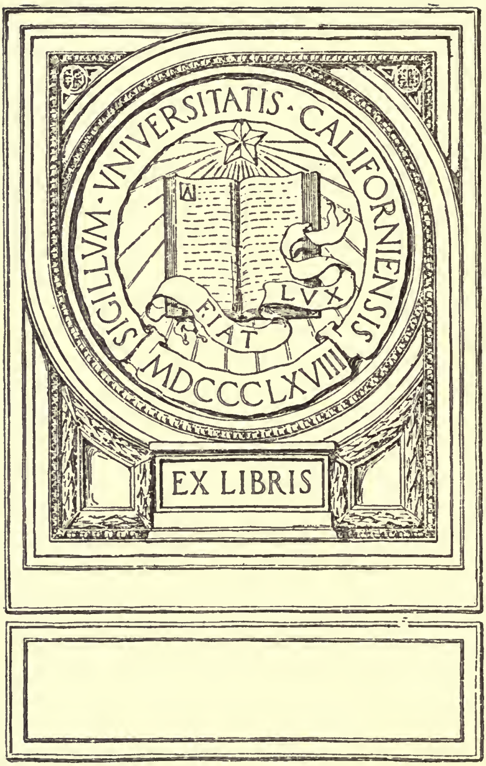
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LONDON:
CHARLES GRIFFIN AND COMPANY, LIMITED,
EXETER STREET, STRAND, W.C. 2.
1919.

PREFACE.

During the earlier period of chemistry as an exact science a justifiable distinction was created by mineral chemists between common and rare elements. Only a few of the latter had been isolated from a small number of scarce minerals; the methods for their detection and estimation were uncertain; their application in the arts was negligible. Though briefly dealt with in text-books, they were neglected in the lecture-room and in the laboratory.

The advances made by scientific and industrial research, especially during the last decade, have brought about a complete and permanent change. Only the rarest elements have not yet been put to some practical use; others, supposed to be of scanty occurrence, have been found to be universally distributed, though in small quantities; a few have been discovered in local deposits of considerable magnitude; whilst several have now definitely taken their place as indispensable adjuncts of metallurgical and chemical industry.

While this revolution has been, and still is, going on, the old arbitrary separation into common and rare elements is still adhered to by most writers and teachers, with the result that the training of the future chemist can hardly be said adequately to prepare him for present-day requirements. The older professional man, if confronted with the unfamiliar subject in his practical work, has to glean his information from original communications scattered amongst the vast output of technical literature, as not one of the otherwise excellent handbooks on ore analysis contains anything like a complete list of the rarer elements.

The present volume represents an endeavour on the part of its authors to bring the analysis of minerals of the rarer elements into line with that of their more abundant relatives, the descriptions of the operations of mineral analysis being preceded in each case by concise information on the general and analytical chemistry, as well as the mineralogy, of the element under treatment. In this form the book will, we trust, appeal to the analyst or metallurgist in actual practice, as well as to the student who has mastered the chemistry of the common elements, and become proficient in the analysis of their ores.

A uniform plan has been adhered to throughout the book so as to facilitate reference. The elements follow each other in the order of the groups of the Periodic System. The text-matter for each element is arranged in the following sequence, though one or several headings may be omitted :—

GENERAL INFORMATION.

Minerals.
Properties and Compounds.
Quantitative separation.
Estimation (Gravimetric, Volumetric, and Colorimetric).

MINERAL ANALYSIS.

Detection in ores.
Determination in ores.
Impurities in ores.
Complete analysis of ores.
Technical methods.

In writing a book of this kind a certain amount of compilation of the work of others is not only unavoidable, but desirable. No chemist, however experienced, has opportunity to test all the methods covering so vast a subject, and he must therefore rely to a certain extent on the experience and judgment of others if he aspires toward completeness. We have endeavoured as much as possible to describe methods which we have found to be reliable. In some cases processes were specially tested before being included, in others we have devised original methods or combinations.

Whilst some of the best books are claimed by their writers not to be anything but compilations, collation of other standard works sometimes discloses the same omissions of information on certain analytical problems. Thus the fact that we were unable, in spite of diligent search, to find a method for the separation of molybdenum from antimony in chemical literature cannot be due to mere coincidence. The same remark applies to the separation of palladium from silver. In both cases we worked out a new method of separation.

Brevity has been aimed at so as to reduce the size and price of the volume; as it is not intended for beginners, illustrations have been omitted, while equations are almost entirely confined to volumetric methods. With the same object in view no general index has been included, but two smaller ones have been substituted, the first containing the minerals and the second the separations. For the rest, we hope the uniform treatment of the text-matter and the numerous cross-references render a general index unnecessary.

A special feature of this book is the prominence accorded to complete analysis, a scheme for which is given in nearly every case in which a compound of the element under treatment occurs as a distinct mineral species. To avoid undue length and repetition, the directions for complete analyses have been very briefly outlined in tabular form; the tables must be taken as merely showing in what manner the mineral is resolved into its constituents by the treatment indicated, and all details as to the operations involved must be looked up elsewhere in the book. We would even advise those more or less unfamiliar with the subject, before undertaking a complete analysis, to map out the scheme after the model of the table, but with full directions included. Sometimes a constituent will be found placed in more than one section of a table, showing that it is not wholly obtained in one fraction.

This little work is probably the first in which the complete analysis of rare-element minerals has received systematic treatment. We are quite content to draw upon our methods the fire of adverse criticism, provided it be constructive as well as destructive. In this manner will progress be achieved, for hitherto the methods of complete analysis have been very inadequately discussed. Hillebrand, in his admirable *exposé* of rock analysis, has shown the multitude of pitfalls that beset the determination of the most common constituents of the Earth's crust; what, then, must be the position with regard to the complex mixtures of the rarer minerals? We shall therefore welcome any suggested improvements, which will be embodied and acknowledged in a possible future edition.

The following books and treatises have been consulted for data reproduced in these pages: Dana's *System of Mineralogy*, Cahen and Wootton's *Mineralogy of the Rarer Metals*, Levy's *Rare Earths* for mineralogical data; Newton-Friend's *Text-book of Inorganic Chemistry*, Roscoe and Schorlemmer's *Treatise on Chemistry*, Gmelin-Krant's *Handbuch der anorganischen Chemie* for the general chemistry; Crookes's *Select Methods of Chemical Analysis*, Mellor's *Treatise on Quantitative Inorganic Chemistry*, Rüdisüle's *Nachweis, Bestimmung und Trennung der chemischen Elemente*, and numerous original papers and communications for details of analytical procedure.

W. R. S.
A. R. P.

LONDON.

PERIODIC TABLE.

Periods.		Group 0.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
First short period		He 4·00	H 1·008 Li 6·94	Be 9·1	B 11·0	C 12·005	N 14·01	O 16·00	F 19·0	
Second short period		Ne 20·2	Na 23·00	Mg 24·32	Al 27·1	Si 28·3	P 31·04	S 32·06	Cl 35·46	
First long period	Even series	A 39·88	K 39·10	Ca 40·07	Sc 44·1	Ti 48·1	V 51·0	Cr 52·0	Mn 54·93	Fe 55·84 Co 58·97 Ni 58·68
	Odd ,,	. .	Cu 63·57	Zn 65·37	Ga 69·9	Ge 72·5	As 74·96	Se 79·2	Br 79·92	
Second long period	Even series	Kr 82·9	Rb 85·45	Sr 87·63	Y 88·7	Zr 90·6	Cb 93·1	Mo 96·0	. .	Ru 101·7 Rh 102·9 Pd 106·7
	Odd ,,	. .	Ag 107·88	Cd 112·4	In 114·8	Sn 118·7	Sb 120·2	Te 127·5	I 126·92	
Third long period	Even series	X 130·2	Cs 132·81	Ba 137·37		. .	. .	. .	. .	. . . . . .
	Odd ,,	. .	. .	. .	Rare Earth Metals	. .	. .	. .	. .	
Fourth long period	Even series	. .	. .	. .		. .	Ta 181·5	W 184·0	. .	Os 190·9 Ir 193·1 Pt 195·2
	Odd ,,	. .	Au 197·2	Hg 200·6	Tl 204·0	Pb 207·20	Bi 208·0	. .	. .	
Fifth long period		Nt 222·4	. .	Ra 226·0	. .	Th 232·4	. .	U 238·2	. .	. . . . . .

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ERRATA

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22. *Procedure* 8, under F^1: the third and fourth lines should read as follows:
"dryness, take up with 2 c.c. of HCl, add slight excess of $NaNH_4HPO_4$, make ammoniacal, add $\frac{1}{10}$ the volume of"

50. Seventh line from top: the bracket "(see Rare Earths, § III)" should read: "(see Cerium, § II, (*a*))."

57. Footnote [1]: second line should read:
"and Sterba-Böhm, *loc. cit.*, p. 55."

and the water slowly decanted into a similar basin. Washing and decantation are repeated until the slimed material has been separated from the fine sandy matter. The latter is rinsed back into the mortar with very little water, again ground, and all the operations repeated until the whole of the sample has been slimed. The aqueous suspension is evaporated to dryness on a steam-bath; the residue after thorough mixing is ready for weighing.

In many cases, especially with minerals containing ferrous compounds, it is advisable to grind the sample under absolute alcohol free from fixed residue, and to allow the alcohol to evaporate at room temperature. These precautions have been found necessary to prevent oxidation of the fine powder during crushing and drying.

(*b*) **Contamination in Crushing.**—When a mineral is being crushed or ground it tends to exert an abrading action on the grinding surfaces, and if it is harder than the material of the crusher, a more or less considerable amount of the latter will find its way into the sample. Con-

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THE
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CHAPTER I.

INTRODUCTION.

General information concerning certain manipulations and apparatus, of importance in mineral analysis, has been placed in this introductory section.

All temperature readings are given in degrees Centigrade.

(*a*) **Crushing Samples for Analysis.**—The success of a mineral analysis depends in many cases on the amount of care with which the crushing has been carried out. If the material is a sulphide ore, fine grinding is not so essential, a fineness of −100-mesh being in most cases sufficient. Oxide minerals, however, require much more elaborate grinding, especially the crystallised varieties found in metamorphic rocks and alluvials. Such material must be crushed to an impalpable powder, which is best done in the following manner: The sample is first crushed to −100-mesh size as usual, screened, and carefully quartered down until the weight is reduced to 2–3 grm. This is placed in an agate mortar, and enough water added to form a thick paste, which is thoroughly ground for fifteen minutes or until all grittiness has disappeared. The contents of the mortar are then transferred to a flat basin with a minimum of distilled water from a wash-bottle; the dish is given a rotary motion, and the water slowly decanted into a similar basin. Washing and decantation are repeated until the slimed material has been separated from the fine sandy matter. The latter is rinsed back into the mortar with very little water, again ground, and all the operations repeated until the whole of the sample has been slimed. The aqueous suspension is evaporated to dryness on a steam-bath; the residue after thorough mixing is ready for weighing.

In many cases, especially with minerals containing ferrous compounds, it is advisable to grind the sample under absolute alcohol free from fixed residue, and to allow the alcohol to evaporate at room temperature. These precautions have been found necessary to prevent oxidation of the fine powder during crushing and drying.

(*b*) **Contamination in Crushing.**—When a mineral is being crushed or ground it tends to exert an abrading action on the grinding surfaces, and if it is harder than the material of the crusher, a more or less considerable amount of the latter will find its way into the sample. Contamination is greater in the case of friction than when concussion is employed. Thus a muller and slab (bucking plate) should not be used for any but very soft material; it has its use in preparing samples for works assays, but the risk of contamination is too great for exact analytical work. A cast-iron or steel mortar answers well for breaking up lumps by pounding them, but it should be carefully tested for its resistance to abrasion by friction, using quartz powder or sand previously extracted with strong hydrochloric acid. Porcelain or Wedgwood mortars and pestles suffer a decided loss when used on material the hardness of which exceeds 6. Agate is most commonly used for fine grinding, but it is likewise worn away by minerals of hardness 7 and over. For such products, the best procedure consists in grinding them in a steel mortar that has been in use for some time, and extracting the fine powder under water with a horseshoe magnet or magnetised knife-blade. This mode of working is not applicable to ores containing strongly magnetic minerals, *e.g.* magnetite. The hardest minerals being almost invariably insoluble in acids, the powder may also be extracted with very weak hydrochloric acid or, what is preferable, iodine water. The procedure to be adopted depends on the nature of the material.

(*c*) **Contamination by Fusion.**—This may be due to (1) corrosion of the crucible, or (2) impurities in the fluxes used.

(1) *Corrosion of the Crucible.—Platinum* is slightly attacked by fused alkaline carbonate, more so by bisulphate or nitrate, and rather strongly by cyanide, hydroxide, or peroxide. The metal introduced into the analysis is eliminated by precipitation with hydrogen sulphide.

Silver crucibles are very useful for fusions with alkaline hydroxide and nitrate; though a little silver goes into solution, it is readily eliminated as chloride or sulphide. The metal being easily obtained in the pure state, no other impurities are introduced through the use of a crucible obtained from a reliable source. The decomposition of silicates can be accomplished by fusion with sodium hydroxide in a silver crucible; the only precaution to be observed is, not to use a blast, Teclu, or other powerful burner, for fear of melting the silver.

Copper is a very good substitute for silver; the metal is almost chemically pure, and though a good deal of attack takes place in a peroxide fusion, the removal of the dissolved copper by hydrogen sulphide gives no trouble.

Nickel crucibles are widely used for peroxide fusions in the determination of single constituents. They must not be employed for fusion assays involving the estimation of base metals, because the degree of purity of the metal is rather uncertain. Thus a crucible analysed by one of the authors ("Reinnickel" brand) was found to contain 0·14 per cent. of copper, 0·31 of iron, 0·31 of manganese, 0·07 of cobalt, and 0·06 of magnesium. Silicon is also a likely impurity. The above remarks apply also to *iron* crucibles.

Silica crucibles cannot, of course, be used for fusions with alkaline fluxes, but are very serviceable for bisulphate, and fairly so for cyanide, fusions.

(2) *Impurities in the Fluxes.*—Contamination due to this cause can be guarded against and allowed for by running blank tests on every fresh supply of material, even that sold as chemically pure. If the blank is excessive, the bottle should be rejected. The most difficultly obtainable pure flux is probably potassium (sodium) cyanide. This should be tested particularly as to its sulphide content, by shaking a solution of 5–10 grm. with a little bismuth hydroxide, the darkening of which indicates the presence of sulphur.

(*d*) **Jones' Reductor.**[1]—This apparatus is very convenient for the rapid reduction of solutions prior to titration with permanganate. It consists of a cylindrical funnel (100 c.c. capacity) mounted on a glass tube 18 in. long and ½ in. wide. The upper end of the tube carries a glass tap just below the funnel; the lower drawn-out end reaches through a rubber stopper into, and below the side tube of, a vacuum filtration flask. The funnel contains a 1-in. layer of coarsely-powdered calcined quartz supported by a filter plate, while the tube is filled with 20- to 30-mesh ordinary, or preferably amalgamated, zinc as free from iron as possible.

The reductor is prepared for use by pouring 100 c.c. of cold 5 per cent. sulphuric acid into the funnel and gently opening the tap whilst applying suction to cause a slow current of acid to flow through the zinc. The zinc is then washed five times with water, and the tap closed while the tube is full of water. The filtration flask is then emptied and washed. This acid wash is always applied before use.

For the reduction, the solution is transferred to the funnel, and slowly passed through the zinc column. When the funnel is nearly empty its sides are rinsed down, after which the reductor is washed with acid followed by water as above, taking care to keep the zinc column always covered with liquid. The solution is titrated immediately, the reductor being again ready for use. The deduction for iron in the zinc is ascertained by a blank test.

(*e*) **Filtration and Ignition of Gelatinous and Slimy Precipitates.**—The tedious operation of filtering and washing precipitates of a gelatinous nature is greatly accelerated by adding pulped filter fibre to the solution before precipitating. The pulp is prepared by beating and stirring an ashless 9 or 11 cm. filter with a little hot water in a beaker until completely disintegrated. In addition to the greater speed thus obtained the filtrate is generally free from cloudiness, while the precipitate upon ignition yields a light, finely subdivided product easily attacked by solvents or fluxes. Ferric oxide thus obtained is readily soluble in hydrochloric acid. Other elements in the determination of which this expedient is of great value are aluminium, titanium, columbium, tantalum, zirconium, etc.

(*f*) **Use of Spectroscope in Analysis.**—The various kinds of spectra and their use in analysis are :—

(1) *Flame spectra* are produced when the light from an incandescent compound of the element is examined through the spectroscope. The

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[1] For a photograph of Jones' reductor see Mellor's *Quantitative Inorganic Analysis*, p. 191.

compound chosen for the test should be slightly volatile; usually the chloride gives the best results. The alkalies, alkaline earths, indium, and thallium give characteristic flame spectra; in fact the latter two metals as well as cæsium and rubidium were discovered by means of the spectroscope.

(2) *Spark spectra* are produced by allowing a powerful spark to pass between poles made of pure porous carbon and impregnated with a solution of a salt (preferably the chloride) of the metal under examination. They may also be produced by connecting the solution of the salt with the negative terminal of an induction coil and passing the spark from a positive pole of platinum suspended just above the surface of the liquid. This latter method is usually employed in the identification of the rare earths, solutions of whose salts give characteristic spark spectra.

(3) *Arc spectra.*—The substance under investigation is placed on the positive carbon, or in a hole bored along its axis. The arc is then struck between the poles, and the spectrum examined as usual.

(4) *Absorption spectra* are best observed by allowing the light from a Nernst lamp to pass through a dilute solution of the substance, contained in a parallel-walled glass vessel. Absorption occurs not only in the visible region but also in the ultra-violet and infra-red; gadolinium salts, in fact, have an absorption spectrum in the ultra-violet, but none in the visible region. If it is desired to examine such invisible absorption spectra, recourse must be had to photography; a quartz prism and lenses must then be used, as glass absorbs the ultra-violet rays.

The spectra are measured by comparison with an iron arc spectrum, and, if a permanent record is required, the two spectra are photographed slightly overlapping one another. The part of the band measured is that in which absorption is most intense (*i.e.* the darkest part). This is called the "head," and need not necessarily be in the middle of the band, but its position is always very nearly the same and is independent of the dilution. The width and intensity of the bands vary inversely with the concentration and directly with the thickness of the absorbing layer. As the intensity of the bands is a measure of the concentration of the material producing them, an examination of the absorption spectrum of a solution furnishes valuable data as to the progress of a fractional crystallisation for the separation of the rare earths, especially of the cerium metals, all of which give characteristic spectra.

The strength, width, and position of the bands are usually affected by the nature of the solvent; mineral acids, for example, render the neodymium bands weaker, more diffuse, and wider towards the red end of the spectrum. Again, other substances in solution usually diminish the intensity of the bands, whereas rise of temperature has the opposite effect. All these points require to be considered when examining absorption spectra, otherwise erroneous conclusions are likely to be drawn.

(5) *Phosphorescence spectra* are produced when substances are subjected to the cathode discharge in Crookes's tubes. This method has proved very useful in work on the rare earths.

(6) *Spectra of gases* are observed by passing an electric discharge through the rarefied gas enclosed in a Geissler tube.

(*g*) **Electroscope.**—The following description of an electroscope for the accurate determination of radium is taken from Bulletin No. 104 of the U.S. Bureau of Mines; it is that used by C. L. Parsons and his collaborators in the National Radium Institute.[1]

The instrument consists essentially of two nickel-plated brass chambers connected by a collar of the same metal, filled with sealing-wax. The upper or leaf chamber is a cylinder, 3¼ in. in diameter and 1¼ in. deep, the axis of which is horizontal. An aperture at the top of the cylinder, of the same dimensions as the collar at the bottom, is also filled with sealing-wax, into which is embedded a rectangular brass bar 2¼ in. long, which serves to carry the leaf system. The leaf itself is 2 in. long and ¼ in. broad; it is made of aluminium, and is affixed to the upper part of the brass bar; the lower part of the latter carries a brass spring which lightly touches the knob of a cross-rod, which latter passes through the collar into the emanation or gas chamber, where it terminates in a cylindrical brass electrode ½ in. in diameter.

A brass rod for charging the instrument is threaded through a hard-rubber connection in the side of the leaf chamber; a wire runs at an angle of 45° from the rod to the leaf system, which it touches just above the junction of the leaf and bar. The rod and wire may be rotated for the purpose of removing them from the neighbourhood of the leaf system when the latter has been charged.

The ends of the leaf chamber are covered with glass, or preferably mica, windows, the insides of which are covered with fine wire gauze to conduct away stray currents. A circular hole in the gauze enables observation of the leaf to be taken through a telescope carrying a micrometer scale set parallel to the leaf.

The lower chamber, in which the emanation is collected, is a hollow, gas-tight cylinder 4 in. high and 3½ in. in diameter, set upright and screwed into the neck of the leaf chamber. The bottom of the gas chamber consists of a brass plate ⅛ in. thick; the chamber is also fitted with two holes, ½ in. in diameter, diagonally opposite each other; they are fitted with glass tubes carrying ground-in glass stoppers; the rubber connections are secured with wire. The method of using the apparatus is described under Radium, § IV.

A simpler form of apparatus for rough determinations of the activity of uranium minerals has a lower chamber about 2 in. high, fitted with a movable door carrying a brass table of the same size as the chamber. The ore, crushed to a suitable size, is spread evenly over the table and the chamber closed. By comparing the rate of fall of the leaf when the unknown material is used against that observed with an ore of known uranium content the amount of uranium can be approximately ascertained (*see* Uranium, § IX, (*c*)).

(*h*) **Electromagnet.**—This instrument is indispensable in mineralogical analysis (*q.v.*). The particulars given below refer to a magnet described

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[1] A photograph of the electroscope faces p. 90 of the Bulletin.

in R. H. Richard's *Text Book of Ore Dressing* (1909), p. 609, but modified so as to attract the more weakly magnetic minerals.

The magnet itself consists of two cores of slowly-annealed iron, joined at the top by a yoke of cast iron. The pole shoes are slotted, to allow of adjustment of the air gap, and bevelled towards each other at an angle of 45°. Each core is wound with 5000 ft. of No. 21 cotton-covered copper wire, making 6760 coils. The turns are held in place top and bottom by brass rings, and are protected by layers of paper and tarred marline. The magnet is run on a 110-volt circuit, and by the introduction of suitable resistances in series its strength may be so adjusted as to effect separation of a mineral mixture into fractions of different magnetic susceptibility.

The separation of the more important magnetic minerals by means of the above electromagnet may be effected by inserting the following resistances :—

(*a*) 16 candle-power lamp, 50 volt. Resistance about 96 ohms.
(*b*) 16 ,, ,, ,, 50 ,, ,, ,, 96 ,,
(*c*) 8 ,, ,, ,, 50 ,, ,, ,, 48 ,,
(*d*) 8 ,, ,, ,, 50 ,, ,, ,, 48 ,,

The mode of applying the resistances, and the selective attraction exerted on various minerals, are as follows :—

Resistances in Circuit.	Approximate Current (Amp.).	Mineral Attracted.
$a+b+c+d$ . . .	0·27	Ilmenite.
$a+b+c$	0·37	Garnet.
$a+b$	0·55	Wolfram.
a	0·75	Monazite.
All out	1·1	Stannine.

MINERALOGICAL ANALYSIS.

A thorough knowledge of mineralogy is indispensable to the metallurgical chemist for solving the problems relating to the economic recovery of the valuable constituents of ores. To take a well-known example : If an ore be found to contain substantial amounts of tin and tungstic acid, it becomes more important to identify the form in which the latter occurs than to ascertain its percentage in the ore ; for a tin-wolfram ore is valuable for both its tin and tungsten contents, whereas certain grades of tin-scheelite ore are, up to the present, almost worthless.

In the laboratory, the application of the determinative methods of mineralogy constitutes a most valuable help in analytical work. A qualitative analysis is not only supplemented, but may be entirely replaced, by a mineralogical examination. The latter is both quicker and simpler, because it substitutes mechanical separation and simple tests (physical, blowpipe, etc.) on the picked fragments of mineral, for the elaborate operations of opening up, separating into groups, resolving these into elements, and identifying the latter. It is also more delicate, because a few particles or crystals of a mineral occurring in traces can be picked out and identified in a sample weighing many pounds; in chemical analysis this small quantity would probably be overlooked. Finally, it conveys information as to the mode of combination of elements in an ore mixture which chemical analysis cannot give, since the latter starts by destroying the mineral constituents.

It has been mentioned that mineralogical separation is done by mechanical means. Even separation may often be dispensed with, *e.g.*, when the ore under investigation is in the form of coarse lumps, and the operator possesses sufficient experience to recognise mineral species by inspection, aided, if necessary, by determination of the hardness, streak, cleavage, etc. The coarse lumps are next broken up to expose fresh surfaces: in this manner all the minerals present can be identified in lump ore. Since fine grinding obliterates the megascopic characteristics of a mineral mixture, crushing previous to analysis should only be done after the nature of an ore has been satisfactorily ascertained. When asked to report on an ore, the chemist should insist on receiving it in a natural or coarse condition.

The more important rarer elements are extracted from detrital deposits formed by the disintegration of igneous and metamorphic rocks in which these elements occur in minute quantities.[1] The minerals containing them, being heavier and more resistant to atmospheric agencies than the mother rock, have been accumulated in river beds and on sea and lake shores during the present and past geological periods, the deposits being known as alluvials, placers, black sands, etc. They occur in every degree of comminution, generally in the form of water-worn, rounded or flattened grains. On account of their importance as a source of many rarer elements, a mineralogical analysis of alluvial deposits is frequently necessary. The separation of the material into its component minerals is based upon differences in their physical properties.

The more important operations in mineralogical analysis are :—

(*a*) **Water Concentration.**—In the case of alluvials, this has been effected by Nature. In the laboratory, it is carried out by panning, on a larger scale by jigs and shaking-tables.

(*b*) **Separation by heavy liquids,** such as bromoform (sp. gr. 2·9), methylene iodide (3·33), mercury potassium iodide (3·17), cadmium borotungstate (3·28). The mineral mixture is sprinkled upon the

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[1] The rarer elements not found in metamorphic rocks occur in very minute quantities in sulphide ores such as zinc blende, copper and nickel ores, pyrites, pyrrhotine, etc. They are gallium, germanium, indium, and thallium; selenium and tellurium. Traces of platinum metals are also found in pyrrhotine, etc., as well as in igneous rocks.

Titanium, zirconium, and vanadium are universally found in small quantities in rocks of various description.

Lithium, cæsium, and rubidium are primarily found in micas and felspars, and are dissolved in the weathering of the mother rock.

liquid contained in an ordinary funnel, the lower end of which carries a rubber tube closed by means of a pinchcock.

(*c*) **Magnetic Separation.**—A number of minerals are attracted by a strong electro-magnet (see Introduction), while magnetite and pyrrhotine are practically the only ones attracted by a horseshoe magnet. By using the different powers of the electromagnet the other magnetic minerals may be subdivided into strongly, moderately, and weakly magnetic (see below).

(*d*) **Radioactivity**[1] is tested for by means of the electroscope (see Introduction) or a photographic plate. The fractions obtained in the analysis are disposed along lines in the shape of numerals on the black paper wrapping containing the plate; this is left in the dark for twelve to forty-eight hours, after which the negative is developed and fixed in the ordinary way, when the design will be reproduced in dark lines if radioactive minerals are present.

A scheme for the mineralogical analysis of alluvials, based on differences in magnetic properties, colour, and specific gravity, is given below. If the material contains coarse particles, it is first passed through a sieve (8, 10, or 12 mesh) and the oversize sorted by hand into homogeneous fractions. The undersize is submitted to electromagnetic separation. The non-magnetic fraction is separated by means of bromoform if quartz apparently predominates; if not, it is first sorted with the help of forceps into coloured and colourless fractions, and the latter separated by bromoform. The magnetic fraction is further divided into strongly and weakly magnetic portions; each of these is then sorted. When apparently homogeneous fractions have been obtained, they are identified by mineralogical or, if necessary, chemical tests. The streak of small particles is taken by crushing them on the streak plate with a knife-blade. If the sand is very fine, the fractions may be examined under a weak-power microscope (1½ in.) in reflected as well as in transmitted light.

TABLE FOR THE EXAMINATION OF ALLUVIALS.[2]

A. NON-MAGNETIC MINERALS.

(1) **Of Metallic Appearance:**—

Gold: characteristic colour; sectile.
Platinum (*q.v.*): see note below, after B (3).
Osmiridium, *q.v.*
Molybdenite, *q.v.*

(2) **Dark, Opaque:**—

Cassiterite: colourless streak. Treated with zinc dust and hydrochloric acid, it acquires a tin-white coating which can be polished.
Rutile (*q.v.*): pale brown streak.

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[1] For radioactive minerals see columbium, uranium, thorium, radium.

[2] For tests and description of minerals of the rarer elements the reader is referred to the different chapters.

(3) **Coloured :—**

Paler varieties of cassiterite and rutile : see (2).
Titanite or *sphene* (*q.v.*) : brownish, streak white.
Chrysoberyl (*q.v.*) : greenish, streak white.
Corundum : H 9, various colours.
Beryl : see (4).
Baddeleyite (*q.v.*) : grey or brown ; zirconium reaction with turmeric paper.
Zircon (*q.v.*) : red.

(4) **Colourless, or Slightly Coloured :—**

(α) *Lighter than bromoform :—*
Quartz and its varieties.
Beryl (*q.v.*) : green to white.

(β) *Heavier than bromoform :—*
Scheelite (*q.v.*) : boiled with hydrochloric acid, the particles assume a canary-yellow colour.
Zircon (*q.v.*) : pale pink (see also (3)) ; turmeric paper test.
Topaz : wine-yellow, H 8 ; gives fluorine reaction.
Apatite : greenish to white. Reactions for fluorine, chlorine, phosphoric acid.
Diamond : transparent, highly refractive. H 10.

B. MAGNETIC MINERALS.

(NOTE.—*The subdivision into strongly, etc., magnetic minerals is approximate, as the magnetism of a mineral species varies with its chemical composition.*)

(1) **Strongly Magnetic :—**

(α) *Brown to black, opaque :—*
Magnetite : black, attracted by knife-blade.
Ilmenite (*q.v.*) : black ; streak black to brownish-red. Titanium reactions.
Menaccanite, iserine : varieties of ilmenite.
Black garnet : fusible.

(β) *Coloured :—*
Garnet : generally red to pink, also brownish. Rhombic dodecahedra frequent.

(2) **Moderately Magnetic :—**

Brown to black, opaque :—
Wolframite (*q.v.*) : reddish-brown streak. The powder turns yellow when boiled with *aqua regia.*
Chromite : brown streak. Green borax bead.
Tantalite, columbite (*q.v.*) : streak dark red to black. Tantalum and columbium reactions.

(3) **Weakly Magnetic :—**

(α) *Black, opaque :—*
Pleonaste : black spinel ; colourless streak ; infusible.

Schorl : black tourmaline. Reaction for boric acid. Colourless streak.
Emery : greyish-black corundum.

(β) **Coloured :—**

Spinel : generally red, resembling garnet, but infusible.
Tourmaline : blue, green, red (see (α)).
Monazite (*q.v.*) : pale-yellow to dark reddish-brown ; radioactive. Reactions for phosphoric acid and rare earths.

(*Note.*—Native platinum is sometimes magnetic. The following minerals not found in alluvials are frequently, but not invariably, attracted by an electromagnet : chalybite, hematite, limonite, franklinite, biotite, hornblende, augite, epidote, olivine, serpentine.)

It is thought advisable to give two examples of mineralogical analyses from actual practice, since it is hard to describe a systematic procedure applicable in all cases.

Example A.—All finer than 12-mesh. Electromagnetic separation gave :—

(*a*) Non-magnetic fraction 69·3 per cent., sp. gr. 6·7.
(*b*) Weakly magnetic ,, 21·3 ,, ,, 5·4.
(*c*) Strongly ,, ,, 9·4 ,, ,, 5·0.

(*a*) The non-magnetic fraction was treated with zinc dust and acid, and the few colourless particles picked out from among those of metallic appearance (*i.e. cassiterite*) ; they were separated by bromoform into *quartz* and *topaz* (fluorine reaction).

(*b*) The weakly magnetic fraction was sorted into two homogeneous portions : (α) the bulk consisted of dull black water-worn grains. After powdering and fusing with bisulphate, strong columbium reactions were obtained, tantalum being subordinate. These and the low specific gravity prove *columbite.* (β) Subordinate fraction : brown, opaque, soft, water-worn grains, giving titanium reactions : *iserine.*

(*c*) The strongly-magnetic fraction was hand-sorted into five homogeneous portions : (α) pale pink transparent grains, and (β) red transparent grains. Both these were found to consist of *garnet* rich in manganese (*spessartite*). (γ) Dull black grains, identical with *columbite* of fraction (*b*). (δ) Brown grains identical with *iserine* of fraction (*b*). (ε) Black, lustrous, angular particles found to consist of *ilmenite.*

Example B.—The sample was screened through a 10-mesh sieve. The oversize, part of which gave a brown, and part a colourless streak, was treated with zinc dust and acid as in the previous case. The non-metallic-looking black particles were found to give strong tantalum, but no columbium reactions ; sp. gr. 7·1 ; hence *tantalite.* The metallic-looking particles constituting the bulk were *cassiterite.* The undersize was treated electromagnetically. The strongly- and weakly-magnetic products looked very similar, and were united previous to hand-sorting. They contained chiefly *ilmenite* and a little *garnet* ; some more *tantalite* was also found. The non-magnetic portion was sorted according to appearance into : (α) black grains, found to be *cassiterite* ; (β) a subordinate amount of *muscovite* ; (γ) a few tiny grains of *gold* ; and (δ) colourless particles. These were treated with bromoform, giving *quartz* as the lighter mineral, and a small heavy fraction which became yellow on boiling with hydrochloric acid : *scheelite.*

Quantitative Mineralogical Analysis.—A quantitative mineralogical analysis of alluvial material is often required. The procedure is the same as that outlined above ; in addition, every product is weighed. If the amount of material at the operator's disposal is small, the identification tests have to be carried out after the products have been separated and weighed.

Example C.—A little over 2 grm. of sample was available. It was separated electromagnetically into :—

(*a*) Strongly-magnetic	fraction,	0·23 grm.
(*b*) Weakly ,,	,,	0·04 ,,
(*c*) Non-magnetic	,,	2·04 ,,
	Total . .	2·31 grm.

(*a*) This product was homogeneous and brownish-black ; no magnetite was found (knife-blade test). It was identified as *ilmenite.*

(*b*) This was of a pale brown colour. After fusing with bisulphate, one-half of the solution was tested with molybdate solution, the other half with ammonium oxalate : positive tests for phosphoric acid and rare earths proved *monazite.*

(*c*) The non-magnetic portion (practically colourless : absence of cassiterite) was separated by bromoform, the lighter portion (*quartz*) weighing 1·92 grm. The heavy product (pale pink) was fused with sodium peroxide, the acidified solution giving strong turmeric reaction : *zircon.* Hence the composition of this alluvial was :—

Ilmenite	10·0 per cent.
Monazite	1·7 ,, ,,
Zircon	5·2 ,, ,,
Quartz	83·1 ,, ,,
	100·0 per cent.

Quantitative Mineralogical Analysis by Selective or Fractional Decomposition.—This procedure, the principle of which is explained under Complete Analysis (p. 33), is of limited applicability in the case of minerals of the rarer elements, because the majority have to be opened up by fusion. The weighed quantity of material is treated with the solvent and filtered on an alundum filter ; the insoluble residue is washed off, dried, and weighed, and the dissolved mineral taken by difference. The following are examples of this class of work : Separation of tungstic ochre from wolfram and scheelite by hot dilute caustic soda, tungstic ochre dissolving. Separation of wolfram from scheelite (finely powdered) by nitric acid, followed by filtration and treatment with ammonia: wolfram is left almost unattacked; the separation is not quite quantitative. Separation of molybdine from molybdenite by hydrochloric acid, in which the latter is insoluble. Separation of bismuth from molybdenite by weak nitric acid, which dissolves bismuth. Separation of molybdenite from galena by hot hydrochloric acid (1 : 1), which dissolves the latter.

QUALITATIVE CHEMICAL ANALYSIS.

Tests and characteristic reactions for the detection of each of the rarer elements discussed in this book will be described in every individual case. It is intended here to present a general scheme of systematic qualitative analysis applicable to any ore or mineral mixture, and including nearly all the metallic elements. Such a scheme, in order to be of general applicability, must include a uniform procedure for obtaining the mineral in solution, from which the analytical groups are successively thrown down, and each group precipitate further separated into its constituent elements.

The method here adopted for preparing the solution is that of A. A. Noyes,[1] in which the solvents are applied in the following order:—

(1) Nitric acid dissolves sulphides as well as most substances attacked by hydrochloric acid (but not the acid-earth compounds enumerated under (2)), while obviating the precipitation or volatilisation of some elements as chlorides.

(2) The residue from (1) is treated with hydrofluoric acid, which decomposes silicates (except cyanite, andalusite, tourmaline, beryl, zircon, and topaz), tungstates, tantalates, columbates, and some titanium minerals.

(3) The residue from (2) is attacked with hydrochloric acid, then with *aqua regia*. This dissolves cinnabar, molybdenite, ferric oxides, manganese peroxide, lead sulphate, and gold.

(4) The residue from (3) is fused with sodium carbonate, bisulphate, or peroxide, according to its nature.

By carrying out this procedure the metallic constituents of any mineral mixture are dissolved and obtained in several solutions, occasionally in one. The various fractions may, as a rule, be combined before examination, or tested separately if desired; the hydrofluoric solution of the acid-earth group, however, must always be examined by itself.

A comprehensive scheme of qualitative analysis, based on the work of Noyes, Browning, and others,[2] is given below in condensed tabular form. Table I. contains the directions for effecting solution of the mineral; Tables II. to VIII. are devoted to the examination of the analytical groups, more particularly to the separation of the elements. For the sake of brevity, the confirmatory tests for the common metals have not been included in the tables. Directions for washing the precipitates have likewise been omitted in most cases.

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[1] *Chem. News*, 1906, **93**, 146.

[2] For references to the original papers consult Browning's *Introduction to the Rarer Elements* (4th edition, 1917), pp. 207–226.

TABLE I.[1]—OPENING UP.

Digest 1 grm. of slimed mineral with 10 c.c. HNO_3 (1 : 1) till action is over. Dilute with 20 c.c. of hot H_2O, decant and filter.

F^1: evaporate to dryness, heat to 120° for 1 hour. Treat as, or combine with, final residue from R^1 after like treatment.

R^1: transfer to Pt dish, evaporate or decant water, digest with 5–10 c.c. pure strong HF on water-bath. Evaporate twice to dryness with 5 c.c. strong HNO_3, boil with 10 c.c. HNO_3 (1 : 3). If solution is complete after HF or HNO_3 treatment, evaporate to dryness once more, heat to 120° for 1 hour. If complete solution has not taken place, evaporate to dryness, add 10 c.c. strong HNO_3 and 1 grm. pure SiO_2 (Note *a*). Cover, digest for three-quarters of an hour; evaporate to dryness, heat to 120° for an hour. Powder residue (and that from F^1), add 5 c.c. HNO_3 (1 : 1), boil, dilute, decant and filter.

R^2: pour 5–10 c.c. strong HF on to filter (rubber funnel), receive filtrate in Pt dish containing balance of residue. Heat 5 minutes, dilute, decant and filter into another Pt dish.

F^2: evaporate to dryness, take up with 40 c.c. H_2O, add 4 c.c. HCl (2 : 1 water), warm. If ppte forms, filter it off and boil with H_2O; filter into HCl filtrate, test residue for Ag. Filtrate: Table IV.

F^3: Table II.

R^3: boil gently in porcelain with 15 c.c. strong HCl, dilute and filter, digest residue with *aqua regia*, dilute, filter into HCl solution. Dry or ignite residue.

F^4: evaporate to dryness, take up with HCl (1 : 4), filter.

R^4: fuse with (*a*) Na_2CO_3, (*b*) $NaHSO_4$, or (*c*) Na_2O_2; see below.

R^5: digest with NH_4OH, filter.

F^5: Table IV.

F^6: test for Ag.

R^6: boil with $CH_3CO_2NH_4$, filter.

R^7: $SrSO_4$ or $BaSO_4$. Fuse with Na_2CO_3; see Table VII., P^1.

F^7: test for Pb.

(*a*) If non-metallic and light-coloured, or in doubtful cases, fuse with Na_2CO_3, leach, filter.

R^8: digest with HCl, filter.

R^9: see (*b*).

F^9: see Table IV.

F^8: evaporate with HCl, heat to 120°, digest with HCl (1 : 1), filter.

R^{10}: see R^2.

F^{10}: see Table IV.

(*b*) If non-metallic and light-coloured, and thought to consist of oxides, fluorides, or phosphates, fuse with bisulphate in silica crucible, leach, filter.

R^{11}: treat as R^2, filter.

F^{11}: Table IV.

R^{12}: if $BaSO_4$ or $SrSO_4$, see R^7; if SiO_2 or silicates, see (*a*); if SnO_2, see (*c*).

F^{12}: Table II.

(*c*) If metallic, or non-metallic and dark, fuse with Na_2O_2 in Ni crucible, leach, acidify with HCl, evaporate to dryness, heat to 120° for an hour, boil with dilute HCl, filter (see Note *b*).

R^{13}: dissolve in HF; see Table II.

F^{13}: examine separately (Table IV. *et seq.*). Reject nickel filtrate.

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[1] In the tables throughout this book, P denotes precipitate; R, residue; F, filtrate; S, solution; D, distillate; L, loss.

Note a (to R^1).—The SiO_2 used must be pure and free from residue. It is prepared by diluting water-glass with three volumes of water, adding HCl in slight excess, decanting, boiling two to three times with water, and drying. The residue is boiled two to three times with strong HCl, washed free from acid, dried, and ignited.

Note b (to R^4 (*c*)).—If from appearance of residue the presence of platinum metals or osmiridium is inferred, proceed as in Table III.

TABLE II.—ACID-EARTH GROUP.

The solution (F^3, F^{12}, or R^{10}, R^{13} dissolved in HF; see Table I.) is ppted with H_2S (rubber tube). Filter through rubber funnel.

P^1 (may contain Sb, Mo, As, Bi): digest with $(NH_4)_2S$, filter.

R^2: test for Bi.

F^2: add to F^3.

F^1 (Ta, Cb, Ti, Zr, W, Si): evaporate to fumes with H_2SO_4; add NH_4OH and $(NH_4)_2S$, filter (Note *a*).

F^3: add F^2, acidify with H_2SO_4, filter.

P^3: dissolve in HF, evaporate to fumes with H_2SO_4, dilute, let settle, filter.

F^6: evaporate to fumes, dilute, add HCl + Zn: blue ppte = W.

P^6: dry, heat in H_2S current.

Sublimate^7: test for As.

R^7: boil with strong HCl, dilute, filter.

R^4: test for Ta and Cb as directed under Columbium, § VII, (*g*).

F^4: test for Ti and Zr as in Table V., S^8.

F^8: test for Sn and Sb.

R^8: boil with HNO_3, evaporate to fumes with H_2SO_4, cool, add three volumes of H_2O, filter.

F^9: add Zn + KCNS. Red colour = Mo.

R^9: add Zn + HCl. Blue ppte = W.

Note a (to F^1).—If much W and/or Mo are present, the ppte is re-dissolved in HF, the solution evaporated with H_2SO_4, and the pption with NH_4OH and $(NH_4)_2S$ repeated. Combine filtrates.

TABLE III.—PLATINUM GROUP.

Fuse the material (R^4 (*c*), Table I.) with Na_2O_2 in Ni crucible. Leach with H_2O, transfer to retort, acidify with HCl, add HNO_3, distil into NaOH.

D^1: if yellow, acidify with HCl, add a few drops $Na_2S_2O_3$, warm; brown ppte = Os.

S^1: extract with ether.

S^2: evaporate ether, boil with $CH_3CO_2NH_4 + HCO_2H$ for several hours under reflux. Filter, reject filtrate, boil ppte with HCl, filter.

Ether^2: evaporate, test residue for Au, Fe.

F^3: test for Sn.

R^3: heat with NaCl in Cl current, extract with boiling H_2O. Filter.

F^4: add NH_4Cl, let stand, filter.

R^4 (if any): repeat treatment with NaCl + Cl; add filtrate to F^4, residue to F^6.

P^5 (Pt, Ir, Ru): dissolve in hot H_2O, add NH_2OHHCl, cool, add NH_4Cl.

P^6: yellow: $(NH_4)_2PtCl_6$.

F^6: add residue from R^4; evaporate to dryness, ignite, fuse residue with KOH + KNO_3 (Ag crucible). Leach, filter.

R^7: heat with NaCl in Cl current, leach, add NH_4Cl. Red-black ppte = Ir.

F^7: distil in Cl current (see Ruthenium, § III, (*f*)) into C_2H_5OH + HCl. To distillate add NH_4OH, $Na_2S_2O_3$, and warm: violet colour = Ru.

F^5 (Pd, Rh): add freshly ppted AgI. Filter.

P^8: boil with a little *aqua regia*, filter, reject residue, evaporate filtrate, take up with dilute HCl, add a few drops KI: black ppte = Pd.

F^8: ppte with Zn, filter, reject filtrate. Heat ppte with NaCl in Cl current, extract with alcohol, filter.

F^9: contains a little Ru. Reject.

R^9: soluble in H_2O with rose colour; no ppte with NH_4Cl. Add excess KOH + C_2H_5OH. Black ppte = Rh.

TABLE IV.—HYDROGEN SULPHIDE GROUP.

(Germanium and rarer platinum metals omitted. For germanium a separate test should be made (Germanium, § V.); for platinum metals, see preceding table.)

Precipitate the solutions referred to this table in Table I., separately or combined, with H_2S. Filter, again pass H_2S through filtrate; if ppte forms, add it to the first.

P^1: digest, hot, with $(NH_4)_2S$. Filter. | F^1: see Table V.

R^2: boil with HNO_3 (1 : 1); filter.

F^3: test for Pb, Bi, Cu, Cd. | R^3: digest with Br, filter.

F^4: add KCl, evaporate to low volume, let stand, filter. | R^4: SnO_2.

P^5: K_2PtCl_6. | F^5: add NaOH and $C_2O_4H_2$, boil, filter.

F^6: test for Hg. | P^6: Au.

F^2: ppte with dilute HCl, filter, reject filtrate. Boil ppte with strong HCl; filter.

R^7: dissolve in $HCl+KClO_3$, evaporate, take up with a little H_2O; filter. | F^7: test for Sb, Sn.

P^8: K_2PtCl_6. | F^8: add NH_4Cl, NH_4OH, and Mg mixture. Let stand overnight, filter.

F^9: boil with excess of $C_2O_4H_2$. Filter. | P^9: test for As.

F^{10}: evaporate nearly to dryness, add 10 c.c. of strong HCl, reduce in the cold with 0·2 grm. Na_2SO_3; let stand, filter. | P^{10}: Au.

P^{11}: red, soluble in KCN = Se. | F^{11}: add equal volume of H_2O and a little KI and Na_2SO_3. Filter.

F^{12}: boil to expel SO_2, add KCNS + Zn: red colour = Mo. | P^{12}: black, soluble in H_2SO_4 with red colour: Te.

TABLE V.—AMMONIA-AMMONIUM SULPHIDE GROUP.

(Exclusive of Indium and Gallium, which see.)

To F^1, Table IV., add 5 grm. NH_4Cl and a slight excess of NH_4OH; pass H_2S. Filter.

P^1: add P^2, dissolve in HCl, boil, add HNO_3, evaporate, add H_2O, ppte with $C_2O_4H_2$ (see Rare Earths, § V.). Filter.

F^1: acidify with CH_3CO_2H, boil, filter.

P^2 (if any): add to P^1. | F^2: see Table VII.

P^3: see Table VI. | F^3: evaporate to fumes with H_2SO_4, dilute. If any white crystalline ppte remains, fuse it with Na_2CO_3, and proceed as in Table VII., P^1. To filtrate, or original F^3, add NaOH, Na_2O_2, Na_2CO_3; boil and filter.

P^4: dissolve in HCl, destroy HCl with HNO_3, boil with $KClO_3$. Filter.

P^5: MnO_2. | F^5: test for P_2O_5; if present, test first for Fe, then add sufficiency of $FeCl_3$, neutralise with Na_2CO_3, add 2 grm. CH_3CO_2Na, boil, filter.

F^6. | P^6.

F^4: add faint excess of HNO_3, dilute to 100 c.c., treat with excess of 2–3 grm. of $NaHCO_3$, heat 20–30 minutes in a pressure bottle. Filter.

P^{11}: dissolve in HCl, add NH_4OH, filter. | F^{11}: neutralise with HNO_3, add $Pb(CH_3CO_2)_2$, filter.

P^{12}. | F^{12}. | F^{14}. | P^{14}.

(Table continued overleaf.)

Table V.—Ammonia-Ammonium Sulphide Group—*Continued.*

<table>
<tr><td colspan="2">F^6: pass H_2S, filter.</td><td colspan="4">P^6: dissolve in HCl (1 : 1), extract with ether.</td><td colspan="2">P^{12}: dissolve in HNO_3, evaporate almost to dryness, extract with amyl alcohol. Filter.</td><td rowspan="3">F^{12}: test for Zn.</td><td colspan="2">F^{14}: ppte with H_2S, filter, reject PbS; to filtrate add Br, boil, neutralise with NH_4OH; add CH_3CO_2H and Na_2HPO_4. Filter.</td><td rowspan="3">P^{14}: $PbCrO_4$.</td></tr>
<tr><td rowspan="2">P^7: test for Co, Ni, Zn.</td><td rowspan="2">F^7: see Table VII.</td><td colspan="2">S^8: evaporate with H_2SO_4, adjust acidity to 1 per cent., add $H_2O_2 + Na_2HPO_4$. Filter.</td><td colspan="2">Ether^8: evaporate, take up with H_2SO_4, add KI and SO_2, filter.</td><td rowspan="2">R^{13}: test for Al.</td><td rowspan="2">F^{13}: evaporate to dryness; test for Be.</td><td rowspan="2">P^{15}: yellow = U.</td><td rowspan="2">F^{15}: add NH_4OH, pass H_2S; red, pink, or violet solution = V.</td></tr>
<tr><td>F^{10}: yellow to orange = Ti.</td><td>P^{10}: Zr phosphate. For confirmatory test, see Zirconium, § V.</td><td>F^9: Fe.</td><td>P^9: yellow = Tl.</td></tr>
</table>

Table VI.—Rare-Earth Group.

<table>
<tr><td colspan="6">Digest P^3, Table V., with fuming HNO_3 (1·5), evaporate to dryness, destroy HNO_3 by evaporation with HCl, dry again, take up with water, boil with $Na_2S_2O_3$; filter.</td></tr>
<tr><td colspan="2">P^1: extract with strong HCl, filter, reject residue, neutralise filtrate with Na_2CO_3, pour into large excess of 20 per cent. Na_2CO_3, boil, filter.</td><td colspan="4">F^1: ppte with NH_4OH, reject filtrate, dissolve ppte in HCl, saturate with Na_2SO_4 cryst., filter, wash with saturated Na_2SO_4 solution.</td></tr>
<tr><td rowspan="3">P^2: dissolve in HCl, neutralise with NH_4OH, pour into 20 per cent. neutral ammonium tartrate, boil clear solution with NH_4OH: crystalline ppte = Sc.</td><td rowspan="3">F^2: acidify with HCl, boil off CO_2, ppte with NH_4OH. Dissolve ppte in HNO_3, evaporate to dryness, take up with H_2O, add NH_4NO_3 and H_2O_2: voluminous white ppte = Th.</td><td colspan="3">P^3: digest with NaOH, filter, reject filtrate. Dissolve in HNO_3, boil with $KBrO_3$ and lump marble, filter.</td><td rowspan="3">F^3: add NH_4OH. White ppte = Yttria earths. Dissolve in HNO_3. Absorption spectrum = Er, etc. (Rare Earths, § III, (*b*) (3).)</td></tr>
<tr><td colspan="2">F^4: ppte with NH_4OH, filter, reject filtrate. Dissolve ppte in NHO_3, evaporate to dryness, heat residue to 450° for ½ minute. Extract with H_2O, filter.</td><td rowspan="2">P^4: dissolve in strong HNO_3, add citric acid, NH_4OH, and H_2O_2; yellow to brown colour = Ce.</td></tr>
<tr><td>F^5: add a few drops of CH_3CO_2H and solution of iodine in KI, then NH_4OH drop by drop till brown colour nearly disappears. Warm gently; blue colour = La.</td><td>R^5: ignite; brown colour = Di (Rare Earths, § I, (*a*) (2)).</td></tr>
</table>

Table VII.—Alkaline-Earth Group.

<table>
<tr><td colspan="4">To F^2, Table V., add $(NH_4)_2CO_3$ solution. Boil, filter.</td></tr>
<tr><td colspan="3">P^1: dissolve ppte, and the residue from leaching the soda fusion of any residues obtained in R^7, R^{12}, Table I., and F^3, Table V., in HNO_3. Evaporate to complete dryness, heat to 140°. Extract with ether-alcohol (1 : 1), filter.</td><td rowspan="3">F^1: Table VIII.</td></tr>
<tr><td rowspan="2">F^2: evaporate to dryness, test residue for CaO.</td><td colspan="2">R^2: dissolve in H_2O, add a few drops of CH_3CO_2H and K_2CrO_4. Filter.</td></tr>
<tr><td>F^3: concentrate, add $NH_4OH + (NH_4)_2CO_3$, boil, filter, test ppte for Sr.</td><td>P^3: yellow = Ba.</td></tr>
</table>

TABLE VIII.—ALKALI GROUP.

<table>
<tr><td colspan="2">Evaporate F^1, Table VII., to dryness. Ignite gently to expel NH_4 salts. Add solution of 1 grm. $C_2O_4H_2$, evaporate to dryness, ignite. Extract with hot H_2O, filter.</td></tr>
<tr><td>R^1: test for Mg.</td><td>F^1: evaporate to dryness with HCl, extract with amyl alcohol, filter.</td></tr>
<tr><td>R^2: add a few drops of H_2O, excess of H_2PtCl_6, let stand, filter.</td><td>F^2: evaporate to dryness, test residue spectroscopically for Li.</td></tr>
<tr><td>P^3: test spectroscopically for Rb, Cs.</td><td>F^3: add equal volume of alcohol, filter, wash with 50 per cent. alcohol.</td></tr>
<tr><td>F^4: Na (see Note *a*). Add a few drops of 1 per cent. alcoholic H_2SO_4: crystalline ppte of Na_2SO_4. If no ppte is formed, saturate solution with HCl gas: crystalline ppte of NaCl.</td><td>P^4: test spectroscopically for K.</td></tr>
</table>

Note a (to F^4).—Not applicable to solutions resulting from the fusion of R^4, Table I., with Na_2CO_3, $NaHSO_4$, or Na_2O_2.

COMPLETE CHEMICAL ANALYSIS.[1]

In addition to the descriptions of individual analyses given in the succeeding chapters, it is thought useful here to present some general information on the subject of complete analysis, including the resolution of group precipitates of greater or lesser complexity into their constituents. Since a general scheme taking into account nearly all the elements would be far too involved, the directions here given refer only to the commoner ones. The separation of the rarer metals will be discussed under their respective headings, and, to simplify the tables, reference to this chapter will be made whenever a separation product containing only common elements has been obtained.

§ I. Methods for Determining Elements.—In assaying for single constituents, a fairly considerable amount of the element to be determined is generally obtained by weighing out a suitable quantity of ore; whereas in a complete analysis the same portion is used for estimating a number of constituents, some being present in large, others in minute, quantity. The method of estimation used will often depend on the amount present; a colorimetric process is frequently adopted for small quantities (*e.g.* bismuth, titanium); sometimes it is preferable to weigh small precipitates rather than use a volumetric method (*e.g.* zinc, antimony). We may therefore distinguish between methods more suitable for moderate to large, and others for minute, quantities. Table I. shows the different methods of estimating some of the commoner elements

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[1] This article is substantially an amplified reprint of a paper entitled "General Principles governing the Complete Analysis of Minerals and Ores," by W. R. Schoeller (*Analyst*, 1915, **40**, 90).

by way of illustration; alumina, barium, silica, sulphur, and the alkalis have not been included, as they are practically always weighed.

TABLE IX.

Abbreviations: G., gravimetric, V., volumetric, E., electrolytic, C., colorimetric, determination.

Element.	Moderate to Large Amounts.	Minute Quantities.
Antimony . .	V. with permanganate, bromate, or iodine. E. as metal.	G. as SbO_2.
Arsenic . .	V. with iodine or bromate. G. as $Mg_2As_2O_7$.	V. with iodine.
Bismuth . .	G. as Bi_2O_3, $BiOCl$, or $BiPO_4$.	E. as metal. C. as BiI_3.
Calcium . .	V. with permanganate.	G. as $CaSO_4$ or CaO.
Cobalt . .	V. with thiosulphate, or by alkalimetry. G. as $Co_2P_2O_7$. E. as metal.	G. as $CoSO_4$, or nitroso-β-naphthol.
Copper . .	V. with thiosulphate. E. as metal. G. as Cu_2S.	C. with ammonia or ferrocyanide. V. with thiosulphate.
Iron . . .	V. with permanganate or bichromate.	G. as Fe_2O_3. C. with thiocyanate.
Lead . .	V. with thiosulphate. G. as $PbSO_4$ or $PbMoO_4$.	V. with thiosulphate. C. with H_2S. G. as $PbMoO_4$.
Magnesium .	V. by alkalimetry. G. as $Mg_2P_2O_7$.	G. as $Mg_2P_2O_7$.
Manganese .	V. with permanganate, or oxalic acid and permanganate.	G. as Mn_3O_4. C. as $HMnO_4$.
Nickel . .	E. as metal. V. with cyanide.	G. with dimethylglyoxime. V. with cyanide.
Phosphorus .	V. by alkalimetry. G. as $Mg_2P_2O_7$.	G. as $PbMoO_4$.
Silver . .	V. with thiocyanate or sodium chloride. E. as metal. G. as AgI.	Scorification or crucible fusion.
Tin . . .	V. with iodine.	V. with iodine. G. as SnO_2.
Zinc . . .	V. with ferrocyanide or sodium sulphide. G. as $Zn_2P_2O_7$.	G. as ZnO.

Speaking generally, a gravimetric process is preferable for small quantities to a volumetric where a certain excess of reagent is required to produce a good end-point, or still more to an indirect titration. Again, with still smaller quantities, the disadvantage of gravimetric methods lies in the fact that a small alteration in the weight of a crucible several thousand times heavier than its contents causes a considerable relative error in the determination, and if available a colorimetric process is much to be preferred.

§ **II. Separation of Elements.**—For the quantitative separation of the common elements into groups the procedure is similar to that followed in qualitative analysis, while that of the elements from one another often requires different methods in order to carry out their subsequent estimation. A subdivision into groups and quantitative separation of the common elements in an abridged form is given below.

A. HYDROGEN SULPHIDE PRECIPITATE.

First Case: Mercury is absent.

Digest H_2S-precipitate, hot, with $Na_2S + NaOH$. Filter, wash with hot dilute Na_2S-solution.

Filtrate: Procedure 1. Residue: Procedure 2.

Procedure 1.

Filtrate contains As, Sb, Sn, and a little Cu. Add Na_2SO_3 whilst boiling until yellow colour is discharged. Let settle, filter, wash with dilute Na_2S-solution.

P^1: CuS. Add to Procedure 2.

F^1: add excess of CH_3CO_2H, pass H_2S, boil, let settle, filter, reject filtrate. Boil ppte with strong H_2SO_4 until clear and sulphur has volatilised. Dilute with 1 vol. H_2O, cool, add 2·5 vol. strong HCl, pass H_2S, filter, wash with HCl (2·5 : 1 water), then with 5 per cent. H_2SO_4 to displace HCl.

P^2: As_2S_3. Dissolve in strong H_2SO_4, neutralise with $NaHCO_3$, titrate with I.

F_2: partially neutralise with NH_4OH, dilute, pass H_2S, filter, reject filtrate. Dissolve ppte in HCl + Br, boil gently to expel Br, reduce hot with piano wire (about 20 minutes), filter, wash with 5 per cent. HCl.

F^3: reduce with soft iron nails, cool in running water in CO_2 current, titrate Sn with I.

P^3: dissolve in HCl + Br, evaporate Br, ppte with H_2S, dissolve ppte in strong H_2SO_4, add H_2O and $\frac{1}{8}$ vol. of strong HCl, titrate Sb with $KMnO_4$.

Procedure 2.

Residue from Na_2S treatment: Ag, Pb, Bi, Cu, Cd sulphides. Add P^1, Procedure 1. Dissolve in HNO_3(1 : 3 H_2O), filter off sulphur, dilute to 200 c.c., add 10 c.c. of 10 per cent. KI, then 20 c.c. of HNO_3 (1 : 1); boil till I is expelled. Filter, wash with 5 per cent. HNO_3, then H_2O.

P^1: AgI. Dry, ignite, weigh.

F^1: evaporate with H_2SO_4 to fumes. Dilute with 5 vols. H_2O, boil, cool, filter, wash with 5 per cent. H_2SO_4.

F^2: add slight excess of Na_2CO_3, then 1–2 grm. KCN free from sulphur, digest hot, filter, wash.

P^2: $PbSO_4$. Wash with alcohol, dry, ignite, weigh.

P^3: dissolve in HNO_3, dilute till acid is N/3, heat almost to boiling, add small excess of N/5 Na_2HPO_4 solution, slowly, with constant stirring. Let settle, filter, wash with hot H_2O. Dry, incinerate filter separately, add ppte, ignite, weigh $BiPO_4$.

F^3: boil with dilute H_2SO_4 till HCN is expelled. Ppte feebly acid solution with H_2S, filter, digest ppte with hot H_2SO_4 (1 : 5 H_2O), filter, wash with 5 per cent. H_2SO_4.

P^4: CuS. Dissolve in HNO_3, apply iodide titration.

F^4: partly neutralise, ppte CdS; weigh as $CdSO_4$, or $Cd_2P_2O_7$.

Note.—If much Bi is present, omit H_2SO_4 treatment of F^1, and ppte Pb and Bi together with $Na_2CO_3 + KCN$. Dissolve ppte in HCl, boil with 1–2 grm. of piano wire till the latter is nearly dissolved; filter, wash with hot water. Dissolve ppte in HCl + Br, boil, ppte Bi with H_2S, filter, wash free from Fe; dissolve Bi_2S_3 in HNO_3, ppte $BiPO_4$ as under P^3. The filtrate from the iron pption is diluted and treated hot with H_2S; the ppte of PbS is converted into and weighed as $PbSO_4$.

Second Case: Mercury is present, Tin and Cadmium absent.

Procedure 3.

<table>
<tr><td colspan="3">Digest H_2S ppte with Na_2S, filter, and wash, as under First Case.</td></tr>
<tr><td>R^1: see Procedure 2.</td><td colspan="2">F^1: boil with excess of NH_4Cl; filter, wash with dilute $(NH_4)_2S$.</td></tr>
<tr><td colspan="2">P^2: HgS. Dissolve in $HCl+KClO_3$, expel Cl, ppte with $SnCl_2$, weigh Hg.</td><td>F^2: As, Sb, little Cu. See Procedure 1.</td></tr>
</table>

Third Case: Mercury, Tin, and Cadmium are present.

Procedure 4.

The simultaneous presence of mercury, tin, and cadmium in the H_2S precipitate (an exceptional case in ore analysis) complicates the procedure so much that it is not worth while determining all the constituents of the group in the same portion. Mercury and tin are best determined separately, while the other metals are separated as follows :—

<table>
<tr><td colspan="5">Digest H_2S ppte with Na_2S, filter, and wash, as under First Case.</td></tr>
<tr><td colspan="2">F^1: boil with excess of NH_4Cl, filter, wash with dilute $(NH_4)_2S$.</td><td colspan="3">R^1: evaporate to dryness with dilute HNO_3, heat residue to 110°, take up with hot dilute HNO_3, filter, wash with dilute HNO_3.</td></tr>
<tr><td>F^2: boil with Na_2SO_3, filter, wash.</td><td>P^2: reject.</td><td rowspan="2">F^4: add solutions from P^3 and R^5, add slight excess of Na_2CO_3, then 2–3 grm. KCN free from sulphur, digest hot, filter, wash.</td><td colspan="2">R^4: dry, ignite gently, fuse with Na_2CO_3+S, leach, filter, wash.</td></tr>
<tr><td>P^3: dissolve in HNO_3, add to F^4.</td><td>F^3: treat as F^1, Procedure 1, but reject filtrate containing Sn(F^3).</td><td>F^5: reject.</td><td>R^5: dissolve in dilute HNO_3, add to F^4.</td></tr>
<tr><td colspan="3">F^6; add slight excess of dilute HNO_3, warm gently, filter on tared paper, wash.</td><td colspan="2">P^6: Pb, Bi. See Note to Procedure 2.</td></tr>
<tr><td colspan="2">P^7: AgCN. Dry, weigh.</td><td colspan="3">F^7: add excess of Na_2CO_3, and KCN. Pass H_2S, adding more KCN if necessary to dissolve CuS. Filter, wash.</td></tr>
<tr><td colspan="2" rowspan="2">F^8: Cu. Boil with excess of H_2SO_4, ppte with H_2S, determine Cu by iodide.</td><td colspan="3">P^8: treat with hot dilute H_2SO_4 (1 : 5 H_2O). Filter, wash.</td></tr>
<tr><td colspan="2">F^9: Cd. See F^4, Procedure 2.</td><td>R^9: reject.</td></tr>
</table>

Separate mercury determination: Holloway-Eschka method.

Separate tin determination: Evaporate 1 grm. of the ore with HNO_3 to dryness, heat residue to 110°; take up with dilute HNO_3, filter, wash with dilute HNO_3, ignite residue gently, and fuse with Na_2O_2, etc., as in Pearce's method.

B. AMMONIA-AMMONIUM SULPHIDE GROUP.

First Case: Chromium is absent.

Procedure 5. (*Note.*—For materials containing little titanium and phosphoric acid. If the ore is rich in titanium, consult Titanium, § IX.; if rich in phosphoric acid, apply Procedure 13, and in F^3 thereof determine all the metals according to Procedures 1–10. If alkalies have to be determined in the same portion, precipitate the whole of this group with ammonia and ammonium sulphide, as in Procedure 7.)

Oxidise filtrate from H_2S ppte with HNO_3, and, if the introduction of much sodium salt is considered undesirable, evaporate nearly to dryness. Take up with a little HCl, and neutralise with Na_2CO_3. If no evaporation is made, neutralise at once with Na_2CO_3. Add 2–3 drops CH_3CO_2H, 2–3 grm. CH_3CO_2Na, 300–400 c.c. of hot H_2O, boil 1 minute; filter on ashless 11 or 12·5 cm. paper; dissolve ppte in a little HCl, repeat pption.

Combined F^1: see Procedure 6.

P^1: dissolve in HCl, pulping the filter. Ppte with slight excess of NH_4OH, filter, wash, ignite wet, weigh. If ppte is rich in Fe, dissolve in strong HCl; if Al predominates, fuse with $NaHSO_4$. Adjust acidity to 1 : 1 HCl, filter into separating funnel, wash with HCl (1 : 1).

R^2: Ignite in silica crucible, fuse with $NaHSO_4$, leach, add to S^3.

F^2: extract 3 times with ether.

S^3: evaporate ether, add solution from R_2, evaporate to strong fumes with 2 c.c. H_2SO_4. Take up with cold water, transfer to Nessler tube, add a few drops of H_2O_2 free from P_2O_5, determine TiO_2 colorimetrically.

Ether^3: evaporate on water-bath, take up with HCl, ppte with NH_4OH, weigh Fe_2O_3, or titrate.

Transfer to beaker, boil to decompose H_2O_2, add NH_4NO_3 and molybdate reagent, determine P_2O_5. Weight of mixed ppte − $(Fe_2O_3 + TiO_2 + P_2O_5) = Al_2O_3$.

Procedure 6.

Treat combined filtrates F^1, Procedure 5, with H_2S, and digest on steam-bath till the precipitate has settled. Filter, wash with H_2S-water containing a few drops of CH_3CO_2H.

P^1: dissolve in HCl + Br, evaporate excess of Br, carefully neutralise with NH_4OH, add 8–10 drops 2N-HCl and 2 grm. $(NH_4)_2SO_4$ per 100 c.c. bulk; heat to 50°, saturate with H_2S, allow to settle, filter, wash with 2 per cent. $(NH_4)_2SO_4$ solution saturated with H_2S.

P^2: ZnS. Dissolve in HCl and titrate, or weigh $Zn_2P_2O_7$.

F^2: boil to expel H_2S, concentrate to 50 c.c., add 2 grm. $NH_4H_2PO_4$, heat to boiling, add NH_4OH whilst stirring, finally drop by drop, till blue amorphous ppte becomes pink and crystalline. Filter, wash with hot H_2O. If much Co or Ni is present, dissolve in HCl and re-precipitate.

P^3: $CoNH_4PO_4$. Titrate, or weigh $Co_2P_2O_7$.

F^3: cool, add a drop of KI, titrate Ni with KCN.

F^1: boil to expel H_2S; neutralise almost completely with Na_2CO_3, boil, add 20 c.c. of bromine-water and 1–2 grm. CH_3CO_2Na; boil to expel Br. Filter, wash with hot H_2O.

P^4: MnO_2. Dissolve in $C_2O_4H_2$, titrate back with $KMnO_4$; or weigh as Mn_3O_4.

F^4: concentrate to 100–200 c.c.; apply Procedure 8 or 9, rejecting filtrate containing alkalies.

Second Case: Chromium is present.

Procedure 7. (See Note to Procedure 5 concerning P_2O_5 and TiO_2.)

Oxidise filtrate from H_2S ppte with HNO_3. To the hot solution add 5 grm. of NH_4Cl, a slight excess of NH_4OH, and freshly prepared $(NH_4)_2S$. Allow to stand warm overnight, filter, and wash with dilute $(NH_4)_2S$. If considerable quantities of alkaline earths are present, dissolve ppte in HCl, repeat pption, combine filtrates.

F^1: apply Procedure 8 or 9.

P^1: dissolve in HCl + Br, expel Br, cool, neutralise almost completely with Na_2CO_3, add 5 grm. NH_4Cl per 100 c.c. bulk and a slight excess of $BaCO_3$ emulsion. Let stand several hours, shaking frequently. Filter, decant 3 times with water; wash.

F^2: ppte with $(NH_4)_2S$, filter. Dissolve ppte in HCl + Br, boil, add 5 grm. NH_4Cl and NH_4OH, repeat pption with $(NH_4)_2S$. Filter off ppte, wash with $(NH_4)_2S$, reject filtrates. Dissolve ppte in HCl + Br, boil, neutralise with Na_2CO_3, add 2 grm. of CH_3CO_2Na and a few drops of CH_3CO_2H; continue as in Procedure 6, but reject filtrate from MnO_2.

P^2: dissolve in dilute HCl, boil to expel CO_2. Ppte with NH_4Cl, NH_4OH, and $(NH_4)_2S$; repeat pption, reject filtrates. Dissolve ppte in small excess of HCl, add 20 c.c. Br-water, pour into freshly-made NaOH in porcelain basin. Boil a minute, filter into small excess of HNO_3. Dissolve, repeat pption with NaOH + Br; combine filtrates.

P^3: dissolve in H_2SO_4; if solution is not clear, evaporate to fumes, cool, and dilute. Add tartaric acid (3 times the weight of $Fe_2O_3 + TiO_2$), pass H_2S to reduce Fe, boil to expel H_2S. Make faintly ammoniacal, saturate with H_2S. Filter, wash quickly with dilute $(NH_4)_2S$.

F^3: make faintly ammoniacal, boil, filter.

F^4: Exactly neutralise with NHO_3, ppte with $HgNO_3$, ignite ppte, weigh Cr_2O_3.

P^4: ignite, weigh, fuse with $NaHSO_4$, ppte P_2O_5 with molybdate, take Al_2O_3 by difference.

P^5: dissolve in H_2SO_4 for titration with $KMnO_4$; or oxidise solution, ppte with NH_4OH, weigh Fe_2O_3.

F^5: boil with 20 c.c. H_2SO_4 (1 : 1). When fuming, cover with watch-glass and continue heating till acid becomes colourless. Dilute, ppte with NH_4OH, ignite ppte, weigh TiO_2.

C. ALKALINE EARTHS.

First Case: Barium, Strontium, and Alkalies are absent.

Procedure 8.

The concentrated filtrate (F^4, Procedure 6, or F^1, Procedure 7) is treated with 5 grm. NH_4Cl if not already present, made ammoniacal, and ppted with $(NH_4)_2C_2O_4$. If much Mg is present, re-dissolve and repeat pption; combine filtrates.

P^1: CaC_2O_4. Titrate with $KMnO_4$, or weigh as CaO or $CaSO_4$.

F^1: concentrate, digest at a gentle heat with strong HNO_3 (3 times the weight of NH_4Cl present), evaporate nearly to dryness, take up with 2 c.c. of HCl, make ammoniacal, add slight excess of $NaNH_4HPO_4$, followed by $\frac{1}{10}$ the volume of strong NH_4OH. Filter next day, wash ppte with 10 per cent. NH_4OH, ignite, and weigh as $Mg_2P_2O_7$; or wash with 50 per cent. alcohol and titrate with N/5 acid.

Note.—If F^1 contains acetates added in the previous treatment, it is necessary to add more HNO_3 than indicated above.

Second Case: All the Alkaline Earths and Alkalies are present.

Procedure 9.

The concentrated filtrate (F^4, Procedure 6, or F^1, Procedure 7) is treated with 5 grm. of NH_4Cl if not already present, made ammoniacal, and ppted with $(NH_4)_2CO_3$. Filter and wash with hot water.

P^1: dissolve in HNO_3, add solution from P^4. Evaporate to dryness in a flask, heat residue for 1–2 hours at 140° in a current of warm air. Treat dry residue with ten times its weight of absolute alcohol in a stoppered flask, allow to stand 2 hours. Add equal volume of ether, set stoppered flask aside overnight. Filter, wash with ether-alcohol (1 : 1).

F^1: add 3–4 drops dilute H_2SO_4 and 1 c.c. $(NH_4)_2C_2O_4$, let stand overnight, filter.

P^4: ignite, fuse with Na_2CO_3, dissolve washed residue in HNO_3, add to P^1.

F^4: apply Procedures 10 or 11.

F^2: evaporate to dryness, take up with water, ppte CaO as oxalate.

R^2: dissolve in H_2O (300 c.c. per 1 grm. of mixture), boil, add 6 drops of CH_3CO_2H and 10 c.c. of 10 per cent. $(NH_4)_2CrO_4$. Let stand 1 hour. Filter, wash by decantation with very dilute $(NH_4)_2CrO_4$, then hot H_2O. Rinse back ppte, dissolve in little dilute HNO_3, dilute to 200 c.c., boil, add slowly 5 c.c. of $CH_3CO_2NH_4$ and enough $(NH_4)_2CrO_4$ to neutralise CH_3CO_2H (absence of smell). Let stand 1 hour, filter, wash with H_2O. Combine filtrates.

P^3: dry, ignite gently, weigh $BaCrO_4$.

F^3: concentrate, add excess of dilute H_2SO_4 and an equal volume of alcohol. Let stand overnight, filter, wash with 50 per cent. alcohol. Ignite, weigh $SrSO_4$.

D. MAGNESIA AND ALKALIES.

Procedure 10. (If sulphates are present, apply Procedure 11.)

Evaporate filtrate F^4, Procedure 9, to dryness in platinum. Gently ignite residue, take up with a little H_2O, add 1 grm. $C_2O_4H_2$, evaporate to dryness, ignite gently. Extract with a little H_2O, filter, wash.

R^1: MgO. Dry, ignite, weigh.

F^1: add small excess of HCl, evaporate in platinum, ignite gently, weigh $KCl + NaCl$ containing a little $MgCl_2$. Take up with a little H_2O and 1 drop HCl, add excess of H_2PtCl_6, evaporate to dryness, take up with strong alcohol, filter, wash with alcohol.

P^2: dry, separate from filter, rinse paper with hot water, evaporate washings to dryness, add ppte, heat to 160°, weigh K_2PtCl_6. Calculate KCl.

F^2: evaporate to dryness, take up with very dilute HCl, ppte Pt with H_2S (hot), filter, evaporate filtrate to small bulk, ppte small quantity of Mg as $MgNH_4PO_4$. Calculate $MgCl_2$. NaCl is obtained by difference.

Procedure 11.

The filtrate F^4, Procedure 9, is acidified with HCl and treated with sufficient $BaCl_2$ to ppte sulphates, followed by NH_4OH and $(NH_4)_2CO_3$ to remove excess of $BaCl_2$. Filter, reject ppte, evaporate filtrate to dryness, gently ignite residue, take up with a few drops of HCl, add $Ba(OH)_2$ till slightly alkaline, boil, filter, wash with hot water.

P^1: dissolve in slight excess of HCl, ppte hot with H_2SO_4, filter off $BaSO_4$, ppte MgO in filtrate as $MgNH_4PO_4$.

F^1: ppte with $NH_4OH + (NH_4)_2CO_3$, filter, evaporate filtrate to dryness, gently ignite residue, take up with a little H_2O, repeat pption to remove last traces of Ba. Evaporate filtrate, moisten residue with HCl, again evaporate, ignite residue gently, weigh $KCl + NaCl +$ small amount of $MgCl_2$. Apply Procedure 10, F^1.

E. COMMON ACID RADICLES.

These are assumed to have been converted into sodium salts by fusion with sodium carbonate.

First Case: Silica, Sulphuric Acid (as Barytes), Alumina, and small amounts of Titanic and Phosphoric Acids. Halogens and Boric Acid absent.

Procedure 12.

<table>
<tr><td colspan="4">Digest Na_2CO_3 melt with H_2O, acidify with HCl, evaporate to complete dryness on water-bath. Digest residue with strong HCl for 10 minutes. Add hot H_2O, filter by decantation, again pour decanted solution through filter, wash with acidulated water.</td></tr>
<tr><td colspan="2">R^1: add R^4. Ignite wet in platinum, weigh. Evaporate with $HF + H_2SO_4$, ignite with $(NH_4)_2CO_3$, weigh again.</td><td colspan="2">F^1: evaporate to complete dryness on water-bath. Take up with dilute HCl, filter, wash.</td></tr>
<tr><td>L^2: SiO_2.</td><td>R^2: fuse with $NaHSO_4$, leach with cold water. Filter, wash.</td><td rowspan="2">R^4: 2nd SiO_2. Add to R^1.</td><td rowspan="2">F^4: pass H_2S, filter, reject ppte. Oxidise filtrate with HNO_3, add F^3, ppte with $NH_4Cl + NH_4OH$, dissolve, re-ppte.</td></tr>
<tr><td>R^3: $BaSO_4$. Ignite, weigh.</td><td>F^3: add to F^4.</td></tr>
<tr><td colspan="4">Dissolve ppte in HCl (1 : 1), apply ether extraction (Procedure 5. F^2 *et seq.*).</td></tr>
</table>

Second Case: Phosphoric and Arsenic Acids, Fluorine, Chlorine, Silica, and Titanic Acid (*e.g.* in Apatite Group Minerals).

Procedure 13. (*Note.*—The fluorine determination is preferably carried out in a separate portion.)

<table>
<tr><td colspan="7">Extract Na_2CO_3 melt with hot water, filter, wash with 2 per cent. Na_2CO_3.</td></tr>
<tr><td colspan="3">R^1: dissolve in HCl in porcelain basin, evaporate to dryness, take up with HCl, filter.</td><td colspan="4">F^1: add 10 grm. of solid $(NH_4)_2CO_3$, let stand at 40° overnight. Filter, wash with $(NH_4)_2CO_3$-water.</td></tr>
<tr><td>R^2: 1st SiO_2. Add to R^3.</td><td colspan="2">F^2: evaporate to dryness, take up with HCl, filter.</td><td>P^5: add to P^6.</td><td colspan="3">F^5: add a few c.c. of ammoniacal ZnO-solution, boil till all NH_3 is expelled. Filter, wash.</td></tr>
<tr><td rowspan="3">F^3: pass H_2S, filter, reject Pt ppte; treat filtrate with NH_4OH, dissolve ppte in H_2SO_4, and continue as under P^3 *et seq.*, Procedure 7, to obtain TiO_2; add R^4, fuse with $NaHSO_4$, determine TiO_2 colorimetrically. (See Note *a.*)</td><td colspan="2">R^3: 2nd SiO_2. Add R^2, R^7, and R^8. Ignite and weigh. Treat with $HF + H_2SO_4$, ignite with $(NH_4)_2CO_3$, weigh again.</td><td colspan="2">P^6: add P^5; evaporate to dryness with HCl, filter, wash.</td><td colspan="2">F^6: add phenolphthalein, cautiously neutralise with HNO_3; add $AgNO_3$ solution, filter, wash with minimum of cold water.</td></tr>
<tr><td rowspan="2">L^4: SiO_2.</td><td rowspan="2">R^4: add to TiO_2 from F^3.</td><td>R^7: add to R^3</td><td>F^7: evaporate again with HCl, filter, wash.</td><td rowspan="2">F^9: contains F. See Note *b*, below.</td><td rowspan="2">P^9: extract with dilute HNO_3, filter, wash.</td></tr>
<tr><td>R^8: add to R^3.</td><td>F^8: add to solution from F^{10}.</td></tr>
<tr><td colspan="3"></td><td colspan="3">F^{10}: ppte with HCl, filter, wash, reject ppte, add F^8,</td><td>R^{10}: AgCl. Ignite, weigh.</td></tr>
<tr><td colspan="7">ppte with H_2S. Filter.</td></tr>
<tr><td colspan="4">P^{11}: determine As_2O_5.</td><td colspan="3">F^{11}: determine P_2O_5. (See Note *a.*)</td></tr>
</table>

Note a (to F^3).—If the metals are to be determined in the same portion, this filtrate is examined according to Procedures 1–10: F^{11} should then be examined for Al as well as for P_2O_5.

Note b.—Treatment of F^9. Ppte Ag with NaCl, filter, reject ppte. Add 1 c.c. of 2N-Na_2CO_3 solution to filtrate, boil, add excess of $CaCl_2$ solution, filter, wash with hot water. Transfer dried ppte to Pt dish, add filter ash. Ignite, digest with dilute CH_3CO_2H, take to dryness, extract with H_2O, filter, wash, dry; separate ppte from paper, ignite, weigh CaF_2.

Third Case: Silica, Fluorine, Boric Acid.

Procedure 14.

(*a*) *First Portion:* Boron. The solution of the Na_2CO_3 melt is faintly acidified with CH_3CO_2H, using litmus as indicator. Add slight excess of $Ca(CH_3CO_2)_2$, distil the whole with pure CH_3OH several times into a receiver containing a known weight of pure CaO previously slaked. The distillate is evaporated at very low temperature, the residue gently heated, transferred to a tared crucible with water, and ignited to constant weight. The increase in weight over CaO is B_2O_3.

(*b*) *Second Portion:* Silica and fluorine. Apply Procedure 13, obtaining SiO_2 in R^1, P^5, and P^6; in this case the three precipitates are mixed and treated as described under R^1. For fluorine, the filtrate from the ammoniacal ZnO treatment is treated with 1 c.c. of 2N-Na_2CO_3 solution, etc., as under F^9, Procedure 13.

§ **III. Other Methods of Separation.**—Besides the above group separations, a number of shorter methods can be applied where only two elements have to be separated, or where it is not intended to estimate every constituent in the same portion. Two elements belonging to different groups need not necessarily be separated by the group reagent. As with the actual estimation, the best method for separation will frequently depend on the quantities present; in making one's choice one should, if possible, aim at leaving or obtaining the predominant element in solution and at precipitating the subordinate, so as to avoid or minimise occlusion and co-precipitation and the washing of bulky precipitates; or at producing a crystalline or heavy, rather than an amorphous or voluminous, precipitate. Table X. is intended to illustrate this principle. The term " converse " may be applied to two methods if they can be used alternatively for the separation of two elements, subject to one being predominant or subordinate in quantity. To facilitate the use of the table, the number of each method is followed by that of its converse in brackets. Some separations are not perfect because a small quantity of the predominant element is carried down with the precipitated subordinate; in this case the precipitate is subjected to a second treatment by the same or the converse method, which is easily done on account of its small bulk. Thus in 18 (Table X.) the insoluble tin oxide takes down a small quantity of lead as stannate, and is treated as in 13: this is far better than extracting tin from lead sulphide by sodium sulphide.

Examples of separations by repeating the same treatment are found under 20, 31, 36, etc. Most of these methods can be used for separating

TABLE X.

Large Quantities of—	From Small Quantities of—					
	Arsenic.	Antimony.	Tin.	Lead.	Copper.	Bismuth.
A. Arsenic . .	. .	1 (6). Ammonium carbonate.	2 (11). Ammonium carbonate.	3 (16). Sodium sulphide.	4 (21). Sodium sulphide.	5 (26). Sodium sulphide.
Antimony . .	6 (1). H_2S in strong HCl.	. .	7 (12). Metallic iron.	8 (17). Potassium sulphide.	9 (22). Potassium sulphide.	10 (27). Potassium sulphide.
Tin . . .	11 (2). H_2S in strong HCl.	12 (7). H_2S in oxalic acid.	. .	13 (18). Sodium sulphide.	14 (23). Sodium sulphide.	15 (28). Sodium sulphide.
Lead . . .	16 (3). H_2SO_4.	17 (8). H_2SO_4 and tartaric acid.	18 (13). Nitric acid.	. .	19 (24). H_2SO_4.	20 (29). As BiOCl.
Copper . .	21 (4). By ferric chloride and ammonia.	22 (9). Same as 21; or thiocyanate and tartaric acid.	23 (14). Nitric acid.	24 (19). H_2SO_4; or electrolysis.	. .	25 (30). H_2S and potassium cyanide.
Bismuth . .	26 (5). H_2S in strong HCl.	27 (10). As BiOCl in tartaric acid.	28 (15). Metallic iron.	29 (20). As $PbSO_4$ in 1 : 5 H_2SO_4, or metallic iron.	30 (25). Thiocyanate.	. .
	Iron.	Aluminium.	Manganese.	Zinc.	Nickel.	Calcium.
B. Iron . . .	. .	31 (36). As phosphate, or by ether.	32 (41). Zinc oxide, or by ether.	33 (46). H_2S in formic acid, or by ether.	34 (51). Zinc oxide, barium carbonate, or by ether.	35 (56). As calcium oxalate in oxalic acid.
Aluminium .	36 (31). NaOH.	. .	37 (42). NaOH + Br.	38 (47). H_2S in acetic acid.	39 (52). NaOH + Br.	40 (57). Same as 35.
Manganese .	41 (32). Zinc oxide.	42 (37). Zinc oxide.	. .	43 (48). H_2S in acetic acid.	44 (53). Ammonium sulphide, followed by acetic acid.	45 (58). H_2SO_4 and alcohol.
Zinc . . .	46 (33). Ammonia.	47 (38). Ammonia.	48 (43). Bromine.	. .	49 (54). NaOH + Br.	50 (59). Oxalate.
Nickel . .	51 (34). Ammonia.	52 (39). Ammonia.	53 (44). Bromine.	54 (49). H_2S in faintly acid solution.	. .	55 (60). Oxalate.
Calcium . .	56 (35). Ammonia.	57 (40). Ammonia.	58 (45). Bromine.	59 (50). Ammonium sulphide.	60 (55). Ammonium sulphide.	. .

three or more elements (compare 7 and 28; 18 and 23; 41 and 42; 36, 37, and 39).

§ IV. Separation into Insoluble Residue and Soluble Fraction.—The usual acid treatment of minerals, etc., commonly results in a solution of the metals and an insoluble residue. Where the latter contains no metallic compounds, such as oxides of tin or antimony, chromite, tungstic acid, silver chloride, etc., it consists of the insoluble part of the gangue, chiefly silica, barium sulphate, or silicates.[1] The silica was either originally present as quartz or liberated from a silicate by the acid treatment. Most silicates and rocks, though termed insoluble, yield a small soluble fraction, the amount of which may vary with the size of grain and degree of weathering of the mineral, the nature and quantity of acids used, the time of contact, and the temperature of decomposition. Thus the insoluble is generally higher with sulphuric than with hydrochloric acid. Even when working under the same conditions the results of duplicate trials may sometimes disagree; of this the following is an example (from H. Ries, *Clays*, 1908, p. 69):—

Successive Treatment with HCl and H_2SO_4.	Muscovite.		Biotite.	
1. Soluble in hydrochloric acid . .	18·64	17·80	77·73	73·34
2. „ in sulphuric acid . . .	38·75	41·80	2·04	7·88

Another source of error lies in the fact that silicic acid resulting from decomposition of silicates is not quite insoluble even after careful dehydration, a few mgrms. being always recovered from the filtrate upon evaporation to dryness; even then a small fraction still remains soluble, and part of this is precipitated along with alumina in the subsequent treatment.

Generally speaking, hydrochloric is to be preferred to sulphuric acid in the separation of the insoluble. Barytes is soluble in hot concentrated sulphuric acid, and reprecipitated on dilution; the precipitate almost invariably carries down other sulphates, especially lead, which it tenaciously retains. Fluorite in the gangue will cause loss in silica if the usual acid treatment is applied, while glass or porcelain may be slightly attacked and yield soluble bases. The method of Berzelius is available for the determination of fluorine and silica in ores containing them (Procedures 13 and 14).

Unless the gangue is entirely composed of altogether insoluble material, such as quartz or barytes, the insoluble figure gives no exact indication of the amount of gangue; the weight is simply that of the unattacked portion, *plus* any silica that may have separated. The distinction between, and separation into, a soluble and insoluble fraction is thus more or less arbitrary and imperfect, and merely based upon

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[1] For the complete analysis of silicate rocks consult Hillebrand, *U.S. Geol. Survey Bull.* 422; Washington, *Manual of the Chemical Analysis of Rocks* (1904).

the action of the common acids on minerals. In order to obviate the errors to which the separation of the insoluble is liable, the following points should be kept in mind :—

(*a*) The decomposition is done, wherever possible, with hydrochloric acid, with or without a nitric acid treatment ; the assay is evaporated to complete dryness, preferably on a water-bath.

(*b*) The filtrate from the insoluble is again evaporated to complete dryness to recover soluble silica.

(*c*) The portion in which the insoluble is determined must also serve for the estimation of all the earths and silicate-forming bases, because silicates are not always attacked to the same extent.

(*d*) It must not be forgotten that hydrated silicates may be present, which lose their water on ignition. Weighing the latter on a tared filter previous to igniting would not give the whole of the combined water, as some may have been lost through the partial decomposition of silicates in the acid treatment. (For estimation of combined water see § VII.)

(*e*) Many mineral products contain organic or carbonaceous (graphitic) matter, which remains with the insoluble residue. In case hydrated silicates are present, the usual method of weighing the insoluble before and after ignition would produce erroneous results ; it is therefore best to treat the insoluble from another portion with hydrochloric and hydrofluoric acids to break up the silicates, and to collect on a tared filter after evaporating and taking up with dilute acid. After weighing, the filter is incinerated and the ash subtracted.

§ V. Determination of Heavy Metals.—In order to minimise chances of error in the analysis of ores the decomposition of which is tedious or difficult, the heavy metals present should be determined in the same portion as the bases and insoluble residue. On the other hand, while the behaviour of silicates to acids may be uncertain, the decomposition of sulphides is in most cases a simple matter ; therefore, where several heavy sulphide metals are present, the separation of which would entail much care and manipulation, it is legitimate, for the sake of expediency in technical work, to estimate some of them along with the lighter metals, and the remainder in a separate portion. A few examples may here be given :—

(*a*) If copper, antimony, and tin are present in the hydrogen sulphide precipitate, it is convenient to determine the tin in the first portion after precipitating copper and antimony by means of metallic iron ; while in the other portion copper is separated by treating the sulphides with potassium sulphide, tin not interfering in the volumetric determination of antimony by permanganate.

(*b*) If the filtrate from iron and alumina contains zinc, lime, and magnesia, the two latter are precipitated as usual, zinc not interfering ; in another portion, the same filtrate is used for the volumetric assay of zinc.

(*c*) With ores containing lead, antimony, or arsenic as principal or important constituents, the decomposition by strong sulphuric acid alone presents advantages as regards separation and estimation of these metals. Lead is converted into sulphate, which is filtered off and dissolved in ammonium acetate. The solution is filtered from the gangue, re-precipitated with sulphuric acid, and concentrated by evaporation. The original sulphate precipitate is apt to include small quantities of antimony, bismuth, iron, or lime, which remain dissolved in the liquor on re-precipitating the lead. Arsenic and antimony are converted into their lower oxides, or, if present in the pentavalent state, are reduced by adding filter paper to the strong acid and boiling till colourless. Trivalent arsenic, unlike pentavalent, is readily precipitated by hydrogen sulphide, and at the same time separated from antimony by adding twice the volume of strong hydrochloric acid to the filtrate from the lead sulphate. The filtrate from the arsenic precipitate is partially neutralised for the precipitation of antimony sulphide, to which is added the small quantity recovered from the filtrate of the re-precipitated lead sulphate.

The simultaneous determination of the insoluble residue and all the soluble metals may also be carried out by taking 2·5 grm. of ore and making up the volume of the filtrate from the insoluble to 250 c.c. Two 100 c.c. portions are then measured off, and worked upon separately for different metals, as explained above.

§ VI. Separate Determination of Certain Constituents.—In addition to the general method outlined in §§ IV. and V., special trials will be required for elements present in minute quantity, or determinations necessitating the use of certain apparatus and reagents undesirable in the combination scheme.

Elements Present in Small Quantities.—The most important and common example is the gold and silver assay, which is done by crucible fusion or scorification. Any element occurring in small quantity may at times have to be tested for separately on a larger quantity of ore, especially where it constitutes an objectionable impurity. Of this the determination of cadmium in zinc blende is a typical example: the fact that it always occurs in small proportion, and that its precipitation by hydrogen sulphide is a delicate operation, renders a separate estimation desirable, especially as the result is of great importance to the smelter.

The other assays of this class include :—

(*a*) *Sulphur.*—Whether the assay involves a fusion or not, sulphur is always estimated separately. It should not be determined in solutions having undergone treatment with hydrogen sulphide, as small quantities of sulphuric acid may have formed in presence of oxidising compounds.

(*b*) *Fusion assays*, such as :—

Potassium cyanide for tin (in presence of tungsten).
Sodium hydroxide or peroxide, for tin or antimony.
Sodium carbonate and potassium nitrate, for arsenic or antimony.
Sodium carbonate and sulphur, for arsenic or antimony.
Calcium carbonate and ammonium chloride, for alkalies.

(*c*) *Distillation assays,* for mercury, arsenic, fluorine, boric acid.
(*d*) *Gasometric methods.*—Nitric acid, carbon dioxide.
(*e*) *Decompositions* by means of hydrofluoric acid.
(*f*) *Determinations* involving the use of organic acids.

§ **VII. Oxidised Minerals.**—Besides the operations so far described, the analysis of minerals other than sulphides may require the determination of combined water, carbon dioxide, or of oxygen present in various forms of combination. Thus oxides, peroxides, hydroxides, carbonates, sulphates, or hydrated silicates may be present. The analysis is carried out as follows:—

1. *Silica and total metals* are determined in one portion, or two if more convenient.

2. *Total combined water* (in hydroxides, hydrated sulphates, and silicates, etc.); direct estimation by Penfield's method.[1]

3. *Carbon Dioxide.*—This is most conveniently estimated in a Geissler or similar apparatus by decomposition with an acid.[2] For clean carbonates, fusion with borax answers well.[3]

4. *Sulphuric Anhydride.*—Sulphates of barium and strontium require fusion with sodium carbonate; those of lead and lime are opened up by boiling with ammonium carbonate; basic sulphates dissolve in dilute acids. The determination differs from that of sulphur in that no oxidising agent is used.

5. *Differentiation between Higher and Lower Oxides.*—The following commoner elements occur in ores in different states of oxidation: iron, manganese, cobalt, chromium, antimony, and arsenic. Therefore, if found to be present, it will be necessary to ascertain their state of oxidation.

Iron.—Ferrous oxide is usually determined by decomposing the ore in an atmosphere of carbon dioxide and titrating with permanganate, ferric oxide being found by difference. Chalybite and vivianite are soluble in dilute sulphuric acid; magnetite and ilmenite are opened up by fusion with bisulphate, silicates by hydrofluoric acid.[4] Very often the direct determination of ferric iron is more convenient, since ferric compounds are more readily dissolved than ferrous (*e.g.* in silicates, spinels, etc.). The ore is attacked with hydrochloric acid in an atmosphere of carbon dioxide, and the hot solution titrated with stannous chloride till colourless. Copper or arsenates must not be present.

Manganese.—The intermediate oxides act like mixtures of the proto- and the peroxide, which latter is determined by oxalic acid, or ferrous ammonium sulphate, and permanganate. The higher oxides of manganese interfere with the determination of ferrous oxide, and *vice versa*; they react upon one another with formation of ferric and manganous salts, though the amount of excess oxygen can, of course, be correctly ascertained.

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[1] *Amer. Journ. Sci.*, 1894, **48**, 30.
[2] "Direct Determination," Hillebrand, *U.S. Geol. Survey Bull.* 422, p. 179.
[3] Fresenius, *Quantitative Chemical Analysis*, 7th edition (1876), 336.
[4] Hillebrand, *U.S. Geol. Survey Bull.* 422, p. 161.

Cobalt.—The sesquioxide occurs in the mineral asbolan. It can be determined like manganese dioxide, also by distillation with hydrochloric acid and potassium iodide.

Chromium.—Chromic oxide is found in some bauxites; combined with ferrous oxide it occurs as chromite, which always contains more or less ferric iron. The ferrous oxide is determined by heating 0·5 grm. of the finely-powdered mineral with 10 c.c. of sulphuric acid (sp. gr. 1·34) in a pressure tube at 250° to 300° for ten hours (paraffin bath) and titrating the solution with permanganate. Chromates are determined similarly to manganese peroxide, by dissolving the mineral in an acid solution of ferrous sulphate and ascertaining the excess of the latter.

Antimony.—Oxidised ores may contain tri- and tetroxide, the former being soluble in tartaric or dilute hydrochloric acid. Total antimony is determined by fusion with sodium carbonate and sulphur, and the insoluble oxide found by difference.

Arsenic.—To differentiate between arsenious and arsenic acid the mineral is boiled with caustic alkali. The arsenite in the filtrate may be titrated with iodine, or the arsenate with iodide and thiosulphate.

§ VIII. Mixed Oxide and Sulphide Ores.—If the sample under examination contains both oxidised minerals and sulphides, the latter will interfere with the determination of combined water and carbonic acid described under § VII. It also becomes necessary to estimate the metals present as oxides.

1. *Combined Water.*—Direct estimation in a Penfield tube by adding ignited litharge or bismuth oxide as a retainer for sulphur. In presence of fluorides, ignited lime is mixed with the substance.

2. *Carbon Dioxide.*—The ore is decomposed by a mineral (but not hydrochloric) acid, and sufficient potassium chromate to oxidise the sulphides, or an organic acid, such as tartaric acid, may be used. Calcite is decomposed by bichromate solution alone, without the addition of an acid.

3. *Sulphur as Sulphides and Sulphates.*—Minerals containing sulphur may be classified as follows according to their solubilities :—

(*a*) Sulphates soluble in water (" vitriols ").

(*b*) Sulphates of calcium and lead, and basic sulphates (*e.g.* brochantite), soluble in hydrochloric acid, or decomposed by boiling ammonium carbonate solution.

(*c*) Sulphides soluble in hydrochloric acid (*e.g.* galena, blende, stibnite).

(*d*) Sulphides insoluble in hydrochloric acid (*e.g.* pyrites, sulphides of copper).

(*e*) Insoluble sulphates (of barium and strontium).

Extraction with ammonium carbonate solution yields a solution of sulphur trioxide from (*a*) and (*b*); nitric acid and potassium chlorate dissolve the sulphur from (*c*) and (*d*); the sulphuric anhydride in the insoluble residue from this treatment is determined after fusion with sodium carbonate.

TABLE XI.

	1.	2.	3.	4.	5.	6.	7.
	Water.	A. Acetic, or B. Tartaric Acid.	A. Caustic Soda, or B. Ammonia.	Hydrochloric Acid. A. Dilute. B. Strong.	Nitric Acid.	Fusion with Sodium— A. Bisulphate, or B. Carbonate.	A. Hydroxide, or B. Peroxide.
Lead . .	. .	A. Carbonate.	A. Sulphate.	A, B. Sulphide. →	Sulphide.	. .	. .
Copper . .	Sulphate.	A. Carbonates, Oxides, Basic sulphates, Oxychloride.	→ B.	B. Silicates.	Sulphides, Arsenides, Antimonides. Native.	. .	. .
Silver . .	. .	. .	B. Chloride.	. .	Sulphide, Arsenides, etc. Native.	. .	. .
Antimony .	. .	B. Trioxide →	A. Trioxide, Sulphide. →	A, B. Sulphide. →	Sulphide.[1]	. .	A. Tetroxide.
Tin . .	. .	. .	. .	. .	Sulphide.[2]	. .	B. Oxide.
Iron . .	Sulphate.	A, B. Carbonate.	. .	B. Oxides.[3] A, B: Hydroxides, Pyrrhotine. →	. . Pyrites, Arsenides, Pyrrhotine.	A. Ilmenite, Magnetite, Chromite. → B. Silicates.	B. Chromite.
Zinc . .	Sulphate.	A. Carbonate (in 50 per cent. acid). →	A. Carbonate, Silicate.	A, B. Sulphide. →	Sulphide.	A, B: Zinc spinels.[4]	. .
Nickel (cobalt)	Sulphates.	Carbonates.	. .	Arsenates. B. Ni-silicate.	Sulphides. Arsenides.	A, B. Ni-silicate.	. .
Manganese .	. .	Carbonate.	. .	Sulphide,[5] Peroxides.	Sulphide.	B. Silicates.	. .
Calcium . .	Sulphate.[6]	Carbonate.	. .	A. Phosphate.	. .	B. Silicates.	. .
Barium . .	. .	Carbonate.	. .	. .	. .	B. Sulphate.	. .

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[1] Separation of sulphide from tetroxide by hydrochloric or nitro-tartaric acid.
[2] Stannine: dissolve in *aqua regia*.
[3] Some oxide ores are difficultly soluble in hydrochloric acid: fuse with bisulphate.
[4] Addition of borax glass advisable when sodium carbonate is used.
[5] In zinc blende.
[6] If much sulphate is present, extract with sodium sulphate or chloride solution.

Barium (or strontium) carbonate, which forms an occasional gangue mineral of sulphide ores, interferes with the determination of sulphide sulphur by being converted into insoluble sulphate. In such a case the alkaline earth carbonate is removed by a preliminary treatment with acetic acid.

4. *Differentiation between Oxides, Sulphides, etc.*—In estimating oxides of metals in presence of their sulphides, advantage is taken of the different behaviour of minerals towards certain reagents which dissolve some while leaving others unaffected. The same principle is applied in separating various oxidised minerals from one another.

The percentage of total metals, sulphur, silica, etc., having been determined as described in the preceding paragraphs, a fresh portion of sample is attacked with a suitable solvent and the resulting solution examined for metals by the usual methods, while the residue is subjected to extraction by another solvent if necessary.

A scheme for the separation of the more important minerals of the common metals is outlined in Table XI., in which the vertical columns indicate the order in which the reagents are used; these are distinguished by lettering (A, B). The horizontal lines show the order of solution of the minerals. Some are soluble in reagents placed in successive vertical columns; this is indicated by arrows inserted between the names.

The procedure outlined in the table separates the ore into an "insoluble residue" and "soluble fraction," much in the same manner as does hydrochloric acid or *aqua regia* in the determination, described in paragraph IV., of the insoluble gangue and total metals; but what has been said there with regard to the behaviour of silicates towards acids applies to a much greater extent to the separation of minerals by selective decomposition. Not only does the degree of decomposition vary with the temperature, quantity, and concentration of solvent used, the time of contact. and the degree of comminution, but the dissolved constituents themselves may exert a slight solvent action. Moreover, crystalline varieties are often less soluble than amorphous ones. The solubility may also be affected by impurities or isomorphous replacements. In this manner a small amount may escape solution, or be dissolved, by a reagent contrary to the ordinary behaviour of the mineral. If thereby metals present as sulphides are calculated to oxides, or *vice versa*, the final summation will be affected. It should therefore be borne in mind that separations by fractional decomposition, while quantitative in many cases, are far from satisfactory in others. At times it is practically impossible to establish the exact composition of a complex ore by direct analysis, in which case it is legitimate to compute the quantity of one or more oxides present by calculation on the assay results. The mineralogical examination is the most valuable help where chemical methods fail.

Where hydrochloric acid dissolves both the sulphides and oxides of the same metal, the order of the reagents in columns 4 and 5 of the table may be inverted, thus :—

	4.	5.	6.
	Nitric acid.	Hydrochloric acid.	A. Sodium bisulphate. B. ,, carbonate.
Iron . .	Pyrites, arsenides, pyrrhotine.	Hydroxides, oxides.	A. Oxides.
Manganese .	Sulphide.	Peroxides.	B. Silicates.

Pyrrhotine may also be separated from pyrites, limonite, etc., by means of a horseshoe magnet.[1]

§ **IX. Determinations by Difference.**—When making determinations by difference, the following rule is observed wherever possible: After the sum of the constituents has been ascertained, the subordinate is estimated direct and the predominant found by difference. If the reverse is done, though this may not affect the final result, the experimental error is all thrown on the side of the subordinate element, and the smaller its amount the less reliable will be the figure so obtained. To take one constituent by difference, by subtracting the sum of all the others from 100·00, is an objectionable practice in mineral analysis; it is admissible only in the case of refined metals, the fineness of which is ascertained by determining the impurities.

The "loss on ignition method" for the estimation of combined water can only be used occasionally, as with some oxidised minerals, such as bauxite, limonite, and certain silicates. Organic matter, carbonates, sulphides, sulpharsenides, etc., cause high results, while ferrous compounds lower them. With a little practice, Penfield's direct determination of combined water is almost as simple as that by loss on ignition.

In a few cases carbon dioxide and combined water can be estimated together by loss on ignition—viz. with oxidised ores free from sulphur, consisting of carbonates of copper, zinc, or lead, with or without ferric oxides or hydroxides. This is done at a gentle heat in a porcelain crucible, avoiding reduction of its contents by the burner gases.

§ **X. Accuracy. "Traces."**—Concerning the degree of accuracy to be attained, a final error of ±0·50 per cent. should not be greatly exceeded, and a complete analysis which sums up to between 99·50 and 100·50 is very satisfactory. The results are calculated to the second decimal place. To go beyond this is useless in practical ore analysis.

The use of the term "trace" may here be considered, as opinions differ regarding the amount to which it should be applied. However, from the point of view of technical ore analysis, we may define as "trace" a quantity that does not affect the final result, *i.e.* less than 0·01 per cent. (This does not, of course, apply to noble metals, which are calculated to ounces per ton.)

In scientific work (*e.g.* geochemistry, genesis of ore deposits, distri-

[1] Lunge-Keane, *Technical Methods of Chemical Analysis*, vol. i. part 1, p. 289.

bution of elements, etc.) a full analysis also includes the determination of elements present in " spectroscopic " traces, and often involves the working up of large quantities of material. The description of such work is beyond the scope of this book, and it must be understood that the term " complete analysis " is applied throughout to the estimation of the major constituents of minerals, as carried out by the more elementary methods here described.

CHAPTER II.

THE FIRST GROUP.

LITHIUM—RUBIDIUM—CÆSIUM.

GENERALITIES.

Of the three rarer metals of the alkali group, lithium is related to sodium. Thus the chloroplatinates of the two metals crystallise with six molecules of water, and are very soluble in water and in alcohol. On the other hand, the comparative insolubility of lithium carbonate, fluoride, and phosphate establishes a certain similarity with calcium.

Rubidium and cæsium bear such a close resemblance to potassium as to render almost impossible their identification by chemical methods in presence of each other. All the more important salts of the three metals are isomorphous, and they are precipitated together by all the reagents used for the precipitation of potassium.

The spectroscope is indispensable in all analytical work on the rarer alkali metals.

LITHIUM.

§ I. Minerals.—(*a*) *Lepidolite*, lithium mica, $Li_3Al(SiO_3)_3$, closely resembles muscovite except in colour, which is violet, lilac, or rose-red, though sometimes white. H 2·5–4; sp. gr. 2·8–3. Often contains rubidium, cæsium, and fluorine. *Zinnwaldite* is another (hydrous) variety of lithium mica.

(*b*) *Spodumene*, $LiAl(SiO_3)_2$, belongs to the monoclinic pyroxene group. Greenish or greyish, translucent crystals of pearly lustre. H 7; sp. gr. 3·1.

(*c*) *Petalite*, $LiAl(Si_2O_5)_2$, is usually massive, rarely crystallised. Colourless or white, transparent to translucent. H 6; sp. gr. 2·5. This, like the preceding minerals, is practically unattacked by acids.

(*d*) *Amblygonite*, lithium aluminium fluophosphate, $Li(AlF)PO_4$. White, yellow, green, or brown triclinic crystals of perfect cleavage. Soluble in sulphuric acid. H 6; sp. gr. 3.

(*e*) *Triphylite* and *lithiophylite* are lithium iron manganese phosphates, $Li(Fe,Mn)PO_4$. Orthorhombic, lustre vitreous to resinous. H 4·5; sp. gr. 3·5. The colour of the former, in which iron predominates, is greenish-grey to bluish; the latter, containing more manganese, is salmon-coloured to yellow-brown.

(*f*) *Beryl* (*q.v.*) often carries lithia.

(*g*) The element is widely distributed in small quantities in alkali minerals, *e.g.* felspars, micas, and rocks containing them. Through the disintegration of the latter it is converted into soluble salts, hence it occurs in spring and mineral waters and in soils. It is absorbed by vegetable organisms, and has been detected in many plant ashes.

§ **II. Properties and Compounds.**—(*a*) The *metal* is obtained, like sodium, by heating the carbonate with charcoal. It is silver-white on fresh surfaces, softer than lead, and the lightest solid (sp. gr. 0·59). Its melting-point is 180°; it combines directly with oxygen to Li_2O, hydrogen to LiH, nitrogen to Li_3N, and the halogens. Acids dissolve it with ease, while water is decomposed by it, though not violently.

(*b*) *Lithium hydroxide*, $LiOH.H_2O$, is formed by the action of the metal on water, or by double decomposition between lithium sulphate and barium hydroxide. Colourless crystals, which lose their water of hydration when heated in a current of hydrogen.

(*c*) *Lithium chloride*, $LiCl$, obtained by dissolving the hydroxide or carbonate in hydrochloric acid, forms colourless, extremely deliquescent, crystals, very soluble in water, also in various alcohols and in pyridine. The salt melts at 606°. Evaporation of its aqueous solution to dryness causes very slight hydrolysis; the residue is not quite soluble in pyridine, and imparts alkaline reaction to water.

(*d*) *Lithium chloroplatinate*, $Li_2PtCl_6.6H_2O$, resembles the sodium salt, and is readily soluble in water as well as in a mixture of alcohol and ether.

(*e*) The *nitrate*, $LiNO_3$, is isomorphous with sodium nitrate; very soluble in water and in alcohol.

(*f*) *Lithium sulphate*, $Li_2SO_4.H_2O$; soluble in water and in alcohol.

(*g*) *Lithium carbonate*, Li_2CO_3, is a white crystalline powder obtained when a strong solution of the chloride is poured into an ammoniacal solution of ammonium carbonate and the liquid heated. 100 parts of water dissolve 1·4 parts at 10°, and 0·73 part at 100°. It is more soluble in presence of salts of sodium and potassium, and much more so in presence of ammonium salts. The carbonate is completely dissociated when heated to 780° in a current of hydrogen.

(*h*) *Trilithium phosphate*, $2Li_3PO_4.H_2O$, is precipitated by addition of sodium phosphate solution to solutions of lithium salts. The precipitation is not complete unless caustic soda is added to neutralise the free acid formed: $3Li_2SO_4+2Na_2HPO_4=2Li_3PO_4+2Na_2SO_4+H_2SO_4$. The crystalline precipitate becomes anhydrous at 100°. It is soluble in 2539 parts of water or 3920 parts of dilute ammonia, but much more soluble in presence of ammonium salts.

(*i*) The *fluoride*, LiF, is precipitated from lithium solutions by ammonium fluoride. Soluble in 800 parts of water.

§ **III. Quantitative Separation.**—(*a*) The separation of lithium from metals of other analytical groups is carried out like that of sodium and potassium. For the separation of alumina the basic acetate process should be adopted, as the hydroxide precipitated by ammonia retains lithium. The separation of the alkaline-earth group with ammonium carbonate must be carried out in presence of considerable ammonium chloride, and the precipitate thoroughly washed with hot water (*cf.* § II. (*g*)); it is advisable to dissolve the precipitate in hydrochloric acid and repeat the precipitation. The combined filtrates and washings, if at all bulky, should be concentrated and tested for calcium (strontium) with sulphuric acid and alcohol. Calcium oxalate precipitated in presence of lithium is always contaminated with the latter, and it is difficult to effect complete removal by washing. Magnesium is precipitated by lime water after expelling ammonium salts. The separation of lithium from the other metals of the alkali group will now be described.

(*b*) *Separation from Large Quantities of Sodium and Potassium.*[1]—The solution of the chlorides is concentrated as much as possible, and saturated with hydrochloric acid gas introduced into the flask by means of a tube, the enlarged end of which terminates just above the level of the liquid. Most of the sodium and potassium are precipitated as chlorides. The acid liquor is filtered through asbestos, and the precipitate thoroughly washed with strong hydrochloric acid. The filtrate and washings, containing all the lithium and a little potassium and sodium, are evaporated to dryness, the residue dissolved in water and a few drops of hydrochloric acid, and treated as under (*c*).

(*c*) *Separation from all other Alkali Metals.*—This is based on the solubility of lithium chloride in certain organic solvents, such as amyl alcohol, pyridine, or a mixture of equal volumes of ethyl alcohol and ether (both absolute). Except the first named, these solvents are added to the dehydrated mixed chlorides and the mixture heated to boiling to dissolve the lithium salt. With pyridine, two (sometimes three) extractions are necessary. If ether-alcohol is used, the chloride mixture is allowed to stand overnight in contact with the menstruum. Gooch's amyl alcohol method [2] is carried out as follows :—

The concentrated solution, containing less than 0·2 grm. of the mixed chlorides and a few drops of hydrochloric acid, is treated in a small conical flask with 10 c.c. of amyl alcohol (B.P. 129°–132°), and cautiously heated on an asbestos gauze; the flask is provided with a capillary tube, passing through a doubly-perforated stopper and dipping into the liquid, through which air is passed by aspiration to facilitate boiling. When all the water and part of the alcohol have been driven off the liquid is allowed to cool; 2–3 drops of strong hydrochloric acid are then added to convert into chloride the small quantity of lithium hydroxide formed by hydrolysis. The liquor is boiled for a short time, and filtered whilst hot through asbestos. The residue is carefully washed with boiled amyl alcohol, the filtrate and washings evaporated to dryness in an air-bath, the residue dissolved in dilute sulphuric acid, and filtered from organic residue into a tared platinum crucible; this solution is evaporated to dryness, the residue gently heated till fused,

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[1] Treadwell-Hall, *Analytical Chemistry*, 1905, vol. ii. 45, 52.

[2] *Amer. Chem. Journ.*, 1887, **9**, 33. 100 c.c. dissolve 6·6 grm. LiCl.

the crucible covered, cooled, and weighed. If the proportion of lithium in the mixed chlorides is small, the residue from the extraction with amyl alcohol should be dissolved in water and the treatment repeated. As the weighed lithium sulphate contains small quantities of the other alkalies, a correction must be applied. For every 10 c.c. of alcoholic filtrate (exclusive of the alcohol used for washing) the following deduction is made from the weight found :—

0·0005 grm. if sodium is present.
0·00059 ,, ,, potassium is ,,
0·00109 ,, ,, sodium and potassium are present.

The solubility of rubidium and cæsium chlorides is of the same order (*i.e.* 0·0009 grm. per 10 c.c.). If sodium and potassium are also determined, corresponding additions must be made to the weight of the chlorides, *i.e.* 0·00041 grm. for sodium and 0·00051 for potassium per 10 c.c. of alcoholic liquor.

(*d*) *Separation from Potassium.*—When potassium is precipitated as chloroplatinate in presence of lithium by the usual process, some lithium is occluded in the precipitate ; hence it is preferable to use the above extraction method.

§ **IV. Gravimetric Determination.**[1]—(*a*) The determination as sulphate has already been described under § III, (*c*). It is the most convenient method, and the precautions required in the case of potassium and sodium are unnecessary, as no acid sulphate is formed.

(*b*) As *phosphate*,[2] Li_3PO_4. This mode of working yields high results. To the chloride solution a concentrated solution of sodium phosphate and a slight excess of caustic soda are added. The residue left after evaporation is taken up with a minimum of warm water followed by an equal volume of ammonia. After standing for twelve hours, the precipitate is filtered off and washed with ammonia ; the filtrate and first washings are evaporated to dryness, and the residue again treated as before ; it should dissolve completely in ammonia, and any residue must be filtered off. The precipitates are dried, separated from the paper, and ignited to constant weight.

§ **V. Volumetric Determination.**—Lithium hydroxide, carbonate, etc., may be determined according to the ordinary processes of alkalimetry.

$$1 \text{ c.c. } \frac{n}{10} \text{ acid} = 0{\cdot}001494 \text{ grm. } Li_2O.$$

§ **VI. Detection in Minerals.**—(*a*) Lithium compounds and minerals impart to the flame a beautiful crimson colour. The reaction is made more sensitive by first moistening the material with strong hydrochloric acid ; some minerals require fusion with potassium bisulphate and acide fluoride in a loop of platinum wire. The colour is masked by the yellow sodium flame, but can be distinguished through blue glass or a thin layer of indigo solution. Potassium in considerable quantity like-

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[1] Estimation as fluoride : Carnot, *Z. anal. Chem.*, 1890, **29**, 332.
[2] Mayer, *Annalen*, 1856, **98**, 193.

wise interferes with the test. For the certain detection of lithium, especially small quantities, recourse must be had to the spectroscope; when observed through it, the spectrum of lithium is seen to consist of two lines in the red, α (32)=6708 and β (45)=6104.[1] The reaction is so sensitive that unweighable traces of lithium can thereby be detected; as little as 0·000,001 mgrm. will produce a transient appearance of the red lines. They are intense and persistent if the mineral under investigation contains weighable quantities.

(*b*) If it is desired to prove the presence of lithium by a wet reaction, the finely-powdered mineral, if a silicate, is opened up with hydrochloric and hydrofluoric acids; the acid liquor is evaporated to decompose fluorides, diluted, and precipitated with baryta or lime water. Phosphate minerals are best treated by L. Smith's method, and the ignited product leached with hot water. In either case the alkaline earths are precipitated in the filtrate with ammonium carbonate or oxalate, the solution filtered and evaporated to dryness, and the ammonium salts expelled by gentle ignition. The residue is extracted with ether-alcohol and two drops of hydrochloric acid, and the filtered extract evaporated to dryness. The residue is dissolved in a little water, and the solution divided into two parts. One is treated with sodium phosphate, as shown under (*b*), § IV.; the phosphate precipitate is soluble in hydrochloric acid, and the solution remains clear on addition of ammonia; but on boiling, a heavy crystalline precipitate is produced. The other half of the solution is heated with ammonium carbonate (§ II, (*g*)); the washed carbonate precipitate may be converted into chloride and the latter submitted to the flame test (*a*).

§ VII. Determination in Minerals.—The procedure for the determination of lithium in minerals does not differ from that followed in the case of sodium and potassium up to the point where the pure mixed alkali chlorides are obtained in a weighable form. If potassium and sodium are also to be determined, the salt mixture is weighed quickly, on account of the hygroscopicity of the lithium compound. Of the various methods available for alkali determinations that of Lawrence Smith is most satisfactory, though decomposition with hydrofluoric acid, or fusion with lead or bismuth oxide, may also be adopted. In every case the (weighed) alkali chlorides are dissolved in a little water and rinsed into a small conical flask; 10 c.c. of amyl alcohol are added, and the determination concluded as explained in § III, (*c*).

§ VIII. Complete Analysis of Minerals.—In complete analyses involving a determination of alkali metals, the latter is nearly always done on a separate portion of the mineral. This mode of working is adhered to in the examples given below.

(*a*) *Silicates.*—The most interesting member of this group is lepidolite, which, in addition to lithia, may contain as much as 3 per cent. of rubidia as well as cæsia (0·7 per cent.).

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[1] The numbers in brackets refer to the position of the lines on the scale comprising 170 subdivisions, in which the yellow sodium line is situated at 50.

First Portion: SiO_2, F, TiO_2, Al, Fe, Mn, alkaline earths.

Fuse 1 grm. with 6–8 grm. Na_2CO_3; leach with water, filter, wash with 2 per cent. Na_2CO_3.

R¹: dissolve in HCl, evaporate to dryness, take up with dilute HCl, filter, wash.

F¹: add 10 grm. $(NH_4)_2CO_3$, let stand at 40° overnight, filter, wash with dilute $(NH_4)_2CO_3$.

F²: pass H_2S, filter, reject ppte, boil off H_2S, add solution from R³, determine Al, Fe, TiO_2, Mn, alkaline earths (Procedure 5 *et seq.*).

R²: add P⁴ and residue from P⁵, ignite, weigh. Treat with $HF + H_2SO_4$, ignite, weigh again.

L³: SiO_2.

R³: fuse with $NaHSO_4$, leach; ppte cold with NH_4OH, dissolve ppte in HCl, add to F².

P⁴: add to R².

F⁴: add a few c.c. of ammoniacal ZnO solution, boil to expel NH_3, filter.

P⁵: dissolve in HCl, evaporate to dryness, take up with dilute HCl, filter, reject filtrate, add residue to R².

F⁵: determine fluorine (Procedure 13, F⁹).

Second Portion: for alkalies.

1 grm. of finely powdered mineral is ground with 1 grm. of purest NH_4Cl, then with 8 grm. of purest ppted $CaCO_3$. Ignite gently in platinum (finger-shaped crucible if available). Extract with hot water, filter, wash thoroughly. The residue must dissolve completely in HCl, showing complete attack. Ppte filtrate with $NH_4OH + (NH_4)_2CO_3$, adding 2–3 grm. NH_4Cl, filter, wash thoroughly, dissolve in HCl, repeat pption. Evaporate the combined filtrates in platinum or porcelain, heat residue in air-bath to expel NH_4 salts. Take up residue with a few c.c. of H_2O, add a drop of $BaCl_2$ solution, a few drops of NH_4OH and $(NH_4)_2CO_3$, heat, let stand, filter. Evaporate filtrate in tared platinum dish, heat residue in air-bath, and weigh. Take up with a little H_2O, filter through a tiny paper into a small conical flask, wash, ignite and weigh the small residue; subtract weight from that previously obtained. Difference=mixed alkali chlorides. Treat filtrate with amyl alcohol; filter, wash with amyl alcohol (§ III, (*c*)).

F¹: evaporate alcohol, weigh LiCl. Test weighed salt with H_2PtCl_6, add any ppte to P².

R¹: rinse into porcelain dish with a little water, add excess of H_2PtCl_6, evaporate, take up with alcohol, filter, wash with alcohol.

P²: add any ppte from F¹. Dissolve in hot dilute HCl, ppte Pt with H_2S, evaporate filtrate to dryness, take up in minimum of H_2O, add $SbCl_3$ solution in strong HCl, filter on hardened paper, wash with strong HCl.

F²: Evaporate alcohol, take up with dilute HCl, boil, ppte Pt with H_2S, evaporate filtrate to dryness, ignite gently, weigh NaCl.

P³: dissolve in dilute HCl, pass H_2S, filter, evaporate filtrate to dryness, gently ignite residue, weigh CsCl.

F³: dilute, pass H_2S, filter, evaporate filtrate to dryness, gently ignite residue, weigh KCl + RbCl. Dissolve in dilute HNO_3, ppte with $AgNO_3$, filter, wash.

F⁴: Remove excess of Ag with HCl, evaporate filtrate to dryness, and once more with HCl, to recover KCl and RbCl for spectroscopic determination (see Rb, § III.). If the quantity of mixed chlorides of K,Rb is very small, the indirect determination by $AgNO_3$ is useless; proceed at once by spectroscopic method.

P⁴: ignite, weigh AgCl, calculate to KCl and RbCl.

Third Portion: for combined water by Penfield's method, using lead oxide as a retainer for fluorine.

(*b*) *Beryl.*—See Beryllium, § VIII.

(*c*) *Phosphates.*

First Portion: for phosphoric acid, fluorine, silica, iron, alumina, titanium, manganese, and alkaline earths, apply Procedure 13 (consult also § III, (*a*)).

Second Portion: for alkalies, see (*a*), second portion.

RUBIDIUM.

§ **I. Minerals.**—(*a*) *Rhodizite*, rubidium aluminium borate, $Rb_2O.2Al_2O_3.3B_2O_3$, is a very rare mineral, which has been found in the form of minute, white, translucent crystals on tourmaline. Tetrahedral. H 8; sp. gr. 3·4. Contains also cæsium and potassium.

(*b*) *Lepidolite* (*q.v.*), though a lithium mineral, is the most abundant source of rubidium, some varieties containing as much as 3 per cent. of rubidia.

(*c*) Rubidium is met with in minute quantities in a number of minerals, such as felspars, micas, leucite, spodumene, carnallite, etc. Like lithium, it is dissolved in the process of weathering, and is found in mineral waters, soils, and plants.

§ **II. Properties and Compounds.**—(*a*) The *metal* is very soft and silver-white, but oxidises rapidly, and takes fire in air. It burns also when brought in contact with water. Sp. gr. 1·52; M.P. 38·5°; B.P. 696°. Its vapour is blue. The following methods can be adopted for the isolation of the element: reduction of the chloride with calcium, or of the hydroxide by means of aluminium or magnesium.

(*b*) The *hydroxide*, RbOH, is prepared from rubidium sulphate and caustic baryta by double decomposition; the solution, freed from barium sulphate by filtration, leaves on evaporation a greyish-white deliquescent mass, which is a stronger base than potassium hydroxide.

(*c*) The *chloride*, *sulphate*, *nitrate*, *carbonate*, and, generally speaking, all rubidium salts, bear a close resemblance to those of potassium. The carbonate is deliquescent. Rubidium *alum*, *perchlorate*, and *cobaltinitrite* are more or less difficultly soluble.

(*d*) *Rubidium chloroplatinate*, Rb_2PtCl_6, is a yellow precipitate obtained like the potassium salt (see Platinum, § II, (*e*)); it is isomorphous with the latter, and less soluble (*cf.* Cæsium, § II, (*d*)).

§ **III. Quantitative Separation.**—(*a*) The separation of rubidium from all other metals, including sodium and lithium (*q.v.*), is effected exactly like that of potassium.

(*b*) *Separation from Potassium.*—No exact method for the separation of these closely-allied metals is known. The separation of the chloroplatinates is one by fractional precipitation or crystallisation, the rubidium accumulating in the less soluble fractions.

(1) If the available quantity of the mixed potassium and rubidium chlorides or sulphates is fairly large and contains a substantial proportion of rubidium salt, the two metals can be estimated accurately by the indirect method, viz. determination of the acid radicle.

(2) In the majority of cases the above procedure is not applicable, and the only alternative consists in determining rubidium spectroscopi-

cally in presence of potassium. Gooch and Phinney[1] proceed as follows: The mixture of alkaline chlorides is first precipitated with chloroplatinic acid to eliminate sodium. The chloroplatinates are converted into chlorides, and the bulk of the potassium precipitated by addition of alcohol to the concentrated solution. The filtrate is evaporated to dryness, and the residue dissolved in a known amount of water. The standard rubidium chloride solution is made to contain between 0·0002 and 0·0005 mgrm. Rb per 1/50 c.c. (or 0·0142–0·0355 grm. RbCl per litre). The coils used in the determination are made of 0·32 mm. platinum wire; each is wound into a 30-turn spiral, 1 cm. long and 2 mm. in diameter, which will hold 1/50 c.c. of liquid. One is dipped into the standard, the other into the test solution; the spirals are brought into two Bunsen flames, and the latter observed through a double-vision spectroscope, the slit of which is adjusted to 0·2 mm. Potassium chloride is first added to the standard until the blue potassium line (β at 153) matches that in the test. The blue rubidium lines (α and β) are then compared, and one of the solutions diluted until the lines are of equal intensity. The concentration of the two solutions in rubidium being equal, the quantity present in the test is found by means of the formula $\frac{\text{Vol. of test} \times \text{Wt. of Rb in standard}}{\text{Vol. of standard}}$. A dark room is essential for the success of the operation, which yields results comparing within 10 to 20 per cent.

(*c*) *Separation from Cæsium.*—See Cæsium, § III, (*c*).

§ **IV. Gravimetric Determination.**—(*a*) *In pure Solutions.*—Rubidium is usually weighed as the neutral sulphate, obtained by evaporating the solution with sulphuric acid and gently igniting the residue with ammonium carbonate. Addition of the latter is essential, as rubidium bisulphate is very stable. The metal may also be weighed as chloride, or chloroplatinate; in every case the operations are conducted as for the estimation of potassium.

(*b*) *In Presence of Potassium.*—See § III, (*b*).

§ **V. Detection in Minerals.**—Rubidium affords exactly the same reactions as potassium, being precipitated as chloroplatinate, cobaltinitrite, perchlorate, hydrotartrate, etc. Nor can it be distinguished from potassium by the flame test, as it also gives a violet coloration. The spectroscope is the only certain means of detecting and identifying rubidium. A small quantity of the powdered mineral (mixed with potassium bisulphate and acid fluoride if necessary) is brought into the flame on a loop of platinum wire. The following principal lines[2] are characteristic:—

α (violet) = 4204 (136–137).
β (blue) = 4216 (135).
γ (red) = 7799 (16).
δ (red) = 7950 (14–15).

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[1] *Amer. Journ. Sci.*, 1892, **44**, 392.

[2] The numbers in brackets refer to the position of the lines on the scale comprising 170 subdivisions, in which the yellow sodium line is situated at 50.

The reaction is of the utmost sensitiveness, as it is given by as little as 0·002 mgrm.

§ **VI. Determination in Minerals.**—This is described under the complete analysis of lepidolite (Lithium, § VIII, (*a*), second portion).

Spectroscopic Method for Rubidium (and Cæsium).—Where the absolute quantity of rubidium and cæsium is very small, the spectroscopic method is the only one available. In W. O. Robinson's process,[1] the concentrated, slightly acid solution of the mixed alkali chlorides is precipitated with 0·05 grm. of chloroplatinic acid; the liquid is well stirred, and evaporated till pasty. The excess of potassium (sodium) chloride is dissolved quickly in a minimum of hot water, the precipitate filtered off on a tiny perforated disc of platinum foil covered with asbestos, and washed with 80 per cent. alcohol. The filter is gently ignited in hydrogen to reduce the platinic chloride, washed with hot water, and the filtrate evaporated to pastiness in a small platinum dish. The mass is taken up with four drops of strong hydrochloric acid; the liquid is filtered into a graduated 2 or 3 c.c. flask, and the residue extracted twice more with the above quantity of acid. The volume is adjusted, and a platinum spiral dipped into the solution, then held in the Bunsen flame, and the latter examined through a spectroscope. The blue rubidium and cæsium lines are compared to those obtained with standard solutions containing known amounts of rubidium and cæsium and excess of potassium chlorides, as in the method of Gooch and Phinney (§ III, (*b*) (2)). An accuracy of 5 to 10 per cent. is claimed to be easily attained.

Complete Analysis.—See Lithium, § VIII.

CÆSIUM.

§ **I. Minerals.**—(*a*) *Pollucite* (Pollux), cæsium aluminium silicate, $H_2Cs_4Al_4(SiO_3)_9$, is colourless and transparent, and occurs crystallised (cubic) as well as massive. Very rare mineral, found chiefly in Elba. Part of the cæsia is replaced by soda, but rubidia is completely absent, or almost so. H 6·5; sp. gr. 2·9.

(*b*) *Lepidolite.*—See Lithium, § I.

(*c*) *Vorobyevite* is a variety of beryl containing up to 3 per cent. of cæsia.

(*d*) The disintegration of rocks composed of silicate minerals which carry minute amounts of cæsium furnishes soluble salts of that metal; hence traces are found in mineral, spring, river, and sea water.

§ **II. Properties and Compounds.**—(*a*) The *metal* is prepared by the same methods as rubidium. Like the latter it is silver-white, and takes fire in the air as well as in water. Sp. gr. 1·88; M.P. 26·4°; B.P. 670°.

(*b*) *Cæsium hydroxide*, CsOH, is prepared like rubidium hydroxide, which it resembles. It is the strongest base known, and cæsium the most electro-positive metal.

(*c*) The salts of cæsium are isomorphous with, and closely resemble,

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[1] *Journ. Indust. Engin. Chem.*, 1918, **10**, 50; *Journ. Soc. Chem. Ind.*, 1918, 76A.

those of rubidium and potassium. The deliquescent carbonate is soluble in absolute alcohol.

(*d*) The *chloroplatinate*, Cs_2PtCl_6, is precipitated by chloroplatinic acid as yellow octahedra ; it is the least soluble of the alkali chloroplatinates ; at 20°, 100 parts of water dissolve

K_2PtCl_6 . . .	1·12	parts.
Rb_2PtCl_6 . . .	0·141	,,
Cs_2PtCl_6 . . .	0·070	,,

(*e*) *Cæsium dichloroiodide*, $CsCl_2I$, is one of the many polyhalides known ; re-crystallisation of this salt has been the means of purifying material used in the determination of the atomic weight of cæsium. Tri- and pentahalides have been prepared.

§ **III. Quantitative Separation.**—(*a*) *Separation from Lithium.*—See Lithium, § III, (*c*).

(*b*) *Separation from Sodium.*—Cæsium is precipitated as chloroplatinate, like potassium.

(*c*) *Separation from Rubidium and Potassium.*—(1) The concentrated solution of the chlorides containing one-third to one-half its bulk of hydrochloric acid is treated with a strongly acid solution of antimony trichloride, when the cæsium separates as a white crystalline precipitate, consisting of $3CsCl.2SbCl_3$. This is filtered off on hardened paper, washed with strong hydrochloric acid, and dissolved in dilute acid. The antimony is eliminated as sulphide, and the filtrate evaporated to dryness, giving cæsium chloride.[1]

(2) Stannic chloride solution added to the concentrated solution of the chlorides produces a crystalline precipitate of cæsium chlorostannate, Cs_2SnCl_6, from which cæsium chloride is obtained in the same manner as in the previous procedure. Ammonium salts must not be present in this case.[2]

(3) The solution is treated with a slight excess of lead nitrate, saturated with chlorine, and allowed to stand overnight. The precipitate produced is cæsium chloroplumbate, Cs_2PbCl_6, the solubility of which is less than 0·1 grm. per litre. The salt is decomposed by hydrogen sulphide as before.[3]

§ **IV. Gravimetric Determination.**—(*a*) In pure solutions the procedure is exactly the same as for rubidium (*q.v.* § IV, (*a*)).

(*b*) In presence of only one other alkali metal the indirect determination is applicable (Rubidium, § III, (*b*) (1)).

§ **V. Detection in Minerals.**—Cæsium cannot be distinguished by chemical reactions either from rubidium or potassium, except in that it gives insoluble double salts with the chlorides of antimony, tin, or lead (see § III, (*c*)) ; this reaction can be carried out only in the case of minerals rich in cæsia. All the other precipitation tests are exactly the same as those for potassium. Cæsium salts colour the Bunsen

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[1] Godeffroy, *Ber.*, 1876, **7**, 375 ; Wells, *Amer. Chem. Journ.*, 1901, **26**, 265.

[2] Sharples, *Amer. Journ. Sci.*, 1869, **47**, 178.

[3] Wells, *Amer. Journ. Sci.*, 1893, **46**, 186.

flame violet; the tint is more reddish than that given by rubidium or potassium salts, but recourse must be had to the spectroscope to identify cæsium in admixture with other alkalies. This highly sensitive test is carried out as for rubidium, cæsium being identified by the following lines:[1] α (blue) = 4555 (109); β (blue) = 4593 (106). A third line, γ (red), at 42, is less prominent.

§ VI. Determination in Minerals.—(*a*) Spectroscopic method for minute quantities: see Rubidium, § VI.

(*b*) Gravimetric method: see § VII., and Lithium, § VIII, (*a*), second portion.

§ VII. Complete Analysis of Minerals.—(*a*) *Pollucite:*—

First Portion: for silica, alumina, and common bases. Fusion with sodium carbonate, etc., as usual.

Second Portion: for alkalies. The mineral is opened up by Lawrence Smith's method (Lithium, § VIII, (*a*)). The pure mixed alkali chlorides are weighed and precipitated with chloroplatinic acid. The precipitate is gently ignited, the residue extracted with water, and the filtrate evaporated. The residue is weighed as CsCl after gentle heating; its purity is checked by a chlorine determination, and spectroscopic tests for rubidium and potassium.

The filtrate from the chloroplatinate precipitate is evaporated to dryness, the residue heated in an air-bath, gently ignited, and extracted with water. The filtrate on evaporation to dryness gives sodium chloride; this may be tested spectroscopically for lithium.

(*b*) *Beryl.*—See Beryllium.

(*c*) *Lepidolite.*—See Lithium.

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[1] The numbers in brackets refer to the position of the lines on the scale comprising 170 subdivisions, in which the yellow sodium line is situated at 50.

CHAPTER III.

THE SECOND GROUP.

BERYLLIUM—RADIUM.

GENERALITIES.

BERYLLIUM is the first member of the second group in the periodic table. The properties of the metal and of its compounds recall those of aluminium, while resembling those of the metals of the magnesium sub-group rather than those of the calcium metals. Thus the metal is of a brilliant white colour, unaltered in the air and soluble in acids, but unattacked (unlike magnesium and aluminium) by water at any temperature. Its hydroxide resembles alumina in being insoluble in a boiling solution of ammonia and ammonium chloride, but soluble in excess of caustic alkalies. Its chloride and sulphate are both readily soluble, but are neither isomorphous with, nor contain the same amount of water of crystallisation as, the corresponding magnesium or aluminium compounds. The oxide is intermediate in properties between those of magnesium and aluminium; it is soluble in acids and alkalies unless strongly ignited.

Radium resembles barium very greatly in all its properties and compounds, the one outstanding difference being the radioactivity and slow disintegration of the element, whether free or combined.

BERYLLIUM.

§ **I. Minerals.**—(*a*) *Silicates.*—(1) *Phenacite*, beryllium silicate, Be_2SiO_4, crystallises in transparent to translucent rhombohedral prisms with a vitreous lustre and conchoidal fracture; colour, brown, pale yellow, pale rose or colourless. H 7; sp. gr. 3·0.

(2) *Bertrandite*, beryllium hydrogen silicate, $Be_4H_2Si_2O_9$; transparent, vitreous yellow tables often twinned, orthorhombic; cleavage perfect. H 6·5; sp. gr. 2·6.

(3) *Trimenite*, beryllium manganese silicate, $BeMnSiO_4$; pale pink to colourless, triclinic tabular prisms. H 6·5; sp. gr. 3·4.

(4) *Beryl*, beryllium aluminium silicate, $Be_3Al_2Si_6O_{18}$; vitreous, transparent to translucent, hexagonal prisms; brittle, uneven fracture; colours, green, pale blue, yellow, white or pale rose. H 8; sp. gr. 2·7.

(5) *Euclase*, hydrated beryllium aluminium silicate, $2BeO.Al_2O_3.$

$2SiO_2.H_2O$; transparent pale green, brittle, monoclinic prisms. H 7; sp. gr. 3·0.

(6) *Leucophanite*, beryllium calcium sodium fluosilicate, $BeCaNaFSi_2O_6$; pale green, transparent, orthorhombic tables; vitreous lustre, brittle; cleavage perfect. H 4; sp. gr. 2·9. On heating or being struck it shows a bluish phosphorescence.

(7) *Meliphanite*, another fluosilicate, $Be_2Ca_2NaFSi_3O_{10}$; tetragonal, usually found massive or in obtuse octahedral crystals; colour, yellow to red.

(8) *Helvite* $(Be,Mn,Fe)_7Si_3O_{12}S$, and *Danalite* $(Be,Mn,Fe,Zn)\ Si_3O_{12}S$, are complex beryllium manganese iron zinc sulphides and silicates; colours, yellow, brown, green or grey; translucent, brittle minerals with vitreous lustre. Isometric, usually occurring in tetrahedra. H 6; sp. gr. 3·3.

(*b*) *Other Minerals.*—(1) *Chrysoberyl*, beryllium aluminate, $BeAl_2O_4$; brittle, translucent to transparent, green orthorhombic crystals, often twinned; vitreous lustre, nearly perfect cleavage. H 8·5; sp. gr. 3·3.

(2) *Beryllonite*, beryllium, sodium phosphate, $BeNaPO_4$; occurs in transparent, orthorhombic, colourless to pale yellow prisms, with a brilliant vitreous lustre and perfect cleavage. H 5·5; sp. gr. 2·8.

(3) *Herderite*, beryllium calcium fluophosphate, $BeCaFPO_4$; yellowish to greenish-white short hexagonal pyramids and prisms; translucent, with sub-conchoidal fracture and vitreous lustre. H 5; sp. gr. 3·0.

(4) *Hambergite*, basic beryllium borate, $4BeO.B_2O_3.H_2O$; greyish-white, translucent orthorhombic prisms, vitreous lustre, perfect cleavage. H 7·5; sp. gr. 2·3.

§ **II. Properties and Compounds.**—(*a*) The *metal* is obtained by electrolysis of the double sodium fluoride. It is of a bright silver-white colour, melts at 1278°, and becomes superficially coated with oxide on heating in the air. The fine powder readily burns on heating, forming the oxide, and is readily soluble in acids, but does not decompose water even at a red heat. The compact metal is not attacked by cold dilute sulphuric or concentrated nitric acid, and only dissolves slowly on heating. Sp. gr. 1·93.

(*b*) The *oxide*, BeO (beryllia), is an amorphous white powder (sp. gr. 3·02), which on fusing in the electric furnace becomes harder than ruby, denser and crystalline. After strong ignition it is insoluble in dilute acids. It may be prepared by ignition of the hydroxide, nitrate, carbonate, or sulphate.

(*c*) The *hydroxide*, $Be(OH)_2$, is thrown down as a gelatinous white precipitate on the addition of alkalies to solutions of its salts. It is insoluble in ammonia, but soluble in caustic alkalies, alkaline carbonates, and ammonium carbonate.

(*d*) The *chloride*, $BeCl_2.4H_2O$, deliquescent crystals yielding basic salts when heated.

(*e*) The *carbonates*: basic salts are precipitated on the addition of alkaline carbonates to a cold solution of a beryllium salt. These are soluble in excess of the precipitant, but are re-precipitated on boiling.

§ **III. Quantitative Separation.**[1]—Beryllium accompanies aluminium in qualitative analysis, being precipitated from its solutions as hydroxide on the addition of ammonia and ammonium chloride. The separation of the other metals precipitated at the same time is carried out as follows:—

(*a*) *Separation from Iron, Aluminium, Titanium.*[2]—(1) The mixed hydroxides (precipitated by ammonia) are dissolved in hydrochloric acid and the solution neutralised with ammonia. The cold neutral solution is then treated with 10 grm. of solid sodium bicarbonate for every 100 c.c. of solution, the beaker covered, and the contents rapidly raised to boiling. After boiling one minute the beaker is cooled by immersion in cold water, and the precipitated iron, aluminium, and titanium hydroxides are filtered off and washed three times with a warm (70°–80°) 10 per cent. solution of sodium bicarbonate. The precipitate is dissolved in hydrochloric acid and the precipitation repeated from a bulk of 100 c.c. The joint filtrates are carefully acidified with hydrochloric acid, boiled to expel carbon dioxide, and the solution treated with excess of ammonia to throw down the beryllium hydroxide.

(2) If the metals have been separated from the alkaline earths by the basic acetate method the precipitate may be dried at 100° and digested two or three times with hot glacial acetic acid.[3] The insoluble iron and aluminium compounds are filtered off on a hot-water funnel and washed with hot glacial acetic acid. The filtrate on cooling deposits basic beryllium acetate, which is filtered off and washed with cold glacial acid. Small quantities of iron and aluminium acetates remain dissolved in the filtrate from the beryllium.

(*b*) *Separation from Zirconium.*[4]—The mixed nitrate solution is digested on the water-bath with an excess of caustic soda. The zirconium is precipitated as hydroxide, whereas the beryllium dissolves. If much of the former metal is present, the precipitate must be dissolved and re-precipitated.

(*c*) *Separation from Uranium.*—See Uranium, § III.

(*d*) *Separation from Aluminium*[5] (ether process).—The mixed chloride solution is evaporated nearly to dryness, the residue taken up with 20 c.c. of hydrochloric acid (sp. gr. 1·2) and 25 c.c. of ether added to the clear solution, after which the whole is saturated with hydrogen chloride. The precipitate of $AlCl_3.6H_2O$ is filtered on asbestos (Gooch crucible) and washed with a cold mixture of equal volumes of strong hydrochloric acid and ether saturated with hydrogen chloride. The beryllium in the filtrate is recovered by evaporation and precipitation by ammonia.

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[1] For general analytical chemistry and references see Parsons, *The Chemistry and Literature of Beryllium*, Easton, Pa., 1909.

[2] Parsons and Barnes, *Journ. Amer. Chem. Soc.*, 1906, **28**, 1589.

[3] Parsons, *Journ. Amer. Chem. Soc.*, 1904, **26**, 738 ; Parsons and Robinson, *ibid.*, 1906, **28**, 555.

[4] The phosphate method may also be used (Titanium, § III, (*b*) (2)).

[5] Havens, *Amer. Journ. Sci.*, 1897, **4**, 111 ; *Chem. News*, 1897, **76**, 111.

(*e*) *Separation from Cerium Metals.*[1]—This is best carried out by precipitation of the cerium metals with sodium sulphate (see Rare Earths, § III.). The beryllium in the filtrate is precipitated with ammonia.

(*f*) *Separation from Yttrium Metals.*[2]—The acid solution containing sufficient acid to make it 0·3 N is treated with an excess of oxalic acid (see Rare Earths, § III.). The filtrate is evaporated to fumes with nitric and sulphuric acids to destroy oxalic acid and the beryllium precipitated with ammonia.

§ **IV. Gravimetric Determination.**[3]—Beryllium, like aluminium, is precipitated as hydroxide by the addition of a slight excess of ammonia to its solutions. The operation is best carried out in boiling solutions; the liquid after precipitation should smell only very slightly of ammonia. The precipitate must not be washed with pure water; a 2 per cent. solution of ammonium nitrate or acetate should be used to prevent loss of the colloidal hydroxide. All traces of chlorides must be removed before ignition; the precipitate is ignited wet and weighed as BeO.

§ **V. Detection in Ores.**[4]—The ore is fused with sodium carbonate, the melt leached with hot water, the solution acidified with hydrochloric acid and evaporated to dryness. The dry mass is taken up with hot dilute hydrochloric acid and the insoluble material (SiO_2, Cb_2O_5, etc.) removed by filtration. The solution is treated with hydrogen sulphide, filtered, and the filtrate boiled and oxidised with nitric acid. The solution is nearly neutralised with sodium carbonate, evaporated to 25 c.c. and cooled. It is then treated with 2 grm. of solid sodium peroxide, boiled, and filtered. The filtrate is acidified with nitric acid and a slight excess of ammonia added. If no precipitate forms, beryllium is absent; if a gelatinous precipitate is thrown down, it is filtered off, dissolved in a minimum of hydrochloric acid, 3 grm. of solid sodium bicarbonate added, the mixture boiled one minute, and filtered. The filtrate is diluted with ten times its bulk of water and boiled, when a white precipitate of basic carbonate forms if beryllium is present.[5]

§ **VI. Determination in Ores.**—(*a*) *Silicates.*—From 1 to 2 grm. of finely-powdered ore are fused in a platinum crucible with six times their weight in sodium carbonate. The cold melt is leached with water, the solution acidified with hydrochloric acid and evaporated to dryness. The residue is taken up in dilute hydrochloric acid and the silica filtered off. The solution is treated with hydrogen sulphide, filtered, and the filtrate boiled to expel excess of the gas. After oxidising with a little nitric acid the liquid is nearly neutralised with sodium carbonate, treated with 10 grm. of solid bicarbonate per 100 c.c. and boiled one minute; the precipitate is filtered off, washed, dissolved, and re-precipitated, as described in § III, (*a*). The beryllium in the mixed filtrates is recovered by careful neutralisation with nitric acid, followed by precipi-

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[1] Gibbs, *Amer. Journ. Sci.*, 1864, **37**, 354; Berthier, *Annalen*, 1843, **46**, 182.

[2] *Ibid.*

[3] For general analytical chemistry and references, see Parsons, *The Chemistry and Literature of Beryllium*, Easton, Pa., 1909.

[4] *Ibid.*

[5] Wunder and Chéladzé, *Ann. Chim. anal.*, 1911, **16**, 203.

tation with ammonia in the presence of ammonium chloride. The beryllium hydroxide is well washed with hot 2 per cent. ammonium acetate, ignited wet, and weighed as BeO.

(*b*) *Phosphates.*—One gramme of the very finely-powdered mineral is decomposed by gently boiling with 25 c.c. of *aqua regia.* The solution is evaporated to dryness, the residue taken up with nitric acid and the latter again evaporated to dryness; the mass is once more taken up with nitric acid and the solution treated with an excess of molybdate mixture. After heating to boiling the whole is allowed to stand overnight, the precipitate of ammonium phosphomolybdate filtered off and washed with 2 per cent. nitric acid. The filtrate is precipitated with ammonia, the washed precipitate dissolved in hydrochloric acid, and the solution treated with bicarbonate, as described under (*a*).

§ **VII. Complete Analysis.**—Silicate minerals containing beryllium may contain in addition alumina, iron, manganese, zinc, lime, magnesia, alkalies, fluorine, sulphur, and water. The following table takes into account all these constituents, and is suitable for the analysis of all beryllium minerals except phosphates and borates.

First Portion.—

<table>
<tr><td colspan="9">Fuse 1 grm. of the mineral with 6 grm. of sodium carbonate in platinum. Leach with hot water, filter, wash with 1 per cent. Na_2CO_3.</td></tr>
<tr><td colspan="4">F^1: boil with 10 grm. $(NH_4)_2CO_3$ until smell of NH_3 has disappeared. Filter, wash with hot NH_4OH water.</td><td colspan="5">R^1: dissolve in HCl, evaporate to dryness; take up in dilute HCl; filter, and wash with hot water.</td></tr>
<tr><td colspan="2">P^2: add R^5, ignite, weigh; treat with HF and H_2SO_4, evaporate, ignite, weigh again.</td><td colspan="2">F^2: boil with ammoniacal ZnO until NH_3 is expelled. Filter, wash with hot water.</td><td colspan="2">R^5: add to P^2.</td><td colspan="3">F^5: add solution from R^3. Pass H_2S, filter, and reject precipitate. Boil off excess of H_2S, oxidise with HNO_3, add 5 grm. NH_4Cl and excess of NH_4OH. Boil, filter, and wash precipitate with 5 per cent. NH_4Cl; re-dissolve hydroxides in HCl, add 5 grm. NH_4Cl, re-precipitate with NH_4OH. Unite the two filtrates.</td></tr>
<tr><td>L^3: SiO_2.</td><td>R^3: fuse with $KHSO_4$, leach, add to F^5.</td><td>P^4: Dissolve in HCl, evaporate to dryness, take up in dilute HCl, filter, reject filtrate. Ignite and weigh precipitate. Add weight to L^3.</td><td>F^4: treat with $CaCl_2$ for fluorine. Procedure 13.</td><td colspan="2">P^6: Dissolve in HCl and precipitate the Fe_2O_3 and Al_2O_3 twice with $NaHCO_3$, as described in § III, (*a*).</td><td colspan="3">F^6: pass H_2S, filter, wash with $(NH_4)_2S$.</td></tr>
<tr><td colspan="2">P^8: Fe_2O_3 and Al_2O_3 as hydroxides, separate by Procedure 5.</td><td colspan="4">F^8: acidify with HCl, boil off CO_2, precipitate Be as § IV.</td><td colspan="2">P^7: ZnS and MnS, separate by Procedure 6.</td><td>F^7: CaO, MgO. See Procedure 8.</td></tr>
</table>

Second Portion: for sulphur.

Third Portion: for alkalies (including Cs, Li, Rb) by Lawrence Smith's method.

Fourth Portion: for water, by Penfield's method.

RADIUM.[1]

§ **I. Minerals.**—Radium being a degradation product of uranium is found in all uranium minerals, and the amount present bears a constant ratio to the uranium, which is approximately the same for all minerals unless, like some varieties of autunite, they have been exposed to the constant action of running water, which washes out part of the radium salts. According to Rutherford (1906) the ratio U : Ra is $1 : 3{\cdot}4 \times 10^{-7}$, while Soddy (1914) gives it as $1 : 3{\cdot}24 \times 10^{-7}$, and Lind and Whittemore (1915) find it to be $1 : 3{\cdot}3 \times 10^{-7}$.

§ **II. Properties and Compounds.**—Radium salts resemble those of barium; the *chloride* crystallises as the dihydrate, and is less soluble than the corresponding barium compound; the *sulphate* is the most insoluble sulphate known, its solubility being $\frac{1}{100}$ that of barium sulphate. The metal has been prepared.

§ **III. Quantitative Separation.**—To separate radium from all other metals except barium it is sufficient to add a quantity of barium salt to the mixture and then to separate the barium by the usual methods. All the radium will be found in the barium sulphate obtained. It can be separated from barium only by fractional crystallisation.

§ **IV. Detection and Determination in Ores.**—(*a*) *Detection.*—The ore is examined for the presence of uranium, as described in Uranium, § VI. If the latter is found, it follows that radium is also present.

(*b*) *Determination.*—Radium is always determined electroscopically in ores. The emanation method is based on the fact that the first disintegration product of radium is an inert, radioactive gas; this is removed from the ore and pumped into an exhausted electroscope, where its quantity is measured by observing the rate of discharge. The ore must be kept for one month in a sealed tube to allow the gas (radium emanation or niton) to attain equilibrium with the radium present. This occurs when the rate of production of the niton (*i.e.* the rate of degradation of the radium) is equal to its rate of degradation into the solid element RaA. To ensure obtaining all the niton from the ore it must be completely decomposed, for which two methods are available, fusion or solution. In the first method, from 1 to 0·05 grm. of mineral is fused with 1 to 2 grm. of sodium carbonate in a small platinum boat; when decomposition is complete, the boat is sealed up in a thin-walled glass tube and set aside for one month. In cases where all the uranium and radium are rendered soluble by boiling with nitric acid, a weighed quantity of the ore is sealed up in a thin-walled tube and the emanation allowed to accumulate for one month. In either case, at the end of the month the sealed tube is broken in a small flask containing boiling nitric acid (1 : 1), the evolved gases being passed through caustic soda, then through strong sulphuric acid into a gas burette. When all action is over, the burette is closed and connected up with the exhausted gas-chamber of the electroscope. The gas is then allowed to escape through

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[1] See Moore and Kithil, *U.S. Bureau of Mines Bull.* 70 (1913); Parsons and others, *Bull.* 104 (1915).

a sulphuric acid micro-drying tube into the electroscope and the burette and tube cleaned out by a current of dry air free from dust and carbon dioxide, which is made to flow into the gas-chamber of the electroscope until the pressure therein is normal. After allowing the apparatus to stand for three hours the leaf is charged for fifteen minutes from a battery, and three readings taken of the time required for the leaf to fall through the same hundred divisions as used in standardising. After the experiment is finished the ionisation chamber must be cleaned immediately by passing a current of dry dust-free air through it for several hours. Previous to introducing the emanation into the chamber the natural leak of the instrument should be determined by charging the leaf for fifteen minutes from a battery and observing its fall during five minutes. The rate of fall of the leaf due to the " leak " and that obtained when the emanation is present are calculated in divisions per second; the difference gives the rate due to the emanation alone. The instrument should be calibrated by using a standard pitchblende which has been sealed up for a month and treated in a similar manner to the sample. Its content of uranium being known, the radium present is found by multiplying the uranium figure by $3{\cdot}33 \times 10^{-7}$. A sufficien quantity of ore and standard should be used so that the rate of fall of the leaf is between 1 and 2 divisions per second.

CHAPTER IV.

THE THIRD GROUP.

SCANDIUM—GALLIUM—INDIUM—THALLIUM.

GENERALITIES.

SCANDIUM belongs to the even series of the group, and resembles the other two members, yttrium and lanthanum (see Rare Earths), to a certain extent, but a large number of its properties recall thorium and zirconium ; thus it gives an oxalate insoluble in water or dilute mineral acids, but soluble in ammonium oxalate ; its carbonate is soluble in and forms double salts with alkaline carbonates ; its solutions are precipitated by boiling with thiosulphate (*cf.* zirconium, thorium) and by hydrofluoric acid (*cf.* thorium), and the fluoride is soluble in alkaline fluorides (like zirconium fluoride). Its salts are somewhat easily hydrolysed, and the hydroxide is a weak base, but shows no acidic properties at all.

The compounds of gallium, indium, thallium (odd series) resemble those of aluminium to a greater or lesser degree. The hydroxides (except thallic) are amphoteric, the gallium compound being a weaker base but stronger acid than alumina, and the reverse holding good for indium hydroxide. Gallic and thallic salts are readily hydrolysed, indium salts hardly at all. All three metals form alums ; the thallium compounds, however, are only formed with difficulty. The affinity for sulphur increases with atomic weight, gallium sulphide not having yet been obtained pure, while indium and thallic sulphides are well-defined stable compounds. On heating in a current of hydrogen chloride gallium gives the trichloride, $GaCl_3$; indium, the dichloride, $InCl_2$; and thallium, the monochloride, TlCl. Thallium differs from the other metals of the group in forming a series of stable compounds in which it is monovalent. These compounds resemble either the corresponding potassium (*e.g.* sulphate, nitrate, carbonate) or lead salts (*e.g.* chloride, iodide, chromate).

SCANDIUM.

§ **I. Minerals.**—(*a*) *Thortveitite*, a silicate of scandium and the yttrium earths, $Sc_2O_3.2SiO_2$, is the only mineral in which scandium is the principal basic constituent. Orthorhombic, grey-green, brittle mineral with a brilliant adamantine lustre ; twins common. H 6½ ; sp. gr. 3·57.

(*b*) *Wiikite* is a very complex mineral, containing 1 to 1½ per cent. of scandia, together with large amounts of rare earths and oxides of columbium, tantalum, titanium, zirconium, silicon, thorium, uranium, and iron. Black, amorphous, radioactive. H 6; sp. gr. 4·85.

(*c*) In addition to the above, the element is found in many rare earth minerals, and in some specimens of mica, cassiterite, and wolfram.

§ **II. Properties and Compounds.**—(*a*) *The metal* has not yet been isolated.

(*b*) The *oxide*, Sc_2O_3, is a white powder soluble in hot dilute acids, formed on ignition of a scandium salt of a volatile acid.

(*c*) The *fluoride*, ScF_3, is a white gelatinous precipitate, formed on adding a soluble fluoride or fluosilicate to a boiling solution of a scandium salt. Like zirconium, it forms soluble double salts with the alkali fluorides; their general formula is $ScF_3.3RF$.

(*d*) The *sulphate*, $Sc_2(SO_4)_3.6H_2O$, crystallises in globular aggregates fairly soluble in water. With potassium sulphate it gives a double salt, $Sc_2(SO_4)_3.3K_2SO_4$, insoluble in a saturated solution of the precipitant; the corresponding sodium salt, however, is soluble in a saturated solution of sodium sulphate.

(*e*) The *carbonate*, $Sc_2(CO_3)_3.12H_2O$: white precipitate, soluble in alkaline carbonates; on boiling the solution double salts are thrown down.

(*f*) The *oxalate*, $Sc_2(C_2O_4)_3.5H_2O$, is precipitated by oxalic acid from solutions of scandium salts; slightly soluble in water, readily soluble in ammonium oxalate solution, giving a stable double salt which crystallises out on evaporation.

§ **III. Quantitative Separation.**[1]—Scandium accompanies the rare earth metals in analysis, being precipitated along with them by means of oxalic acid. In the double sulphate separation it accompanies the cerium metals if potassium sulphate is used as precipitant; if the sodium salt is used, however, the scandium passes into the filtrate along with the yttrium metals, and in the subsequent fractional crystallisation it accumulates in the most soluble fraction of the bromates.

(*a*) *Separation from Yttrium Metals.*—The neutral chloride solution derived from the most soluble bromates is boiled with an excess of sodium thiosulphate, whereby the scandium is precipitated as basic thiosulphate. The washed precipitate is extracted with hot dilute hydrochloric acid and the precipitation repeated. The acid extract of the second precipitate is treated with oxalic acid, whereby pure scandium oxalate is thrown down.

(*b*) *Separation from the Cerium Metals.*—This is effected by double precipitation with sodium sulphate (see Rare Earths, § III.). If the scandium is in large excess, it may be separated as under (*a*).

(*c*) *Separation from Thorium.*[2]—This is best accomplished in two stages: (1) The scandium is separated from the bulk of the thorium

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[1] For a general account of the chemistry and reactions of scandium see Meyer, Wassjuchnow, Drapier, and Bodländer, *Z. anorg. Chem.*, 1914, **86**, 257.

[2] For these and other methods see Meyer and Winter, *Z. anorg. Chem.*, 1910, **67**, 398; *Chem. News*, 1910, **102**, 163, 175; Meyer and Goldenburg, *ibid.*, 1912, **106**, 13; Meyer and Wassjuchnow, *Z. anorg. Chem.*, 1914, **86**, 257; Sterba-Böhm, *Z. Elektrochem.*, 1914, **20**, 289.

by pouring the neutral solution of the chlorides into a large excess of sodium carbonate and boiling the mixture, whereby scandium sodium carbonate is precipitated. The precipitate, which contains about 0·5 per cent. of thoria, is filtered off, washed with hot sodium carbonate solution, dissolved in hydrochloric acid, and the remainder of the thorium separated by either of the two following methods :—

(2α) The neutralised solution of the impure scandium salt is added drop by drop with constant stirring to a 20 per cent. solution of neutral ammonium tartrate. The resulting clear liquor is boiled with a small excess of ammonia, whereby scandium ammonium tartrate is precipitated. This is filtered off, washed with hot ammonium tartrate solution, and ignited to oxide.

(2β) The neutralised chloride solution is poured with vigorous stirring into a solution of ammonium fluoride containing at least eight times as much salt as there is scandia present. After boiling a short time the precipitate of thorium fluoride is filtered on a vulcanite funnel and washed with warm water. The scandium in the filtrate is recovered by evaporation with sulphuric acid followed by precipitation with ammonia or oxalic acid.

§ **IV. Gravimetric Determination.**—Scandium is weighed as the oxide Sc_2O_3, formed by ignition of the oxalate or hydroxide. The former is precipitated like the rare earth oxalates (see Rare Earths, § IV.), the latter in a similar manner to alumina. Both precipitates may be washed with warm water and ignited wet to oxide.

§ **V. Detection in Minerals.**[1]—The mineral is opened up as described under Rare Earths, § V. ; the precipitated oxalates will contain all the scandium ; they should be ignited to oxides, the latter dissolved in acid, and the solution precipitated with sodium sulphate. The filtrate containing yttria earths and scandia is treated with oxalic acid, the precipitate ignited to oxides, and the latter dissolved in hydrochloric acid. The arc spectrum of the solution is then examined for the lines 3572·7, 3614·0, 3630·9, 4247·0, which are highly characteristic of scandium.

For the chemical method of detecting scandium, applicable only if much is present, the ignited yttria earths and scandia are fused with sodium bisulphate, and the aqueous solution of the melt saturated with potassium sulphate. The precipitate may contain thoria as well as scandia, for the separation of which see § III, (*c*).

§ **VI. Determination in Minerals.**—(*a*) *In Minerals containing much Rare Earths.*[2]—The ore is opened up as described under Rare Earths (§ VI.), and the earths separated with sodium sulphate into cerium and yttrium groups. The scandium accompanies the latter, and accumulates in the most soluble fractions when the bromates are crystallised. These are treated as under § III, (*a*) for the separation of the scandium.

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[1] Eberhard, *Sitzungsber. K. Akad. Wiss.*, Berlin, 1908, 851 ; 1910, 404 ; *Chem. News*, 1909, **99**, 30 ; 1910, **102**, 211.

[2] Crookes, *Phil. Trans.*, 1908, A, **209**, 15 ; *Proc. Roy. Soc.*, 1908, A, **80**, 516 ; *Chem. News*, 1908, **98**, 274.

(*b*) *In Wolframite.*[1]—100 grm. of the mineral are fused with 230 grm. of sodium carbonate, the melt leached and the solution filtered. The residue is dissolved in hydrochloric acid and the solution evaporated to dryness. The mass is taken up in dilute hydrochloric acid and the silica removed by filtration ; the filtrate is boiled, 3 to 4 grm. of sodium fluosilicate added with constant stirring, and the mixture boiled for half an hour. The insoluble scandium fluoride is filtered off, washed with hot very dilute hydrochloric acid, and dissolved in strong sulphuric acid. The scandium is precipitated from this solution with ammonia, the precipitate dissolved in nitric acid, and the solution boiled with oxalic acid. The oxalate precipitate is ignited to oxide and weighed.

(*c*) *In Thortveitite.*—One gramme of the mineral is fused with 5 grm. of sodium carbonate, the melt taken up with hot water, the solution acidified with hydrochloric acid and evaporated to dryness. The residue is taken up in hot dilute hydrochloric acid, the solution filtered, and the filtrate boiled with 10 grm. of sodium thiosulphate for an hour. The precipitate is filtered off, washed, and digested with 10 per cent. hydrochloric acid. After filtering off the sulphur the precipitation with thiosulphate is repeated. The second precipitate is again extracted as before, the sulphur filtered off, and the filtrate precipitated with oxalic acid. The scandium oxalate is filtered off, washed with hot very dilute nitric acid, and ignited to oxide. It may contain traces of thoria, which are eliminated by dissolving it in hydrochloric acid and applying method (2α) or (2β) in § III, (*c*).

GALLIUM.

§ I. Minerals.—Gallium is one of the rarest elements, and no mineral is yet known in which it is the predominating metallic constituent. It occurs in traces in many zinc-blendes, in a large number of iron ores (*e.g.* magnetite, clay-ironstone, and blackband ore), and in many samples of bauxite and kaolin. The mineral richest in the element contains only one part in 33,000, but in the metallurgical processes carried out for the extraction of zinc, iron, or aluminium the gallium present concentrates in the metal produced.

§ II. Properties and Compounds.[2]—(*a*) The *metal* is hard, brittle, and of a grey colour with a greenish-blue reflex. It melts at 30·15°, and has a great tendency to remain in the superfused state. Its sp. gr. at 24·5° is 5·96 for the solid and 6·07 for the liquid, hence, like water, it expands on freezing. Gallium is only superficially oxidised in air even at a dull red heat, and dissolves very slowly in any single mineral acid, but readily in *aqua regia* ; it dissolves in caustic alkalies with the evolution of hydrogen. It may be prepared by electrolysis of the sulphate.

(*b*) The *oxide*, Ga_2O_3, is formed by ignition of the nitrate or hydroxide

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[1] Adapted from Meyer, *Z. anorg. Chem.*, 1908, **60**, 134 ; *Chem. News*, 1909, **99**, 85, 97 ; and Sterba-Böhm, *loc. cit.*, p. 139.

[2] See article " Gallium " in Wurtz, *Dictionnaire de Chimie*, Supplement, Part 2, 851.

as a white powder insoluble in acids and alkalies after strong ignition, but soluble in fused bisulphate. The hydroxide is precipitated by a slight excess of ammonia; it is soluble in caustic potash.

(*c*) The *trichloride*, $GaCl_3$, resembles aluminium chloride, and is formed by heating the metal in a current of chlorine or hydrogen chloride. It crystallises in white needles, melts at 75°, boils at 220°, and is very deliquescent, giving a solution from which basic chlorides separate on standing.

(*d*) The *sulphate*, $Ga_2(SO_4)_3$, is a white, very soluble crystalline salt, which forms alums with the sulphates of ammonium, potassium, cæsium, rubidium, and thallium; they crystallise in the isometric system.

(*e*) The *ferrocyanide* is a white amorphous precipitate insoluble in hydrochloric acid (1 : 2 water).

§ **III. Quantitative Separation.**[1]—(*a*) *Separation from Silver and the Metals of the Hydrogen Sulphide Group other than Cadmium and Lead.*—This is effected by passing hydrogen sulphide into the acid solution (sulphuric, if silver is present) containing at least 10 per cent. of free acid. Cadmium and lead are not completely precipitated and must be removed from the filtrate, as described under (*b*).

(*b*) *Separation from Cadmium, Lead, Bismuth, Aluminium, Chromium.*—The gallium is precipitated by the addition of a slight excess of potassium ferrocyanide to a hydrochloric acid solution of the metals containing at least one-third its bulk of strong acid. The operation is best carried out at 60° to 70°; the precipitate must be washed with warm dilute (1 : 3) hydrochloric acid.

(*c*) *Separation from Iron, Cobalt, Nickel, Zinc, Manganese, Cadmium, Thallium, Alkaline Earths and Alkalies.*—The solution containing the metals as chlorides is boiled with metallic copper and freshly-precipitated cuprous oxide, whereby the iron is reduced to the ferrous state and gallium hydroxide is precipitated. The precipitate is well washed, dissolved in hydrochloric acid, and precipitation repeated as before. The final precipitate may be freed from copper by treatment of its solution in hydrochloric acid with hydrogen sulphide (*a*).

(*d*) *Separation from Zirconium, Titanium, and Indium.*[2]—The nearly neutral solution of the chlorides is boiled in a platinum dish with excess of pure caustic potash. The precipitated hydroxides of zirconium, titanium, and indium are filtered off, well washed, digested with hydrochloric acid, and the treatment with potash repeated. The combined filtrates are acidified and the gallium precipitated with ammonia.

§ **IV. Gravimetric Determination.**[3]—Gallium is always weighed as the oxide Ga_2O_3; this is obtained on igniting the gelatinous precipitate thrown down on the addition of ammonia to solutions of gallium salts. Owing to the readiness with which basic salts are formed, the nitrate

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[1] For the separation from practically all the metals see Lecoq de Boisbaudran, *Compt. Rend.*, 1882–84 : **94**, 1154, 1227, 1439, 1625; **95**, 157, 410, 503, 703, 1192, 1332; **96**, 152, 1696, 1838; **97**, 66, 142, 295, 521, 623, 730, 1463; **98**, 711, 781; **99**, 526; also Browning and Porter, *Amer. Journ. Sci.*, 1917, **44**, 221.

[2] Uhler and Browning, *Amer. Journ. Sci.*, 1916, **42**, 389.

[3] For electrolytic determination see Uhler and Browning, preceding footnote.

solution is the most suitable from which to precipitate gallium for gravimetric work. The excess of ammonia should be removed by boiling before filtration, otherwise traces of gallium will remain dissolved; the precipitate is best washed with ammonium nitrate; it can be ignited wet to the oxide.

§ **V. Detection in Ores.**—(*a*) *In Zinc-blende.*—The blende is boiled with *aqua regia*, using a slight excess of the mineral to ensure expulsion of all the nitric acid. The solution is allowed to cool, and filtered from the insoluble material, lead chloride, etc.; the filtrate is treated with strips of metallic zinc until no further metallic deposit is obtained. After filtration the liquid is boiled for several hours with a large excess of zinc; the precipitate formed is dissolved in hydrochloric acid, and the solution evaporated as low as possible without separation of salts. Its spark spectrum is then examined in the usual manner, employing a spark of about 2 mm. taken off the surface of the solution. Gallium shows an intense violet line at 4170 and a distinct but much less intense line at 4031.

(*b*) *In Iron Ores.*—The ore is dissolved in hydrochloric acid or fused with potassium bisulphate; the solution is boiled with metallic copper and freshly-precipitated cuprous hydroxide; the precipitate, after washing, is dissolved in hydrochloric acid and the copper removed with hydrogen sulphide. After adding one-third its bulk of hydrochloric acid to the filtrate the gallium is precipitated with potassium ferrocyanide, and the washed precipitate ignited, fused with bisulphate, and the gallium converted into chloride, the solution of which is examined by the spark-spectrum method.

(*c*) *In Bauxite.*—The mineral is fused with bisulphate and the melt leached with warm very dilute sulphuric acid. The filtered solution is treated with ammonium acetate, a little arsenious acid added, and the liquid saturated with sulphuretted hydrogen. A precipitate of arsenious sulphide containing all the gallium and most of the iron is thrown down. The washed precipitate is dissolved in *aqua regia* and evaporated to dryness with excess of hydrochloric acid. The residue is taken up in hydrochloric acid (2 : 1 water), the arsenic removed with hydrogen sulphide, the solution evaporated, and the spark spectrum examined.

§ **VI. Determination in Ores.**—Owing to the very minute amounts of gallium present in any ore, large amounts (say 100 grm.) must be taken for analysis. Blende is dissolved in *aqua regia* and the excess of nitric acid removed by evaporation; iron and manganese ores are dissolved in hydrochloric acid; the filtered solution, in any case, is treated with metallic zinc in the cold to throw down the greater part of the lead, copper, cadmium, arsenic, etc. The filtered solution is boiled with a large excess of zinc, which throws down alumina, and basic salts of gallium, zinc, iron, etc. The precipitate is dissolved in hydrochloric acid and the solution boiled with copper and cuprous oxide; double precipitation is necessary. The copper is removed from the solution of the second precipitate in hydrochloric acid by hydrogen sulphide. The filtrate, after addition of one-third its bulk of strong hydrochloric acid, is treated with ferrocyanide, the precipitate filtered off, washed with dilute hydrochloric acid, ignited gently, and the residue dissolved in hydrochloric acid. The solution is boiled with copper and cuprous oxide, the copper removed from the solution of the washed precipitate in hydrochloric acid as before, the gallium precipitated with ammonia, and the hydroxide ignited to Ga_2O_3 and weighed. It should be fused with bisulphate, and tested for traces of iron, aluminium, and indium. Aluminium may be removed by re-precipitating the gallium as ferrocyanide; indium and iron remain insoluble on digestion of the mixed hydroxides with caustic soda.

Bauxite is best treated as described under § V, (*c*); the solution of iron and gallium obtained after removal of the arsenic is boiled with copper and cuprous oxide, and the gallium precipitated as hydroxide with ammonia after separation of the copper.

INDIUM.

§ I. **Minerals.**—Like gallium, indium is never found as the predominating metallic constituent of a mineral, but it occurs in traces in most zinc-blendes, tin ores, and in many samples of pyrites, siderite, and tungsten ores. Commercial zinc often contains small quantities of the element.

§ II. **Properties and Compounds.**—(*a*) The *metal* is soft, ductile, and silver-white, melts at 155°, and volatilises at a red heat. Sp. gr. 7·28. It burns in air at a red heat, and unites directly with sulphur and the halogens when heated. Neither boiling water nor aqueous caustic alkalies affect the metal, but it dissolves in mineral acids fairly readily. It may be precipitated from solutions of its salts by metallic zinc or by electrolysis.

(*b*) The *sesquioxide*, In_2O_3, is a yellow powder, soluble in acids if formed at a low temperature, but highly resistant if it has been ignited strongly. It is produced by ignition of the salts of volatile acids, and is reduced to the metal when heated in hydrogen or ammonia, or with aluminium, carbon, or sodium. On heating above 850° it loses oxygen and is converted into In_3O_4.

(*c*) The *sulphide*, In_2S_3, is a yellow flocculent precipitate produced by hydrogen sulphide in a neutral or acetic acid solution of the metal. It is soluble in strong mineral acids, also in a large excess of alkaline sulphide. Potassium sulphide produces in indium solutions a white precipitate of hydrated potassium sulphindate, $K_2In_2S_4.xH_2O$, soluble in excess. Lower sulphides may be prepared in the dry way.

(*d*) The *chlorides*. Three are known: InCl, dark red; $InCl_2$, white crystals; and $InCl_3$, lustrous white tablets. The first two are decomposed by water with the formation of a solution of the third compound and the deposition of the metal. The trichloride is a very deliquescent stable compound, only slightly hydrolysed in aqueous solution. It forms double compounds with chlorides of the alkali metals of the types $R_3InCl_6.2H_2O$ and $R_2InCl_5H_2O$.

(*e*) The *sulphate*, $In_2(SO_4)_3$, is a very soluble compound formed by dissolving the metal or its oxide in sulphuric acid. It forms alums with cæsium, rubidium, and ammonium sulphates.

(*f*) The *basic sulphite*, $In_2(SO_3)_3.2In(OH)_3.5H_2O$, is precipitated by boiling the solution of an indium salt with excess of alkali bisulphite.

§ **III. Quantitative Separation.**[1]—The hydrogen sulphide group is separated in the usual manner, the gas being passed through a hot solution containing 5 per cent. of free acid. Precipitation of the oxidised filtrate by ammonia yields a mixture of indium hydroxide with the hydroxides of the metals of the iron group. The precipitate is well washed, dissolved in dilute sulphuric acid, and the indium precipitated on pure zinc. When the zinc is nearly all dissolved the precipitate is filtered off, dissolved in nitric acid, and the solution evaporated to fumes with a slight excess of sulphuric acid. The cold mass is taken up with water and boiled with a slight excess of ammonia and ammonium chloride, the precipitate filtered off, washed, and dissolved in a slight excess of dilute hydrochloric acid. The nearly neutral solution is boiled with 5 grm. of sodium bisulphite, the precipitate of basic indium sulphite filtered off, washed with cold water, and dissolved in a strong solution of sulphurous acid. The solution is boiled until no more sulphur dioxide is evolved whereby the pure basic sulphite of indium is precipitated.

§ **IV. Gravimetric Determination.**—Indium is always weighed as the oxide In_2O_3. The solution of the metal, preferably as nitrate, is boiled with a slight excess of ammonia [2] and the precipitate filtered off and well washed with hot water. It is ignited wet, gently at first, finally to a dull red heat (the temperature must not exceed 800° [3]), and the residue weighed as In_2O_3.[4]

§ **V. Detection in Ores.**[5]—The ore is dissolved in hydrochloric acid (tin ores must be fused with sodium peroxide; pyrites requires *aqua regia*); the solution containing about 10 per cent. of free acid is precipitated with hydrogen sulphide. After expulsion of the gas the filtrate is treated with metallic zinc, which throws down the rest of the lead and cadmium together with the indium. The precipitate is treated as described under § III. to obtain basic indium sulphite; this is dissolved in hydrochloric acid and tested on platinum wire in the Bunsen flame. The latter is coloured bluish-violet, and the spectroscopic examination

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[1] Mathers (*Journ. Amer. Chem. Soc.*, 1908, **30**, 209) states that indium is very difficult to separate completely from iron. He recommends depositing the indium electrolytically from the solution of the mixed sulphates and then to dissolve the deposit in nitric acid, neutralise with ammonia, add an equal bulk of 50 per cent. acetic acid, and precipitate the iron with a slight excess of nitroso-β-naphthol dissolved in 50 per cent. acetic acid.

[2] Renz (*Ber.*, 1901, **34**, 2763; 1903, **36**, 2751, 4394) recommends the use of methylamine, dimethylamine, or ethylamine in place of ammonia, as the hydroxide has a tendency to dissolve in excess of the latter.

[3] Thiel and Koelsch, *Z. anorg. Chem.*, 1910, **66**, 288. (*Cf.* § II, (*b*).)

[4] For an electrolytic method see Kollock and Smith, *Journ. Amer. Chem. Soc.*, 1910, **32**, 1248.

[5] Hoppe-Seyler, *Annalen*, 1866, **140**, 247; microchemical detection as rubidium indium chloride; Kley, *Chem. Zeit.*, 1901, **25**, 563.

reveals the two very characteristic lines α (blue)=4511·5 (111)[1] and β (violet)=4102 (148).[2]

§ **VI. Determination in Ores.**—The ore is opened up as described under § V. and the indium precipitated with zinc, then twice as basic sulphite (§ III.). The sulphite is dissolved in hydrochloric acid and the solution precipitated with a slight excess of ammonia (§ IV.), the precipitate being ignited and weighed as oxide. On account of the very small quantities in which indium occurs in ores, at least 100 grm. should be taken for the determination.

THALLIUM.

§ **I. Minerals.**—(*a*) *Crookesite*, a selenide, $(Cu,Tl,Ag)_2Se$, is an amorphous, brittle, lead-grey mineral with metallic lustre. H 3; sp. gr. 6·9.

(*b*) *Lorandite*, thallous thioarsenite, $TlAsS_2$, is a deep red, translucent, monoclinic mineral possessing a metallic to adamantine lustre. It is usually found in modified tablets, which have a perfect basal cleavage. Streak dark red. H 2½; sp. gr. 5·5.

(*c*) *Hutchisonite* consists of the sulphides of thallium, silver, copper, lead, and arsenic. Colour and streak vermilion. Transparent to translucent, brittle, orthorhombic, flat prisms, with adamantine lustre and good cleavage. H 1½; sp. gr. 4·6.

(*d*) *Vrbaite*, $TlAs_2SbS_5$, occurs in deep red, translucent, orthorhombic crystals.

(*e*) In addition to the above, thallium is also found in very small quantities in rocks and minerals associated with the alkali metals, zinc, lead, iron, etc.; *e.g.* in sylvine, carnallite, lepidolite, alunite, zincblende, pyrites, hæmatite, braunite, etc.; it tends to concentrate in some of the products when these minerals are worked up. Thus, small amounts of the element are sometimes met with in zinc, cadmium, platinum, bismuth, tellurium, etc., and in chamber mud and flue-dust from sulphuric acid plants.

§ **II. Properties and Compounds.**—(*a*) The *metal* is soft, of a bluish-white colour, and easily cut by a knife, the exposed surface exhibiting a bright metallic lustre, which soon tarnishes. It exists in two enantiotropic modifications, melts at 302°, and has a sp. gr. of 11·85. A bar of the metal gives a "cry," like tin, when bent. It readily dissolves in sulphuric or nitric but only slowly in hydrochloric acid, and combines with oxygen slowly at ordinary temperatures, rapidly at 100°.

(*b*) *Thallous oxide*, Tl_2O, is a heavy, black powder formed by oxidation of the metal in warm air or oxygen, or by dehydration of the corresponding hydroxide at 100°. It readily absorbs moisture from the air, melts at 300°, and, when fused, attacks glass.

(*c*) *Thallous hydroxide*, TlOH, crystallises in yellow needles readily

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[1] The numbers in brackets refer to the position of the lines on the scale comprising 170 subdivisions, in which the yellow sodium line is situated at 50.

[2] Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911).

soluble in water, giving a colourless, strongly-alkaline solution, which readily absorbs carbon dioxide, and attacks glass and porcelain. It is produced by the action of baryta on the sulphate.

(*d*) *Thallic oxide*, Tl_2O_3, a black powder formed by oxidation of the metal between 600° and 700°, or small black crystals obtained by heating thallous nitrate to 450°; melts at 725°, decomposes above 800°, and is insoluble in water, alkalies, or cold sulphuric acid. With hot sulphuric acid it gives thallous sulphate and oxygen; with hydrochloric acid, chlorine and thallous and thallic chlorides.

(*e*) *Thallic hydroxide*, $TlO.OH$, is a brown powder, produced by the action of a slight excess of alkali in solutions of thallic salts. It is insoluble in water.

(*f*) *Thallous chloride*, $TlCl$, crystallises as white cubes from a solution of thallous salt to which a soluble chloride has been added. One part dissolves in 400 parts of cold and 40 of hot water.

(*g*) *Thallous chloroplatinate*, Tl_2PtCl_6, is a pale yellow crystalline precipitate, soluble in 15,585 parts of cold and 1948 of boiling water. At a red heat it gives a thallium-platinum alloy.

(*h*) *Thallous iodide*, TlI, is precipitated as citron-yellow, orthorhombic crystals when a soluble iodide is added to a solution of a thallous salt. If heated to 168° it becomes red and cubic; the freshly-precipitated compound turns green on exposure to the light. 100 parts of water dissolves 0·006 parts of the salt at 20° and 0·12 at 100°.

(*i*) *Thallous sulphide*, Tl_2S, is thrown down on passing hydrogen sulphide through a neutral, alkaline, or acetic acid solution of a thallous salt as a black precipitate insoluble in alkaline cyanide, sulphide, or hydroxide, or in acetic acid. It forms definite compounds with tin and arsenic sulphides, *e.g.* Tl_4SnS_4 and Tl_3AsS_4, which may be used for its gravimetric estimation.

(*j*) *Thallous sulphate*, Tl_2SO_4, is soluble in 20 parts of cold and 5 of hot water. It crystallises in anhydrous rhombic prisms isomorphous with potassium sulphate, and may be fused without decomposition.

(*k*) *Thallous nitrate*, $TlNO_3$, is isodimorphous with potassium nitrate.

(*l*) *Thallic halides, sulphate and nitrate*, are soluble in water, but readily hydrolyse, giving brown basic salts or thallic hydroxide. They readily combine with thallous salts, giving rise to many series of thallothallic compounds (see § III, (*a*) (2)).

§ III. Quantitative Separation.[1]—Thallous salts, like those of lead, are precipitated by hydrochloric acid in the cold, and the chloride dissolves fairly readily in hot water; hydrogen sulphide in acid solution gives no precipitate with thallous salts, but in the presence of members of the hydrogen sulphide group other than cadmium, traces of thallium are co-precipitated. Thallous salts are not precipitated by ammonia or sodium carbonate, but alkaline solutions give, with hydrogen sulphide, a black precipitate of thallous sulphide. In the general scheme of qualitative analysis, thallium, if present, will be found in the ammonium sulphide precipitate, together with zinc, nickel, etc.

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[1] See also Crookes, *Select Methods of Chemical Analysis.*

(*a*) *Separation from Silver.*—(1) Silver may be precipitated by hydrogen sulphide from a solution of the sulphates of the two metals slightly acidified with sulphuric acid.

(2) The mixed chloride precipitate is boiled with *aqua regia.* The solution is diluted considerably with hot water and filtered hot, the residue of silver chloride being well washed with boiling water. The thallium is in the filtrate as thallo-thallic chloride.

(3) The hot solution of the mixed nitrates or sulphates is treated with hydrochloric acid and saturated with chlorine. Silver chloride alone is precipitated, the thallium remaining dissolved as thallic chloride, $TlCl_3$.[1]

(*b*) *Separation from Lead, Bismuth, Copper, Arsenic, Antimony, Tin.*—The solution of the metals is treated with a small excess of sodium carbonate, then with sodium cyanide (free from sulphide), warmed gently, and set aside overnight. The precipitate is filtered off and well washed with warm water; the filtrate is warmed gently with a slight excess of colourless ammonium sulphide, whereby thallous sulphide is precipitated. It is filtered off and washed with warm very dilute ammonium sulphide solution.

(*c*) *Separation from Mercury and Cadmium.*—The cold nearly neutral sulphate or nitrate solution is treated with a solution of potassium iodide drop by drop until any red precipitate of mercuric iodide has re-dissolved, leaving pure yellow thallous iodide.

(*d*) *Separation from Iron, Aluminium, Chromium, Cobalt, Nickel, Zinc, Manganese, Alkaline Earths and Alkalies.*—The cold nearly neutral solution of the sulphates is saturated with sulphur dioxide and treated with potassium iodide in slight excess. Yellow thallous iodide is precipitated.

(*e*) *Separation from Cobalt, Nickel, Zinc, and Manganese.*—The sulphate or nitrate solution is treated with a little sulphur dioxide (to ensure that all the thallium is in the monovalent state), and treated with an excess of sodium carbonate. The precipitated carbonates of the above metals are filtered off and well washed with hot water. The thallium may be recovered from the filtrate by precipitation with colourless ammonium sulphide.

(*f*) *Separation from Lead alone.*—The solution is evaporated to strong fumes with sulphuric acid, the cold mass taken up in water, and the lead sulphate filtered off and washed as usual. The thallium in the filtrate may be separated as iodide after neutralisation with ammonia.

(*g*) *Separation from Copper alone.*—The two metals are precipitated together as iodides with potassium iodide and sulphur dioxide in a nearly neutral solution. The precipitate is filtered off, washed with cold 1 per cent. potassium iodide solution, and digested with dilute ammonia until the residual thallous iodide is pure yellow. It is then filtered off, and washed with dilute ammoniacal potassium iodide solution, then with 80 per cent. alcohol.

(*h*) *Separation from Cadmium alone.*—The neutral solution is treated

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[1] Spencer and Le Pla, *Trans. Chem. Soc.*, 1908, **93**, 958.

with an excess of potassium bichromate, then made slightly ammoniacal, whereby yellow thallous chromate is precipitated (see § IV, (*b*)).

(*i*) *Separation from Gallium.*—(1) The neutral sulphate solution is boiled with a sheet of metallic copper, or with a little freshly-precipitated cuprous oxide, until no further precipitate is formed ; gallium is thrown down as hydroxide. The copper may be removed from the filtrate by method (*g*).

(2) The neutral solution is treated with a little sulphur dioxide, followed by excess of ammonia. The precipitate of gallium hydroxide is filtered off, well washed with hot water, re-dissolved in dilute sulphuric acid, and re-precipitated as before.

§ **IV. Gravimetric Determination.**—(*a*) *As Thallous Iodide.*[1] — The hot, neutral solution of the nitrate or sulphate, containing all the metal as proto-salt, is treated with sufficient potassium iodide to give a 1 per cent. solution after precipitation is complete. After cooling to room temperature, the precipitate of thallous iodide is filtered off on tared paper, and washed with cold 1 per cent. potassium iodide, which is then displaced by 82 per cent. alcohol. Filter and precipitate are dried at 110° and weighed. If thallic salt is present in the original solution, it must be reduced with sulphur dioxide.

(*b*) *As Thallous Chromate*, Tl_2CrO_4.[2]—The solution, containing all the metal as thallous salt, is treated with potassium carbonate or ammonia to alkaline reaction, heated to 70°, and potassium chromate solution added slowly until in slight excess. After standing cold overnight, the precipitate of thallous chromate is filtered off on asbestos felt in a Gooch crucible, washed with cold water, and dried over a low flame until the weight is constant.

(*c*) *As Chloroplatinate.*[3]—The neutral thallous nitrate or sulphate solution contained in a conical flask is boiled, and a solution of chloroplatinic acid added in slight excess. The flask is stoppered, shaken for five minutes, allowed to cool, and the precipitate filtered on a Gooch crucible, washed with cold water, dried at 100°, and weighed as Tl_2PtCl_6. The precipitate shows no tendency to run through the filter if the operation is carried out as described.

(*d*) *As Thiostannate.*[4]—To the hot very slightly acid solution of the metal a slight excess of sodium thiostannate is added, followed by a 15 per cent. solution of sodium monosulphide drop by drop until the liquid reacts neutral. An excess of 25 c.c. of the same reagent is then added and the boiling continued for five minutes while stirring. The solution is diluted with twice its bulk of hot water and allowed to stand three hours, after which the precipitate is filtered off on a Gooch crucible, washed well with cold water, dried at 105°, and weighed as Tl_4SnS_4.

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[1] Baubigny, *Compt. Rend.*, 1891, **113**, 544 ; Werther, *Z. anal. Chem.*, 1864, **3**, 1 ; Long, *ibid.*, 1891, **30**, 342, gives data showing the solubility of thallous iodide in various wash-liquors.

[2] Browning and Hutchins, *Chem. News*, 1899, **80**, 226.

[3] Neumann, *Annalen*, 1888, **244**, 349 ; improved by Cushman, *Amer. Chem. Journ.*, 1900, **24**, 222.

[4] Hawley, *Journ. Amer. Chem. Soc.*, 1907, **29**, 1011; also recommends precipitation as thallous orthothioarsenate.

The precipitant is prepared by adding strong sodium sulphide solution to a 10 per cent. solution of stannic chloride until the precipitate first formed just re-dissolves.[1]

§ **V. Volumetric Determination.**—The determination of thallium by volumetric methods is based on its ability to behave as a monovalent and a trivalent metal; owing, however, to the readiness with which the trivalent salts are hydrolysed, titration with permanganate in sulphuric acid solution does not give satisfactory results. Hydrochloric acid solutions may be used, but the process is complicated by the presence of the acid, and stoichiometric results are not obtained. By working as described under (*a*), however, Hawley [2] states that good results may be obtained.

(*a*) *Permanganate Method.*—The solution of thallium chloride should contain 4 c.c. of hydrochloric acid (sp. gr. 1·2) in a bulk of 60 c.c. Less than 0·16 grm. of the metal should be present, and the titration should be carried out in a cold solution. The permanganate is standardised against a weighed amount of pure thallous chloride, approximately equal to that in the assay.

(*b*) *Bromate Method.*[3]—A slight excess of standard potassium bromate solution (2·730 grm. per litre; 1 c.c = 0·01 grm. Tl) is added to the faintly acid solution of thallous sulphate. The excess of bromate is ascertained by adding 1 grm. of potassium bromide and a considerable excess of hydrochloric acid to the solution and distilling it down to one-third its bulk, the liberated bromine being caught in a solution of potassium iodide. The iodine set free is titrated with sodium thiosulphate (5 grm. per litre; 1 c.c. = 0·002 grm. Tl): $3TlCl + KBrO_3 + 6HCl = 3TlCl_3 + KBr + 3H_2O$; $KBrO_3 + 5KBr + 6HCl = 6KCl + 3Br_2 + 3H_2O$.

(*c*) *The Ferricyanide Method.*[4]—The solution of thallous nitrate in 100 c.c. of water is treated with an excess of potassium ferricyanide solution, followed by dilute caustic potash till the liquid reacts alkaline. The precipitate of thallic oxide is filtered off on an asbestos pad and washed with hot water; the filtrate is acidified with dilute sulphuric acid and the ferrocyanide present determined by titration with permanganate. As a check, the precipitate of thallic oxide may be dried at 200° and weighed as Tl_2O_3.[5]

§ **VI. Detection in Ores.**—The ore is dissolved in *aqua regia*, the solution evaporated to strong fumes with sulphuric acid, the cold mass

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[1] Other gravimetric methods that have been recommended are: Weighing as Tl_2SO_4 or $TlHSO_4$, Browning, *Amer. Journ. Sci.*, 1900, **9**, 137. Treating the thallous salt with bromauric acid and weighing the precipitated gold, Thomas, *Compt. Rend.*, 1902, **134**, 655. As thallous cobaltinitrite, Cunningham and Perkin, *Trans. Chem. Soc.*, 1909, **95**, 1569. Electrolytic methods: Mordern, *Journ. Amer. Chem. Soc.*, 1909, **31**, 1045; Gallo and Cenni, *Atti R. Accad. Lincei*, 1908, **17**, ii. 276.

[2] *Journ. Amer. Chem. Soc.*, 1907, **29**, 300.

[3] Marshall, *Journ. Soc. Chem. Ind.*, 1900, **19**, 994.

[4] Browning and Palmer, *Amer. Journ. Sci.*, 1909, **27**, 379.

[5] Other volumetric methods: Titration of iodine liberated by thallic salts from potassium iodide, Feit, *Z. anal. Chem.*, 1889, **28**, 314; titration of thallous chloride by N/6 bromine, Sponholz, *ibid.*, 1893, **31**, 519.

diluted with water, and any insoluble material filtered off. The filtrate is treated with a little sulphur dioxide, then with a slight excess of sodium carbonate and 2 to 3 grm. of sodium cyanide free from sulphide. After boiling, the precipitate is filtered off, and the filtrate saturated with hydrogen sulphide. Black thallous sulphide is precipitated; it is filtered off, washed, dissolved in sulphuric acid, and the solution tested as follows:—

(*a*) A platinum wire dipped in the solution and then held in the bunsen flame colours the latter green, and the spectroscope shows the characteristic line 5351 in the green.

(*b*) Potassium iodide gives a yellow crystalline precipitate.

(*c*) Potassium chromate gives a yellow precipitate in the faintly ammoniacal solution.

(*d*) Hydrogen sulphide gives no precipitate in acid, but a black sulphide is thrown down from alkaline, neutral, or acetic acid solutions.

(*e*) Ammonia, caustic soda, or sodium carbonate give no precipitate.[1]

§ VII. Determination in Ores.—(*a*) *Determination in Thallium Minerals* (§ I.).—One gramme of finely-powdered mineral is heated with 10 c.c. of strong sulphuric acid and 2 grm. of potassium sulphate in a 250 c.c. flask over a free flame. When completely decomposed, the mass is allowed to cool, diluted with water, boiled, again cooled, and filtered. The filtrate is neutralised with sodium carbonate and 2 grm. excess added, followed by 2–3 grm. of pure sodium cyanide. The liquid is boiled, allowed to settle, and filtered; the precipitate is well washed with hot water, and the filtrate and washings treated with ammonium sulphide until no further black precipitate forms. After cooling, the thallous sulphide is filtered off, washed with dilute ammonium sulphide, and dissolved in 20 per cent. sulphuric acid. The solution is treated with a few drops of sulphurous acid, nearly neutralised with sodium carbonate, filtered if necessary, and the thallium precipitated with potassium iodide (§ IV, (*a*)).

(*b*) *Determination in Pyrites, Blende, etc.*—A large quantity (from 10 to 100 grm.) is dissolved in hot hydrochloric acid, to which nitric is added from time to time, so that, eventually, there is very little excess of the latter left. After cooling, the insoluble material is filtered off, two or three sheets of pure zinc are introduced into the slightly acid filtrate, and the whole set aside overnight. The clear liquor is decanted through a filter, the metallic residue containing all the thallium, indium, cadmium, copper, etc., is washed two or three times with hot water, extracted with dilute sulphuric acid, and the solution treated with sodium carbonate and cyanide, as described under (*a*).

(*c*) *Complete Analysis.*—See Tellurium, § VIII.

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[1] Other typical reactions are: formation of red precipitate of cobaltinitrite (footnote [1], p. 66); formation of double iodide $3TlI.2SbI_2$, Ephraim, *Z. anorg. Chem.*, 1908, **58**, 353.

CHAPTER V.

THE RARE-EARTH GROUP.

§ **I. Generalities.**—The "Rare Earth Group" comprises a series of some sixteen very closely allied metals, which are usually found together in Nature, and are extremely difficult to separate from one another, no exact quantitative method being known except in the case of cerium. They may, however, be roughly separated into three groups by a method based on the solubilities of their double sodium sulphates in a saturated solution of sodium sulphate.

Cerium Group.	Terbium Group.	Yttrium Group.
Double sodium sulphates are insoluble in saturated Na_2SO_4 solution.	Double sodium sulphates are sparingly soluble in saturated Na_2SO_4 solution.	Double sodium sulphates are readily soluble in saturated Na_2SO_4 solution.
(1) Lanthanum. La = 139·0	(1) Europium. Eu = 152·0	(1) Yttrium. Y = 88·7
(2) Cerium. Ce = 140·25	(2) Gadolinium. Gd = 157·3	(2) Dysprosium. Dy = 162·5
(3) Praseodymium. Pr = 140·9	(3) Terbium. Tb = 159·2	(3) Holmium. Ho = 163·5
(4) Neodymium. Nd = 144·3		(4) Erbium. Er = 167·7
(5) Samarium. Sm = 150·4		(5) Thulium. Tm = 168·5
		(6) Ytterbium. Yb = 173·5
		(7) Lutecium. Lu = 175·0
		(8) Celtium. Ct = ?

The metals hold an anomalous position in the periodic classification; with the exception of yttrium, their atomic weights are intermediate between those of barium and tantalum; hence they may be regarded as forming a transition between these two elements without each member having a separate place in the table. Cerium acts either as a triad or tetrad, while the other elements are always trivalent (samarium and europium, however, give dichlorides). The trihydroxides are strongly basic compounds, the salts of which are only very slightly hydrolysed in dilute solutions. Perhaps their most characteristic property is the insolubility of the oxalates in oxalic or dilute mineral acids, which serves to separate them from all other metals except thorium and scandium.

§ **II. Minerals.**—(*a*) *Those in which the Cerium Group predominates.*—(1) *Carbonates.*—(a) *Parisite,* a fluocarbonate of cerium metals and lime, $CaCe_2F_2(CO_3)_3$, occurs as brownish-yellow to red, acute double hexagonal pyramids with perfect cleavage and strong positive double refraction. H 4½; sp. gr. 4·26.

(β) *Cordylite*, the barium analogue of the above, has similar properties.

(γ) *Bastnäsite*, cerium fluocarbonate, $CeFCO_3$, occurs as yellow to brown hexagonal prisms of H 4; sp. gr. 5·0.

(δ) *Lanthanite*, hydrated carbonate of the cerium metals, chiefly lanthanum, $La_2(CO_3)_3.8H_2O$. White to yellowish, opaque, orthorhombic tables. Cleavage perfect. Usually found amorphous as an alteration product. H 2; sp. gr. 2·6.

(2) *Silicates.*—(α) *Cerite*, a hydrated silicate of cerium metals, lime, and ferrous oxide, is a brittle, opaque, brown to red, orthorhombic mineral, usually occurring massive. No cleavage, dull resinous lustre. H 5½; sp. gr. 4·9.

(β) *Allanite* (*Orthite*) is an epidote containing rare earths. Brown to black, opaque monoclinic crystals. H 6; sp. gr. 3·5–4·2. On heating it becomes amorphous, and heavier.

(γ) *Hellandite*, complex hydrous silicate, $3H_2O.(Ca_2,Th,Mg_2)O_2$, $3(Al,Fe,Mn,Ce)_2O_3.4SiO_2$. Red-brown monoclinic prisms. H=5¼; sp. gr. 3·7.

(δ) *Beckelite*, zirconosilicate of cerium metals and lime, $Ca_3Ce_4(Si,Zr)_3O_{15}$, is found in brown transparent octahedra and dodecahedra with cubic cleavage. Sp. gr. 4·1.

(3) *Miscellaneous.*—(α) *Aeschynite.* See Columbium, § I.

(β) *Monazite.* See Thorium, § I.

(*b*) *Those in which Yttria Earths predominate.*—(1) *Silicates.*—(α) *Gadolinite*, ferrous beryllium yttrium silicate, $2BeO.FeO.Y_2O_3.2SiO_2$; brown to greenish-black, brittle, massive; no cleavage, conchoidal fracture. H 7; sp. gr. 4·0–4·5. Glows when heated to 430°, and is then insoluble in acids, the amorphous variety becoming crystalline and denser

(β) *Rowlandite*, yttrium silicate, $2Y_2O_3.3SiO_2$, pale green, massive, translucent. Sp. gr. 4·5.

(γ) *Yttrialite*, yttrium silicate, $Y_2O_3.2SiO_2$, massive, amorphous, translucent, olive-green. H 5½; sp. gr. 4·6.

(δ) *Thalenite*, hydrated yttrium silicate, $H_2O.2Y_2O_3.4SiO_2$, contains much nitrogen and helium. Flesh-red, translucent, monoclinic tables with greasy lustre, no cleavage. H 6½; sp. gr. 4·2.

(2) *Titanosilicates and Titanates.*—(α) *Yttrotitanite or Keilhauite*, complex titanosilicate of iron, lime, alumina, and yttria. Brown to black, monoclinic. Streak grey-brown, distinct cleavage, resinous lustre. H 6½; sp. gr. 3·6.

(β) *Yttrocrasite*, complex titanate of yttrium, with calcium, thorium, uranium, lead, iron. Radioactive, black, with bright pitchy lustre. H 5½; sp. gr. 4·8.

(γ) *Delorenzite*, ferrous uranium yttrium titanate, $2FeO.UO_2.2Y_2O_3.24TiO_2$, resinous, black, orthorhombic crystals; radioactive. H 5·5; sp. gr. 4·7.

(3) *Miscellaneous.*—(a) *Xenotime*, yttrium phosphate, YPO_4, brown to red-brown or yellow, transparent to opaque. Tetragonal; cleavage perfect. H 4½; sp. gr. 4·5.

(β) *Yttrofluorite*, yttrium calcium fluoride, $2YF_3.3CaF_2$, yellow to brown, transparent cubes with poor octahedral cleavage. Vitreous to greasy lustre, brittle. H 4½; sp. gr. 3·6.

(γ) *Yttrocerite*, yttrium cerium calcium fluoride, $(Y,Ce)_2Ca_3F_{12}.2/3H_2O$; violet-blue to white, massive; vitreous to pearly lustre. H 4½; sp. gr. 3·4.

(δ) *Samarskite*, *Fergusonite*, *Euxenite*, etc. See Columbium, § I.

CERIUM.

§ I. Properties and Compounds.—(*a*) The *metal* is obtained by electrolysis of the fused chloride. It is white, and readily combines on heating with oxygen or hydrogen. It slowly decomposes water in the cold, but rapidly at the boiling point. Owing to its great affinity for oxygen it is a powerful reducing agent. M.P. 623°.[1]

(*b*) *Cerium dioxide*, CeO_2, is formed by igniting any cerium compound of a volatile oxyacid in air as a dense white powder insoluble in nitric or hydrochloric acid unless a reducing agent is present; difficultly soluble in strong sulphuric acid.

(*c*) *Cerous oxide*, Ce_2O_3, is produced by heating the dioxide with metallic calcium. It readily oxidises in moist air to the dioxide.

(*d*) *Cerous hydroxide*, $Ce(OH)_3$, produced by the addition of an alkali to solutions of cerous salts, is a powerful reducing agent. In presence of air it gradually turns violet, and is finally completely oxidised to yellow ceric hydroxide.

(*e*) *Ceric hydroxide*, $Ce(OH)_4$, is precipitated on the addition of alkalies to ceric solutions or by oxidation of cerous hydroxide with hydrogen peroxide or chlorine. It is a yellow gelatinous precipitate, soluble in nitric acid to a deep red solution; in sulphuric acid to a yellow solution, with liberation of part of the excess oxygen; in hydrochloric acid with the formation of cerous chloride and evolution of chlorine. It has a tendency to form colloidal solutions, but is precipitated therefrom by electrolytes.

(*f*) *Ceric nitrate*. The neutral salt is unknown, basic compounds only being formed on dissolving the hydroxide in strong nitric acid. It forms an unstable yellow solution, which on the addition of ammonium nitrate turns deep red, due to the formation of a double salt, $(NH_4)_2Ce(NO_3)_6$; this is fairly stable in nitric acid solution, readily soluble in water and alcohol, but nearly insoluble in moderately strong nitric acid.

(*g*) *Cerous oxalate*, $Ce_2(C_2O_4)_3.10H_2O$, is precipitated by the addition of oxalic acid to a solution of a cerous or ceric salt. It is insoluble in water, dilute acids, ammonium oxalate, or in excess of the precipitant. On ignition it yields the dioxide.

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[1] Muthmann and Weiss, *Annalen*, 1904, **331**, 1. Hirsch (*Trans. Amer. Electrochem. Soc.*, 1911, **20**, 57) gives the M.P as 635°, and sp. gr. 6·92.

§ II. Quantitative Separation.—Cerium is a member of the third analytical group, and can be readily separated from all other members of this group (except thorium and the other rare earths) by precipitation with oxalic acid as follows :—

(*a*) *Separation of Cerium* (*and the Rare Earths*) *from Members of the Ammonia Group.*—The chloride solution, containing not more than 1 grm. of the oxides per 60 c.c., is adjusted to an acidity equivalent to 0·3 N and treated with a saturated solution of oxalic acid sufficient to leave 3 grm. of oxalic acid per 100 c.c. of final solution. The flocculent precipitate of the rare earth oxalates rapidly becomes crystalline. The solution is allowed to stand at 60° for twelve hours, or overnight, after which the precipitate is filtered off and thoroughly washed with hot slightly acidified water. If much foreign metals are present it is advisable to digest the precipitate with caustic soda, filter, wash with boiling water till free from oxalates, dissolve the hydroxides in nitric acid, and re-precipitate as before.[1]

(*b*) *Separation from Thorium.*—This may be effected by any of the following methods (for details of which see Thorium, § III.) :—

(1) By precipitation of the thorium from the neutral solution of the nitrates with hydrogen peroxide.

(2) By precipitation of the thorium from neutral solution of the chlorides with sodium thiosulphate.

(3) By precipitation of the thorium from strong nitric acid solution with potassium iodate.

(4) By precipitation of the thorium from sulphuric or hydrochloric acid solution as pyrophosphate or hypophosphate. In the filtrate from the thorium the other rare earths are precipitated with an excess of caustic soda, the hydroxides filtered off and well washed with boiling water till free from the precipitant. Double precipitation may be necessary.

(*c*) *Separation from the other Rare Earths.*—All methods of separating cerium from the other rare earths are based on the fact that this metal can exist in a quadrivalent state, and these compounds are readily hydrolysed with the separation of ceric hydroxide or basic ceric salt. In every case the separation must be repeated several times to ensure a complete separation. The following are the chief methods that have been used :—

(1) *Mosander's Chlorine Method.*[2]—The mixture of rare earths obtained by ignition of the oxalates is dissolved in hydrochloric acid with the addition of a little hydrogen peroxide. The clear liquid is boiled to destroy the excess of the latter reagent, treated with caustic soda until precipitation of the hydroxides is complete, heated to boiling, the precipitate allowed to settle, the clear liquid decanted through a

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[1] Precipitation of rare earth oxalates : Hintz and Weber, *Z. anal. Chem.*, 1897, **36**, 213 ; Drossbach, *Z. angew. Chem.*, 1901, **14**, 655 ; Benz, *ibid.*, 1902, **15**, 297 ; Hauser and Wirth, *ibid.*, 1909, **22**, 484 ; Glaser, *Z. anal. Chem.*, 1897, **36**, 213 ; Ruer, *Z. anorg. Chem.*, 1904, **42**, 48.

[2] Mosander, *Phil. Mag.*, 1843, **23**, 241 ; Hauser and Wirth, *Z. anal. Chem.*, 1909, **48**, 679 ; Browning and Roberts, *Amer. Journ. Sci.*, 1910, **29**, 45 ; Johnstone, *Journ. Soc. Chem. Ind.*, 1914, **33**, 55.

filter, and the precipitate washed several times by decantation. The small quantity on the filter is washed back into the beaker with the minimum of water, the liquid in the beaker made up to 200 c.c. with strong (25 per cent.) caustic soda, and saturated with chlorine until it no longer reacts alkaline. It is then boiled five minutes and allowed to stand overnight, after which the ceric hydroxide is filtered off, washed with boiling water, dissolved in hydrochloric acid, and the above process repeated. After six or seven repetitions the ceria precipitate will be substantially pure, although still containing traces of the other earths.

(2) *The Permanganate Method.*[1]—The neutral solution of the nitrates containing all the cerium as cerous nitrate is heated to boiling in a capacious basin and potassium permanganate solution added in small quantities at a time until the red colour just begins to be permanent. A solution of potassium permanganate and sodium carbonate in the exact ratio $KMnO_4 : 4Na_2CO_3$ is now added very slowly with constant stirring to the nearly boiling solution, so that the pink colour never actually fades away. If, however, this should happen, the colour is restored by the addition of a little pure permanganate. As the precipitation nears completion, the colour disappears more slowly after each addition of the reagent and the effervescence becomes less marked; the solution should then be tested with litmus paper from time to time and permanganate-carbonate or pure carbonate added until it is very nearly neutral, taking care that the pink colour is never actually discharged. After simmering for ten minutes with stirring the precipitate is filtered off, washed with boiling water, dissolved in concentrated hydrochloric acid, the solution diluted, and the cerium precipitated with an excess of oxalic acid. The oxalate is filtered off, washed free from manganese with acidulated water, and dissolved by digestion with fuming nitric acid on a water-bath. The solution is evaporated to dryness, the residue moistened with water which is again evaporated, taken up in water, and the permanganate precipitation repeated. The oxalate obtained this time is ignited and weighed as CeO_2. Traces of cerium are left in the filtrates from the permanganate precipitation; they may be removed by neutralising with sodium carbonate, adding sufficient permanganate to give a permanent pink tint, and boiling for ten minutes. The small precipitate which contains minute amounts of the other earths is treated as before for purification.

(3) *The Bromate Method.*[2]—The neutral, fairly concentrated solution of the nitrates is heated to boiling and treated with potassium bromate. Immediately the red fumes of bromine commence to appear two or three small lumps of marble are added and the liquid boiled for several hours, making good loss by evaporation from time to time. As soon as a test of the filtered solution shows only a trace of cerium by the peroxide test (§ VI, (*f*)) the vessel is removed from the heat, the

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[1] Roberts, *Amer. Journ. Sci.*, 1911, **31**, 350. See also James, *Journ. Amer. Chem. Soc.*, 1908, **30**, 982; Meyer, *Z. anorg. Chem.*, 1903, **37**, 378; Meyer and Schweitzer, *ibid.*, 1907, **54**, 104.

[2] James and Pratt, *Journ. Amer. Chem. Soc.*, 1911, **33**, 1326.

marble taken out, the precipitate allowed to settle, filtered, and washed with 5 per cent. ammonium nitrate solution. This precipitate is practically pure, but may, if thought desirable, be re-dissolved in nitric acid (with the aid of hydrogen peroxide if necessary), the solution evaporated to dryness, etc., and re-precipitated as before. The filtrates are united and boiled with more bromate and marble till the solution ceases to give the peroxide test. This small precipitate is purified as before.

§ **III. Gravimetric Determination.**—Cerium is always weighed as dioxide:—

(*a*) *Oxalic Acid Precipitation.*—The solution of the pure cerous nitrate, slightly acid with nitric acid, is heated to boiling, and an excess of a cold saturated solution of oxalic acid added. The solution is allowed to stand overnight, the precipitate filtered off, washed with warm acidulated water (nitric acid), dried, ignited in platinum, gently at first, finally over the blast, and weighed as CeO_2. Precipitation from a chloride solution leads to co-precipitation of oxalochloride, which on ignition yields a basic chloride, and consequently high results. Alkaline salts, especially potassium, are liable to give serious contamination of the precipitate.

(*b*) *Ammonium Sebacate Precipitation.*[1]—The neutral solution of the nitrate is heated to boiling and a small excess of ammonium sebacate added. After allowing to settle, the precipitate is filtered off, dried, ignited as above, and weighed as CeO_2.

§ **IV. Volumetric Determination.**—(*a*) *Von Knorre's Permanganate Method.*[2]—This is based on the fact that ammonium persulphate in dilute sulphuric acid solution oxidises cerous to ceric sulphate. On the addition of a slight excess of hydrogen peroxide the ceric is again reduced to cerous salt; the excess of peroxide is then determined by titration with permanganate:

$$2Ce(SO_4)_2+H_2O_2=Ce_2(SO_4)_3+H_2SO_4+O_2$$
$$2KMnO_4+5H_2O_2+3H_2SO_4=K_2SO_4+2MnSO_4+8H_2O+5O_2.$$

The procedure is as follows:—The cold solution of cerous salt is acidified with dilute sulphuric acid, 2 grm. of ammonium persulphate added, and the solution boiled two minutes. It is then cooled to about 50° by immersion of the flask in cold water, a further half grm. of persulphate added, and the solution again boiled for five minutes, cooled to 50°, treated with yet another half grm. of persulphate and a little more sulphuric acid, and boiled until no further bubbles of gas are evolved. (This takes about fifteen minutes, at the end of which all the persulphate has been decomposed.) The flask is cooled in running water, and a standard solution of hydrogen peroxide added until the yellow colour is just discharged. This is followed by a small excess, which latter is titrated back with N/20 permanganate solution. The permanganate can be standardised against

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[1] Whittemore and James, *Journ. Amer. Chem. Soc.*, 1912, **34**, 772; 1913, **35**, 129.

[2] *Z. angew. Chem.*, 1897, **10**, 685, 717; *Ber.*, 1900, **33**, 1924; Power and Shedden, *Journ. Soc. Chem. Ind.*, 1900, **19**, 636.

oxalic acid, and the hydrogen peroxide solution then standardised against the permanaganate. 1 c.c. N/20 $KMnO_4 = 0{\cdot}0070125$ grm. Ce. The above method gives very fair results in the presence of the other rare earths; phosphates and titanium, however, interfere.

(*b*) *Sodium Bismuthate Method.*[1]—The solution of cerous sulphate containing 20 c.c. of concentrated sulphuric acid in a bulk of a 100 c.c., is treated with 2 grm. of ammonium sulphate and 1 grm. of sodium bismuthate, and boiled for five minutes. After cooling a little, 50 c.c. of 2 per cent. sulphuric acid are added, and the excess of bismuthate filtered on a Gooch crucible packed with asbestos previously well washed, first with acidified permanganate, then with distilled water. The crucible is washed with 100 to 150 c.c. of 2 per cent. sulphuric acid, the filtrate cooled to room temperature, a small excess of hydrogen peroxide or ferrous sulphate added, and the excess titrated back with N/20 permanganate. Rare earths, zirconium, thorium, and titanium do not interfere.

(*c*) *The Ferricyanide Method.*[2]—The neutral solution of cerous sulphate is poured into an excess of potassium ferricyanide solution made alkaline with 2–3 grm. of caustic soda. The precipitated hydroxides are filtered off, well washed with warm water, the filtrate and washings acidified with sulphuric acid, and the ferrocyanide present titrated with N/20 potassium permanganate:

$$Ce_2(SO_4)_3 + 2K_3Fe(CN)_6 + 8KOH = 2Ce(OH)_4 + 2K_4Fe(CN)_6 + 3K_2SO_4.$$

§ V. Colorimetric Determination.—Cerium may be determined in thorium oxide by the following process:[3]—The material is fused with bisulphate, the solution of the melt precipitated with ammonia, and the precipitate dissolved in nitric acid. The liquid is evaporated to dryness, the residue taken up in water, and filter fibres removed by filtration. The filtrate is heated with a measured excess of citric acid and hydrogen peroxide, neutralised with ammonia, and transferred to a cylinder. The standard is prepared by adding an approximately equal amount of pure thorium nitrate to a small quantity of cerium solution (0·0005 grm. Ce), and equal quantities of citric acid, hydrogen peroxide, and ammonia. The tints are matched by withdrawing a suitable amount of solution from the cylinder in which the colour is stronger.

§ VI. Detection in Ores.—The ore is opened up by one of the methods described in § VII., the total rare earths precipitated as oxalates, and the latter digested with fuming nitric acid, which is finally evaporated to dryness on a water-bath; the residue is taken up with water, the thorium removed with hydrogen peroxide, and the rare earths in the filtrate precipitated with ammonia after boiling off the excess of peroxide. The precipitate is filtered off, well washed, dissolved in nitric acid with a few drops of hydrogen peroxide, the solution evaporated to dryness, and the following tests applied after taking up with water:—

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[1] Metzger, *Journ. Amer. Chem. Soc.*, 1909, **31**, 523; Metzger and Heidelberger, *ibid.*, 1910, **32**, 642. *Cf.* also Wägner and Müller, *Ber.*, 1903, **36**, 282, 1732.

[2] Browning and Palmer, *Amer. Journ. Sci.*, 1908, **26**, 83; *Chem. News*, 1908, **98**, 106

[3] Benz, *Z. angew. Chem.*, 1902, **15**, 300.

(*a*) Caustic soda or alkalies give a white precipitate insoluble in excess, turning yellow on addition of hydrogen peroxide.

(*b*) The solution is poured into a large excess of potassium carbonate solution so as to yield a clear liquid ; on adding a few c.c. of hydrogen peroxide the solution turns yellow if cerium is present.[1]

(*c*) Tartaric acid is added, the solution made ammoniacal, and boiled with a few drops of hydrogen peroxide. A dark brown colour develops if cerium is present.[2]

(*d*) Ammoniacal silver nitrate solution is warmed with the neutral cerous solution, when a brown colour or black precipitate (according to the amount of cerium present) is produced.[3]

(*e*) The solution is rendered alkaline with caustic soda, evaporated to dryness, and a drop of a solution of strychnine in excess of sulphuric acid added. The solution turns blue or violet, and finally red.

(*f*) One part of ceria in 10,000 of liquid may be detected by treating the neutral or slightly acid solution with ammonium acetate in excess and hydrogen peroxide. A yellow precipitate or colour, due to the formation of basic perceric acetate, is formed.[4]

§ **VII. Determination in Ores.**—(*a*) *Gravimetric.*—(1) *Opening up the Ore.*—(α) *Monazite Sand.*—5 grm. of the powdered sand are heated with 10 c.c. of concentrated sulphuric acid at 200°–300° until completely decomposed (2–3 hours), avoiding as far as possible loss of acid by evaporation. The pasty mass is allowed to cool, stirred into a large excess of cold water so that all soluble matters dissolve, and the solution made up to 250 c.c. It is filtered, and 50 c.c. (=1 grm.) pipetted off.

(β) *Aeschynite.*—2·5 grm. of the slimed mineral are strongly heated with 10–12 c.c. of sulphuric acid until the excess of the latter is expelled. The residue of anhydrous sulphates is dissolved in ice-cold water, the solution made up to 250 c.c., allowed to stand overnight, and 100 c.c. (=1 grm.) filtered off.

(γ) *Cerite, Orthite, Gadolinite.*—2·5 grm. of the finely divided mineral are made into a paste with water, 5 c.c. of concentrated sulphuric acid added, and the mixture heated to drive off all volatile matter, finishing up at a dull red heat. After cooling, the mass of anhydrous sulphates and silica is powdered and stirred into 200 c.c. of ice-cold water. The solution is made up to 200 c.c., allowed to stand overnight, and 100 c.c. (=1 grm.) filtered off.

(2) *Separation of the total Rare Earths.*—(α) The solution obtained from monazite sand is treated cold with an equal bulk of cold saturated solution of oxalic acid, allowed to stand an hour, stirred vigorously, and set aside overnight. The crystalline oxalate precipitate is filtered off, well washed with acidified water, ignited to oxide, and the latter dissolved in nitric acid with the addition of a little hydrogen peroxide

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[1] Job, *Compt. Rend.*, 1898, **126**, 246 ; Meyer, *Z. anorg. Chem.*, 1904, **41**, 94.

[2] Wirth, *Chem. Zeit.*, 1913, **37**, 773.

[3] Biltz and Zimmermann, *Ber.*, 1907, **40**, 4979.

[4] Hartley, *Trans. Chem. Soc.*, 1882, **41**, 202.

to reduce ceric oxide. After expelling excess of peroxide, the solution is cooled, diluted to 150 c.c., the acidity adjusted to 0·3 N nitric acid, and the rare earths re-precipitated as oxalates by the addition of a moderate excess of a saturated (cold) oxalic acid solution to the warm (60°) solution of the earths. The precipitate is now free from phosphoric acid and other members of the ammonia group, and contains all the thorium, scandium, and rare earths; it is ignited to oxides.

(β) The solution of the cerite, orthite, or aeschynite earths is treated with ammonia to remove the greater part of the lime which remains in solution. After heating to boiling, the precipitate of earth hydroxides, together with iron, etc., is filtered off, washed with hot water, dissolved in the minimum quantity of nitric acid with a few c.c. of hydrogen peroxide to reduce any ceric salt, boiled, and treated with a cold saturated oxalic acid solution in moderate excess. After stirring vigorously the whole is allowed to stand (preferably at 60° overnight), filtered, the precipitate well washed with hot water, ignited, dissolved in nitric acid, re-precipitated, and again ignited.

(3) *Separation of the Thoria.*—The ignited earth oxides are dissolved in nitric acid with the aid of a few c.c. of hydrogen peroxide added from time to time, the solution evaporated to dryness on the water-bath, the residue moistened with water, and again dried. The neutral nitrates are now dissolved in water and the thorium precipitated as peroxide by the addition of hydrogen peroxide and a large amount of ammonium nitrate (see Thorium, § III.). The precipitate after washing is dissolved in nitric acid, the excess of which is removed by evaporation as before, and the thorium re-precipitated.

(4) *Separation and Estimation of Cerium.*—The combined filtrates are treated hot with an excess of ammonia, the precipitate filtered, washed well, dissolved in nitric acid, and the cerium precipitated as described in § II, (*c*). The precipitate produced by any of the methods there enumerated is dissolved in hydrochloric acid, boiled to expel chlorine, the acidity adjusted to 0·3 N, the solution diluted to 200 c.c., and the cerium precipitated as oxalate (§ III.). The precipitate and paper are digested with fuming nitric acid, evaporated to dryness on the water-bath, taken up with water, and the cerium precipitated as in § III. This precipitate is ignited and weighed as CeO_2. The colour of the ignited oxide is a fair test of purity; it should be very pale yellow to nearly white, without a trace of a salmon or pink colour.

(*b*) *Volumetric.*[1]—0·5 grm. of cerite, orthite, or other silicate is fused with 5 grm. of sodium bisulphate, the cold melt dissolved in 350 c.c. of cold water containing 5 c.c. of strong sulphuric acid, and the solution allowed to stand overnight. 0·6 grm. of monazite is heated to 200–300° with 5 c.c. of strong sulphuric acid; after complete decomposition the cold mass is stirred into 350 c.c. of ice-cold water and set aside overnight. In either case the solution is filtered, the residue washed with cold dilute sulphuric acid, and 100 c.c. of cold saturated solution of oxalic acid added to the boiling filtrate. After standing

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[1] Metzger and Heidelberger, *Journ. Amer. Chem. Soc.*, 1910, **32**, 642.

overnight the precipitate is filtered off, washed with warm 1 per cent. oxalic acid, rinsed off the paper into the original beaker, and well boiled with an excess of caustic soda. The hydroxides are filtered off, washed free from oxalates, and dissolved in 80 c.c. of water and 2 c.c. of strong sulphuric acid; 2 grm. of ammonium sulphate are added, the solution boiled, treated with 1 grm. of sodium bismuthate, and the analysis finished as described in § IV, (*b*).

RARE EARTH METALS OTHER THAN CERIUM.

§ I. Properties and Compounds.—Cerium having been dealt with separately, the other rare earth metals will now be described collectively in three groups, viz. cerium metals, terbium metals, and yttrium metals.

(*a*) *Cerium Metals.*—(1) The *metals* are produced by electrolytic reduction of the fused anhydrous chlorides. They are white to yellowish in colour, tarnish slowly in moist air, decompose water slowly in the cold but rapidly on boiling with evolution of hydrogen, and dissolve readily in acids. They combine directly with oxygen, hydrogen, nitrogen, and carbon on heating. The physical properties are tabulated below:—

Metal.	Colour.	Melting Point.[1]	Specific Gravity.[1]
Cerium . . .	Iron-grey.	623°	7·02
Lanthanum . .	Tin-white.	810	6·15
Praseodymium . .	Yellow.	940	6·48
Neodymium . .	Yellow tinge.	840	6·96
Samarium . . .	Pale grey.	1350	7·7

An alloy known as *Mischmetall*, consisting chiefly of cerium metals, is prepared by the electrolysis of the molten anhydrous chlorides. These are prepared from monazite residues obtained in the manufacture of thorium nitrate.

(2) The *oxides* are fairly strong bases, which liberate ammonia from ammonium salts, and are soluble in dilute acids after ignition. They may be prepared by ignition of the oxalates, nitrates, or hydroxides.

(*α*) *Lanthana*, La_2O_3, is a white powder which readily absorbs carbon dioxide from the air. Like lime, it hisses when slaked, and turns red litmus blue.

(*β*) *Praseodymia*, Pr_2O_3, is a greenish-yellow powder which, when heated, readily absorbs oxygen from the air, being converted into a brown oxide, probably Pr_4O_7, which is also formed on ignition of the oxalate or nitrate in the air. The dioxide, PrO_2, is obtained as a black powder by heating the nitrate to 440°.

(*γ*) *Neodymia*, Nd_2O_3, is a light blue to lilac powder with a faint reddish fluorescence; very small amounts of impurities, however, turn it brown. The colour of salts of neodymium is complementary to

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[1] Muthmann and Weiss, *loc. cit.* (p. 70).

that of praseodymium salts (this is also the case with erbium and thulium, see (*c*)). The usual neodymium : praseodymium ratio in minerals is 2 : 1.

(δ) *Samaria*, Sa_2O_3, is a yellowish-white powder of density 8·3.

(3) The *hydroxides* are precipitated by the addition of alkali to hot dilute solutions of the salts. They are insoluble in excess of the precipitant, absorb carbon dioxide from the air, and give rise to unstable peroxides with hydrogen peroxide. Lanthanum hydroxide is white, turns red litmus blue, and gives a blue colour with solid iodine. Praseodymium hydroxide is bright green, the neodymium compound blue, and that of samarium yellowish-white. Solutions of the salts with colourless acids are, in the case of lanthanum, colourless; praseodymium, green; neodymium, red to reddish-violet; samarium, topaz-yellow. The basic power of the hydroxides decreases in the order La, Ce^{iii}, Pr, Nd, Sa, Ce^{iv}.

(4) The *chlorides*, $\text{M}^{\text{iii}}\text{Cl}_3$, are produced by solution of the metals, oxides, hydroxides, or carbonates in hydrochloric acid. They crystallise as hexahydrates with the exception of the praseodymium salt, which forms a heptahydrate. Dark brown samarous chloride, SmCl_2, is obtained by reduction of SmCl_3 in hydrogen.

(5) The *fluorides* are insoluble in water and dilute mineral acids, but somewhat soluble in strong hydrofluoric acid. They may be precipitated as hydrated salts by addition of hydrofluoric acid to solutions of the chlorides. The anhydrous salts are isomorphous with fluorspar.

(6) The *sulphates* are produced by treating the oxides with excess of sulphuric acid and subsequently heating to 500°. They readily dissolve in ice-cold water, with the formation of hydrates whose solubilities are lower than those of the anhydrous salts and decrease with rise in temperature. This is an important property, which is made use of for the final purification of the elements.

	Hydrate stable at 25°.	Other Hydrates.	Crystal form of stable Hydrate.	Solubility (grm. anhydrous sulphate in 100 H_2O) at		
				0°	18°	100°
Lanthanum sulphate	$\text{La}_2(\text{SO}_4)_3.9\text{H}_2\text{O}$	16; $6\text{H}_2\text{O}$	Hexagonal	3·0	2·1	0·7
Praseodymium ,,	$\text{Pr}_2(\text{SO}_4)_3.8\text{H}_2\text{O}$	5; 6; 12; $15\frac{1}{2}\ \text{H}_2\text{O}$	Monoclinic	19·8	14·05	1·0
Neodymium ,,	$\text{Nd}_2(\text{SO}_4)_3.8\text{H}_2\text{O}$	none	,,	9·5	7·0	2·25
Samarium ,,	$\text{Sm}_2(\text{SO}_4)_3.8\text{H}_2\text{O}$	none	,,	3·42 at 25°.		

On addition of a large excess of sodium or potassium sulphate to a solution of the chlorides, crystalline double sodium (potassium) sulphates are precipitated. These are insoluble in saturated sodium or potassium sulphate solutions.

(7) The *oxalates* are precipitated as decahydrates by the addition of oxalic acid to a solution of the metals. They are insoluble in water,

very slightly soluble in dilute mineral acid, and readily soluble in hot concentrated hydrochloric or nitric acid, from which oxalo-chlorides or oxalo-nitrates may be crystallised.

(8) The *double nitrates* have the general formula: $2[M^{iii}(NO_3)_3].3[M^{ii}(NO_3)_2].24H_2O$, where M^{iii}=rare earth metals; the bismuth salts are isomorphous with those of the rare earths, and their solubilities are intermediate between those of the corresponding salts of samarium and europium and those of gadolinium and dysprosium, while they are nearly equal to those of terbium; M^{ii}=magnesium, manganese, nickel, cobalt, zinc. The formula of the double ammonium nitrates is $M^{iii}(NO_3)_3.2NH_4NO_3.4H_2O$.

(*b*) *Terbium Metals.*—The general methods of preparation of the metals and their salts are the same as for the cerium metals. Little is known concerning the pure metals. The properties of the most important compounds are given in the following table:—

	Europium.	Gadolinium.	Terbium.
Oxides . .	Eu_2O_3; pale pink.	Gd_2O_3; white.	Tb_2O_3, white; Tb_4O_7, dark brown, formed on igniting oxalate.
Chlorides . .	$EuCl_3.6H_2O$, pale rose. $EuCl_2$, colourless, soluble in H_2O, formed by reduction of $EuCl_3$ in hydrogen.	$GdCl_3.6H_2O$, colourless, deliquescent.	$TbCl_3$, deliquescent colourless prisms.
Sulphates . .	$Eu_2(SO_4)_3.8H_2O$.	$Gd_2(SO_4)_3.8H_2O$. 2·98 parts of anhydrous salt dissolve in 100 H_2O at 25°.	$Tb_2(SO_4)_3.8H_2O$.

The double sodium or potassium sulphates are slightly soluble in saturated alkali sulphate solution.

(*c*) *Yttrium metals.*—Yttrium, erbium, and ytterbium are the three most abundant metals of this group; the others are rare, and little is known of their chemistry.

(1) The *metals.* Yttrium and erbium have been prepared as grey metallic powders; the other metals have not yet been described.

(2) The *oxides* are prepared by ignition of the oxalates, hydroxides, or nitrates.

(α) *Yttria*, Y_2O_3, is a pure white, feebly diamagnetic powder which absorbs carbon dioxide from the air and liberates ammonia from its salts. Yttrium salts are colourless.

(β) *Dysprosia*, Dy_2O_3, is a white, highly paramagnetic solid giving yellow salts.

(γ) *Holmia*, Ho_2O_3, is a pale yellow, highly paramagnetic powder; its salts are orange-yellow.

(δ) *Erbia*, Er_2O_3, is a heavy, rose-coloured powder (density 8·6). Its salts are rose-coloured, have a sweet astringent taste, and yield characteristic absorption spectra.

(ε) *Thulia*, Tm_2O_3, a dense white powder with a greenish tinge; gives pale green salts, the colour of which is complementary to that of erbium salts. When strongly heated it gives a carmine-red glow which is very characteristic.

(ξ) *Ytterbia*, Yb_2O_3, white powder which dissolves in acids, giving colourless salts.

(η) *Lutecia*, Lu_2O_3, is a white powder; salts colourless.

(θ) *Celtia*, Ct_2O_3, is white. It has only recently been discovered (1911).

(3) The *chlorides* crystallise with six molecules of water, with the exception of the thulium salt, which has seven.

(4) The *sulphates* crystallise as monoclinic octahydrates and form double salts with sodium or potassium sulphates, which are soluble in a saturated solution of the alkali sulphate.

(5) The *oxalates* are precipitated in a similar manner to those of the cerium metals.

§ II. Quantitative Separation from other Elements.—(*a*) The rare earths are separated from other elements of the ammonia group by means of oxalic acid (see Cerium, § II, (*a*)).

(*b*) *Separation from Thorium.*—See Thorium, § III.

(*c*) *Separation from Cerium.*—See Cerium, § II.

(*d*) *Separation from Scandium.*—See Scandium, § III.

§ III. Separation of the Rare Earths from one another.—(*a*) *Approximate Separation of the Cerium from the Yttrium Group.*—(1) *The Metals are in Solution as Chlorides or Nitrates.*[1]—The solution is evaporated to dryness on a water-bath, the residue taken up in a minimum amount of water, and 200 to 300 c.c. of a saturated solution of potassium sulphate added, followed by 5 grm. of the powdered salt. The mixture is well stirred, set aside overnight, filtered, the precipitate washed with a saturated solution of potassium sulphate, and digested with hot caustic soda solution. The resulting hydroxides are filtered off, well washed with hot water, dissolved in hydrochloric acid, the solution evaporated to dryness, the residue taken up in a minimum of water, and the cerium metals precipitated as before. The precipitate is transformed into nitrate and the metals precipitated with oxalic acid. The combined filtrates from the double sulphate precipitate are treated with oxalic acid to throw down the yttrium earth oxalates.

(2) *The Metals are Present as Sulphates.*—The solution is evaporated to dryness, and the residue heated to 450° until no further fumes of sulphuric acid are evolved. The cold mass is broken up and dissolved in ice-cold water to a nearly saturated solution, which is diluted with an equal bulk of water, and solid sodium sulphate added with constant stirring until the solution is saturated. After standing overnight the precipitate is filtered off, washed with saturated sodium sulphate solu-

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[1] Johnstone, *Journ. Soc. Chem. Ind.*, 1914, **33**, 55.

tion, and digested hot with caustic soda ; the hydroxides are filtered off, washed with hot water, dissolved in hydrochloric acid, and the solution re-precipitated with sodium (or potassium) sulphate as in (1). The precipitate of double alkali sulphates after the second precipitation contains all the lanthanum, praseodymium, and neodymium, and nearly all the samarium, europium, and gadolinium, together with a minute amount of yttrium metals, but a small part of the terbium metals will be found in solution together with the yttrium group.

(*b*) *Separation of the Rare Earths from one another.*—Except for the separation of thorium and cerium from the other rare earths, no exact quantitative separation of these metals is known. The only method by which a separation can be accomplished is that of fractional crystallisation, which is applicable to the rare earths because their corresponding salts are usually isomorphous and capable of forming mixed crystals. It has been found that the order in which these salts separate from solutions is generally as follows :—

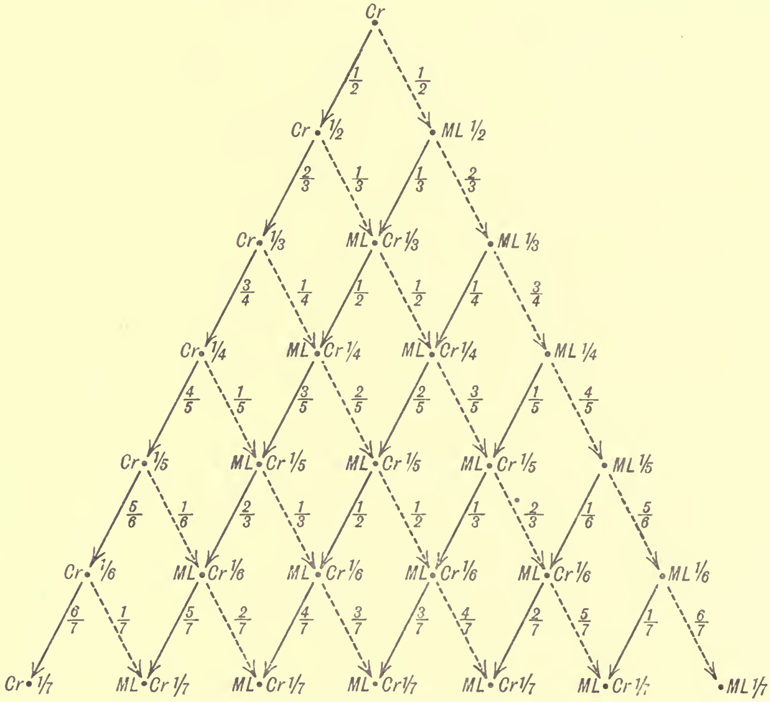
$$\underbrace{\text{La Ce Pr Nd Sm}}_{\text{Cerium group.}} \qquad \underbrace{\text{Eu Gd Tb}}_{\text{Terbium group.}} \qquad \underbrace{\text{Dy Ho Y Er Tm Yb Lu Ct}}_{\text{Yttrium group.}}$$

Hence, with the exception of yttrium, this "serial order" corresponds with the sequence of the elements according to increase in atomic weight. The usual procedure for fractionating a mixture of rare earth salts is carried out in two stages :—

(1) *First Stage.*—The original mixture of salts (A) is dissolved in the hot solvent and the solution evaporated until on cooling about one-half the original mixture crystallises out. After standing overnight the mother-liquor (B) is decanted into a new vessel and again evaporated, so that about one-third of the remaining salt crystallises on cooling. The first crystals (C) are dissolved in hot solvent, so that on cooling two-thirds of the mixture crystallises out. Both vessels are allowed to stand overnight ; the liquor (D) from the evaporation of B is poured off from the crystals (E) and again evaporated. The liquor (F) from the re-crystallisation of C is poured on to crystals E, the whole warmed until the crystals dissolve, adding more solvent if necessary, and the solution allowed to crystallise. The crystals from F are re-dissolved and re-crystallised as before. The process is continued in like manner until about 20 fractions have been obtained, the first crystals in each series being re-crystallised from fresh solvent, the mother-liquors from each crop being used to dissolve the next crop, and the final mother-liquor being evaporated in stages (see diagram, p. 82).

(2) *Second Stage.*—In this stage the number of fractions is kept constant. The fractions, numbered from one to twenty, are heated until any crystals dissolve, and evaporated so that on cooling about three-fourths of the solid separates. The mother-liquor from fraction 2 is poured into a new vessel (21), the liquor from 19 on to the crystals in 20, that from 18 into crystals 19, and so on down to the liquor from 1, which is poured on to crystals 2. New solvent is placed in vessel 1, the whole series from 1 to 20 heated till the crystals dissolve, and again

allowed to crystallise. The same process is gone through as in the first case; the liquor from 20 is poured into 21, that from 19 on to crystals 20, and so on. Crystals 1 are again taken up in fresh solvent and the entire series of operations repeated. After a time crystals 1 become very small in bulk; they therefore miss a crystallisation, after which they are added to the crystals in vessel 2, which thenceforward constitutes the "head" fraction. When the liquor in vessel 21 gets to a sufficient bulk it is added to the series and becomes the new "tail" fraction; by continuing in this manner, fractions 1, 2, 3, etc., gradually disappear, and new fractions, 21, 22, 23, etc., appear at the end of the series. As each head or tail fraction becomes a pure salt it is removed from the series, and thus after a time the fractions begin to get less as more and more of the pure salts are removed from each end.



Continued until 20 fractions are obtained.

Cr = crystals; ML = mother-liquor.

Crystals move in the direction of the continuous lines; mother-liquors, in that of the broken lines.

The figures at the nodal points (written thus: $^1/_6$) represent the weight of salts in the products as fractions of the original mixture. Those on the arrows (written thus: $\frac{3}{7}$) show in what proportion each fraction should be split up into crystals and mother-liquor.

(3) *Control of the Fractionation.*—Several methods are available for ascertaining the progress of the fractionation:—

(*a*) *Spectroscopic Methods.* (See Introduction).—Where a metal gives an absorption spectrum (praseodymium, neodymium, erbium, thulium), the inspection of the latter is a rapid means for detecting the presence of the metal. The spark spectrum may be applied to all the rare earths, while the examination of the arc spectrum supplies the final proof of purity.

(β) *Determination of Equivalent Weight.*—A weighed amount of the oxide, prepared from the oxalate, is dissolved in hydrochloric acid, a small excess of sulphuric acid added, the solution evaporated to dryness, and the residue heated slowly to 500° to constant weight. This method answers well for cerium metals and yttrium, but the less basic members of the yttrium group are best converted into anhydrous sulphates, a weighed amount of which is ignited to oxide.

(γ) *Determination of the Magnetic Susceptibility*[1] is said to be a rapid and useful method.

(4) *The Separation.*—The procedure tabulated below, which will give the best possible results in the shortest time, is substantially that worked out by C. James.[2] The thorium having been removed by one of the methods described under Thorium, § III., the rare earths in the filtrate are precipitated hot with caustic soda, the precipitate dissolved in hydrochloric acid, the solution precipitated with oxalic acid, and the precipitate ignited to oxides. The further treatment depends on the proportion of yttrium earths present: if this exceeds 20 per cent., the mixed oxides are dissolved in hydrochloric acid and the analysis proceeded with as under (α); if well below 20 per cent., the procedure should commence at (β). It should be kept in mind that these operations do not give a quantitative separation, as it is impossible entirely to eliminate the intermediate fractions between two elements; but these may be reduced to small amounts.

TABLE XII.

<table>
<tr><td colspan="4">(α) Dissolve mixed oxides in HCl, saturate with $Na_2SO_4.10H_2O$, filter.</td></tr>
<tr><td colspan="3">P^1: double sulphates of Ce, La, Pr, Nd, Sa, Eu, Gd; small amounts of Tb, Dy, Ho. Digest with NaOH, filter, wash free from sulphates, dissolve in HNO_3, evaporate to dryness, take up with H_2O.</td><td>F^1: yttria earths; add to F^5.</td></tr>
<tr><td colspan="4">(β) Dissolve in HNO_3, evaporate to dryness, take up with H_2O. Either solution is boiled with $KBrO_3$ and marble until most of the Ce is ppted. Filter.</td></tr>
<tr><td rowspan="2">P^2: bulk of Ce. Add P^4, dissolve in HCl, ppte with $H_2C_2O_4$, ignite to CeO_2.</td><td colspan="3">F^2: boil with more $KBrO_3$ and marble until all Ce is ppted. Filter.</td></tr>
<tr><td>F^3: add F^4. Ppte with NH_4OH, filter, reject filtrate, dissolve ppte in HCl, add Na_2SO_4, filter.</td><td colspan="2">P^3: remainder of Ce with small amounts of other earths. Dissolve in HCl, ppte with NH_4OH, filter, reject filtrate, dissolve ppte in HNO_3, and repeat $KBrO_3$ treatment.</td></tr>
<tr><td>F^5: add F^1 (in the case of (α)); treat for yttria earths (Table XIII.).</td><td>P^5: digest with NaOH, filter, reject filtrate, dissolve ppte in HNO_3, ppte with $H_2C_2O_4$, reject filtrate, ignite oxalates, dissolve oxides in known minimum of HNO_3; neutralise an equal amount of HNO_3 with MgO, mix solutions, and subject to fractional crystallisation so as to eventually obtain four groups of fractions, according to their composition.</td><td>P^4: add to P^2.</td><td>F^4: add to F^3.</td></tr>
</table>

(T.O.)

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[1] Urbain, *Compt. Rend.*, 1908, **146**, 406, 922; Urbain and Jantsch, *ibid.*, 1908, **147**, 1286.

[2] *Journ. Amer. Chem. Soc.*, 1908, **30**, 979; *ibid.*, 1912, **34**, 757. See also Meyer and Hauser, *Die Chemische Analyse der Seltenen Erden*, Stuttgart, 1912.

TABLE XII.—*Continued.*

GROUP 1.—Least soluble. Colourless—pale green ; La, Pr.

Treat each fraction separately as follows : Ppte with $H_2C_2O_4$, ignite ppte, dissolve in known minimum of HNO_3, neutralise two-thirds the amount of HNO_3 with NH_4OH, continue fractionation from water containing one-tenth the weight of mixed oxides in HNO_3. Each crop of crystals is washed with strong HNO_3, which is added to the next more soluble crop.

Fraction 1.—Least soluble. La-NH_4 nitrate. Dissolve in H_2O, add a little HNO_3, ppte with $H_2C_2O_4$, ignite to La_2O_3. Purify if desired by dissolving in strong H_2SO_4; heat to 500° until all free acid is expelled. Dissolve in water at 1°, heat to 32°, filter, using suction, wash with hot H_2O. Ppte : pure $La_2(SO_4)_3.9H_2O$. Filtrate : La and a little Pr.	*Fraction* 2.—Small intermediate product, contains La and Pr.	*Fraction* 3.—Pr-NH_4 nitrate. Ppte with $H_2C_2O_4$, ignite to Pr_4O_7. Add ignited oxide from Fraction 1 of Group 2.

GROUP 2.—Colourless—pale pink. Pr, Nd.

Treat each fraction separately as follows : Ppte with $H_2C_2O_4$, ignite, dissolve in known minimum of HNO_3, neutralise an equal amount of HNO_3 with $MnCO_3$, mix solutions, continue fractionation from HNO_3 of sp. gr. 1·3, allowing most of the salts to crystallise out in each operation, so the volume of mother-liquor is small compared to the bulk of the crystals. By this method the two elements may be separated with the loss of very little material in Fraction 2.

Fraction 1.—Least soluble. Pr-Mn nitrate. Dissolve in dilute HNO_3, ppte with $H_2C_2O_4$, ignite to Pr_4O_7, add to Fraction 3 of Group 1.	*Fraction* 2.—Intermediate. (Pr + Nd.)	*Fraction* 3.—Nd-Mn nitrate. Treat like Fraction 1, add Nd_2O_3 to Fraction 2 of Group 3.

GROUP 3.—Amethyst. Crude Nd.

Continue fractional crystallisation of double Mg nitrates until the absorption spectrum in the blue stands out clearly, showing elimination of Pr and Sm. (Fractionation of the simple nitrates from strong HNO_3 will concentrate the Pr in the *most* soluble fractions.)

Fraction 1.—Small. (Pr + Nd.)	*Fraction* 2.—Nd-Mg nitrate (main Nd fraction). Ppte acid solution with $H_2C_2O_4$, ignite to Nd_2O_3, add Fraction 3 of Group 2.	*Fraction* 3.—Small. (Sm + Nd.)

GROUP 4.—Yellow. Sm, Eu, Gd ; small amounts of yttria earths.

Evaporate each fraction separately to dryness ; continue fractionation of the double Mg nitrates from HNO_3 of sp. gr. 1·3. After a time, when the head fractions, examined through a thickness of 12 cm., show no absorption bands (of Eu) at 5337 and 5251, they are removed from the series. The fractionation of the remainder is continued, with the addition of Bi-Mg nitrate to each mother-liquor ; the head fractions, as they become free from Eu, are again removed. Finally, a head fraction of pure Bi-Mg nitrate is obtained, and thus a quantitative separation of Sm from Eu (Gd) is accomplished.

Fraction 1.—Double Mg nitrates of Sm and a little Nd, with much Bi. Dissolve in H_2O, ppte with H_2S, filter, ppte filtrate with $H_2C_2O_4$, ignite to Sm_2O_3, again convert into double Mg nitrate, add equal weight of Bi-Mg nitrate, continue fractionation. Nd concentrates in the head fractions.	*Fraction* 2.—Eu-Mg nitrate with much Bi. Treat as Fraction 1.	*Fraction* 3.—Small intermediate fractions, chiefly Gd with a little Eu.	*Fraction* 4.—Gd with Tb and a little of the yttria earths. Convert into simple nitrates, fractionate from HNO_3 of sp. gr. 1·3 whilst continually adding $Bi(NO_3)_3.5H_2O$ to the mother-liquors. Eventually a quantitative separation of Gd from the other earths may be carried out, Gd accumulating in the head fractions. The intermediate fractions, containing Tb, are freed from Bi and added to Fraction 1, Group 2, Table XIII.

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TABLE XIII.

<table>
<tr><td colspan="3">Ppte F^5 (Table XII.) with $H_2C_2O_4$, ignite, dissolve in H_2SO_4, heat to 450° to drive off excess of acid; dissolve in ice-cold water, pour over slight excess of $Ba(BrO_3)_2$, filter off $BaSO_4$; subject to fractional crystallisation to obtain four groups of fractions.</td></tr>
<tr><td colspan="3">GROUP 1.—Gd and Tb bromates, with small quantities of Nd and Sm. Convert to double Mg nitrates, and fractionally crystallise with addition of Bi-Mg nitrate (Table XII., Group 4). The final fractions are substantially the same as the more soluble ones of Group 4, Table XII.</td></tr>
<tr><td colspan="3">GROUP 2.—Tb, Dy, Ho, Y bromates. Convert into simple nitrates, fractionate from HNO_3 (1·3) with addition of $Bi(NO_3)_3.5H_2O$, so as to obtain three fractions.</td></tr>
<tr><td><i>Fraction</i> 1.—Tb. Any small quantity of Gd may be extracted in the less soluble portion from the fractionation of the double Ni nitrates.</td><td><i>Fraction</i> 2.—Dy. Convert into ethylsulphates, and continue fractionation, obtaining Tb in the least soluble, and Ho in the most soluble, fraction.</td><td><i>Fraction</i> 3.—Ho, Y. Subject to fractional pption with NH_4OH, Ho concentrating in the least basic fractions. The Ho fractions may be purified by fractionation of the simple nitrates in presence of Bi nitrate.</td></tr>
<tr><td colspan="3">GROUP 3.—Crude yttrium bromate (chief impurities: Ho, Er). Ppte with $H_2C_2O_4$, ignite, dissolve in HNO_3, evaporate to dryness, heat residue gently until surface acquires a characteristic steely appearance. Pour fused mass into cold water, heat to boiling and allow to cool, when basic nitrates of the less basic earths crystallise out. Filter, dissolve residue in HNO_3; repeat evaporation and fusion. Evaporate filtrate to dryness, subject residue to same process. Continue treatment, adding filtrate from one fraction to basic salts from the next. Yttria is most difficult to obtain free from other earths.</td></tr>
<tr><td colspan="3">GROUP 4.—Y, Er, Tm, Yb, Lu, Ct bromates. Continue bromate fractionation, obtaining finally three principal groups of fractions.</td></tr>
<tr><td><i>Fraction</i> 1.—Y, Er. Apply fusion of nitrates as under Group 3. Erbium being the less basic earth, its nitrate is decomposed first. Erbia has not yet been obtained perfectly pure.</td><td><i>Fraction</i> 2.—Tm. Continue bromate fractionation, if desired, for further purification.</td><td><i>Fraction</i> 3.—Yb, Lu, Ct. Convert each fraction into simple nitrates, and continue fractionation from HNO_3. Yb concentrates in the least soluble crystals, Ct in the mother-liquors. Neither Lu nor Ct have yet been obtained in the pure state.</td></tr>
</table>

(*c*) *Approximate Separation of Lanthanum from Didymium* (i.e. *Praseodymium + Neodymium*).[1]—The solution of the nitrates is evaporated to dryness in a porcelain dish, the residue gently heated to about 450° for a few minutes, and removed from the heat before decomposition is complete. The mass is taken up, whilst warm, with hot water, the mixture left to stand a few hours, boiled, and filtered. Most of the didymium remains undissolved as basic nitrate. The filtrate, which is usually pale pink, is again evaporated to dryness and the fusion repeated on the residue. This treatment is continued until the filtrate is colourless (usually 2–3 repetitions suffice). The insoluble residue is ignited in air, then in hydrogen, and weighed as Di_2O_3; the filtrate of lanthanum nitrate is evaporated and the residue ignited to La_2O_3. The latter should be white. The results for didymia are usually a little high, those for lanthana correspondingly low; it is preferable to repeat the fusion several times rather than attempt the separation at too high a temperature.

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[1] Damour and Deville, *Bull. Soc. Chim.*, 1864, **2**, 339. Schützenberger and Boudouard, *Compt. Rend.*, 1896, **122**, 697; **123**, 782; 1898, **126**, 1648; Nilson, *ibid.*, 1879, **88**, 642, 647.

(*d*) *Separation of the Cerium from the Terbium Group.*[1]—This can be accomplished quantitatively by the fractional crystallisation of the double magnesium nitrates in the presence of bismuth magnesium nitrate, as described under (*b*) (4), Table XII., Group 4. It is a lengthy operation, but not so protracted as the isolation of the individual earths.

(*e*) *Separation of the Terbium from the Yttrium Group.*[2]—The best method for effecting this separation consists in the fractional crystallisation of the ethylsulphates in the presence of metals of the cerium group. The metals do not separate in the " serial order " (see (*b*)), the neodymium salt being the least soluble, and the lanthanum salt approximately equal in solubility to that of gadolinium ; from the latter onwards the " serial order " holds good. After a prolonged treatment by fractionation all fractions containing lanthanum are removed : they contain the terbium together with the cerium group, which latter must be removed as under (*d*).

§ **IV. Gravimetric Determination.**—(*a*) *Determination of the Sum of Rare Earths other than Ceria.*—The solution from which the cerium has been removed by one of the methods given under Cerium, § II., is acidified with nitric acid (about 5 c.c. per 100 of solution) and precipitated hot with excess of saturated oxalic acid solution. After standing overnight the precipitate is filtered off, well washed with very dilute nitric acid, and rinsed into a porcelain basin. Nitric acid is added, and evaporated to dryness on a water-bath ; the residue is heated with fuming nitric acid until all oxalic acid is destroyed ; the nitrate residue is taken up in water and the solution re-precipitated with oxalic acid as before. The washed residue is dried, and ignited gently at first in a porcelain crucible. The ignited oxides are more or less coloured, due to the presence of the higher oxides of praseodymium and terbium. The excess oxygen may be removed by ignition in hydrogen, after which the material is weighed as sesquioxides ; alternatively, the weighed oxides are digested with hydrochloric acid and potassium iodide in a stoppered flask, and the liberated iodine measured with N/10 thiosulphate solution. 1 c.c. = 0·0008 grm. oxygen. The oxides should be weighed in a covered crucible, as they readily absorb moisture and carbon dioxide.

(*b*) *Determination of the Individual Earths.*—In the case of fractional crystallisations, each final fraction of purified earth compound is dissolved in water and any bismuth precipitated with hydrogen sulphide. In the case of double nickel nitrates, the earth is first precipitated with ammonia to eliminate the bulk of the nickel. The nitrate solution is precipitated with oxalic acid (twice in the case of magnesium or manganese double nitrates) and the determination finished as under (*a*). The reduction in hydrogen or titration of excess oxygen is necessary only in the case of praseodymium and terbium.

§ **V. Detection in Minerals.**—The powdered mineral is opened up with hydrochloric or sulphuric acid, or, if necessary, by fusion with sodium bisulphate or carbonate ; in the latter case the insoluble residue

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[1] Demarçay, *Compt. Rend.*, 1900, **130**, 1019, 1185.

[2] Urbain, *Journ. Chim. Phys.*, 1906, **4**, 58.

from the aqueous extract of the melt is dissolved in hydrochloric acid. The acid solution obtained by any of the above processes is treated with hydrogen sulphide to remove metals of that group. The filtrate is boiled, oxidised with nitric acid, and precipitated with ammonia in the presence of ammonium chloride. This precipitate is dissolved in hydrochloric acid and the warm solution treated with excess of oxalic acid. After standing overnight the precipitate is filtered off, dissolved in fuming nitric acid, and the thorium precipitated from the neutral nitrate solution with hydrogen peroxide (Thorium, § III.). After destroying the excess of the latter by boiling the filtrate, sodium sulphate is added to saturation. Any white crystalline precipitate proves the presence of cerium earths. The filtrate is acidified with nitric, and again treated with oxalic acid, whereby the oxalates of the yttrium earths are precipitated. (See also Qualitative Analysis, Table VI.)

§ **VI.—Determination in Minerals.**—The methods for opening up minerals in which the cerium metals predominate have already been described under Cerium, § VII. Tantalo- and titano-columbates are fused with potassium hydroxide (Columbium, §§ V. and VII.), or dissolved in hydrofluoric acid. In the latter case the rare earths are converted into insoluble fluorides, which are filtered off and evaporated with a small excess of sulphuric acid to dryness. The residue is taken up with ice-cold water and the solution precipitated with oxalic acid in the usual manner. The separation of thorium and cerium is described under Cerium, § II. ; the filtrate from the cerium precipitate is then treated as under § IV.

§ **VII. Complete Analysis of Ores.**—(*a*) *Monazite Sand.*—The sand may contain, besides monazite, zircon, ilmenite, rutile, tantalite, and titano-columbates.

First Portion.—

<table>
<tr><td colspan="8">Heat 1 grm. of finely powdered sample with 5 c.c. of strong H_2SO_4 in a small porcelain dish at 180°–200° for 2–3 hours, avoiding undue loss of acid by volatilisation. Pour slowly into 100 c.c. of cold water, let stand ½ hour, filter, wash with cold very dilute H_2SO_4.</td></tr>
<tr><td colspan="4">R^1 : ignite in Pt crucible, fuse with 2–3 grm. Na_2CO_3, leach with H_2O, filter, wash with 1 per cent. Na_2CO_3.</td><td colspan="4" rowspan="2">F^1 : add F^3 and F^4. Dilute to 600 c.c., nearly neutralise with NH_4OH, add 10 c.c. of strong HCl, ppte with $(NH_4)_2C_2O_4$, filter next day, ignite ppte, repeat pption. Combine filtrates.</td></tr>
<tr><td colspan="2">R^2 : fuse with $NaHSO_4$, leach, filter.</td><td colspan="2" rowspan="2">F^2 : acidify with HCl, evaporate to dryness, heat to 110°, take up with dilute HCl, filter, wash.</td></tr>
<tr><td>R^3 : add to R^4.</td><td>F^3 : add to F^1.</td><td colspan="2" rowspan="3">F^6 : evaporate with 10 c.c. H_2SO_4 and 20 c.c. HNO_3 to fumes. Dilute, ppte with NH_4OH, reject filtrate, ignite ppte, fuse with Na_2CO_3, leach with H_2O, filter.</td><td colspan="2" rowspan="3">P^6 : ignite, dissolve in HNO_3 and a little H_2O_2, neutralise with NH_4OH, add NH_4NO_3 and H_2O_2. Filter, repeat pption (Thorium, § III, (*a*)).</td></tr>
<tr><td colspan="2">R^4 : add R^3, ignite and weigh. Treat with $HF+H_2SO_4$, ignite, weigh.</td><td colspan="2">F^4 : add to F^1.</td></tr>
<tr><td>L^5 : SiO_2.</td><td colspan="3">R^5 : $Ta_2O_5+Cb_2O_5$ containing small amount of TiO_2 ; determine the latter colorimetrically.</td></tr>
<tr><td colspan="4"></td><td>R^7</td><td>F^7</td><td>F^9</td><td>P^9</td></tr>
</table>

(Continued overleaf.)

<table>
<tr><td colspan="2">R^7: Fuse with $NaHSO_4$, ppte cold with $NH_4Cl + NH_4OH$. Filter, repeat pption, combine filtrates.</td><td>F^7: acidify with HCl, ppte with NH_4OH, ignite, weigh $AlPO_4$.</td><td>F^9: ppte with NH_4OH, reject filtrate, dissolve ppte in $HNO_3 + H_2O_2$, evaporate to dryness, take up with H_2O, ppte Ce with $KBrO_3$ and marble (Cerium, § II.). Repeat pption.</td><td>P^9: ignite, weigh ThO_2.</td></tr>
<tr><td>P^8: Ti, Zr, Fe, Al.</td><td>F^8: determine CaO.</td><td colspan="2" rowspan="2">F^{10}: ppte with $NH_4Cl + NH_4OH$, reject filtrate, dissolve ppte in HCl, evaporate to dryness, take up in 5 c.c. H_2O, add 200 c.c. saturated K_2SO_4 solution and 5 grm. of finely powdered K_2SO_4. Let stand 12 hours with occasional stirring, filter, wash with saturated K_2SO_4 solution. Repeat pption (§ III, (a)).</td><td rowspan="2">P^{10}: see Cerium, § VII, (a) (4).</td></tr>
<tr><td colspan="2">See Titanium, § III.</td></tr>
<tr><td colspan="3">F^{11}: yttrium metals. Ppte with $H_2C_2O_4$, ignite and weigh as Y_2O_3, etc.</td><td colspan="2">P^{11}: cerium metals. Boil with 400 c.c. $H_2O + 5$ c.c. HCl. Ppte with $H_2C_2O_4$, ignite in H current, weigh as La_2O_3, Di_2O_3, etc.</td></tr>
</table>

Second Portion.—Phosphoric acid. Fuse 0·5 grm. with 5 grm. Na_2CO_3. Leach with water, wash with 1 per cent. Na_2CO_3, repeat fusion on residue. A third fusion may be required to extract the whole of the phosphoric acid. Acidify combined filtrates with HNO_3, evaporate to remove silica, take up with HNO_3, filter, precipitate with molybdate solution, dissolve precipitate in ammonia, add magnesia mixture.

Third Portion.—Loss on ignition.

(*b*) *Fluorides* (*Fluocarbonates*).

First Portion.—

<table>
<tr><td colspan="2">Attack 1 grm. of powder with strong H_2SO_4 in platinum. Volatilise excess of acid, take up with H_2O and 5–10 grm. of NH_4Cl, ppte with NH_4OH. Dissolve ppte in HCl, add NH_4Cl, repeat pption. Combine filtrates.</td></tr>
<tr><td>P^1: dissolve in HNO_3, adjust acidity to 0·3 N, ppte with $H_2C_2O_4$, filter.</td><td>F^1: determine CaO(BaO).</td></tr>
<tr><td>F^2: determine Fe and Al.</td><td>P^2: treat like P^6 in preceding table.</td></tr>
</table>

Second Portion.—Fluorine. Fusion with SiO_2 and Na_2CO_3.

Third Portion.—Carbon dioxide and water; direct determination. One grm. of mineral is fused with 2–3 grm. of dehydrated borax in a platinum boat or bulb tube in a current of air previously passed over soda-lime. The tube contains a heated layer of previously fused and powdered litharge between plugs of glass wool, which serves to retain any escaping fluorine compounds. The gases then pass through a calcium chloride tube and a soda-lime tube, both weighed. When quiet fusion has been attained, the system is swept with a current of pure dry air.

CHAPTER VI.

THE FOURTH GROUP.

TITANIUM—ZIRCONIUM—THORIUM—GERMANIUM.

GENERALITIES.

THE rarer elements of this group, like silicon, give oxides of the type MO_2, in which form they are usually weighed. Titanium, zirconium, and thorium belong to the same (even) series, the basicity of which increases, according to the general rule, with the atomic weight; thus titanic salts are most easily hydrolysed, zirconium salts less so, while thorium compounds are the most stable. The three metals are not precipitated by hydrogen sulphide, and their hydroxides can be dissolved in nitric acid. Germanium, like the other members of the odd series (tin, lead), is precipitated by hydrogen sulphide, and behaves towards nitric acid like tin.

TITANIUM.

§ I. **Minerals.**—(*a*) *Oxides.*—Titanium dioxide (TiO_2), the only naturally occurring oxide, is found in three distinct crystalline modifications:—

(1) *Rutile* crystallises in the tetragonal system, and is isomorphous with tinstone, thorite, and zircon. It occurs as reddish-brown to black prisms, terminated by pyramids, the sides of the prisms being vertically striated. Twins are common. Brittle, fracture sub-conchoidal; sub-metallic to admantine lustre. Streak pale brown. H 6·5; sp. gr. 4·2.

(2) *Anatase or Octahedrite* is a distinct tetragonal form crystallising in pyramids or tables. H 5·5; sp. gr. 3·8 to 4·0.

(3) *Brookite*, the orthorhombic variety of the dioxide, crystallises in short tabular prisms. H 6; sp. gr. 3·9 to 4·2.

(*b*) *Titanates.*—(1) *Ilmenite* is an iron-black mineral with sub-metallic lustre, essentially a ferrous titanate, but of very variable composition, ferric oxide often partly replacing the titanium dioxide. Rhombohedral tables; conchoidal fracture; brownish-black streak; magnetic to weak electromagnet. H 5·5; sp. gr. 4·5 to 5·0.

Iserine and *Menaccanite* are varieties of ilmenite occurring in alluvials.

(2) *Pseudobrookite*, ferric titanate, $2Fe_2O_3.3TiO_2$, occurs as dark brown to black, sub-translucent, horizontally striated tables belonging

to the orthorhombic system. Streak yellow to brown. H 6; sp. gr. 4·4.

(3) *Pyrophanite*, manganese titanate, $MnTiO_3$, crystallises in the rhombohedral system as deep blood-red, transparent tables, giving an ochre-yellow streak with a tinge of green. H 5; sp. gr. 4·5.

(4) *Perovskite*, calcium titanate, $CaTiO_3$, occurs in pale yellow to red-brown cubes with an adamantine lustre; transparent to opaque, brittle. H 5·5; sp. gr. 4.

(*c*) *Titanosilicates*.—(1) *Sphene* or *Titanite*, calcium titanosilicate, $CaSiTiO_5$, occurs variously coloured, yellow, brown, green, red, or black. Transparent to opaque mineral crystallising in the monoclinic system. Lustre resinous to adamantine. Twins common. Also found massive. H 5·5; sp. gr. 3·5.

(2) *Guarinite* is a yellow translucent orthorhombic variety of calcium titanosilicate crystallising in thin tables with an adamantine lustre. H 6; sp. gr. 3·5.

(*d*) In addition to the above, titanium occurs in many rare and unimportant silicates of very complex composition, which usually contain the rare earths, thorium, or zirconium. It is also an essential constituent of various titanocolumbates, such as the euxenite-polycrase series (see Columbium, § I.). As a subordinate constituent it is present in most rocks, especially the more basic ones, and in clays.

§ II. Properties and Compounds.—(*a*) The *metal* has a brilliant white colour, is very brittle and hard. It has a powerful affinity for carbon, oxygen, and nitrogen, and therefore is very difficult to prepare pure, although it can be made by reducing the dioxide with carbon in the electric furnace in the absence of air. It is soluble in acids, and decomposes steam at a red heat. Sp. gr. 4·87; melting point 1800°.

(*b*) The *dioxide* is trimorphous (see § I, (*a*)). As usually obtained artificially, it is a white amorphous powder, insoluble in water, hydrochloric or nitric aids, and only with difficulty soluble in concentrated sulphuric acid. Rendered soluble by fusion with bisulphate. Readily obtained by igniting the precipitate produced by ammonia in a solution of titanium salt.

(*c*) *Orthotitanic acid*, H_4TiO_4, is precipitated from a *cold* hydrochloric acid solution of a titanium salt on the addition of alkalies as a voluminous white precipitate readily soluble in dilute acids. On long standing under water it gradually changes to metatitanic acid, and, on ignition, yields the dioxide with the evolution of light.

(*d*) *Metatitanic acid*, H_2TiO_3, is produced by boiling a nearly neutral hydrochloric acid solution of the ortho-acid as a white voluminous precipitate. On ignition it is converted into the anhydride without evolution of light. It is insoluble in acids, with the exception of hot strong sulphuric or hydrofluoric acids.

(*e*) *Sodium titanates*.—Three compounds, viz. $Na_2Ti_2O_5$, $Na_2Ti_3O_7$, and $Na_4Ti_3O_8$, are produced by fusion of the dioxide with sodium carbonate. They are insoluble in water.

(*f*) *Titanium peroxide*, TiO_3, is produced when hydrogen peroxide acts on a sulphuric acid solution of the dioxide. It gives an intense orange-brown solution in acids, which decomposes on boiling.

(*g*) *Titanium sesquioxide* (Ti_2O_3).—Salts of this oxide (*e.g.* titanous chloride, $TiCl_3$) are produced by the reduction of tetravalent titanium in acid solution with zinc. Their solutions are of a deep violet colour, and, being readily oxidised, are powerful reducing agents.

(*h*) *Titanium cyanonitride*, probably $Ti(CN)_2.3Ti_3N_2$, is formed by the strong ignition of the dioxide and charcoal in a current of nitrogen, and is often found in iron blast-furnaces as copper-red cubes. On ignition in steam it yields ammonia, and has been proposed as the basis of a method for the fixation of atmospheric nitrogen.

(*i*) *Titanium tetrafluoride* (TiF_4).—When metatitanic acid is dissolved in hydrofluoric acid, hydrogen fluotitanate, H_2TiF_6, is believed to be formed. Unlike silicon, titanium is not volatilised by evaporation of hydrofluoric solutions in the presence of sulphuric acid, but if the latter is omitted a considerable proportion of the titanium is volatilised.

(*j*) *Potassium fluotitanate*, $K_2TiF_6.H_2O$, is produced by the addition of potassium fluoride to a solution of the preceding compound. Ninety-six parts of water dissolve 1 part of the anhydrous salt at ordinary temperature.

§ **III. Quantitative Separation.**—Titanium belongs to the third analytical group, being precipitated from acid solutions by ammonia or by the basic acetate method. Its separation from the other metals of this group is carried out as follows :—

(*a*) *Separation from Iron*[1] (*Nickel, Cobalt, Zinc, Manganese, Uranium*).—(1) The hydrochloric acid solution of the metals is treated with hydrogen sulphide to reduce ferric iron, an excess of tartaric acid equal to three times the weight of metallic oxides present is added, and the solution made faintly ammoniacal. Hydrogen sulphide is again passed through the solution to precipitate the sulphides of the above metals, and the solution heated to 60°–80° to coagulate the precipitate, which is then filtered off and thoroughly washed with dilute colourless ammonium sulphide water. The filtrate is boiled with excess of dilute sulphuric acid to expel sulphuretted hydrogen, and the tartaric acid destroyed by boiling with two and a half times its weight of potassium permanganate[2] to produce a permanent pink colour, which is then discharged with sulphurous acid solution. The tartaric acid may also be removed by evaporation with sulphuric acid and nitric acid[3] until the liquid is colourless.

(2) Titanium may be separated from iron, zinc, beryllium, rare earths, and uranium by precipitation with sodium thiosulphate[4] from a neutral solution of the chlorides or sulphates of the metals. The cold acid solution is treated with sodium carbonate solution until the precipitate that forms re-dissolves only with difficulty (a permanent precipitate

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[1] Cathrein, *Z. Kryst.*, 1882, **6**, 244 ; 1883, **7**, 250 ; see also the next two footnotes.

[2] Lindet, *Chem. News*, 1897, **76**, 212.

[3] Wdowiszewski, *Stahl u. Eisen*, 1907, **27**, 781 ; Thornton, *Amer. Journ. Sci.*, 1912, **34**, 214.

[4] *E.g.* Dittrich and Freund, *Z. anorg. Chem.*, 1907, **56**, 337.

should be avoided). A solution of 10 grm. of sodium thiosulphate in cold water is then added and the whole boiled for one hour. After settling, the precipitate is filtered off on a loose filter, well washed with boiling water, ignited, fused with potassium bisulphate, and the melt dissolved in cold 5 per cent. sulphuric acid. This solution will contain all the titanium, thorium, zirconium, and aluminium, with traces of impurities that may be removed by a second precipitation.

(3) If iron alone has to be removed, the separation can be effected by ether.[1]

(*b*) *Separation from Zirconium.*—Zirconium is a very troublesome constituent of titanium minerals, as in its presence it is not possible to precipitate the titanium completely by hydrolysis. Hillebrand [2] states that 0·2 per cent. of ZrO_2 inhibits the hydrolysis of 0·3 per cent. of TiO_2.

(1) Zirconium is obtained with the titanium, aluminium, and thorium in the precipitate produced with thiosulphate, (*a*) (2). The ignited precipitate is fused with bisulphate, the solution of the melt treated cold with a small excess of ammonia, and the precipitated hydroxides filtered on a loose filter, washed with cold 2 per cent. ammonium nitrate, and dissolved in nitric acid. The cold solution is treated with sodium carbonate until as nearly neutral as possible, but avoiding a permanent precipitate, and poured drop by drop into a boiling solution of 10 grm. of ammonium salicylate in 50 c.c. of water. Boiling is continued until the bulk is reduced to 100 to 120 c.c.; the precipitate is then filtered off and washed with 5 per cent. ammonium salicylate solution until quite white.[3] In case this precipitate, which contains all the zirconium and thorium, is considerable, it should be ignited, fused with potassium bisulphate, and the above process repeated. The combined filtrates, which contain the titanium and aluminium, are treated with ammonia, the hydroxides filtered off, washed free from salicylic acid, ignited, fused with potassium bisulphate, and separated as under (*d*) below.

(2) In case the titanium is considerable and the zirconium small the latter is best precipitated as phosphate according to Hillebrand,[4] as follows :—

The solution (preferably that from the thiosulphate precipitation) is adjusted so that the acidity does not exceed 1 per cent. of free sulphuric acid, the bulk being 200 c.c. One c.c. of sodium phosphate solution (saturated) is then added after oxidising the titanium with an excess of hydrogen peroxide (20 vols. $=$ 6 per cent. H_2O_2). The solution is allowed to stand forty-eight hours, with occasional addition of a few drops of hydrogen peroxide to keep the titanium in the higher state of oxidation. The small precipitate of zirconium phosphate is then filtered off, washed with cold 0·5 per cent. sulphuric acid, ignited, and fused with sodium carbonate. The melt is leached with hot water, the insoluble zirconium

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[1] Barneby and Isham, *Journ. Amer. Chem. Soc.*, 1910, **32**, 957.

[2] *Bull.* 422, *U.S. Geol. Surv.*, 136.

[3] Dittrich and Freund, *Z. anorg. Chem.*, 1907, **56**, 344.

[4] *Bull.* 176, *U.S. Geol. Surv.*, 75. See also Bailey, *Journ. Chem. Soc.*, 1886, **49**, 149, 481 ; Dittrich and Pohl, *Z. anorg. Chem.*, 1905, **43**, 236 ; Wedekind, *ibid.*, 1903, **33**, 83.

hydroxide filtered off, washed with hot water, ignited and fused with potassium bisulphate. The zirconium is then re-precipitated as phosphate with sodium phosphate and hydrogen peroxide as before. The combined filtrates are treated with ammonia, whereby the phosphates of thorium, titanium, and aluminium are precipitated. The precipitate is filtered, washed with boiling 2 per cent. ammonium nitrate, ignited and fused with ten times its weight of sodium carbonate. The melt is leached with water, the solution boiled with ammonium nitrate, filtered, and the precipitate well washed, ignited, and fused with potassium bisulphate. Thorium and aluminium are removed as described under (*c*) and (*d*).

(*c*) *Separation from Thorium.*[1]—(1) This may be effected by treating the nearly neutral hydrochloric acid solution with ammonium oxalate until the precipitate first formed dissolves again. The solution is heated to boiling, and hydrochloric acid added drop by drop until no further precipitate is produced. After standing overnight the thorium oxalate is filtered off and well washed with warm water acidified with hydrochloric acid. The filtrate is evaporated to fumes with sulphuric acid, cooled, diluted with water, and the titanic acid precipitated with ammonia. Rare earths also are separated from titanium by this process.

(2) The nearly neutral sulphate solution is treated with dilute hydrofluoric acid[2] and warmed till the gelatinous thorium fluoride becomes dense and sandy. The solution is filtered through a rubber funnel into a platinum dish, the precipitate well washed with very dilute hydrofluoric acid, and the combined filtrate and washings evaporated to strong fumes with sulphuric acid to expel hydrofluoric acid. From the sulphate solution thus obtained the titanium is precipitated with ammonia.

(*d*) *Separation from Aluminium.*[3]—The solution of the two metals in sulphuric acid is neutralised with dilute sodium carbonate solution, and 20 grm. of sodium acetate and acetic acid (sp. gr. 1·04) equal to one-sixth of the total bulk of the solution, added. The contents of the beaker are heated to boiling and boiled one minute, when all the titanium is precipitated as flocculent metatitanic acid. After settling, the precipitate is filtered off, washed with 5 per cent. acetic acid, then with boiling water, ignited, fused with sodium carbonate to remove traces of silica and phosphoric or vanadic acids ; the melt is leached with hot water, and the insoluble sodium titanate filtered off, washed with hot water, ignited and fused with potassium bisulphate. The cold melt is dissolved in warm 5 per cent. sulphuric acid and the titanium re-precipitated as before.

(*e*) *Separation from Phosphoric, Tungstic, Molybdic, Vanadic, and Chromic Acids.*—The ore is fused repeatedly with sodium carbonate,

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[1] Ammonium salicylate (see (*b*) (1)) precipitates thorium as well as zirconium.

[2] Hillebrand, *loc. cit.* (p. 92) ; Rosenheim, Samter, and Davidsohn, *Z. anorg. Chem.*, 1903, **35**, 424.

[3] Gooch, *Proc. Amer. Acad. Sci.*, 1885, **12**, 435 ; *Chem. News*, 1885, **52**, 55, 68 ; Chatard, *ibid.*, 1891, **63**, 269 ; Neumann, *Stahl u. Eisen*, 1910, **30**, 457 ; Hillebrand, *loc. cit.* (p. 92) ; Wdowiszewski, *Eng. and Min. Journ.*, 1908, **85**, 1200 ; Thornton, *ibid.*, 1912, **94**, 353.

each fusion being followed by extraction of the melt with boiling water and filtration of the insoluble sodium titanate, etc. The process is repeated until the solution of the melt after filtration and neutralisation with nitric acid gives no precipitate with mercurous or silver nitrate.

(*f*) *Separation from Columbic and Tantalic Acids.*—See Columbium, § III.

§ **IV. Gravimetric Determination.**—Titanium is always weighed as the dioxide after precipitation by one of the reagents enumerated below. If precipitated from a solution containing sulphates, the dioxide should be ignited with ammonium carbonate.

(1) The acid solution is heated to boiling, treated with a slight excess of dilute ammonia, the precipitate allowed to settle, filtered off, washed with 2 per cent. ammonium nitrate, ignited, and weighed as TiO_2.

(2) The acid solution is nearly neutralised with cold dilute sodium carbonate solution and then boiled with 10 grm. of sodium thiosulphate for one hour. The precipitate of sulphur and metatitanic acid is filtered on a loose paper, washed with boiling water, ignited, and weighed as TiO_2.

(3) The neutral solution of the sulphate is diluted to 300 c.c., saturated with sulphur dioxide,[1] and boiled for two hours in a flask fitted with a reflux condenser. Where a number of determinations have to be made, the use of several Liebig condensers is rather cumbersome. They may be replaced by air condensers in the form of glass tubes 3–4 feet long and ½ in. wide. Metatitanic acid is produced by hydrolysis of the sulphate, and is filtered off, ignited, and weighed as TiO_2. The solution is tested for unprecipitated titanium with hydrogen peroxide.

(4) The titanium may be precipitated by the basic acetate process described under § III, (*d*). This precipitate is ignited and weighed as TiO_2. Its purity is ascertained by a second precipitation.

§ **V. Volumetric Determination.**[2]—Titanium salts in acid solution are reduced by zinc to the trivalent condition, and a volumetric process has been based on this property.

The sulphuric acid solution containing 20 per cent. of free acid is transferred to a 250 c.c. round flask, 10 grm. of coarsely-granulated zinc added, the flask stoppered with a cork carrying two holes to admit the passage of a slow current of hydrogen, and the reduction allowed to proceed until the zinc is completely dissolved. The solution is then titrated to the usual pink tinge with potassium permanganate :

$$5Ti_2(SO_4)_3+2KMnO_4+8H_2SO_4=10Ti(SO_4)_2+K_2SO_4+2MnSO_4+8H_2O.$$

The hydrogen should pass through the apparatus at the rate of a bubble a second during the whole assay. A blank should be run on the zinc and due allowance made. Iron interferes with this method ; therefore,

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[1] *E.g.* Röer, *Chem. Zeit.*, 1909, **33**, 1225.

[2] Hinnchsen, *Chem. Zeit.*, 1907, **31**, 738 ; Newton, *Amer. Journ. Sci.*, 1908, **25**, 130 ; Hibbert, *Journ. Soc. Chem. Ind.*, 1909, **28**, 189 ; Gemmel, *Analyst*, 1910, **35**, 198 ; Ball and Smith, *Journ. Amer. Chem. Soc.*, 1914, **36**, 1838 ; Neumann and Murphy, *Z. angew. Chem.*, 1913, **26**, 613.

if present, the titration of the reduced solution should be carried out with a standard solution of ferric alum (14 grm. per litre) in presence of a large excess of ammonium thiocyanate (5 c.c. of saturated solution). The completion of the reaction is indicated by a pale red tinge :

$$Ti_2(SO_4)_3+Fe_2(SO_4)_3=2Ti(SO_4)_2+2FeSO_4.$$

The permanganate or ferric alum solutions are standardised against a weighed amount of pure titanium dioxide dissolved by fusion with bisulphate.

§ **VI. Colorimetric Determination.**—(*a*) Titanic sulphate yields intense orange-yellow coloured solutions on the addition of hydrogen peroxide. This has been made the basis of a colorimetric method by E. Weller.[1] The colour is best compared when it is of a deep straw-yellow tint, *i.e.* when the titanium present corresponds to 0·0015 to 0·002 grm. per 100 c.c. of test solution. The colour is bleached by hydrofluoric acid even in minute quantity and by large amounts of phosphoric acid and potassium sulphate, but the presence of considerable free sulphuric acid tends to overcome the interference of the latter, which is present from the bisulphate fusion. Uranium, vanadium, molybdenum, and chromates interfere by giving a colour with the peroxide. Iron interferes if present in sufficient quantity ; the yellow tint is discharged by phosphoric acid, due to the formation of ferric phosphate, but the acid itself has a slight bleaching effect (see above). Therefore it is best to proceed as follows :—

The titanium solution is treated with 5 c.c. of phosphoric acid (sp. gr. 1·38), 5 c.c. of 6 per cent. hydrogen peroxide, and 9 c.c. of strong sulphuric acid, and made up to 100 c.c. in the Nessler tube. A standard tube is prepared with the same quantities of reagents as the assay, including potassium sulphate, and diluted nearly to 100 c.c. A solution of titanium sulphate of known strength is slowly added to the standard until the colours match. The standard is diluted exactly to the mark and the colours again matched.

Preparation of the Standard.—3·000 grm. of pure, feebly calcined potassium fluotitanate are weighed into a platinum basin and evaporated to strong fumes three times with sulphuric acid in order to ensure complete expulsion of the fluorine. The cold mass is diluted with water and made up to 1 litre so as to contain at least 7 per cent. of free sulphuric acid. One c.c. of this solution equals 0·001 grm. TiO_2.

(*b*) Other colorimetric methods have been proposed, based on the colours developed when a phenol[2] or phenolcarboxylic[3] acid is added to a solution of titanium sulphate in strong sulphuric acid. The high concentration of the acid is rather a drawback to these methods.

(*c*) Fenton[4] has proposed to use dihydroxymaleic acid in the colori-

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[1] Weller, *Ber.*, 1882, **15**, 2599 ; Baskerville, *Journ. Soc. Chem. Ind.*, 1900, **19**, 419 ; Brakes, *ibid.*, 1901, **20**, 23 ; Pamfil, *Monit. Scient.*, 1911, **24**, 643. See also Hillebrand, *loc. cit.* (p. 92).

[2] Lehner and Crawford (*Journ. Amer. Chem. Soc.*, 1913, **35**, 138) recommend thymol.

[3] *E.g.* salicylic acid, Jorissen, *Bull. Acad. Roy. Belg.*, 1903, 902.

[4] *Journ. Chem. Soc.*, 1908, **93**, 1064.

metric determination of titanium. One part of titanium in one million parts of solution gives a distinct straw-yellow colour with this acid, whereas 1 part in 15,000 gives an intense orange-red colour. Vanadium salts give no colour ; uranyl salts give a brown colour destroyed by acid in the cold ; and molybdates a red-brown colour, destroyed on boiling with acids. Tungstic acid gives a brown colour which rapidly changes to blue. The analysis is carried out as in (*a*), but 0·2 grm. of the dihydroxymaleic acid is added instead of the hydrogen peroxide, and the colour should be allowed to develop for an hour before comparison with a series of previously prepared standards. Iron must be absent, as ferric salts destroy the reagent.

§ **VII. Detection in Ores.**—The ore is first fused with ten times its weight of sodium carbonate, the melt leached out, and the insoluble residue filtered off, ignited, and fused with potassium pyrosulphate. The cold melt is dissolved in warm 7 per cent. sulphuric acid and the following tests tried :—

(1) Hydrogen peroxide gives an intense orange-brown colour if much titanium is present, yellow to orange if the amount is small.

(2) Dihydroxymaleic acid gives a pale yellow to orange colour with traces, a deep orange colour with larger amounts.[1]

(3) Reduction with zinc and sulphuric or hydrochloric acid gives a deep violet solution with considerable titanium.

(4) Thymol gives an intense red colour with titanium salts in strong sulphuric acid.

(5) If the solution is nearly neutralised and boiled, a flocculent white precipitate of metatitanic acid is thrown down, insoluble in acids except hydrofluoric or hot concentrated sulphuric acid.

(6) Ammonium salicylate gives an intense orange-yellow colour in neutral titanium solutions, and no precipitate even on boiling. (Distinction from zirconium, thorium, tantalum, and columbium.)

§ **VIII. Determination in Ores.**—(*a*) *Determination in Rutile and Ores low in Iron and free from Zirconium.*—0·5 grm. of ore is fused with 5 grm. of sodium carbonate in platinum for half an hour over a blast. The cold melt is boiled with water until thoroughly disintegrated, and the insoluble residue containing all the titanium as sodium titanate filtered off, washed thoroughly with 2 per cent. sodium carbonate, ignited wet in platinum, and fused with 4 grm. of potassium pyrosulphate until completely dissolved. When cold, 2 c.c. of concentrated sulphuric acid are added and the melt warmed up to thoroughly incorporate the acid ; the mass is allowed to cool, transferred to a beaker, and dissolved in 5 per cent. sulphuric acid at 40°. The solution should not be warmed above 60° ; addition of 50 c.c. of sulphurous acid solution assists the dissolution of the cake. When quite dissolved, any small quantity of silica is filtered off and the solution neutralised with ammonia, avoiding formation of any permanent precipitate. Twenty grm. of sodium acetate, 10 c.c. of sulphurous acid, and one-sixth the total bulk of the solu-

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[1] Vanadium gives a similar colour to titanium with hydrogen peroxide, but no colour with this reagent.

tion in acetic acid (about 50 per cent.) are then added, and the whole boiled one minute. The flocculent metatitanic acid is allowed to settle, filtered off, washed with 5 per cent. acetic acid, then with hot water, ignited wet, and weighed as TiO_2.[1] Its purity should always be tested by re-precipitation, as described under § III, (*d*).

(*b*) *Determination in Ilmenite and Iron Ores generally.*—(1) *Gravimetric Method for Ores high in* TiO_2.—0·5 to 1 grm. of ore is fused with 5 to 7 grm. of potassium pyrosulphate till all black specks have completely dissolved. The cold melt is leached with 5 per cent. sulphuric acid and gently warmed until all soluble matters have dissolved. Any insoluble material is filtered off, fused with sodium carbonate, and the melt extracted with water. The precipitate is filtered off, well washed, dissolved in fused bisulphate, and the solution of the cake in 5 per cent. sulphuric acid added to that obtained above. The united filtrates are neutralised with sodium carbonate without producing any precipitate, 10 grm. of sodium thiosulphate dissolved in a small quantity of water are added, and the solution boiled for one hour. The precipitate is filtered off, well washed with boiling water, ignited wet in platinum, fused with potassium bisulphate, and the titanium precipitated from the solution of the melt with sodium acetate and acetic and sulphurous acids, as under (*a*).

(2) *Colorimetric Method for Traces of Titanium.*—The ore is fused with potassium bisulphate and the melt dissolved in water containing 9 c.c. of sulphuric acid per 100 c.c. The solution is treated with phosphoric acid and hydrogen peroxide, as described in § VI., and the colour compared with that of a solution containing a known weight of titanium.

(*c*) *Determination in Columbates, Tantalates, and Ores containing Zirconium.*[2]—One grm. of the slimed ore is fused with potassium pyrosulphate (5 to 7 grm.) until completely decomposed, leached with warm 5 per cent. sulphuric acid until all soluble matters have dissolved, and filtered. The residue, which may contain some titanium, is set aside to be worked as described later (A). The filtrate containing most of the titanium is nearly neutralised with sodium carbonate, and boiled with 10 grm. of thiosulphate in 250 c.c. bulk for one hour. The precipitate of titanium, zirconium, thorium, and aluminium hydroxides is filtered off, washed with boiling water, ignited, and fused with pyrosulphate. The sulphates are then transformed into nitrates, and the thorium and zirconium separated from the titanium and aluminium by the ammonium salicylate method (§ III, (*b*) (1)). The residue (A) is dissolved in a little hydrofluoric acid, and evaporated to strong fumes with sulphuric acid to expel all fluorine. The mass is diluted with cold water and an excess of ammonia added ; the precipitate of hydroxides is filtered off, washed free from sulphates with 2 per cent. ammonium nitrate, and digested with 2 grm. of salicylic acid in 100 c.c. of water on a hot plate until the bulk of solution is reduced to 50 c.c. The insoluble

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[1] Blair, *The Chemical Analysis of Iron*, 1908, 184 ; Bain, *Journ. Amer. Chem. Soc.* 1903, **25**, 1073 ; Waterhouse, *Chem. News*, 1902, **85**, 198.

[2] After Dittrich and Freund, *Z. anorg. Chem.*, 1908, **56**, 344, 346.

columbic and tantalic acids are filtered off and washed with hot 1 per cent. salicylic acid. Any titanium present shows in the filtrate by imparting to it an orange colour. It is precipitated by ammonia, and added to the bulk of the titanium obtained above. The combined TiO_2 precipitate is ignited, fused with sodium carbonate, the melt boiled with water, the residue washed with 2 per cent. sodium carbonate, ignited, fused with bisulphate, and the resulting solution precipitated as under § III, (*d*).

(*d*) *Colorimetric Method for Traces in Rocks.*[1]—One grm. of the rock powder is fused with 10 grm. of sodium carbonate for half an hour over the blast. The cold melt is extracted with boiling water, the insoluble residue filtered off, washed with 2 per cent. sodium carbonate, and brought into solution by fusion with potassium pyrosulphate, as previously described. The solution is treated with sufficient sulphuric acid to give 9 c.c. of strong acid per 100 c.c. bulk, and diluted to 250 c.c. Sufficient solution is pipetted into the test-glass to give 1·5 to 5 mg. TiO_2, 5 c.c. phosphoric acid and 5 c.c. of 6 per cent. hydrogen peroxide added, and the test compared with a standard made up in a similar manner (see § VI, (*a*)).

§ IX. Complete Analysis of Ores.—This includes determination of impurities such as aluminium, phosphorus, vanadium, manganese, lime, and magnesia.

(*a*) *Rutile.*—

<table>
<tr><td colspan="4">0·5 to 1 grm. crushed to —100 mesh. Fuse with 3–6 grm. $NaHSO_4$; leach with warm 5 per cent. H_2SO_4. Filter.</td></tr>
<tr><td colspan="2">R^1 : ignite and weigh in platinum, treat with $HF+H_2SO_4$, ignite, weigh.</td><td colspan="2" rowspan="2">F^1 : add leach from R^2. Add 5 grm. NH_4Cl and excess of NH_4OH in the cold. Repeat pption, adding filter pulp. Combine filtrates.</td></tr>
<tr><td>L^2 : SiO_2.</td><td>R^2 : fuse with $NaHSO_4$, leach, add solution to F^1.</td></tr>
<tr><td colspan="3">P^3 : ignite, fuse with Na_2CO_3, leach with H_2O, filter, wash with 2 per cent. Na_2CO_3-solution.</td><td>F^3 : determine Mn, Ca, Mg.</td></tr>
<tr><td colspan="2">R^4 : ignite, fuse with $NaHSO_4$, dissolve in warm 5 per cent. H_2SO_4, pass H_2S, filter, reject ppte. Saturate filtrate with H_2S, neutralise with Na_2CO_3 avoiding ppte, add 20 grm. CH_3CO_2Na and $\frac{1}{6}$ of the bulk of 50 per cent. CH_3CO_2H. Boil one minute, filter, wash with 5 per cent. CH_3CO_2H, then with hot H_2O.</td><td colspan="2">F^4 : acidify with H_2SO_4, add H_2O_2 free from Al and P_2O_5, determine V_2O_5 colorimetrically. Boil, reduce with SO_2, expel excess by boiling. Cool, add NH_4NO_3, HNO_3, and molybdate mixture. Let stand, filter.</td></tr>
<tr><td>P^5 : ignite, weigh TiO_2; if not quite white (Fe), repeat fusion with $NaHSO_4$ and pption.</td><td>F^5 : boil off H_2S, oxidise with Br, add pulp, ppte with NH_4OH, reject filtrate. Dissolve ppte in HNO_3, pour into excess of NaOH, boil, filter.</td><td>P^7 : determine P_2O_5.</td><td>F^7 : ppte with NH_4OH, filter, reject filtrate. Dissolve ppte in HNO_3, neutralise with NH_4OH, add 1 grm. of $(NH_4)_2CO_3$, let stand, warm, for some time. Filter.</td></tr>
<tr><td>P^6 : $Fe(OH)_3$. Add Fe from P^5 if necessary, titrate Fe.</td><td>F^6 : acidify with HNO_3, ppte with NH_4OH, add to P^8.</td><td>P^8 : add ppte from F^6, ignite, weigh Al_2O_3.</td><td>F^8 : reject.</td></tr>
</table>

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[1] Hillebrand, *loc. cit.* (p. 92).

(*b*) *Ilmenite.—First Portion.*—

<table>
<tr><td colspan="3">1 grm. crushed to −100 mesh. Fuse with 6 grm. $NaHSO_4$, leach with warm 5 per cent. H_2SO_4. Filter.</td></tr>
<tr><td colspan="2">R^1 : SiO_2, etc. See R^1, L^2, R^2, preceding table.</td><td>F^1 : add leach from R^2. Pass H_2S, filter, reject ppte. To filtrate add 3 grm. of tartaric acid, a slight excess of NH_4OH, saturate with H_2S. Filter, wash with colourless NH_4SH.</td></tr>
<tr><td colspan="2">P^3 : dissolve in HCl, boil, oxidise Fe, ppte as basic acetate. Filter.</td><td rowspan="2">F^3 : evaporate with $HNO_3+H_2SO_4$ to strong fumes until colourless. Boil with excess of Na_2CO_3, filter, dissolve, repeat pption, wash with 2 per cent. Na_2CO_3, combine filtrates.</td></tr>
<tr><td>P^4 : titrate Fe.</td><td>F^4 : ppte Mn with Br.</td></tr>
<tr><td colspan="2">F^5 : see (*a*), F^4 *et seq.*</td><td>P^5 : ignite, fuse with $NaHSO_4$, leach, ppte with NH_4Cl+NH_4OH in the cold, repeat pption, combine filtrates.</td></tr>
<tr><td colspan="2">F^6 : determine Ca, Mg.</td><td>P^6 : $TiO_2+Al_2O_3$ (partly). Separate according to § III, (*d*). Ppte filtrate from TiO_2 with NH_4OH, dissolve ppte in HNO_3 ; add to Al_2O_3 from F^5.</td></tr>
</table>

Second Portion.—Ferrous oxide. Fuse 0·5 grm. with 3 grm. $NaHSO_4$ and 5 c.c. H_2SO_4 in a conical flask, cool, add boiled water and H_2SO_4 ; when dissolved, titrate with $KMnO_4$. All operations to be carried out in CO_2 atmosphere.

Third Portion.—Sulphur. Fuse with $Na_2CO_3+KNO_3$, leach, filter, determine SO_3 in filtrate.

(*c*) *Other Minerals* (*Titanosilicates, etc.*).—The mineral is fused with ten times its weight of Na_2CO_3, and the melt leached with water. The solution contains most of the silica, aluminium, and vanadium. The residue, consisting of sodium titanate and the carbonates or oxides of the common metals, is fused with bisulphate. Both solutions are examined according to (*a*) or (*b*).

(*d*) *Titanocolumbates.*—See Tantalum, § VII.

ZIRCONIUM.

§ I. Minerals.—(*a*) *Oxides.*—(1) *Baddeleyite*, zirconium dioxide, ZrO_2, occurs as monoclinic tables often twinned. They have a greasy to vitreous lustre and a nearly perfect cleavage. The colour varies, according to the percentage of iron, from white through yellow, brown and red, to black. H 6 ; sp. gr. 5·7.

(2) *Brazilite* is compact, hard, amorphous baddeleyite containing zircon, another unnamed zirconium silicate, silica, iron oxide, and titanium oxide in variable proportions. The colour varies from red-brown to brownish-white. It is also sometimes black or grey. The most abundant source of zirconium.

(3) *Zirkelite* is a complex mixture of iron oxide, lime, zirconia, titania, and thoria. It is found as brittle, resinous, black octahedra having a conchoidal fracture. H 5·5 ; sp. gr. 4.

(4) *Uhligite*, complex mineral found in bright black octahedra. It is a mixture of lime, alumina, titania, and zirconia.

(*b*) *Silicates.*—(1) *Zircon*, zirconium orthosilicate, $ZrSiO_4$, is found as brittle tetragonal prisms isomorphous with rutile, thorite, and cassiterite. Colour variable; it has been found colourless, red, brown, green, yellow, and black. Lustre adamantine, double refraction strong. No cleavage. H 7·5; sp. gr. 4·7.

(2) *Naegite*, a radioactive variety of the above, contains yttrium, thorium, and tantalum.

(3) *Lavenite*, complex silicate of iron, manganese, and zirconium containing tantalum. Yellow to brown monoclinic tables, with vitreous lustre and perfect cleavage. H 6; sp. gr. 3·5.

(4) *Hainite*, complex silicate of calcium, sodium, titanium, and zirconium containing tantalum. Pale yellow triclinic needles or plates with vitreous lustre.

(5) *Eudialyte*, silicate of zirconium, sodium, calcium, and iron containing chlorine. Red to brown translucent rhombohedral tables. Lustre resinous. H 5·5; sp. gr. 2·9.

(6) *Rosenbuschite*, silicate and fluoride of zirconium, titanium, sodium, and lime. Orange, vitreous, monoclinic crystals. H 5·5; sp. gr. 3·3.

§ **II. Properties and Compounds.**—(*a*) The *metal* is produced by reduction of potassium fluozirconate with sodium in the presence of sodium chloride. The fused metal has a white colour, is very hard (7 to 8 on Mohs' scale) and brittle. It melts at about 1500°, and is very resistant to acids, being attacked only by *aqua regia* and hydrofluoric acid. It readily combines on heating with oxygen (to ZrO_2), nitrogen (to Zr_3N_2), and hydrogen (to ZrH_2).

(*b*) The *dioxide*, ZrO_2, is a dense white powder, very resistant to acids and alkalies. It is used as a refractory on account of its inertness and high melting-point (about 2700°). It volatilises at 3000°. Formed by ignition of the nitrate, oxalate, or hydroxide.

(*c*) *Zirconium hydroxide* is precipitated by ammonia or caustic alkali from zirconium solutions. It is white, gelatinous, insoluble in excess, and contains an indefinite amount of water. When precipitated in the cold, it is soluble in dilute acids; if thrown down from hot solutions, or after washing with hot water, it is soluble only in strong acids.

(*d*) The *oxychloride*, $ZrOCl_2.8H_2O$, is formed on dissolving the hydroxide in hydrochloric acid. It is readily soluble in water, but only slightly so in hydrochloric acid, from a solution of which it crystallises in tetragonal prisms.

(*e*) The *fluoride*, $ZrF_4.3H_2O$, is soluble in water containing free hydrofluoric acid (difference from thorium). The addition of potassium fluoride causes deposition of crystals of potassium fluozirconate, K_2ZrF_6, which is soluble in seventy parts of cold and four parts of boiling water.

(*f*) *Zirconyl oxalate* is a white powder formed on mixing the requisite quantities of solutions of a zirconium salt and a soluble oxalate. It is soluble in ammonium oxalate or oxalic acid.

(*g*) *Zirconium sulphate*, $Zr(SO_4)_2.4H_2O$, is obtained by dissolving the hydroxide in sulphuric acid. Potassium sulphate gradually precipitates potassium zirconyl sulphate from the cold solution.

(*h*) *Sodium orthozirconate*, Na_4ZrO_4, is formed when the oxide is fused with excess of sodium carbonate. Decomposed by water with formation of the hydroxide.

§ III. Quantitative Separation.—Zirconium is a metal of the third analytical group, being precipitated by ammonia in the presence of ammonium chloride. It is separated from the other members of this group in the following manner:—

(*a*) *Separation from Iron, Nickel, Cobalt, Manganese, Zinc, Uranium.*[1]—The solution of the metals in hydrochloric or sulphuric acid is treated with hydrogen sulphide until all the iron is reduced to the ferrous condition. Three times the weight of oxides present in tartaric acid is added and the solution made faintly ammoniacal. Hydrogen sulphide is again passed through the warm (60°) solution until all the above metals are precipitated as sulphides and the precipitate has coagulated. After settling, the solution is filtered, and the precipitate well washed with hot water containing a little colourless ammonium sulphide. The filtrate is boiled with excess of dilute sulphuric acid to expel hydrogen sulphide, 20 c.c. of strong nitric and 10 c.c. of strong sulphuric acid added, and the solution carefully evaporated to strong fumes to destroy tartaric acid. The solution now contains zirconium sulphate, and titanium, thorium, aluminium, beryllium, and rare earths if present.

(*b*) *Separation from Rare Earths* (*also from Manganese, Beryllium, and Small Amounts of Iron*).[2]—The solution is neutralised with sodium carbonate so that no permanent precipitate is formed, treated with 10 grm. of sodium thiosulphate dissolved in a small quantity of water, diluted to 300 c.c., and boiled for one to two hours, adding hot water to replace that lost by evaporation. The precipitate is allowed to settle, filtered through a loose paper, ignited and fused with bisulphate. The melt is extracted with dilute sulphuric acid; the solution may now contain zirconium, thorium, titanium, and aluminium.

(*c*) *Separation from Aluminium.*[3]—(1) The solution (preferably in hydrochloric acid) is diluted so that it contains not more than 0·1 grm. $ZrO_2+TiO_2+ThO_2$ per 100 c.c., and treated with a dilute solution of sodium carbonate until a faint opalescence remains on stirring; this is then removed by the cautious addition of dilute hydrochloric acid. A saturated solution of sodium iodate [4] is now added in slight excess, the solution heated to boiling, boiled fifteen minutes, and allowed to stand overnight, after which the precipitate is filtered off and washed

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[1] Cathrein, *Z. Kryst.*, 1882, **6**, 244; 1883, **7**, 250; Lindet, *Chem. News*, 1897, **76**, 212; Wdowiszewski, *Stahl u. Eisen*, 1907, **27**, 781; Thornton, *Amer. Journ. Sci.*, 1912, **34**, 214.

[2] Dittrich and Freund, *Z. anorg. Chem.*, 1907, **56**, 337.

[3] Separation by cupferron: Ferrari, *Annali Chim. Appl.*, 1914, **2**, 276; Thornton and Hayden, *Amer. Journ. Sci.*, 1914, **38**, 137.

[4] Davis, *Journ. Amer. Chem. Soc.*, 1889, **11**, 26; see also Meyer and Speter, *Chem. Zeit.*, 1910, **34**, 306, and Meyer, *Z. anorg. Chem.*, 1911, **71**, 65, who precipitate with a large excess of iodate in a nitric acid solution, as for thorium (*q.v.*); this also separates phosphoric acid and rare earths from zirconium, but precipitates thorium, titanium, and ferric salts.

with boiling water. It is then dissolved in hydrochloric and sulphurous acids to reduce the iodate, the cold solution treated with a slight excess of ammonia, the precipitate filtered and washed with dilute ammonium nitrate till free from iodide. It is dissolved in nitric acid; titanium and thorium, if present, are removed according to (*d*) and (*e*).

(2) Zirconium is precipitated as phosphate (Titanium, § III, (*b*) (2)).

(3) The mixed oxides are fused with thirty times their weight of sodium carbonate, the aqueous extract of the melt digested with a little caustic soda, and filtered. The alumina is in the filtrate, and the zirconium in the residue, which is fused with bisulphate.[1] Alternatively, the mixed oxides may be fused with sodium hydroxide.

(*d*) *Separation from Titanium.*—See Titanium, § III, (*b*).

(*e*) *Separation from Thorium.*—The precipitated hydroxides are dissolved in hydrochloric acid; the solution is nearly neutralised with dilute ammonia, heated to boiling, and ammonium oxalate added until the precipitate first formed is re-dissolved completely. An equal volume of boiling water is added, followed by concentrated hydrochloric acid drop by drop until no further precipitate forms. After standing overnight the precipitate is filtered off and washed with warm water. The filtrate contains the zirconium; it must be evaporated to strong fumes with sulphuric and nitric acids to destroy oxalates.

(*f*) *Separation from Beryllium.*—See Beryllium, § III, (*b*).

§ IV. Gravimetric Determination.—Zirconium is usually weighed as dioxide, obtained by igniting the precipitate produced by ammonia or sodium thiosulphate. The precipitation by ammonia is carried out in the same manner as in the case of aluminium, and the precipitate must similarly be washed with 2 per cent. ammonium nitrate to avoid loss of colloidal hydroxide. If sodium thiosulphate is used, the precipitation is carried out as shown in § III, (*b*). The precipitate in this case filters more readily than that produced by ammonia owing to the presence of sulphur, but is liable to occlude salts; it is washed with boiling water alone. The precipitate produced by either method is ignited to constant weight and weighed as ZrO_2.

§ V. Detection in Ores.—The ore is fused with acid potassium fluoride, the melt boiled with dilute hydrofluoric acid, the solution filtered, and evaporated to strong fumes with sulphuric acid. The acidity of the solution thus obtained is adjusted to 1 per cent., the zirconium precipitated as phosphate, and this precipitate converted into sulphate as described in § VI, (*b*). The solution is now tested as follows:—

(1) A piece of turmeric paper dipped in the solution acidified with hydrochloric acid, and dried, turns red-brown. Titanium gives a similar reaction.

(2) Oxalic acid gives a precipitate soluble in excess (distinction from thorium). Ammonium oxalate produces the same reaction.

(3) Hydrogen peroxide gives a white gelatinous precipitate of hydrated peroxide in neutral (sulphate) solutions (distinction from titanium).

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[1] Ferguson, *Eng. and Min. Journ.*, 1918, **106**, 356, 793.

(4) Sodium iodate gives a white flocculent precipitate of basic iodate in neutral solution (distinction from aluminium).

(5) Caustic alkalies give a white precipitate insoluble in excess (distinction from aluminium and beryllium).

(6) Ammonium carbonate gives a white precipitate soluble in large excess (distinction from titanium).

(7) Hydrofluoric acid gives no precipitate (distinction from thorium).

(8) Zirconium dioxide, moistened with cobalt solution and heated on charcoal, gives a dirty violet mass.

§ VI. Determination in Ores.[1]—(*a*) *Determination in Zircon, Baddeleyite, Brazilite, and Oxide and Silicate Minerals high in Zirconia.*—0·5 grm. of the slimed mineral is fused with 5 grm. of sodium carbonate in a platinum crucible over a blast for an hour. The cold melt is boiled out with water, and the insoluble residue containing the zirconium filtered, washed with 2 per cent. sodium carbonate, ignited and fused with 5 grm. sodium bisulphate at a low red heat in a silica or platinum crucible. The cold melt is dissolved in warm dilute sulphuric acid, the insoluble fumed with hydrofluoric and sulphuric acids, any residue again fused, and the solutions united. The solution is precipitated with thiosulphate as in § III, (*b*), the precipitate calcined, fused with sodium bisulphate, dissolved in dilute sulphuric acid, the solution neutralised, and the thorium precipitated as in § III, (*e*). The filtrate is evaporated with nitric and sulphuric acids to fumes to decompose oxalates; the acid solution is diluted with water, precipitated in the cold with ammonia, the washed precipitate dissolved in nitric acid, and the neutralised solution precipitated with ammonium salicylate (see Titanium, § III, (*b*) (1)). The precipitate is ignited, and fused with bisulphate; the solution of the melt is precipitated with ammonia or thiosulphate, the precipitate well washed, ignited wet in platinum, and weighed as ZrO_2. If no thorium is present and but little titanium (*e.g.* brazilite) the oxalate separation may be dispensed with; the titanium and zirconium are precipitated together as basic iodates, converted into hydroxides, ignited and weighed as ZrO_2+TiO_2 (§ III, (*c*)). The oxides are fused with bisulphate, the titania determined colorimetrically (Titanium, § VI.), and deducted from the weight of mixed oxides.

(*b*) *Determination in Rocks.*[2]—Two grm. of the rock powder are fused with 10 grm. of sodium carbonate in a platinum crucible. The melt is boiled out with water, the insoluble residue filtered off, washed with 2 per cent. sodium carbonate solution, boiled with a small excess of 5 per cent. sulphuric acid, and the liquid filtered through the original filter. After well washing with dilute acid the filter and contents are ignited in platinum, the residue treated with hydrofluoric and sulphuric acids, and evaporated to strong fumes. The mass is diluted with water and the solution filtered into the original acid filtrate, the acidity of which is adjusted so that there is not more than 1 per cent. free acid in the solution. Ten c.c. of 6 per cent. hydrogen peroxide and 1 c.c. of

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[1] See also Wedekind and Lewis, *Journ. Chem. Soc.*, 1909, **95**, 456.

[2] Hillebrand, *Bull.* 176, *U.S. Geol. Survey*, 75.

saturated sodium phosphate solution are added and the liquid allowed to stand twenty-four to forty-eight hours, after which the precipitate is filtered off and washed with very dilute sulphuric acid (0·5 per cent.). Even if small in amount the precipitate is ignited, fused with 2 to 3 grm. of sodium carbonate, the melt extracted with boiling water, and the residual impure zirconia filtered and washed with 2 per cent. sodium carbonate. It is then ignited, fused with 1 grm. of sodium bisulphate, the melt dissolved in a small quantity of dilute sulphuric acid, the solution adjusted to 1 per cent. free acid, and the precipitation repeated. After standing two days the precipitate is filtered off, washed with 0·5 per cent. sulphuric acid, then with water, ignited, and weighed as zirconium phosphate. This contains 51·8 per cent. of ZrO_2.

§ **VII. Complete Analysis of Ores.**—(*a*) *Zircon, Baddeleyite, or Brazilite.*—

<table>
<tr><td colspan="5">Heat 0·5–1 grm. of slimed ore in tared Pt crucible, take loss on ignition.
Fuse residue with 6 grm. Na_2CO_3 over a blast for one hour. Boil with water, filter, wash with hot water.</td></tr>
<tr><td colspan="2">F^1: acidify with HCl, evaporate to dryness, take up with dilute HCl, filter.</td><td colspan="3">R^1: fuse with $NaHSO_4$, leach with 5 per cent. H_2SO_4, filter.</td></tr>
<tr><td>R^2: SiO_2; add to R^4.</td><td>F^2: again evaporate, take up with HCl, filter.</td><td rowspan="2">F^4: add F^3 and leach from R^5, pass H_2S, filter, reject ppte, nearly neutralise filtrate with Na_2CO_3, pass CO_2 and heat to expel H_2S, ppte with $Na_2S_2O_3$ and filter pulp (§ III, (*b*)), filter, wash well with hot water.</td><td colspan="2">R^4: add R^2 and R^3. Ignite and weigh; treat with $HF + H_2SO_4$; ignite, weigh.</td></tr>
<tr><td>F^3: add to F^4,</td><td>R^3: SiO_2; add to R^4.</td><td>R^5: fuse with $NaHSO_4$, leach, add to F^4.</td><td>L^5: SiO_2.</td></tr>
<tr><td colspan="2">F^6: evaporate with HNO_3, determine Fe, Mn, Ca, Mg.</td><td colspan="3">P^6: ignite gently, leach with H_2O, filter off, ignite strongly, weigh $ZrO_2 + TiO_2 + Al_2O_3$. Fuse with Na_2CO_3 and leach as under § III, (*c*) (3). Filter.</td></tr>
<tr><td colspan="4">R^7: fuse with $NaHSO_4$, leach, determine TiO_2 colorimetrically in aliquot portion. Weight of $P^6 - (Al_2O_3 + TiO_2) = ZrO_2$. If more than 5 per cent. TiO_2 is present, treat leach as under Ti, § III, (*b*) (1); ppte salicylate filtrate with NH_4OH, filter off, ignite and weigh TiO_2.</td><td>F^7: determine Al_2O_3.</td></tr>
</table>

(*b*) *Minerals containing Thoria, Rare Earths, etc.*—Minerals in which zirconia predominates are opened up by fusion with bisulphate, or, if siliceous, by fusion with sodium carbonate, with subsequent fusion of the insoluble residue with bisulphate (see (*a*)). Thorium minerals containing small amounts of zirconia are opened up with hydrochloric acid (for silicates), sulphuric acid (for phosphates), or bisulphate (for oxides). The analysis of the solution thus obtained is conducted as described under Thorium, § VII. (See also Tantalum, § VII.)

THORIUM.

§ **I. Minerals.**—All thorium minerals are radioactive.

(*a*) *Oxides.*—(1) *Thorianite* is essentially thorium oxide (ThO_2) containing uranium oxide (10–30 per cent.) and rare earths (1–8 per cent.).

Jet-black, lustrous, rhombohedral crystals of cubic habit. Brittle. H 7; sp. gr. 8–9·7. Evolves helium on heating.

(2) *Mackintoshite* is a complex mixture containing about 45 per cent. of thoria, together with oxides of uranium, zirconium, tantalum, iron, magnesium, lead, and sodium. Black, opaque, tetragonal crystals resembling thorite (*q.v.*). H 5½; sp. gr. 5·4.

(3) *Cleveite*, *Bröggerite*, and *Uraninite* are uranium minerals containing variable amounts of thoria (see Uranium, § I.).

(*b*) *Silicates.*—(1) *Thorite* and *Orangite* are varieties of thorium silicate, $ThSiO_4$, differing in colour and specific gravity. Orangite is heavier (5·2–5·4) than thorite (4·4–4·8); the former possesses a fine orange colour, while the latter is dark brown to black. Both crystallise in the tetragonal system, and are isomorphous with zircon, rutile, and cassiterite. H 4½–5. Uranium oxide and rare earths often present.

(2) *Calciothorite* is a deep red, translucent, amorphous variety of thorite containing lime. H 4½; sp. gr. 4·1.

(3) *Eucrasite* is a black, opaque mineral resulting from the alteration of thorite. H 4½–5; sp. gr. 4·4. It is usually found amorphous, and contains large amounts of rare earths.

(4) *Freyalite* is a brown, amorphous, resinous silicate containing thoria 28 per cent., cerium earths 30 per cent., and zirconia 6 per cent. H 6; sp. gr. 4·1.

(5) *Pilbarite*, *Thorogummite*, and *Yttrogummite* are yellow to brown, opaque silicates of thorium and uranium (see Uranium, § I.).

(*c*) *Phosphates.*—(1) *Monazite* (a phosphate of the cerium metals and thorium).—Small, yellow, brittle, monoclinic crystals, with a resinous lustre, usually translucent. H 5; sp. gr. 5–5·2. Occurs generally as water-worn, yellow, translucent grains in alluvial deposits, together with quartz, ilmenite, rutile, and garnet. It is the most important source of thorium. Magnetic, but less so than ilmenite.

(2) *Xenotime* (a phosphate of yttrium metals with a small amount of thorium). See Rare Earths, § II, (*b*) (3).

(*d*) *Titano- and tantalocolumbates.*—See Columbium, § I.

§ II. Properties and Compounds.—(*a*) The *metal* is a dark grey powder of sp. gr. 11·3, melting about 1700°. It readily combines with oxygen, hydrogen, and nitrogen. Soluble in *aqua regia*, very difficultly in other acids.

(*b*) The *oxide*, ThO_2, is prepared by ignition of the hydroxide, oxalate, or nitrate as a dense white powder. Insoluble in acids, except boiling strong sulphuric acid; soluble in fused bisulphate. Forms tetragonal crystals when fused with borax, and octahedral crystals on fusion with sodium phosphate. The oxide formed by igniting the nitrate containing 1 per cent. of sulphate is a voluminous white powder, and, as such, is used in the mantle industry.

(*c*) *Thorium hydroxide*, $Th(OH)_4$, is a white, amorphous precipitate thrown down by ammonia or caustic alkalies from solutions of thorium salts; it is insoluble in excess of the reagents. Barium carbonate in cold, or sodium thiosulphate in boiling solutions, cause complete precipitation of the hydroxide. The last reaction enables thorium to be separated from the rare earths.

(*d*) *Thorium peroxide* is precipitated by strong hydrogen peroxide solutions from a neutral solution of thorium nitrate as thorium peroxynitrate. Gelatinous, colourless precipitate decomposed by acids; it yields the dioxide on ignition.

(*e*) *Thorium fluoride*, $ThF_4.4H_2O$, is a white, gelatinous precipitate, insoluble in water or mineral acids, formed by adding hydrofluoric acid to a solution of the chloride.

(*f*) *Thorium chloride*, $ThCl_4$, is soluble in water, alcohol, and ether, and crystallises as octahydrate from aqueous solutions.

(*g*) *Thorium iodate*, $Th(IO_3)_4$, is a white, amorphous precipitate, insoluble in nitric acid in presence of a large excess of alkali iodate.

(*h*) *Thorium sulphate*, $Th(SO_4)_2$, is very important commercially as being the salt used to purify thorium preparations by fractional crystallisation. It forms supersaturated solutions at 0°, which, on heating to 20°, deposit the octahydrate, and above 43° the tetrahydrate.

(*i*) *Thorium nitrate*, $Th(NO_3)_4.12H_2O$, is very soluble in water and alcohol. Important in the incandescent mantle industry.

(*j*) *Thorium pyrophosphate* is a white, amorphous precipitate, insoluble in water and dilute sulphuric acid. (See § III, (*c*).)

(*k*) *Thorium oxalate*, $Th(C_2O_4)_2.6H_2O$, is a white crystalline precipitate, formed when acid solutions of thorium salts are treated with oxalic acid. Insoluble in water, oxalic acid, or dilute acids, and unattacked by concentrated nitric acid; soluble in alkaline oxalate solutions, re-precipitated on addition of mineral acids. On ignition it is converted into the dioxide.

(*l*) *Thorium carbonate* is a white amorphous precipitate produced by alkaline carbonates. It is soluble in excess; the solution is precipitated when heated, but clears again on cooling.

§ III. Quantitative Separation.—Precipitation with oxalic acid from a slightly acid solution separates thorium from the common metals, bases, and from titania and zirconia (Titanium, § III., and Zirconium, § III.), but not from the rare earths. The latter are separated from thorium by one of the following methods:—

(*a*) *The Hydrogen Peroxide Method.*[1]—The neutral solution of the nitrates is diluted to 100 c.c., 10 grm. of ammonium nitrate are added, the solution heated to 60°–80°, and the thorium precipitated by adding 20 c.c. of 3 per cent. hydrogen peroxide. The gelatinous precipitate is filtered off, washed with 2 per cent. ammonium nitrate, re-dissolved in dilute nitric acid, the solution evaporated to dryness, the residue moistened with water, again dried, dissolved in 100 c.c. of 10 per cent. ammonium nitrate, and the thorium re-precipitated by the addition of hydrogen peroxide. The precipitate is washed with 2 per cent. ammonium nitrate, dried, and ignited to ThO_2.

(*b*) *The Iodate Method.*[2]—The solution is diluted to 100 c.c., treated

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[1] Benz, *Z. angew. Chem.*, 1902, **15**, 297.

[2] Meyer and Speter, *Chem. Zeit.*, 1910, **34**, 306.

with 50 c.c. of concentrated nitric acid, and cooled. A solution of 15 grm. of potassium iodate in 30 c.c. water and 50 c.c. of nitric acid is added, the mixture cooled again, and allowed to stand for half an hour with frequent stirring. The white, flocculent precipitate of thorium iodate is left to settle, filtered off, and washed with 200 c.c. of a solution containing 8 grm. of potassium iodate and 200 c.c. nitric acid (1·2 sp. gr.) per litre. The precipitate is washed back into the beaker with 100 c.c. of the washing liquid and again filtered ; it is now rinsed back into the beaker with hot water, and dissolved by adding 30 c.c. concentrated nitric acid. The thorium is re-precipitated by adding to the cooled solution 4 grm. of potassium iodate dissolved in a little concentrated nitric acid and water, the precipitate filtered, and washed as before. The above procedure separates thorium oxide from phosphoric acid and the common metals as well as from the alkaline earths. Titanium and zirconium, however, are also precipitated under the above conditions. To remove these the precipitate is dissolved in hydrochloric acid and a little sulphur dioxide, the thorium, zirconium, and titanium precipitated with ammonia, washed free of iodides, re-dissolved in hydrochloric acid, and the thorium alone precipitated by the addition of a saturated solution of oxalic acid in large excess (§ IV.); the oxalate is ignited and the thoria weighed.

(*c*) *The Pyrophosphate Method.*[1]—The solution, the acidity of which in hydrochloric acid is adjusted to 0·3 N, is heated to boiling, and sodium pyrophosphate slowly added until no further precipitate is formed. The boiling is continued for five minutes, the solution allowed to stand ten minutes, then filtered, and washed with 0·3 N hydrochloric acid. The precipitate and filter are heated with 10 c.c. of strong sulphuric acid and a little ammonium perchlorate to oxidise organic matter, the mass allowed to cool, diluted slowly with water, and poured into excess of hot sodium hydroxide solution. The precipitate of thorium hydroxide is boiled with hydrochloric acid, a little sulphur dioxide water added, the acidity adjusted to 0·3 N, and the thorium again precipitated with pyrophosphate. The precipitate is treated as before, and the final thorium chloride solution precipitated with oxalic acid (§ IV.) to remove zirconium and titanium. This method also obviates the necessity of precipitating all the rare earths with oxalic acid in the first place.

(*d*) *Separation by Sodium Thiosulphate.*[2]—The hydrochloric solution of the ignited oxalates is evaporated to dryness on the water-bath, the residue moistened with 5 c.c. of water, and again dried. It is then taken up with 200 c.c. of water, 9 grm. of sodium thiosulphate crystals dissolved in 30 c.c. of water are added, and the whole allowed to stand overnight. The solution is boiled ten minutes, and the precipitate of thorium hydroxide and sulphur filtered off and well washed with water. The filtrate is vigorously boiled for one hour, and any precipitate that

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[1] Carney and Campbell, *Journ. Amer. Chem. Soc.*, 1914, **36**, 1134.

[2] Fresenius and Hintz, *Z. anal. Chem.*, 1896, **35**, 530 ; Drossbach, *Z. angew. Chem.*, 1901, **14**, 656 ; Benz, *ibid.*, 1902, **15**, 302 ; White, *Thorium and its Compounds* (Institute of Chemistry, 1912).

forms filtered on a fresh small filter and set aside for further treatment. The main precipitate is washed back with a minimum of water into the same beaker, boiled with 10 c.c. of hydrochloric acid, the liquid filtered into a small evaporating basin, and the residual sulphur well washed. The filtrate is evaporated to dryness, the residue moistened with water, dried again, dissolved in 150 c.c. of water, and treated with 3 grm. of sodium thiosulphate in strong solution. After standing overnight the solution is boiled ten minutes, filtered, and the washed precipitate extracted with hydrochloric acid. This solution is evaporated, etc., and again put through the entire process, finally giving a solution of thorium chloride, which is precipitated with oxalic acid (§ IV.).

The filtrates from the second and third thiosulphate precipitations are treated with ammonia; if the precipitate thus produced in the third filtrate is appreciable—showing that the thoria is contaminated with rare earths—a fourth precipitation must be made. The precipitate produced by the one hour's boiling of the filtrate from the first thiosulphate precipitation, the ammonia precipitates, and the sulphur residues are ignited together with the filters; the ignited product contains traces of thoria, which are recovered as follows: fusion with bisulphate, leaching with warm water, precipitation with ammonia, solution of the precipitate in hydrochloric acid, evaporation, precipitation with thiosulphate, extraction of precipitate with hydrochloric acid, and precipitation with oxalic acid. The small quantity of thoria thus found is added to that previously obtained.[1]

§ IV. Gravimetric Determination.—Thorium is always determined gravimetrically [2] as the dioxide, obtained by ignition of the oxalate. The precipitation as oxalate is carried out as follows: The solution of thorium chloride obtained by one of the above methods is evaporated to dryness to remove excess acid, 10 c.c. concentrated hydrochloric acid added, the solution diluted to 150 c.c., heated to 40°–60°, and precipitated by the addition of 30 c.c. of a cold saturated solution of oxalic acid. The warm solution is allowed to stand half an hour, then stirred vigorously, and set aside three to four hours, or, better, overnight at a temperature of 60°. The white crystalline precipitate is filtered off, washed with warm water acidified with hydrochloric acid, and ignited wet to ThO_2.

§ V. Detection in Ores.—The mineral is decomposed by fusion with bisulphate, or by boiling with sulphuric acid, the insoluble filtered off, and the thorium and rare earths precipitated by oxalic acid. The oxalates are filtered off, ignited, and the residue fused with sodium bisulphate. The resulting solution is tested as follows:—

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[1] Other reagents proposed for the precipitation of thoria: (*a*) metanitrobenzoic acid, Neish, *Chem. News*, 1904, **90**, 196, 201; (*b*) potassium azide, Dennis and Kortright, *Journ. Amer. Chem. Soc.*, 1896, **18**, 94; (*c*) sebacic acid, Smith and James, *ibid.*, 1912, **34**, 281; (*d*) sodium hypophosphate, Koss, *Chem. Zeit.*, 1912, **36**, 686; Rosenheim, *ibid.*, 1912, 36, 821; Wirth, *Z. angew. Chem.*, 1912, **25**, 1678.

[2] Metzger and Zons, *Journ. Ind. Eng. Chem.*, 1912, **4**, 493, give a volumetric method based on the precipitation of thorium by ammonium molybdate, using diphenylcarbazide as external indicator. The method is applicable to the determination of thoria in monazite sand.

(1) It is nearly neutralised by sodium carbonate leaving the solution faintly acid; on adding hydrogen peroxide a gelatinous, colourless precipitate of peroxy-salt is obtained.

(2) Sodium pyrophosphate in acid solution gives a white, amorphous precipitate.

(3) Potassium iodate and nitric acid, both in large excess, give a white, amorphous precipitate.

The following method [1] serves to detect traces of thorium in mixtures of rare earths. Two solutions are required: (A) Fifteen grm. potassium iodate, 50 c.c. concentrated nitric acid, 100 c.c. water; (B) 4 grm. potassium iodate, 100 c.c. nitric acid (sp. gr. 1·2) 400 c.c. water. Two c.c. of the solution of the oxides from ignition of the oxalates (free from hydrochloric acid) are mixed with 5 c.c. of solution A. The precipitate formed contains thorium iodate, together with iodates of the other rare earths. The latter are dissolved by boiling with 10 c.c. of solution B, leaving the thorium insoluble. This detects 0·0002 grm. of thoria in 2 c.c. of solution.

§ VI. Determination in Ores.—(*a*) *In Monazite and Ores high in Rare Earths and low in Thoria.*—(1) 12·5 grm. of the sand (uncrushed) are heated in a large porcelain basin with 50 c.c. of sulphuric acid,[2] stirring occasionally until a drop mixed with water on a watch-glass shows no yellow undecomposed grains (about four to six hours are required). After cooling the thick mass is gradually added to cold water with constant stirring, taking care that the temperature never exceeds 20°. When all is in solution, leaving only black ilmenite and white quartz or zircon, together with, perhaps, a small amount of gelatinous silicic or tantalic acids, the solution is diluted to 500 c.c. in a graduated flask. 200 c.c. (=5 grm.) are filtered off through a fluted paper, transferred to a beaker, and treated in the cold with 180 c.c. of a cold saturated solution of oxalic acid. A voluminous precipitate of the oxalates of the rare earths and thorium is thrown down; after standing one hour the solution is vigorously stirred and set aside overnight. The crystalline precipitate of hydrated oxalates is filtered off, washed with dilute hydrochloric acid until the washings cease to show a phosphate reaction, dried, ignited, and the oxides thus formed dissolved in hydrochloric acid. The thorium is now separated from the rare earths by the thiosulphate method (§ III, (*d*)), the final solution of pure thorium chloride precipitated by oxalic acid (§ IV.), the precipitate ignited, and weighed as ThO_2.

(2) 0·5 grm. of the finely-divided sand is intimately mixed with 0·5 grm. of sodium fluoride, and the mixture fused with 10 grm. of sodium bisulphate in a platinum crucible.[3] When tranquil fusion is attained the melt is allowed to cool, extracted with water and a little hydrochloric acid, the liquid heated to boiling, the residue (chiefly silica and tantalic acid) allowed to settle, filtered, washed once or twice with hot water, rinsed back into the beaker, and digested a short time with a little concen-

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[1] Meyer, *Z. anorg. Chem.*, 1911, **71**, 65.

[2] White, *op. cit.* (p. 107).

[3] Benz, *loc. cit.* (p. 106).

trated hydrochloric acid; this is diluted and again filtered. The washed residue is now free from thorium. The combined filtrates are nearly neutralised with ammonia, avoiding a permanent precipitate, heated to boiling, and the rare earth oxalates precipitated as a coarse powder by the addition of 4 grm. of solid ammonium oxalate while vigorously stirring. The beaker is set aside overnight; the precipitate is then filtered, washed with hot water acidulated with nitric acid, rinsed into a porcelain dish with a minimum of water, and the paper repeatedly washed with hot concentrated nitric acid. The contents of the dish are evaporated to dryness on the water-bath, the residue treated with 10 c.c. of nitric (sp. gr. 1·4) and 20 c.c. of fuming nitric acid, and digested on the water-bath (the basin being covered by a clock-glass) until all action has ceased and no further brown fumes form. The clock-glass and sides of the basin are rinsed down with water and the liquid evaporated to dryness, the mass moistened with water, and again dried on the water-bath. The residue is taken up with water, and the thorium separated as peroxide according to § III, (*a*). The second precipitate of peroxynitrate is ignited wet and weighed as ThO_2.

(3) The sand is treated as under (1), using, however, 25 c.c. of sulphuric acid. 100 of 500 c.c. (=2·5 grm.) are filtered off, treated with 50 c.c. of nitric acid, and the thorium precipitated as iodate according to § III, (*b*).

(4) The sand is opened up according to (1), and 100 c.c. (=2·5 grm.) treated with dilute ammonia, taking care to get no permanent precipitate. After adding 3 c.c. of concentrated hydrochloric acid, the thorium is precipitated as pyrophosphate (§ III, (*c*)), finally as oxalate, ignited to oxide, and weighed as such.

(*b*) *In Thorite and other Silicates rich in Thoria and poor in Rare Earths.*—One grm. of the slimed sample is decomposed by digestion with 10 to 15 c.c. of fuming hydrochloric acid and final evaporation to dryness to dehydrate silica. The residue is taken up with 2 c.c. of concentrated hydrochloric acid and a little hot water, and the silica filtered off; copper and lead are separated by hydrogen sulphide in the filtrate. After filtering and boiling off hydrogen sulphide the solution is diluted to 200 c.c., heated to boiling, and the thoria and rare earths are precipitated as oxalates by the addition of 1 grm. of oxalic acid dissolved in a little water. The solution is set aside overnight, and the precipitate filtered off and thoroughly washed with hot water. It is now transferred to an evaporating basin, treated with 60 c.c. of a cold saturated solution of ammonium oxalate, and heated on the water-bath for three hours. The liquid is diluted with 300 c.c. of water and allowed to stand overnight, the insoluble rare earth oxalates filtered off and thoroughly washed with water containing a trace of ammonium oxalate. The residual oxalates are re-treated with 20 c.c. of the ammonium oxalate solution as long as the filtrate gives a precipitate with 1·7 c.c. of hydrochloric acid in 200 c.c. bulk. The first filtrate is treated with 5 c.c. concentrated hydrochloric acid, heated to boiling, and allowed to stand overnight. The precipitate is filtered off, ignited together with the precipitates obtained by the re-treatment of the insoluble oxalates, and weighed as ThO_2 plus a small quantity of rare earths. To purify the thoria it is fused with bisulphate, the melt leached with dilute hydrochloric acid, the solution precipitated with ammonia, the precipitate dissolved in hydrochloric acid, the latter driven off, the mass taken up with water, and the thorium precipitated by boiling ten minutes with 4 grm. of thiosulphate. The precipitate is well washed, extracted with hot hydrochloric acid, the solution precipitated with oxalic acid (§ IV.), and the oxalate ignited to and weighed as ThO_2.

(*c*) *In Thorianite and other Oxide Minerals high in Thoria.*—The ore is opened up by fusion with bisulphate, and the thorium and rare earth oxalates thrown down by oxalic acid from the solution obtained by extracting the melt with dilute hydrochloric acid. The precipitate is ignited and fused with bisulphate, the melt leached with water, the thoria and rare earths precipitated with ammonia, re-dissolved in acid, and thorium separated by any of the methods in § III. As an alternative the oxalate precipitate is treated as in (*b*).

§ VII. Complete Analysis of Ores.—(*a*) *Thorite and its Alteration Products and Varieties.*—

Digest 1 grm. of slimed ore with 10–15 c.c. of fuming HCl, evaporate to dryness, take up with dilute HCl and a few drops of H_2SO_4, filter, wash.

R^1 : ignite, weigh; treat with $HF+H_2SO_4$, ignite and weigh.

L^2 : SiO_2.

R^2 : fuse with 1 grm. $NaHSO_4$, leach, boil in Pt dish, add 1–2 c.c. HF, filter, wash.

F^3 : evaporate with H_2SO_4, dilute, add NH_4OH, filter, boil ppte with salicylic acid.

R^3 : $BaSO^4$.

R^4: $Ta_2O_5+Cb_2O_5$. Ignite and weigh.

F^4 : ppte with NH_4OH, ignite, weigh TiO_2.

F^1 : pass H_2S, filter.

F^5 : boil, oxidise with H_2O_2, ppte hot solution with $H_2C_2O_4$, let stand overnight, filter.

P^5: Cu, Pb.

F^6 : evaporate to dryness, digest with fuming HNO_3, take to dryness, dissolve in dilute HCl, ppte with NH_4Cl+NH_4OH, filter, wash with 2 per cent. NH_4NO_3.

P^6 : dissolve in fuming HNO_3, evaporate to dryness, treat with HNO_3+KIO_3 (§ III, (*b*)).

P^7 : Th. See § III, (*b*).

F^7 : ppte with NH_4OH, filter, dissolve ppte in HCl; for separation see Rare Earths, § III, (*a*).

F^8 : determine Ca, Mg, Na.

P^8 : ignite, fuse with $NaHSO_4$, leach, add tartaric acid, NH_4OH, and $(NH_4)_2S$. Filter.

P^9 : dissolve in HNO_3, boil with excess of Na_2CO_3, filter.

P^{10} : titrate Fe.

F^{10} : see Uranium, § III, (*e*).

F^9 : evaporate with $H_2SO_4+HNO_3$ to destroy tartrates, take up with water, ppte with NH_4OH (cold), and continue as under Zirconium, § VII, (*a*), P^6 *et seq.* (for Al, Ti, Zr).

(*b*) *Thorianite and Oxide Minerals* are opened up by fusion with bisulphate. The melt is extracted with dilute hydrochloric acid; the residue contains silica, barium sulphate, tantalic acid, etc., and is worked up as in (*a*), R^1 *et seq.*; the filtrate is treated like F^1, *ibid.*

(*c*) *Monazite Sand.*—See Rare Earths, § VII, (*a*).

GERMANIUM.

§ **I. Minerals.**—(*a*) *Argyrodite*, silver germanium sulphide, $4Ag_2S.GeS_2$, is a steel-grey metallic-looking mineral occurring in small, indistinct, monoclinic crystals or in compact masses. It gives a shining grey-black streak. H 2·5 ; sp. gr. 6.

(*b*) *Canfieldite* is a variety of the above, in which part of the germanium is replaced by tin. It is of a somewhat darker colour, and has a brilliant metallic lustre. H 2·5 ; sp. gr. 6·3.

(*c*) In addition to the above, germanium occurs in small quantities in some North American zinc blendes.

§ **II. Properties and Compounds.**—(*a*) The *metal* is greyish-white, brittle, and lustrous. It melts at 958°, and has a sp. gr. of 5·47. It is soluble in *aqua regia*, but not in hydrochloric acid. Nitric acids converts it into the dioxide. It may be prepared by reduction of the oxide with hydrogen or magnesium, or by the action of hydrogen or sodium on potassium fluogermanate.

(*b*) *Germanous hydroxide*, $Ge(OH)_2$, is formed on addition of alkali to an acid solution of the corresponding chloride as a yellow precipitate, slightly soluble in water to a yellow solution. With excess of alkali it gives soluble germanite. On being heated in the liquor from which it is precipitated it turns red, and this compound is believed to be the germanium analogue of formic acid, HGeOOH, as the same compound is formed on the addition of water to germanium chloroform, $HGeCl_3$.

(*c*) *Germanium dioxide*, GeO_2, is a dense, white, difficultly fusible powder. It dissolves in 250 parts of water at ordinary temperature and in 95 parts at 100° ; soluble both in acids and alkalies. It is formed on treating the metal or the sulphide with nitric acid.

(*d*) *Germanous sulphide*, GeS, is produced by passing hydrogen sulphide through a solution of the dichloride as a red-brown precipitate soluble in alkalies and in concentrated hydrochloric acid. It is also slightly soluble in water.

(*e*) *Germanic sulphide*, GeS_2, is thrown down as a white precipitate on saturating a strongly acid solution of the dioxide in hydrochloric acid with hydrogen sulphide. It is soluble in 222 parts of cold water, but almost insoluble in concentrated hydrochloric acid. With alkalies it gives thiogermanates, which are not decomposed by weak acids like acetic, but require a considerable excess of mineral acid to completely decompose them.

(*f*) *Germanium chlorides.*—Both the di- and tetra-chlorides are volatile liquids readily decomposed by water, with the separation of the corresponding hydroxides. The tetrachloride boils at 86°.

(*g*) *Potassium fluogermanate*, K_2GeF_6, separates from a solution of the dioxide in hydrofluoric acid on the addition of potassium fluoride as a jelly (like K_2SiF_6), which slowly crystallises.[1] One part is soluble in 174 parts of cold and 34 parts of boiling water.

§ **III. Separation from other Elements.**—(*a*) Germanium may readily

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[1] Kruss and Nelson, *Ber.*, 1887, **20**, 1696.

be separated from most of the metals by taking advantage of the solubility of its sulphide in alkaline sulphides. The sulphide should be precipitated by saturating the solution of the dioxide in hydrochloric acid (1 : 2 water) with hydrogen sulphide. It is filtered off, washed with hydrochloric acid of the same strength saturated with the gas, and dissolved in sodium sulphide. The solution is exactly neutralised with dilute sulphuric acid and allowed to stand overnight. The precipitate of arsenic, antimony, and tin sulphides is filtered off, an equal bulk of strong hydrochloric acid added to the filtrate, and the solution saturated with hydrogen sulphide. Pure white germanic sulphide is precipitated.[1]

(*b*) The solution of the dioxide in strong hydrochloric acid is treated with 0·5 grm. of potassium permanganate and distilled down to half its bulk. Germanium distils over, while arsenic and other metals remain in the residual solution.[2] The distillate is saturated with hydrogen sulphide and the white sulphide filtered off.

§ **IV. Gravimetric Determination.**—(*a*) The sulphide obtained as directed in § III. is washed with hydrochloric acid followed by 90 per cent. alcohol saturated with hydrogen sulphide, dried, detached from the paper, the latter burnt at a low temperature, and the main part of the precipitate added. The whole is gently roasted, treated with nitric acid, dried, and strongly ignited. The residue is weighed as GeO_2.

(*b*) The sulphide may be dissolved in freshly-prepared ammonium sulphide, the solution passed through the original filter which is washed with hot water, the solution and washings being collected in a tared basin, and evaporated on the water-bath to dryness. The dry residue is treated with concentrated nitric acid, the mixture evaporated carefully to dryness, the residue ignited, first gently, then more strongly, and weighed as GeO_2.

§ **V. Detection in Ores.**—The ore is fused with a mixture of sulphur and sodium carbonate, the melt extracted with hot water, the solution filtered, and the filtrate exactly neutralised with dilute sulphuric acid. After standing overnight the precipitate is filtered off and an equal bulk of strong hydrochloric acid added to the filtrate, which is then saturated with hydrogen sulphide. A white precipitate shows the presence of germanium. On heating this precipitate (after drying) in a slow current of hydrogen [3] a red-brown sublimate of germanous sulphide, mixed with a grey-black sublimate of the metal, is obtained.

§ **VI. Determination in Ores.**—(*a*) *Argyrodite* (Canfieldite).—1–2 grm. is fused with five times its own weight of a mixture of equal parts of sulphur and sodium carbonate in a porcelain crucible. The cold melt is leached out with water, the solution filtered from the insoluble silver sulphide, and neutralised exactly with dilute sulphuric acid. The mixture is allowed to stand cold overnight, after which the precipitate of arsenic, antimony, or tin sulphide is filtered off and washed with warm

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[1] Truchot, *Les Terres Rares*, p. 294.

[2] Browning and Scott, *Amer. Journ. Sci.*, 1917, **44**, 313.

[3] Prior and Spencer, *Min. Mag.*, 1898, **12**, 5; see also Haushofer, *Sitzber. Akad. München*, 1887, 133.

water. The solution is treated with an equal bulk of hydrochloric acid (1·16) and saturated with hydrogen sulphide. After settling, the precipitate is treated as shown in § IV.

(*b*) *Blende.*—50–100 grm. are covered with water, and strong nitric acid is added gradually in the cold. When the vigorous action has ceased the mass is heated, evaporated to dryness in a porcelain dish, and the residue gently heated over a free flame until red fumes are no longer evolved. The powdered residue is transferred to a retort fitted with a Liebig condenser. 150 c.c. of strong hydrochloric acid and 1 grm. of permanganate are added through the safety funnel, and solution promoted by shaking the retort. The solution is distilled to one-half its bulk, the distillate diluted with an equal volume of water, and saturated with hydrogen sulphide. The precipitate is filtered off and treated as under § IV.

CHAPTER VII.

THE FIFTH GROUP.

VANADIUM—COLUMBIUM—TANTALUM.

GENERALITIES.

THESE three elements form well-defined pentoxides, which are used for their gravimetric estimation. Vanadium pentoxide is easily reduced in solution, and four lower oxides corresponding to those of nitrogen are known; columbium pentoxide is less readily reduced, and the lower oxides are of indefinite composition; tantalum pentoxide is not reducible by wet methods.

Vanadic acid and its salts bear a great resemblance to the corresponding phosphorus and arsenic compounds, while the appearance and behaviour of columbic and tantalic acids are suggestive of antimonic acid.

The elements are not precipitated by hydrogen sulphide in acid solution, though vanadium has a distinct affinity for sulphur.

VANADIUM.

§ I. **Minerals.**—(*a*) *Sulphides.*—(1) *Patronite*, vanadium pentasulphide, V_2S_5, an amorphous black mineral of sp. gr. 2·5; H 5. Usually the mass is permeated with greenish-blue or black striæ. Often found with asphalt, which then also contains vanadium.

(2) *Rizopatronite*, also amorphous, consists of an intimate mixture of vanadium sulphide, sulphur, coal-like substances, and clay. Lead-grey lustre on fresh surfaces, rapidly tarnished on exposure. The ashes of many coals (and asphalts) are rich in vanadium.

(3) *Bravoite*, vanadiferous iron nickel sulphide, pale yellow octahedra with a faint pink tarnish.

(4) *Sulvanite*, cuprous orthothiovanadate, $3Cu_2S.V_2S_5$, usually occurs as compact bronze-yellow metallic-looking masses giving a black streak. H 3·5; sp. gr. 4.

(*b*) *Silicates.*—(1) *Ardennite*, a manganese epidote containing vanadium sesquioxide. Yellow-brown orthorhombic prisms terminated by pyramids; faces strongly striated. H 6·5; sp. gr. 3·6.

(2) *Roscoelite*, vanadium mica, $2H_2O(K,Na)_2O.3(Al,V)_2O_3.6SiO_2$, resembles muscovite in physical properties, but its colour is clove-brown or olive-green.

(*c*) *Anhydrous Vanadates.*—(1) *Pucherite*, bismuth orthovanadate, $BiVO_4$, a translucent red-brown mineral with vitreous to adamantine lustre and yellow streak. Small orthorhombic tables. H 4; sp. gr. 6·2.

(2) *Vanadinite*, $3Pb_3(VO_4)_2.PbCl_2$, lead chlorovanadate, is the most widely-distributed vanadium mineral. Occurs as yellow to red-brown, subtranslucent, hexagonal prisms with a resinous lustre and conchoidal fracture. Streak white. H 3; sp. gr. 7. Isomorphous with mimetite and apatite.

(*d*) *Hydrous Vanadates.*—(1) *Descloizite*, basic lead-zinc orthovanadate, $(PbZn)_2OH.VO_4$, occurs as orthorhombic prisms or pyramids, varying from red to dark brown in colour; greasy lustre and conchoidal fracture. Streak orange. H 3; sp. gr. 6.

(2) *Mottramite*, basic copper-lead vanadate, $(Cu,Pb)_2OH.VO_4$, dark brown to black crystalline incrustations with yellow streak. Lustre resinous; translucent.

(3) *Volborthite*, basic copper-calcium-barium vanadate $(Cu,Ca,Ba)_2 OH.VO_4$, is a green to grey mineral, with a pearly lustre and greenish-yellow streak. Occurs as tables with a perfect cleavage. H 3·5; sp. gr. 3·5.

(4) *Brackebuschite*, hydrous lead-iron-manganese orthovanadate, $(Pb,Fe,Mn)_2OH.VO_4$, is a black, translucent mineral with a yellow streak.

(5) *Turanite*, basic copper vanadate, $5CuO.V_2O_5.2H_2O$, green, spongy, fibrous aggregates.

(6) *Ferganite*, hydrous uranium vanadate; sulphur-yellow scales.

(7) *Carnotite*, hydrous potassium uranyl vanadate; yellow crystalline powder or incrustations on sandstone and quartz and in the crevices of rocks.

§ II. Properties and Compounds.—(*a*) The *metal* is prepared by the reduction of the pentoxide with a mixture of rare earth metals ("Mischmetall"; see Rare Earths, § I, (*a*)). It is bright silver-white, of sp. gr. 5·5 and M.P. 1730°, is strongly attacked by nitric acid, and readily combines with nitrogen when heated, forming the mononitride, VN.

(*b*) *Vanadium pentoxide*, V_2O_5, is a red-brown crystalline solid melting at 658°, but not volatile in the full heat of the Bunsen flame. It is slightly soluble in water; 1000 parts of cold water dissolve 1 part of V_2O_5.

(*c*) *Vanadium tetroxide*, V_2O_4.—Salts of this oxide are formed when the pentoxide is reduced in acid solution by mild reducing agents, *e.g.* sulphur dioxide, hydrogen sulphide, ferrous sulphate, hydrobromic, oxalic, tartaric acids, alcohol. Their solutions are bright blue, and give a greyish-white voluminous precipitate of the hydrated oxide $V_2O_2(OH)_4.5H_2O$ on adding a slight excess of caustic soda; this precipitate is soluble in excess of the alkali, giving a very dark coloured solution of hypovanadate, $Na_2V_4O_9.7H_2O$.

(*d*) *Vanadium trioxide*, V_2O_3, gives green solutions with acids. It may be prepared as a black powder by igniting the pentoxide in hydrogen.

The salts are prepared by reduction of acid solutions of the pentoxide by potassium iodide or magnesium.

(*e*) *Vanadium dioxide*, V_2O_2, forms lavender-coloured solutions with acids. Its salts are produced on reducing the pentoxide with zinc and hydrochloric acid.

(*f*) *Vanadium monoxide*, V_2O, is formed by slow oxidation of the metal in air.

(*g*) *Ammonium metavanadate*, NH_4VO_3, is a colourless crystalline solid sparingly soluble in water, insoluble in slightly ammoniacal solutions of ammonium chloride. Yields V_2O_5 on ignition in air.

(*h*) *Mercurous vanadate* is formed as a flocculent white precipitate when an excess of neutral mercurous nitrate solution is added to a neutral vanadate solution. It yields V_2O_5 on ignition in air.

(*i*) *Lead Vanadate.*—A yellow basic salt is precipitated by mixing neutral solutions of lead acetate and sodium vanadate. Soluble in acids and concentrated caustic alkalies; insoluble in, and unattacked by, alkaline carbonates.

(*j*) *Pyrovanadic acid*, $H_4V_2O_7$, is formed on boiling sodium vanadate with strong nitric acid as a dark red-brown flocculent precipitate resembling ferric hydroxide.

(*k*) *Ammonium tetravanadate*, $(NH_4)_2V_4O_{11}.4H_2O$.—On adding acetic acid to a boiling solution of ammonium metavanadate until the precipitate re-dissolves, and allowing to cool, crystals of ammonium tetravanadate are deposited. In colour they resemble potassium bichromate.

(*l*) *Pervanadic acid*, HVO_4, is formed when vanadium pentoxide or a vanadate is dissolved in sulphuric acid containing hydrogen peroxide; the solution assumes a deep red colour.

(*m*) *Vanadium pentasulphide*, V_2S_5, is not precipitated from acid solutions by hydrogen sulphide; on passing the gas into ammoniacal solutions of vanadates a deep brown, green, or purple solution is obtained containing thiovanadates: the colour varies with the concentration of the ammonia. The solution on acidification with sulphuric acid gives a brown precipitate of vanadium pentasulphide. The precipitation is rarely quantitative.

§ III. Quantitative Separation.—The gravimetric separation of vanadium involves a preliminary separation from other elements which, in the case of complex mixtures, is an operation of the greatest difficulty. On the other hand, volumetric methods yield reliable results, even in the presence of those elements which are the most troublesome to separate, especially if present together (*e.g.* phosphoric, tungstic, molybdic, silicic, arsenic acids, etc.); hence preference is nearly always given to the volumetric determination. In the cases described below, the separation admits of the subsequent gravimetric estimation. They will be enumerated under two heads: the vanadium is present (*a*) in acid solution with salts of heavy metals or bases, or (*b*) in alkaline solution together with salts of other acids.

(*a*) *Separation from Metals.*—(1) *From Metals of the Hydrogen Sul-*

phide Group.—The solution, free from nitrates, is precipitated with hydrogen sulphide (under pressure if molybdenum is present). Vanadium passes into the filtrate (see § IV, (*e*)).

(2) *From Iron, Titanium, Zirconium, Manganese.*—The solution, oxidised with nitric acid if necessary, is neutralised with 10 per cent. sodium hydroxide, poured into 50 c.c. of the same reagent, boiled for a few minutes, and filtered. The vanadium in the filtrate is precipitated as lead vanadate (§ IV, (*d*)).

(3) *From Uranium, Aluminium, Chromium, Nickel, Cobalt, Manganese, Zinc.*—The solution containing 10 c.c. of nitric acid in 300 c.c. is treated with a slight excess of 25 per cent. lead acetate, followed by 50 c.c. of 25 per cent. ammonium acetate solution. The precipitate is allowed to settle two hours on a steam-bath, filtered off, washed twice with hot water, and dissolved in 5 c.c. of nitric acid; the solution is diluted to 100 c.c. and re-precipitated by the addition of 2–3 c.c. of lead acetate and 25 of ammonium acetate solution. The lead vanadate is washed thoroughly with hot water and treated as under § IV, (*d*).

(4) *From Alkaline Earths.*—(*a*) The material is fused with sodium carbonate and nitrate. On leaching with water the alkaline earths remain undissolved, while the vanadium is obtained in solution (§ IV, (*a*)). (*b*) In presence of much iron, the ammonia or basic acetate separation yields a precipitate containing all the vanadium (see (2)).

(*b*) *Separation from Acids.*—(1) *From Tungstate.*[1]—The two acids are precipitated as mercurous salts; the washed precipitate is digested with strong hydrochloric acid until decomposition is complete, the solution containing vanadyl chloride diluted with 100 c.c. of hot water, and filtered from the tungstic acid and mercurous chloride. The filtrate is evaporated to dryness, the residue again evaporated with nitric acid, taken up with water, and treated as shown in § IV, (*a*).

(2) *From Molybdate.*[2]—The mixed lead vanadate and molybdate is digested hot with a concentrated solution of potassium carbonate. Lead vanadate remains unattacked, mixed with carbonate; it is filtered off and washed with dilute potassium carbonate solution, dissolved in nitric acid, and re-precipitated by adding ammonium acetate ((*a*) (3)).

(3) *From Chromate.*[3]—The alkaline solution is evaporated to 100 c.c., neutralised with acetic acid, and 15 c.c. excess of the glacial acid added, together with a few c.c. of hydrogen peroxide. The solution is boiled until effervescence ceases, the chromate being reduced. The vanadium is then precipitated as in § IV, (*d*).

(4) *From Arsenate, and from Tungstate and Molybdate.*—The solution is evaporated with sulphuric acid to strong fumes to expel nitric acid, cooled, taken up with water, and treated with hydrogen sulphide under pressure. The precipitate consists of arsenic and molybdenum sulphides and tungstic acid. The filtrate is boiled to expel hydrogen sulphide, oxidised with nitric acid, treated with a large excess of

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[1] Friedheim, *Ber.*, 1890, **23**, 353.

[2] Mennicke, *Die Analyse des Vanadins, Molybdäns, und Wolframs.*

[3] Palmer, *Amer. Journ. Sci.*, 1910, **30**, 141.

ammonium acetate, and the vanadium precipitated with lead acetate (§ IV, (*d*)).

(5) *From Phosphate.*—If the quantity of vanadate predominates over the phosphate, the acids are precipitated as mercurous salts and the ignited precipitate weighed as $V_2O_5+P_2O_5$; this precipitate only sinters on ignition. It is fused with sodium carbonate, and the phosphoric acid determined as in § IX, (*a*), vanadium being taken by difference. If phosphoric acid preponderates, it is far preferable to determine the vanadium volumetrically (§ V, (*a*) (1)).

(6) *From Silicate.*—In this case also a volumetric method should be resorted to (§ VIII, (*c*)).

§ **IV. Gravimetric Determination.**—Although vanadium is usually determined volumetrically, the gravimetric methods given below are sometimes used. They can only be applied to alkali vanadate solutions free from any interfering elements. Nitrates of the alkalies are harmless; carbonates must be converted into nitrates.

(*a*) *By Precipitation with Mercurous Nitrate.*—The solution, acidified with a small excess of nitric acid, is treated with mercurous nitrate in slight excess, then with dilute ammonium carbonate drop by drop until the liquor is just neutral, when it is heated to boiling and stirred until the precipitate coagulates and settles clear; the latter is then filtered off, washed with warm water, dried, ignited gently until the filter paper is completely burnt away, then more strongly until the pentoxide just fuses. The cooled mass is weighed as V_2O_5.

(*b*) *By Precipitation as Ammonium Metavanadate.*[1]—The alkaline vanadate solution is evaporated to 50 c.c. and treated with sufficient ammonium chloride to decompose the alkaline salts present and to give a saturated solution. This is heated to boiling on the water-bath and evaporated to 25 c.c., adding, now and again, a little ammonia. After cooling overnight the precipitate is filtered on a Gooch crucible and washed with saturated ammonium chloride solution. If too much ammonium chloride crystallises out, it is partially re-dissolved by the addition of dilute ammonia. The contents of the crucible are dried, heated gently to drive off ammonium salts, and finally ignited at a dull red heat till the V_2O_5 just melts.

(*c*) *By Precipitation as Silver Metavanadate.*[2]—The alkaline vanadate solution is acidified with nitric acid, boiled to expel carbon dioxide, made alkaline with ammonia, and again boiled till all the latter is expelled and the solution just becomes faintly yellow. After diluting to 200 c.c. the vanadium is precipitated by the addition of a slight excess of silver nitrate added slowly whilst stirring. When the precipitate has coagulated and settled, the clear solution is decanted through a filter, the precipitate washed free from silver nitrate by decantation with hot water, finally transferred to the filter, dried, gently ignited apart from the paper, and weighed as $AgVO_3$.

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[1] Berzelius, *Pogg. Annalen*, **22**, 54; Gibbs, *Proc. Amer. Acad.*, **10**, 242, 249; Gooch and Gilbert, *Amer. Journ. Sci.*, 1902, **14**, 205.

[2] Browning and Palmer, *Amer. Journ. Sci.*, 1910, **30**, 220.

(*d*) *By Precipitation as Lead Vanadate.*[1]—The alkaline vanadate solution is nearly neutralised with nitric acid, a small excess of lead acetate added, the solution heated to boiling, and stirred until the precipitate of lead vanadate coagulates and settles well; it is filtered off, washed with very dilute acetic acid, rinsed back into the original beaker, and re-dissolved in nitric acid. The filter paper is ignited and the ash added to the main solution, which is then evaporated with a slight excess of sulphuric acid to strong fumes. After cooling, the mass is diluted with water, the solution heated to boiling, cooled, and the lead sulphate filtered off. The filtrate is received in a tared porcelain basin, evaporated to dryness on the water-bath, and heated gently to drive off all the sulphuric acid; the V_2O_5 is finally fused, allowed to cool, and weighed. The lead may also be removed by hydrogen sulphide in cold dilute hydrochloric acid, or by precipitating as chloride in the presence of alcohol, taking the filtrate to dryness, evaporating the residue twice with strong nitric acid, fusing, and weighing as V_2O_5.

(*e*) Solutions free from other fixed constituents are evaporated to dryness with a little nitric acid in a tared porcelain basin, the residue heated gently at first if sulphuric acid or ammonium salts are present, then to incipient fusion, and weighed as V_2O_5.

§ **V. Volumetric Determination.**—(*a*) *Permanganate Methods.*—(1) *Reduction to V_2O_4 by Sulphur Dioxide.*—The alkaline vanadate solution, free from nitrate, chloride, arsenate, and chromate, is acidified with sufficient dilute sulphuric acid to give a 5 per cent. solution and a current of sulphur dioxide passed through the hot solution till it becomes a pure blue: $V_2O_5 + SO_2 = V_2O_4 + SO_3$. The excess of reducing agent is boiled off while a current of carbon dioxide is passing, and the solution titrated at 80° with potassium permanganate (N/10 or N/20: 1 c.c. N/10 $KMnO_4 = 0{\cdot}0091$ grm. V_2O_5). The colour changes from blue through green to pale yellow until finally the characteristic pink tinge of the permanganate appears. Large quantities of sodium salts are objectionable; hence, if present, a preliminary separation of vanadium as lead vanadate should be made (§ IV, (*d*)), but the lead sulphate need not be filtered off.

The permanganate is standardised against pure iron or ferrous ammonium sulphate. The iron factor multiplied by 1·6296 gives the value in V_2O_5.

(2) *Reduction to V_2O_4 by Oxalic Acid.*[2]—To the vanadium solution are added 30 c.c. of strong sulphuric and 0·2 grm. of oxalic acid, and the whole evaporated to fumes while passing carbon dioxide through the flask: $V_2O_5 + H_2C_2O_4 = V_2O_4 + H_2O + 2CO_2$. After cooling, the mass is diluted to 500 c.c., the solution heated to 80° and titrated with permanganate. 1 c.c. N/10 $KMnO_4 = 0{\cdot}0091$ grm. V_2O_5.

(3) *Reduction to V_2O_2 by Zinc.*[3]—This process is best carried out in the Jones' reductor (see Introduction). The receiver contains a

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[1] Roscoe, *Ann. Chem. Pharm.*, Suppl., 1872, **8**, 102.

[2] Mennicke, *op. cit.* (p. 118).

[3] Gooch and Gilbert, *Amer. Journ. Sci.*, 1903, **15**, 389.

large excess of ferric alum solution and 4 c.c. of syrupy phosphoric acid to decolorise the iron. Through the reductor are passed in succession, using gentle suction, 100 c.c. of hot water, 100 c.c. of 2½ per cent. sulphuric acid, then the solution containing the vanadium (25 c.c. in 2½ per cent. sulphuric acid), and finally 100 c.c. of hot water. The vanadium pentoxide is reduced to V_2O_2, which is oxidised by the ferric alum to V_2O_4, with the production of an equivalent amount of ferrous sulphate. The solution is titrated, first cold, then heated to 80°, and the titration finished, the iron being re-oxidised to $Fe_2(SO_4)_3$, and the vanadium to V_2O_5. Tungstate, molybdate, arsenate, chromate, and iron interfere. 1 c.c. $N/10\ KMnO_4 = 0{\cdot}00303$ grm. V_2O_5.

(4) *Simultaneous Determination of Iron and Vanadium.*[1]—The solution containing both metals as sulphates is first reduced with sulphur dioxide as under (1). After expulsion of the excess of reducing agent the solution is titrated first cold, then at 80°, with N/10 permanganate, giving the sum $Fe+V_2O_5$, according to the equations

$$5V_2O_4+K_2Mn_2O_8+3H_2SO_4=5V_2O_5+K_2SO_4+2MnSO_4+3H_2O.$$
$$10FeO+K_2Mn_2O_8+3H_2SO_4=5Fe_2O_3+K_2SO_4+2MnSO_4+3H_2O.$$

The solution is now concentrated to about 50 c.c., and reduced in the Jones' reductor according to the procedure outlined in (3). The iron is again reduced to the ferrous state, but the vanadium will consume three times as much permanganate as before, thus :

$$5V_2O_2+3K_2Mn_2O_8+9H_2SO_4=5V_2O_5+3K_2SO_4+6MnSO_4+9H_2O.$$

The results are calculated as follows :—

Let n = number of c.c. permanganate required in the 1st titration, and
N = ,, ,, ,, ,, ,, 2nd ,, then
the volume of N/10 permanganate consumed by the vanadium tetroxide will be $\frac{N-n}{2}$ (1 c.c. = 0·0091 grm. V_2O_5) and that equivalent to the iron $\frac{3n-N}{2}$ (1 c.c. = 0·005584 grm. Fe).

(5) *Simultaneous Determination of Molybdenum and Vanadium.*[2]—The solution containing only free sulphuric acid (more than 2 c.c. per 100 c.c.) and less than 0·2 grm. molybdenum per 50 c.c. is reduced with sulphur dioxide, the excess of the latter boiled off, and the vanadium determined as before. It is then passed through the Jones' reductor, when the vanadium is reduced to V_2O_2 and the molybdenum to Mo_2O_3. The reduced solution is collected in ferric alum and phosphoric acid as before (3), and a current of carbon dioxide passed through the receiver during the reduction.

If n = number of c.c. permanganate required in the 1st titration, and
N = ,, ,, ,, ,, ,, 2nd ,, then
n is the volume of N/10 permanganate consumed by vanadium

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[1] Edgar, *Amer. Journ. Sci.*, 1908, **26**, 79 ; 1909, **27**, 174.
[2] *Ibid.*, 1908, **25**, 332.

tetroxide, and N$-3n$ the volume required for the oxidation of molybdenum sesquioxide (Molybdenum, § V, (*b*)).

(*b*) *Iodometric Processes.*—(1) *Liberation of Bromine from Potassium Bromide.*[1]—The solution of alkaline vanadate containing not more than 0·3 grm. V_2O_5 is distilled with 1·5 to 2 grm. of potassium bromide and 30 c.c. of concentrated hydrochloric acid, whereby bromine is liberated and vanadyl chloride remains in the solution, according to the following equation: $V_2O_5+2HBr=V_2O_4+H_2O+Br_2$. The liberated bromine is distilled over into a 10 per cent. solution of potassium iodide, and the resulting iodine titrated with N/10 sodium thiosulphate (1 c.c.$=$0·0091 grm. V_2O_5). This method, although requiring a certain amount of apparatus, is quicker than the permanganate methods, and is exceedingly accurate.

(2) *Liberation of Iodine by Distillation with Potassium Iodide.*[2]—The alkaline vanadate solution, free from nitrates, is boiled down to 25 c.c. and transferred to a small distillation flask fitted with a thistle funnel and connected with an absorption apparatus containing alkaline potassium iodide. The air is driven from the whole apparatus by a current of hydrogen; a saturated solution of 2 grm. of potassium iodide is poured through the thistle funnel, followed by 12 c.c. of strong hydrochloric and 3 c.c. of syrupy phosphoric acid. The solution in the flask is now boiled down to 10–12 c.c. while hydrogen is still passing. At this stage the vanadium is completely reduced to V_2O_3, with the liberation of a corresponding amount of iodine, thus:

$$V_2O_5+4HI=V_2O_3+2H_2O+2I_2.$$

Further distillation leads to the danger of reduction going a little further than V_2O_3, with correspondingly high results. After the distillation is finished the contents of the receiver are acidified with hydrochloric acid, and the liberated iodine titrated with N/10 sodium thiosulphate (1 c.c.$=$0·00455 grm. V_2O_5).

(3) *Simultaneous Determination of Chromium and Vanadium.*[3]—The metals must be present as alkaline chromate and vanadate. The solution is acidified and distilled with potassium bromide as above (1), the vanadium being reduced to V_2O_4 and the chromium to Cr_2O_3, thus:

$$V_2O_5+2HBr=V_2O_4+H_2O+Br_2.$$
$$2CrO_3+6HBr=Cr_2O_3+3H_2O+3Br_2.$$

The bromine is collected in an alkaline iodide solution, which is acidified and the iodine titrated with thiosulphate. The flask is now again connected to the absorption apparatus, and the solution distilled with potassium iodide and hydrochloric and phosphoric acids in a current of hydrogen (see (2)). The chromium is not affected, but the vanadium is further reduced to V_2O_3, thus:

$$V_2O_4+2HI=V_2O_3+H_2O+I_2.$$

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[1] Gooch and Curtis, *Amer. Journ. Sci.*, 1904, **17**, 43.

[2] Browning, *Amer. Journ. Sci.*, 1896, **2**, 185; Friedheim and Euler, *Ber.*, 1895, **28**, 2071.

[3] Edgar, *Amer. Journ. Sci.*, 1908, **26**, 333.

If N=number of c.c. of thiosulphate used in the 1st titration, and
n= ,, ,, ,, ,, ,, 2nd ,, then
n=number of c.c. consumed by vanadium (1 c.c.=0·0091 grm. V_2O_5), and N−n=number of c.c. equivalent to chromium (1 c.c.=0·006667 grm. CrO_3).

(4) *Reduction with Organic Acids to V_2O_4.*—The solution of vanadic acid in sulphuric acid is boiled with 2 grm. of oxalic,[1] tartaric,[2] or citric[1] acid for five minutes, cooled, nearly neutralised with sodium bicarbonate, an excess of N/10 iodine solution added, and neutralisation completed with the bicarbonate. After standing half an hour the excess of iodine is titrated with standard arsenious acid solution, using starch as indicator (1 c.c.=0·0091 grm. V_2O_5). The method is applicable to the determination of vanadium in presence of arsenic, antimony, and tin.

(5) *Simultaneous Determination of Arsenic and Vanadium, or of Antimony and Vanadium.*[3]—The solution is divided into two parts, and the vanadium determined in the first part as directed under (4). The second part is saturated with sulphur dioxide and heated to boiling in a pressure flask for one hour. After cooling, the solution is transferred to a conical flask, the sulphur dioxide boiled off, the solution cooled, neutralised with bicarbonate, excess of iodine added, and the mixture allowed to stand half an hour. The excess of iodine is then titrated with standard sodium arsenite solution. The difference between the two titrations gives the arsenic or antimony, or both if present together.

(*c*) *Miscellaneous Methods.*—(1) *Precipitation as Silver Vanadate.*[4]—The neutral solution of vanadate is treated with a measured excess of silver nitrate solution, the precipitate just re-dissolved by the addition of ammonia, and the solution boiled till all smell of ammonia has disappeared. The precipitate of orthovanadate (Ag_3VO_4) is filtered off, washed with hot water, the filtrate and washings acidified with nitric acid, and the excess of silver nitrate titrated as usual with N/10 ammonium thiocyanate, using ferric alum as indicator (1 c.c. N/10 NH_4CNS=0·00303 grm. V_2O_5).

(2) *Simultaneous Determination of Phosphorus and Vanadium.*[5]—The neutral phosphate-vanadate solution is treated as under (*c*) (1), and the phosphorus and vanadium thus determined together. The precipitate of silver phosphate and vanadate is boiled with dilute sulphuric acid, the liquid reduced with sulphur dioxide, and the vanadium alone titrated with potassium permanganate. Phosphorus is determined by difference.

$$1 \text{ c.c. N/10 } NH_4CNS = \begin{cases} 0{\cdot}00303 \text{ grm. } V_2O_5. \\ 0{\cdot}002368 \text{ ,, } P_2O_5. \end{cases}$$
$$1 \text{ c.c. N/10 } KMnO_4 = 0{\cdot}0091 \text{ ,, } V_2O_5.$$

(3) *Titration with Ferrous Sulphate.*[6]—The alkaline vanadate solution

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[1] Browning and Goodman, *Amer. Journ. Sci.*, 1896, **2**, 355.
[2] Browning, *Z. anorg. Chem.*, 1895, **7**, 158.
[3] Edgar, *Z. anorg. Chem.*, 1909, **62**, 77.
[4] Edgar, *Amer. Chem. Journ.*, 1910, **44**, 467.
[5] *Ibid.*
[6] Lindemann, *Z. anal. Chem.*, 1879, **18**, 102.

free from chromate and arsenate is acidified with hydrochloric or sulphuric acid and titrated cold with N/10 ferrous sulphate, using potassium ferricyanide as external indicator. This method is useful in the presence of much iron (present as ferric salt). 1 c.c. N/10 $FeSO_4$=0·0091 grm. V_2O_5.

§ **VI. Colorimetric Determination.**[1]—The formation of pervanadic acid by the action of hydrogen peroxide on vanadate solutions acidified with sulphuric acid forms the basis of the colorimetric determination of vanadium. The details of the process are the same as for the colorimetric determination of titanium (*q.v.*).

The standard solution is prepared by dissolving 1·286 grm. of ammonium metavanadate in 10 per cent. sulphuric acid and diluting with water to 1 litre. 1 c.c.=0·001 grm. V_2O_5.

§ **VII. Detection in Ores.**—The mineral is fused with five times its weight in sodium carbonate and nitrate or peroxide, the melt leached with hot water, the filtered solution nearly neutralised with nitric acid, and evaporated to dryness. The residue is taken up with water and the filtered solution used for the following tests:—

(*a*) Boiling with a slight excess of acetic acid produces an orange coloration (tetravanadate).

(*b*) Boiling with a large excess of nitric acid causes formation of a deep red-brown flocculent precipitate of pyrovanadic acid.

(*c*) Evaporation of the solution with hydrochloric acid to expel nitrates finally gives a blue solution of vanadyl chloride, with evolution of chlorine; addition of potassium bromide brings this about more readily, bromine being liberated.

(*d*) The solution, slightly acidified with sulphuric acid, gives an intense red-brown colour with hydrogen peroxide (pervanadic acid).

(*e*) Addition of sufficient ammonium chloride to saturate the solution causes all the vanadium to precipitate as ammonium metavanadate, ignition of which gives the pentoxide (see § II.).

(*f*) Lead acetate gives a yellow precipitate in the cold in solutions slightly acid with acetic acid. The precipitate is soluble in nitric acid.

(*g*) If the solution from the water extraction of the melt is acidified with dilute sulphuric acid and treated with zinc the colour changes from yellow-brown to blue, green, violet, and, finally, lavender.

(*h*) Reducing agents (sulphur dioxide, hydrogen sulphide, alcohol, oxalic acid, tartaric acid, or ferrous sulphate) reduce sulphuric acid solutions of vanadates to bright blue vanadyl sulphate.

(*i*) Boiling with potassium iodide and sulphuric acid gives a deep green solution containing V_2O_3.

§ **VIII. Determination in Ores.**[2]—(*a*) *Fusion Methods for Ores low in Silica.*—(1) 0·5 to 1 grm. of ore is mixed with three times its weight

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[1] Hillebrand, *Journ. Amer. Chem. Soc.*, 1898, **20**, 209; *Chem. News*, 1898, **78**, 216; Lindemann, *Z. anal. Chem.*, 1879, **18**, 102.

[2] *Bull.* 70, *U.S. Bureau of Mines*; Low, *Technical Methods of Ore Analysis*; Lunge-Keane, *Technical Methods of Chemical Analysis*, vol. ii. part 1.

of sodium peroxide in a nickel crucible, covered with 1 grm. of the peroxide, and heated till the mass has sintered together and has a uniform black appearance (fusion is unnecessary and objectionable). The cold mass is leached with hot water, the solution heated to boiling and saturated with carbon dioxide. The precipitate is allowed to settle, filtered, and washed with a 2 per cent. solution of sodium carbonate. The filtrate is just acidified with nitric acid, boiled to expel carbon dioxide, an excess of 10 per cent. lead acetate solution added, followed by 3–4 grm. of ammonium acetate, whereby all the vanadium is precipitated as lead vanadate, together with chromium, tungsten, molybdenum, phosphorus, and arsenic. In the case of gravimetric assays these elements must be removed (§ III, (*b*)) ; for the volumetric determination the precipitate is dissolved by boiling with a few c.c. of nitric acid, an excess of dilute sulphuric acid added, and the whole evaporated to strong fumes. The molybdenum, arsenic, and lead are then removed as sulphides by hydrogen sulphide under pressure, and the tungsten will be found as tungstic acid in the sulphide precipitate. In the absence of chromium the filtrate from the sulphides is boiled to expel hydrogen sulphide and titrated with N/20 potassium permanganate; the solution is then reduced with sulphur dioxide, the excess boiled off, and the vanadium again titrated with N/20 permanganate. The last figure is taken as correct.

If chromium is present, the filtrate from the sulphides is evaporated to dryness, the residue fused with sodium carbonate, and the aqueous extract treated with acetic acid and hydrogen peroxide (§ III, (*b*) (3)).

(2) 0·5 to 1 grm. of the finely-powdered ore is fused with six times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate in a platinum crucible. The cold melt is extracted with hot water and the solution filtered ; the residue is washed with hot water, ignited, and again fused with the same mixture. The combined filtered aqueous extracts are nearly acidified with nitric acid and evaporated to dryness (a blank test should be run to ascertain the amount of acid necessary, as an excess would lead to reduction of the vanadate by the nitrite present). The residue is taken up with hot water, the solution filtered, and an excess of lead acetate added. The precipitate of lead vanadate is treated as shown under (1).

(*b*) *Acid Attack for Ores rich in Silica.*—From 1 to 5 grm. of ore are digested with 10 c.c. of *aqua regia* until completely attacked ; the liquid is evaporated to dryness. The residue is boiled with 1 : 1 hydrochloric acid until all soluble matters dissolve and the liquor filtered from silica, which may still contain some vanadium ; it is ignited in platinum, and evaporated nearly to dryness (twice) with a few c.c. of hydrofluoric, then twice with hydrochloric acid to expel the fluorine compounds. The residue is taken up with hot water and a little hydrochloric acid, which is filtered into the main solution ; this is saturated with hydrogen sulphide to remove lead, copper, etc. The filtrate from the sulphides is boiled to expel hydrogen sulphide, oxidised, neutralised, poured into a large excess of sodium hydroxide (6 grm. in 100 c.c. of boiling water), the resultant solution saturated with carbon dioxide, and filtered. The residue is re-dissolved in hydrochloric acid containing a little hydrogen peroxide and the above treatment repeated. The united filtrates are neutralised with nitric acid and the vanadium precipitated as lead vanadate, which is treated as described in (*a*) (1).

(*c*) *Determination of Vanadium in Iron Ores and Rocks.*[1]—Five grm. of ore are fused with 20 grm. of sodium carbonate and 3 grm. of potassium nitrate in platinum over a blast lamp. The cold melt is extracted with hot water, a few drops of alcohol added to decompose manganate, and the solution filtered from the insoluble carbonates, oxides, etc. If much vanadium is present, the residue is ignited and again fused with the above mixture. The combined filtrates are *nearly* neutralised with nitric acid (quantity required ascertained by blank test) and evaporated to dryness, taken up with hot water, and filtered. The residue contains silica, alumina, and part of the chromium if present (should determination of the latter be required, the residue is ignited, treated with hydrofluoric and sulphuric acids, evaporated to dryness, ignited, and fused with soda-nitre, the filtrate being added to the main solution). The cold slightly alkaline solution is treated with an excess of a saturated neutral solution of mercurous nitrate, heated to boiling, filtered, the precipitate washed with hot 1 per cent. ammonium nitrate solution, dried, and ignited at low temperature in platinum. The ignited residue is fused with sodium carbonate, the melt extracted with water (the chromium being determined colorimetrically as neutral chromate if required), the solution acidified with sulphuric acid, and saturated with hydrogen sulphide under pressure. The filtrate from the sulphides is boiled to expel hydrogen sulphide while passing carbon dioxide and the hot solution titrated with N/20 permanganate. To obtain absolutely correct results the solution is again reduced, this time with sulphur dioxide, the excess expelled as usual, and the solution titrated at 80° with permanganate. The mean of the two figures gives the correct result. If more than 5 milligrams of chromium are present a blank test should be made with the same quantity of pure chromate, which is reduced as above with sulphur dioxide and titrated hot.

(*d*) *Determination in Carnotite.*—See Uranium, § VII, (*d*).

§ **IX. Determination of Impurities in Ores.**—The most objectionable impurities are those which form soluble salts on fusion with sodium carbonate, *i.e.* phosphorus and arsenic. Molybdenum and chromium are not so objectionable, as in most cases where vanadium is used in steels these elements are also present.

(*a*) *Determination of Phosphorus.*[2]—From 1 to 5 grm. of ore are fused with sodium peroxide; the aqueous extract of the melt is acidified with nitric acid, again made alkaline with a few drops of dilute caustic soda solution, and the vanadic and phosphoric acids precipitated with mercurous nitrate. The precipitate is ignited, fused with twice its

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[1] Hillebrand, *loc. cit.* (p. 124).

[2] After Treadwell, *Analytical Chemistry*, 1910, vol. ii. 270.

weight of sodium carbonate, the melt leached with hot water, and the solution acidified with dilute sulphuric acid in slight excess. The V_2O_5 is reduced by passing sulphur dioxide, the excess of which is boiled off while passing a current of carbon dioxide through the liquid. After cooling the solution is made up to 100 c.c. with cold water, and 20 c.c. of 75 per cent. ammonium nitrate solution and 50 c.c. of ammonium molybdate solution (75 grm. ammonium molybdate in 500 c.c. of water poured into 500 c.c. of nitric acid, sp. gr. 1·2) are added. The mixture is shaken, heated to 60°, allowed to cool and stand one hour (not more), after which it is filtered and the precipitate washed with a solution containing 50 grm. of ammonium nitrate and 40 c.c. concentrated nitric acid per litre. The washed precipitate is dissolved in 10 c.c. of 8 per cent. ammonia, the solution diluted to 40 c.c., and treated with 10 c.c. of the above ammonium nitrate and 2–3 c.c. of the ammonium molybdate solution. The yellow phosphomolybdate is re-precipitated by the addition of 200 c.c. of 25 per cent. nitric acid, and is now free from vanadium. It is dissolved in ammonia, and the phosphoric acid precipitated in the usual manner with magnesia mixture.

(*b*) *Determination of Arsenic.*[1]—The ore is opened up by a nitric acid attack and taken to fumes with 10 c.c. of strong sulphuric acid. After diluting, silica, lead sulphate, etc., are filtered off, the filtrate reduced with sulphur dioxide, the excess of the latter boiled off, and the arsenic, etc., precipitated with hydrogen sulphide; the precipitate is extracted with sodium sulphide, the solution containing the arsenic evaporated to fumes with strong sulphuric acid, diluted with 25 c.c. of water and 50 c.c. of concentrated hydrochloric acid, and precipitated with hydrogen sulphide. The arsenic sulphide is dissolved in sulphuric acid and titrated as usual with iodine.

§ X. Complete Analysis of Ores.—(*a*) *Vanadinite, Mottramite, etc.*—Ores consisting of vanadates of heavy metals (*e.g.* vanadinite, volborthite, descloizite, pucherite) are usually found associated with lead minerals (such as wulfenite, cerussite, anglesite, pyromorphite, mimetite, crocoisite) and zinc minerals (calamine, etc.). The analysis of such mixtures is most conveniently carried out by working on several portions as illustrated below. Carnotite ores are analysed on similar lines.

First Portion.—

<table>
<tr><td colspan="4">Fuse 1 grm. with 5 grm. Na_2CO_3 and 1 grm. $NaNO_3$, leach, filter, ignite residue with 3 grm. of the same mixture. Leach, filter; unite filtrates. Wash both residues with 1 per cent. Na_2CO_3; combine residues.</td></tr>
<tr><td colspan="2">R^1: dissolve in HCl, pass H_2S, filter.</td><td colspan="2" rowspan="2">F^1: nearly neutralise with HNO_3 (quantity ascertained by blank test), evaporate to dryness, take up with H_2O, filter.</td></tr>
<tr><td>R^2: Bi, Cu, Pb (Procedure 2).</td><td>F^2: add NH_4Cl, NH_4OH, and $(NH_4)_2S$. Boil, filter.</td></tr>
<tr><td>P^3</td><td>F^3</td><td>P^6</td><td>F^6</td></tr>
</table>

(Table continued overleaf.)

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[1] See also Friedheim, Decker, and Diem, *Z. anal. Chem.*, 1905, **44**, 665, for a distillation method.

First Portion.—Continued.

P^3: dissolve in HCl, oxidise with HNO_3, ppte with $BaCO_3$ (Procedure 7).

F^3: Ba, Ca, Mg (Procedure 9).

F^4: determine Zn, Mn.

P^4: add R^7 and P^{10}; remove $BaCO_3$ as in Procedure 7, dissolve sulphides in HNO_3, add NH_4OH, $(NH_4)_2CO_3$, and $(NH_4)_2S$. Filter.

F^5: acidify with HCl, determine U as phosphate (Uranium, §IV, (*c*)).

P^5: dissolve in HCl, ppte Al with $Na_2HPO_4+Na_2S_2O_3$, weigh $AlPO_4$, determine Fe in filtrate.

P^6: ignite, evaporate with $HF+H_2SO_4$ to dryness, fuse residue with $Na_2CO_3+NaNO_3$, leach and filter.

F^6: add F^7, ppte with $HgNO_3$ solution, boil, filter, reject filtrate. Ignite ppte, fuse with $Na_2CO_3+NaNO_3$, leach, acidify with H_2SO_4, evaporate to fumes, cool, ppte with H_2S under pressure, filter, wash with dilute acid.

F^7 (trace Cr): nearly neutralise with HNO_3, add to F^6.

R^7 (trace Al+U): fuse with $KHSO_4$, add to P^4.

F^8: evaporate nearly to dryness, dilute, add a little HNO_3, excess of $CH_3CO_2NH_4$, and one-tenth of the bulk in glacial CH_3CO_2H; ppte with $Pb(CH_3CO_2)_2$, filter.

P^8: dissolve in *aqua regia*, filter, add NH_4OH+Mg Mixture (Molybdenum, § III, (*c*)).

P^9: dissolve in HNO_3, evaporate to fumes with H_2SO_4, titrate V_2O_5 (Vanadium, § V, (*a*) (1)).

F^9: ppte excess of Pb as directed under Uranium, § VII, (*d*). Ppte filtrate from $PbSO_4$ with NH_4OH, filter, reject filtrate. Dissolve in HNO_3, boil with $KClO_3$, ppte with NH_4OH, filter.

P^{11}: weigh as $Mg_2As_2O_7$, or titrate.

F^{11}: acidify with CH_3CO_2H, ppte and weigh $PbMoO_4$.

F^{10}: add CH_3CO_2H, ppte with $BaCl_2$, filter, ignite and weigh $BaCrO_4$.

P^{10}: U, Al. Add to P^4.

Second Portion.—Digest with *aqua regia*, evaporate to dryness, again with hydrochloric acid, filter. Determine silica in residue, and sulphur trioxide in filtrate.

Third Portion.—Chlorine. See Molybdenum, § IX, (*b*), second portion.

Fourth Portion, for phosphoric acid.—See § IX, (*a*).

Fifth Portion.—Determine water by Penfield's method.

Sixth Portion.—Potassium (sodium) in carnotite. Apply hydrofluoric acid or Lawrence Smith's method.

(*b*) *Patronite Ores.*—*First Portion.*—Roast at low temperature in platinum, treat residue as under (*a*) (first portion) for determination of V, Mo, Cu, Fe, Al, Mn, Ni, Ca.

Second Portion.—Fuse with sodium carbonate and nitrate, determine silica and sulphur.

Third Portion.—Water by Penfield's method. If tarry matter distils over, dry the tube in a steam oven and weigh again; the loss is water.

Fourth Portion, for organic matter.—Digest with strong hydrochloric acid, adding a drop of bromine from time to time till all sulphides are decomposed. Warm to expel bromine, rinse into a platinum dish, evaporate with hydrofluoric and hydrochloric acids, filter on tared paper in vulcanite funnel, dry, and weigh. Ignite and weigh again; difference gives organic matter.

Fifth Portion.—Alkalies (hydrofluoric acid, or L. Smith's method).

§ XI. Technical Methods.[1]—(*a*) *Rapid Volumetric Determination of Vanadium in Ores* (*Chromium and Uranium not interfering*).—Two grm. of ore are well mixed with 8 grm. of sodium peroxide, and the mixture heated in an iron crucible until it begins to sinter and becomes dark green on the surface (it should not be fused). The cold mass is extracted with hot water and acidified with 20 c.c. of strong sulphuric acid in 75 c.c. of water. The solution is tinted with permanganate from a burette, ferrous ammonium sulphate added from a second burette until a spot test shows an immediate blue with ferricyanide, after which more permanganate is slowly added until no blue colour develops in a spot test during five seconds. The solution, which now contains vanadyl sulphate, is heated to 70° and titrated with N/20 permanganate. A blank test should be put through the whole process and the result deducted before calculating V_2O_5. If chromium is present, the titration should be made at 40°.

(*b*) *Rapid Method for Vanadium and Uranium in Carnotite.*—See Uranium, § IX, (*b*).

COLUMBIUM.

§ I. Minerals. — (*a*) *Columbite*, iron manganese metacolumbate, $(Fe,Mn)(CbO_3)_2$, is the end-member of the isomorphous columbite-tantalite series. The mineral always contains varying amounts of tantalum, as tantalite is probably never free from columbium. This replacement is the rule with all columbium-tantalum minerals. Likewise the manganous and ferrous oxides replace each other in all proportions. Columbite is orthorhombic, but often found massive; its colour and streak vary from brown to black. H 6. The specific gravity increases with the tantalum content, ranging from 5·3 (columbite) to 7·3 (tantalite); all the minerals of the series are attracted by a strong electromagnet. Columbite is the most plentiful columbium mineral. The metal is also found in a number of very rare minerals which present considerable scientific interest. The best known are :—

(*b*) *Tantalocolumbates.* — (1) *Samarskite*, a pyrocolumbate of rare earth metals, chiefly yttria earths: $R_3''R_2'''(Cb,Ta)_6O_{21}$, where $R''=Fe,Ca,UO_2$, and $R'''=$rare earth metals. Radioactive, contains helium. Orthorhombic, black; streak reddish-brown.

(2) *Annerödite* is a parallel growth of columbite on samarskite.

(3) *Fergusonite*, tetragonal, is an orthocolumbate $R'''(Cb,Ta)O_4$. $R'''=$rare earth metals, chiefly yttrium. Brownish-black. Glows suddenly with evolution of helium when heated to 500°–600°. Radioactive.

(*c*) *Titanocolumbates.* — (1) *Aeschynite*, $Ce(CbO_3)_3.ThTiO_4.\frac{3}{2}TiO_2$. Orthorhombic, nearly black. H 5–6; sp. gr. 4·9–5·7.

(2) *Euxenite-Polycrase, Priorite-Blomstrandine.*—Like the trioxides of antimony and arsenic, these four minerals form an isodimorphous

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[1] Low, *Technical Methods of Ore Analysis.* See also Alvarez, *Chem. Zeit.*, 1909, **33**, 1149.

series, but the end-members—metacolumbate and metatitanate—are unknown. The dimorphous substance euxenite-priorite contains more columbium and less titanium than polycrase-blomstrandine. Though all the minerals of the series are orthorhombic, the measurements for euxenite-polycrase are different from those for priorite-blomstrandine. They are bright black, and contain rare earths, uranium, zirconium, and water.

§ **II. Properties and Compounds.**—(*a*) The *metal* is obtained, like tantalum, by reduction or electrolysis. It is softer, lighter (sp. gr. 8·4), and more easily fusible (M.P. 1950°) than tantalum, and not attacked by acids, with the exception of hydrofluoric.

(*b*) *Oxides.*—The pentoxide, Cb_2O_5, obtained by igniting columbic acid, is a white powder which becomes yellow on heating. Fused bisulphate dissolves it, but on extracting the melt with water most of the columbium is precipitated as columbic acid. The oxide is insoluble in acids, except hydrofluoric. Non-volatile, non-reducible at temperatures attained with a Bunsen burner. Lower oxides, such as Cb_2O_4 and Cb_2O_2, have been prepared by reduction at high temperature. Reduction of columbic acid in acid solution yields an oxide the composition of which closely approaches Cb_3O_5.

(*c*) *Columbic Acid.*—A few properties of this substance are described in § VII, (*a*). In its behaviour towards mineral acids it exhibits a slightly more basic character than tantalic acid (*q.v.*).

(*d*) *Columbates.*—The three types corresponding to those of the phosphates have been recognised in minerals, viz. ortho- ($R_3'CbO_4$), pyro- ($R_4'Cb_2O_7$), and meta- ($R'CbO_3$) columbates. In addition, hexacolumbates, $R_8'Cb_6O_{19}$, are obtained by fusion of insoluble columbates or the pentoxide with caustic alkalies. Potassium hexacolumbate is soluble in water and caustic potash; the sodium salt is slightly soluble in water, but insoluble in caustic soda.

(*e*) *Potassium fluocolumbate*, K_2CbF_7.—See § VII, (*c*).

§ **III. Quantitative Separation of Columbium (and Tantalum) from other Elements.**—The comparative insolubility of the columbic and tantalic acids and anhydrides serves to separate them from most metals, earths, and bases. Only a small number of elements call for a special process of separation, *i.e.* those that form more or less inert acidic oxides or acids. The mixed tantalic and columbic acids will hereunder be referred to as "earth acids."

(*a*) *Separation from Tungsten.*—The precipitated tungstic and earth acids are digested with warm dilute ammonia or ammonium carbonate, which dissolves the former. A better separation is effected by digesting with warm 1 per cent. caustic soda and boiling with excess of ammonium nitrate (Tungsten, § III, (*a*) (2); determination, *ibid.*, § IV, (*b*)). The residual earth acids are filtered off and washed with dilute ammonium nitrate solution.

(*b*) *Separation from Antimony.*—Antimonic acid, if in admixture with the earth acids, may be extracted by digestion with hot yellow ammonium sulphide. It is recommended to ignite and fuse the residue with potassium hydroxide, precipitate the earth acids with hydrochloric acid, and repeat the extraction with ammonium sulphide. The filtrate is acidified and boiled to precipitate antimony sulphide.

(*c*) *Separation from Tin.*—Precipitated stannic acid may be separated from the earth acids as described under antimony, *i.e.* single or double extraction with hot yellow ammonium sulphide. Where large quantities of stannic oxide have to be separated from small amounts of earth acids the mixed precipitate is ignited, transferred to a porcelain boat, and heated in a current of hydrogen. The escaping gas is bubbled through water for the recovery of traces of tin; the residue is boiled with hydrochloric acid, which extracts the tin and leaves the earth acids.

In technical work, tungsten, tin, and antimony are removed together by digestion with ammonia and ammonium sulphide.

(*d*) *Separation from Silica.*—The mixed acids are heated in platinum with hydrofluoric and sulphuric acids. When the whole of the former and the excess of the latter have volatilised the earth acids separate as a thick jelly which is very apt to spirt while being taken to dryness previous to igniting and weighing, unless the evaporation proceeds very slowly. Alternatively the following procedure may be adopted. The acid mixture in the platinum dish is heated with a large excess of sulphuric acid to strong fumes after all the fluorine has been expelled. After cooling it is transferred to a beaker containing distilled water, the dish being cleaned with a rubber-tipped glass rod. The aqueous suspension is made slightly alkaline with ammonia, boiled for some time, and left to settle. The precipitate, consisting of the earth acids, is filtered off and washed with dilute ammoniacal ammonium nitrate solution. Silica is determined by difference, the acids being ignited and weighed before and after the treatment described above.

(*e*) *Separation from Titanium.*—(1) If a small quantity of titanium dioxide is suspected in the weighed mixed pentoxides they are fused with bisulphate, and the melt extracted with cold dilute sulphuric acid. The filtrate is tested colorimetrically with hydrogen peroxide (Titanium, § VI.), and the titanium dioxide deducted from the weight previously found.

(2) Fusion with bisulphate is also applied in technical work for the separation of large quantities of titanium from the earth acids, though the process gives slightly low results for the latter on account of their imperfect insolubility after this mode of attack.

(3) The best separation appears to be by means of salicylic acid.[1] The moist mixed acids are boiled under reflux for three to four hours with a large excess (5–10 grm.) of this reagent; the liquor is filtered, and the yellow filtrate precipitated with ammonia, the precipitate being ignited and weighed as TiO_2. The insoluble residue consists of the earth acids.

(4) Weiss and Landecker[2] describe a process in which the mixed acids, after extraction with ammonium sulphide, are ignited and fused with sodium carbonate and nitrate. The aqueous extract of the melt is

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[1] Dittrich and Freund, *Z. anorg. Chem.*, 1908, **56**, 344, 346.

[2] *Z. anorg. Chem.*, 1909, **64**, 65.

boiled for some time and filtered. The titanium is in the residue. If the filtrate be found to contain more titanium, it is precipitated with hydrogen sulphide, and the two titanium precipitates are dissolved in a mixture of dilute sulphuric acid and hydrogen peroxide ; this solution is reduced with sulphur dioxide and the titanium precipitated with ammonia. The filtrate from the titanium is boiled with excess of sulphuric acid to decompose sodium sulphide ; the earth acids are then precipitated with ammonia.

(*f*) *Separation from Zirconium.*—(1) A technical separation can be effected, as in the case of titanium, by fusion with bisulphate. Zirconium sulphate dissolves, while the earth acids remain almost entirely insoluble. They retain a little zirconia, which is extracted by a second fusion.

(2) Bailey[1] precipitates zirconium from sulphuric acid solutions by means of strong hydrogen peroxide (120 vol.), any tantalic or columbic acid present remaining in solution. This method provides a separation of zirconium from the small quantity of earth acids rendered soluble by the bisulphate fusion.

Note.—The filtration and washing of acid-earth precipitates is greatly facilitated by mixing them with pulped filter fibre. (See Introduction.)

§ IV. Separation from Tantalum, and Gravimetric Determination.—A separation of tantalum and columbium has recently been published by Weiss and Landecker,[2] who direct passing carbon dioxide for one and a half hours through a cold solution of sodium columbate and tantalate, tantalic acid only being precipitated ; however, this method has been found quite unsatisfactory by Foote and Langley[3] and by Meimberg and Winzer.[4]

The only method at present in use for separating the two elements is that of Marignac,[5] or some of its modifications. The process is based on the different solubilities of potassium fluotantalate and the corresponding columbium compound, or potassium columbium oxyfluoride (§ VII, (*c*)). The procedure of fractional crystallisation has to be adopted. The apparatus required consists of a rubber or ebonite funnel (a glass funnel coated internally with paraffin wax may also be used) fitted with a 5·5 cm. filter, and two platinum dishes, A and B. If more platinum vessels are available the operation is a little more convenient, especially if it is desired to collect the fluotantalate precipitate. Even then, this may be rinsed with cold water into a paraffin-coated porcelain dish, the filter washed with cold water, and the tantalum fraction reserved until one of the platinum dishes becomes available.

(*a*) *The Separation.*—The purified mixed acids are transferred from the filter into dish A ; the filter is opened out in B and treated with hot water and a few drops of hydrofluoric acid to dissolve the precipitate still adhering to it. The acid is poured into A and the filter washed several times with water, which is added to that in A. The earth acids are completely dissolved by gently warming dish A and stirring with a

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[1] *Journ. Chem. Soc.*, 1886, **49**, 149, 481.

[2] *Z. anorg. Chem.*, 1909, **64**, 65.

[3] *Amer. Journ. Sci.*, 1910, **30**, 401.

[4] *Z. angew. Chem.*, 1913, **26**, 157.

[5] *Ann. Chim. Phys.*, 1865, **8**, 5, 49.

platinum rod, adding more acid if necessary, but the amount must be carefully limited. To the hot solution is added a boiling solution of potassium fluoride slightly in excess of the quantity required to form the double fluorides. Strangely enough, most text-books direct that one-quarter of the weight of the earth acids in potassium acid fluoride be added, but this is obviously insufficient for the formation of the double salts. More recent directions prescribe the addition of twice the weight of the mixed acids in potassium fluoride. This quantity is also used by the authors. The solution is evaporated on the water-bath to about 10 c.c. and left to cool slowly. The crystals are filtered off and washed with small quantities of cold water, the filtrate and washings being received in B. The latter are evaporated to about 5 c.c. and slowly cooled, when a smaller quantity of fluotantalate separates. Meanwhile the filter is rinsed and washed free from the first fraction. The second fraction is filtered off and washed as before; the filtrate is collected in A and evaporated to dryness. The residue is taken up in less than 5 c.c. of water delivered from a burette (volume *a*), warmed till solution is complete, treated with a drop of hydrofluoric acid, and the liquid left to cool for one hour. The second fraction is rinsed off the filter, added to the first, and the paper well washed. The third fraction is then filtered off and washed three to four times with measured amounts of water, a few drops at a time (washings *b*), into B. The third fraction is rinsed back into A, to which the first and second are now transferred.

(*b*) *Gravimetric Determination of Columbium.*—The contents of dish B are evaporated to fumes with 10 c.c. of sulphuric acid (1 : 1), fuming being continued for twenty minutes to expel all fluorine. The cooled mass is transferred to a beaker containing distilled water and filter pulp, and the dish cleaned with a rubber-tipped glass rod. The liquid is then made slightly alkaline with ammonia and boiled. The precipitate is allowed to settle, filtered off, washed with ammonium nitrate solution, ignited wet in platinum, and weighed. It is again ignited with ammonium carbonate to expel any sulphuric anhydride, ignited strongly, and weighed. An allowance has to be made for tantalum pentoxide in the weighed precipitate, due to the solubility of fluotantalate in the third precipitation. According to Mellor [1] this is calculated as follows :—

For each c.c. of acid liquid (volume *a*) 0·0020 grm. Ta_2O_5.
,, ,, ,, ,, water (washings *b*) 0·00091 grm. Ta_2O_5.

This weight is subtracted from that of the columbium pentoxide and added to the tantalum result. Columbium as well as tantalum is always weighed as pentoxide.

(*c*) *Gravimetric Determination of Tantalum.*—It is generally recommended to determine columbium and tantalum together as pentoxides, and to find the amount of tantalum by difference after determining the columbium, as described above. This is a convenient procedure for tantalite, which contains a small proportion of columbium. It is often desirable to determine the tantalum, and this should be done when the

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[1] *Quantitative Inorganic Analysis*, p. 422.

proportion of the latter element is small (*e.g.* in columbite), on the principle that in a determination by difference the subordinate element should always be determined direct and the predominant by difference.

In order to convert potassium fluotantalate into the pentoxide the precipitate and washings in dish A are evaporated with a large excess (5–10 c.c.) of sulphuric acid to strong fumes and the heating continued for at least twenty minutes. The acid is then poured into water containing filter fibre, neutralised with ammonia, the liquid boiled, the precipitate filtered off, washed, ignited, and weighed, in exactly the same manner as described for the gravimetric estimation of columbium.

(*d*) *Summary of Marignac's Process* :—

<table>
<tr><td colspan="3">Dissolve mixed acids in HF (dish A), evaporate with twice their weight in KF to 10 c.c., filter.</td></tr>
<tr><td>P^1 : rinse and wash into paraffin-coated basin.</td><td colspan="2">F^1 : evaporate in B to 5 c.c., filter.</td></tr>
<tr><td colspan="2">F^2 : evaporate to dryness in A, take up with H_2O, filter.</td><td>P^2 : add to P^1.</td></tr>
<tr><td>R^3 : rinse back into A, add P^1+P^2, evaporate with H_2SO_4.
Tantalum.</td><td colspan="2">F^3 : evaporate in B with H_2SO_4.
Columbium.</td></tr>
</table>

(*e*) *Meimberg and Winzer's Process.*[1]—In this modification of Marignac's process potassium chloride is substituted for the fluoride. The directions are as follows :—

The mixed acids are dissolved in a quantity of hydrofluoric acid sufficient for the formation of the double fluorides ; the solution is mixed with saturated potassium chloride solution and cooled, the volume being so adjusted that potassium fluocolumbate remains dissolved (1 part in 12 of solution). The precipitate is washed with saturated potassium chloride solution, dissolved in water containing a little hydrofluoric acid, the solution again treated with saturated potassium chloride solution, and carefully cooled. The precipitate is filtered off and washed as before, the combined precipitates evaporated in platinum with strong sulphuric acid, and the heating continued for some time after strong fumes have made their appearance. The residue is boiled with water containing a little hydrochloric acid and with ammonia, left to settle, filtered off, washed, ignited, and weighed as tantalum pentoxide. The freedom of this precipitate from columbium is tested colorimetrically (§ VI.). The columbium in the filtrate is determined gravimetrically, and any titanium in the columbium pentoxide by colorimetry (Titanium, § VI.).

§ **V. Volumetric Determination.**—On account of the non-interference of tantalum in the volumetric process this mode of determining columbium is better adapted for the requirements of technical routine work than the gravimetric method, which latter, however, is still up to the present regarded as the standard process.

The volumetric determination of columbium is based on the reduc-

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[1] *Loc. cit.*, p. 132.

tion of columbic acid by zinc in acid solution and oxidation of the lower oxide by permanganate of known strength. Interfering elements (molybdenum, tungsten, titanium) must not be present. Two methods for carrying out the process will here be described :—

(*a*) *Taylor's Method.*[1]—The mixed earth acids are fused with 5 grm. of bisulphate, the melt heated with 10 c.c. of strong sulphuric acid, and the clear liquid transferred to a beaker, the dish being rinsed out with 30 c.c. of strong sulphuric acid. After cooling, 2 grm. of succinic acid are added, followed by 20 c.c. of a saturated solution of the same acid in a fine stream from a burette, whilst continually stirring. Dilution with water to 200 c.c. is gradually effected with constant stirring. The solution, heated to 75°, is passed through a Jones' reductor filled with 20 per cent. sulphuric acid at 75°. When the assay has passed the reductor the latter is rinsed with 50 c.c. of 20 per cent. followed by 200 c.c. of 5 per cent. sulphuric acid. The reduced solution is received in a flask filled with carbon dioxide, and titrated with N/10 permanganate, 1 c.c. of which equals 0·007052 grm. Cb_2O_5. A blank assay should be made, and the volume of permanganate subtracted from that used in the determination.

(*b*) *Levy's Method.*[2]—The weighed mixed oxides are heated with 10 c.c. of hydrofluoric acid, the liquid being heated quickly almost to boiling-point, and kept at that temperature to complete solution, after which it is evaporated as low as possible without separation of solids, or, at most, only a thin scum on the surface. Forty c.c. of strong hydrochloric acid are then added, when everything should dissolve; the acid liquor is transferred to a 500 c.c. conical flask with 20 c.c. of water, and reduced with 10 grm. of fairly massive granulated zinc. Reduction and titration are carried out under hydrogen. This is conveniently done by closing the flask with a three-holed stopper ; two holes are used for the hydrogen supply, while the third carries a short thistle funnel. When the zinc is all dissolved (with brown colour in presence of much columbium), an air-free solution, consisting of 270 c.c. of water, 10 c.c. of strong sulphuric acid, and 20 c.c. of saturated sodium phosphate solution, is introduced through the thistle funnel; the titration is carried out without delay, the permanganate being added through the funnel until a pink tinge is obtained. One c.c. of N/10 permanganate is equivalent to 0·00833 grm. Cb_2O_5.

Levy states that the method tends to give low results with small quantities of columbium in presence of much tantalum, and that his and Taylor's methods give results which appear to be more accurate than those given by Marignac's method in much less time and with less labour.

§ **VI. Colorimetric Determination.**—A colorimetric process for determining columbium in potassium fluotantalate has been worked out by Meimberg.[3] The precipitate is dissolved in hydrochloric containing

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[1] Dissertation, Columbia University; *Journ. Soc. Chem. Ind.*, 1909, **28**, 818.
[2] *Analyst*, 1915, **40**, 204.
[3] *Z. angew. Chem.*, 1913, **26**, 83.

some hydrofluoric acid, and the solution boiled down till a copious precipitate of potassium fluotantalate is formed. After cooling, this is filtered off and washed with cold dilute hydrofluoric acid. The filtrate containing all the columbium is evaporated to dryness on a sand-bath. The residue is dissolved in concentrated hydrochloric acid, the solution transferred to a colorimetric tube, and reduced with tin for fifteen minutes. The colour is matched against a standard, which must be freshly made for each determination. The solution should not contain more than 0·1 per cent. of columbium; the method is stated to be accurate within 0·01 per cent. if 10 grm. are taken for assay.

§ **VII. Detection in Ores.**—All columbium minerals yield by fusion with potassium hydroxide and extraction with water a solution containing potassium hexacolumbate, which gives the following reactions:—

(*a*) On acidification, a white amorphous precipitate of columbic acid is produced. This is very slightly soluble in excess of acid, but easily so in hydrofluoric acid; it also dissolves in hot strong sulphuric acid, and the solution remains clear on dilution. The precipitate does not dissolve in strong hydrochloric acid, but the residue is soluble in water after decanting the acid.

(*b*) Zinc added to the sulphuric acid solution obtained as under (*a*) produces a fine blue colour. Hydrofluoric acid prevents this reaction. Tungsten, molybdenum, and vanadium interfere by giving highly-coloured compounds; the mauve colour of titanium, if present, is less pronounced.

(*c*) The hydrofluoric acid solution obtained as under (*a*) is not precipitated by potassium fluoride, as potassium fluocolumbate, K_2CbF_7, is soluble in 12·5 parts of water. If little free hydrofluoric acid is present, the oxyfluoride, $K_2CbOF_5.H_2O$, is formed, which is still more soluble.

(*d*) Ammonia precipitates columbic acid from the sulphuric acid solution; the precipitate retains ammonia, and is more generally described as "acid ammonium columbate"; tartaric acid prevents the precipitation.

(*e*) Tannin gives an orange-red precipitate in the acid solution.

(*f*) The microcosmic salt bead in a reducing flame assumes a blue, violet, or brown colour with increasing amounts of columbic acid; the heated bead turns red after addition of ferrous sulphate.

(*g*) For the simultaneous detection of columbium and tantalum the white precipitate of columbic and tantalic acids obtained as under (*a*), and extracted with ammonium sulphide to eliminate any tungsten, is dissolved in little hydrofluoric acid, the solution evaporated to small bulk with excess of potassium fluoride, and allowed to cool. A crystalline precipitate, consisting of fine needles of potassium fluotantalate, proves tantalum to be present; the filtrate is evaporated with 10 c.c. of sulphuric acid to expel all fluorine, cooled, diluted gradually with water, and reduced with zinc: a blue coloration shows presence of columbium.

§ **VIII.** (*a*) *Determination in Ores.*—See Tantalum, § V.

(*b*) *Complete Analysis of Ores.*—See Tantalum, § VII.

TANTALUM.

§ I. Minerals.—(*a*) *Tantalite*, iron manganese metatantalate, (Fe,Mn) $(TaO_3)_2$, is the other end-member of the isomorphous columbite-tantalite series; it goes over into columbite by imperceptible gradations. In the same manner, manganous and ferrous oxides are vicarious, and this replacement gives rise to another isomorphous series, the end-members of which are *manganotantalite*, $Mn(Ta,Cb)_2O_6$, and *ferrotantalite*, $Fe(Ta,Cb)_2O_6$. Manganotantalite is more easily decomposed by fusion with potassium hydroxide than ferrotantalite. For a description of this mineral, see Columbite. Tantalite sometimes occurs with wolframite and cassiterite.

(*b*) The other minerals in which tantalum predominates over columbium have no economic interest. The best known are:—

(1) *Microlite*, calcium pyrotantalate, $Ca_2Ta_2O_7$; pale yellow to brown; cubic.

(2) *Stibiotantalite*, antimony tantalate, $Sb_2O_3.(Ta,Cb)_2O_5$; various shades of yellow.

(3) *Yttrotantalite*, yttrium pyrotantalate, isomorphous with samarskite, and of similar composition: $R''R_2'''(Ta,Cb)_4O_{14}.4H_2O$. $R'''=$ chiefly yttrium. Yellow to black.

(*c*) For other tantalum-columbium minerals, see Columbium, § I.

§ II. Properties and Compounds.—(*a*) *Tantalum* is a greyish-white, ductile, tough metal, obtained by electrolysis of fused potassium fluotantalate or of an oxalate solution, or by reduction of the pentoxide by hydrogen in the electric furnace. It can be hardened, and resists all acids except hydrofluoric. Sp. gr. 16·5; M.P. 2475°.

(*b*) The *pentoxide*, Ta_2O_5, is a heavy white powder (sp. gr. 8·71), insoluble in acids, but soluble in hot hydrofluoric acid. The behaviour to fused bisulphate is the same as that of columbium pentoxide. It is non-volatile by itself, but markedly volatile if ignited with ammonium fluoride. Reduction at very high temperature produces black tetroxide, Ta_2O_4.

(*c*) *Tantalic Acid.*—The salient properties of the acid are mentioned in § IV. It has feebler affinities than columbic acid; thus, alkali tantalate solutions are precipitated by a current of carbon dioxide, whereas those of columbate are not.

(*d*) The *tantalates* are of four types, like columbates (*q.v.*). Potassium hexatantalate, $K_8Ta_6O_{19}$, is soluble in water and caustic potash; the sodium salt, slightly soluble in water but insoluble in caustic soda.

(*e*) *Potassium fluotantalate.*—See § IV, (*d*).

§ III. Separation and Estimation.—(*a*) *Separation from other Elements.*—See Columbium, § III.

(*b*) *Separation from Columbium.*—See Columbium, § IV.

(*c*) *Gravimetric Determination.*—Direct determination as Ta_2O_5: see Columbium, § IV, (*c*). Indirect determination: The sum of the mixed oxides, $Cb_2O_5+Ta_2O_5$, having been determined, Cb_2O_5 is determined by gravimetric or volumetric methods, Ta_2O_5 being found by difference. See Columbium, § IV, (*c*) and § V.

(*d*) There is no volumetric or colorimetric method for determining tantalum.

§ IV. Detection in Ores.—The tantalates found in Nature are decomposed by fusion with potassium hydroxide, and extraction of the melt with water yields a solution of potassium hexatantalate. This may be tested as follows :—

(*a*) Sulphuric acid produces a white amorphous precipitate of tantalic acid, insoluble in excess, but soluble in hot concentrated sulphuric acid. The solution is again precipitated on dilution.

(*b*) Hydrochloric acid precipitates concentrated solutions, and the precipitate is soluble in excess to an opalescent liquid.

(*c*) Zinc added to the acid liquid obtained under (*b*) causes no coloration.

(*d*) Tantalic acid is easily soluble in hydrofluoric acid ; the solution on addition of potassium fluoride gives colourless needles of potassium fluotantalate, K_2TaF_7, soluble in about 200 parts of water. It is fusible, and slightly volatile. By boiling a solution of the double fluoride a very insoluble oxyfluoride, $K_4Ta_4O_5F_{17}(=4KF.2TaF_5.Ta_2O_5)$ is precipitated as a white powder. This is a sensitive reaction.

(*e*) Tannin gives a yellowish precipitate in acid solution.

(*f*) Ammonia precipitates from the acid solution white tantalic acid or an acid ammonium tantalate ; tartaric acid prevents the reaction.

(*g*) For the simultaneous detection of tantalum and columbium see Columbium, § VII, (*g*).

§ V. Determination of Tantalum and Columbium in Ores.—The ore is almost always opened up by a fusion, except in a few cases where hydrofluoric acid is employed. A number of fluxes are available, of which the following are the most important :—

(*a*) Potassium hydroxide ; nickel or silver crucible.
(*b*) Potassium carbonate ; iron crucible.
(*c*) Sodium peroxide ; nickel crucible.
(*d*) Sodium bisulphate ; platinum or silica crucible.

Potassium persulphate, potassium acid fluoride, and sodium carbonate and nitrate (Columbium, § III, (*e*)) are also mentioned in literature.

(*a*) *Fusion by Potassium Hydroxide*, recommended by Simpson,[1] answers well for high-grade tantalite (columbite) substantially free from titanium. Six grm. of potassium hydroxide are fused in a nickel crucible supported in a perforated piece of asbestos board, so that only the lower quarter of the crucible extends below the opening. Creeping of the fused alkali is thus prevented. One grm. of the finely ground ore is then added and well mixed by rotating the crucible. The heat is gradually increased, and the covered crucible finally heated for half an hour or more with the full heat of a Teclu burner. When cool, the crucible is placed inside a 500 c.c. beaker and filled with warm water, the beaker being covered to prevent loss by spirting. The liquor is poured into a beaker containing 20 c.c. of strong hydrochloric acid diluted with

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[1] *Chem. News*, 1909, **99**, 243.

water, and the crucible and lid washed with dilute acid, assisted by a rubber-tipped glass rod. The contents of the beaker are now diluted to 300 c.c. and brought to boil, adding a little more acid if the precipitate shows any discoloration, and a few drops of alcohol to destroy permanganate. After twenty minutes' boiling the precipitate is left to settle, the liquid decanted through a 12·5 cm. filter, and the white precipitate thoroughly washed with hot dilute hydrochloric acid ; it contains all the tantalum and columbium, generally mixed with tungsten, tin, and silica, and is purified by rinsing back into the beaker and digesting with hot yellow ammonium sulphide. Tin and tungsten are thus removed. After filtering on the paper previously used and washing with dilute ammonium sulphide the precipitate usually has a greenish tinge, due to adsorbed or incompletely removed iron. It is therefore returned to the beaker once more, digested for a short time with hot dilute hydrochloric acid, filtered off on the same paper, and well washed with acidulated water.

At this stage the mixed acid earths are still contaminated with silica. To remove this the precipitate is transferred to a platinum dish ; what still adheres to the paper is dissolved in dilute hydrofluoric acid in a second platinum vessel, the solution poured into the first, and the filter well rinsed with water. More hydrofluoric acid is added to dissolve the whole of the precipitate and the solution evaporated with 20 c.c. of sulphuric acid (1 : 1) to copious white fumes, after which the heating is continued for at least fifteen minutes. The cooled acid mass is transferred to a beaker containing filter pulp in 300 c.c. of water, the dish well rinsed with a rubber-tipped rod, a slight excess of ammonia added, and the whole boiled for twenty minutes. After settling, the precipitate is filtered off, washed with ammonium nitrate solution, ignited in platinum with ammonium carbonate, heated strongly for fifteen minutes, and weighed as $Cb_2O_5+Ta_2O_5$.

(*b*) *Fusion with Potassium Carbonate* is in all respects the same as with potassium hydroxide, but the salt is much less fusible, hence its use is less convenient.

(*c*) *Fusion with Sodium Peroxide.*—There is no difference between the execution of this process and the preceding ; the attack by peroxide is very quick and energetic.

(*d*) *Fusion with Sodium Bisulphate.*—This is the older process, and is useful for complex minerals, such as titano-columbates and materials containing more subordinate quantities of tantalum and columbium.

The results of this method are a little low, due to the slight solubility of the earth acids after the bisulphate treatment. The slimed mineral is added to ten times its weight of bisulphate previously dehydrated in a platinum dish or crucible. It is fused gently at first, then submitted to a strong heat for half an hour or until dark particles of undecomposed ore are no longer visible. When decomposition is complete the cake is extracted with a large quantity of boiling water, the solution boiled for twenty minutes, left to clear, and filtered. The precipitate, after careful washing with acidulated water, is treated for the removal of tungsten, tin, and a small quantity of iron, exactly as described under (*a*). The precipitate may now contain silica and titanic acid. They are eliminated by first evaporating with hydrofluoric acid and sulphuric acid to strong fumes as before, pouring the acid mass into water, nearly neutralising with ammonia, and boiling with 5–10 grm. of salicylic acid for three to four hours. The clear liquor is decanted, the precipitate transferred to the filter, well washed with dilute salicylic acid, ignited as before, and weighed. (If the ore is found to be free from titanium no change from procedure (*a*) is necessary.)

With ores containing rare earths (*e.g.* monazite sand) the bisulphate melt must be digested with cold water, otherwise hydrated sulphates of cerium, lanthanum, etc., would separate out together with the earth acids. Tin ores are fused with bisulphate after reduction in hydrogen and extraction with hydrochloric acid.

(*e*) The operations described above give the sum of tantalum and columbium pentoxides in the mineral. To ascertain their separate amounts the weighed mixed oxides may be dissolved in hydrofluoric acid for volumetric determination of columbium after Levy; or fused with potassium hydroxide in a silver crucible, the acids precipitated by boiling with hydrochloric acid, dissolved in hydrofluoric acid without any further washing, and separated according to Marignac's or Meimberg and Winzer's method; or they are fused with bisulphate and titrated by Taylor's method (Columbium, §§ IV. and V.).

Some operators prefer to work on two portions of ore, which are treated in the same manner up to the point where the purified mixed acids have been obtained; in one portion the mixed acids are ignited and weighed, the other is used for the determination of tantalum or columbium. It is always advisable to test the weighed tantalum or columbium pentoxide for titanium dioxide and to allow for the quantity thus found (see Columbium, § III, (*e*) (1)).

§ VI. Determination of Impurities in Tantalite.—(*a*) *Columbium.*—The commercial chemist is occasionally required to assay samples of tantalite (generally high-grade picked ores and concentrates) for tantalum and columbium, the latter element being considered harmful in depreciating the quality of tantalum. It is well known that the figures for columbium and tantalum reported by different operators on the same sample often disagree to an extraordinary extent (as much as 20 per cent. and even more), although the sum of the percentages of the earth acids may be in tolerable agreement.

These discrepancies must be attributed to faulty execution of Marignac's process (which, at its best, is accurate to about 1 per cent.) by inexperienced workers, most of whom undoubtedly follow the usual text-book directions as to the quantity of potassium fluoride to be added. That this amount is inadequate for the separation has already been pointed out under Columbium, § IV, (*a*). In the absence of simpler chemical methods of separation a physical method has been proposed by Foote and Langley.[1] It consists in determining the specific gravity

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[1] *Amer. Journ. Sci.*, 1910, **30**, 393.

of the mixed oxides and calculating the proportion of the two constituents from an empirically constructed curve. In our opinion this method requires still more caution in its application than Marignac's; the degree of accuracy is lower (*i.e.* about 2·2 per cent.), and the process requires a fairly large quantity of the pure mixed oxides, hence more ore has to be operated upon; the oxides must be perfectly pure, and always prepared in exactly the same manner, which implies training and practice in the use of the method.

It has also been proposed to determine the specific gravity of the ore itself; this is a very quick method, but still less accurate (*i.e.* to less than 5 per cent.).[1]

We would advise operators unfamiliar with the assay of tantalite to carry out the determination of the mixed acids in duplicate; in one portion the columbium is then determined volumetrically, while the other is treated according to Marignac's (or Meimberg and Winzer's) process.

(*b*) *Other Impurities.*—Small quantities of tin, tungsten, titanium, and silica are the usual impurities of high-grade ores, antimony and yttria earths being less frequent. For the determination of these impurities see § VII.

§ VII. Complete Analysis of Minerals containing Tantalum and Columbium.—A scheme for the complete analysis of tantalum and columbium minerals must embrace the determination of the following constituents: tin, antimony, tungsten, titanium, silica, zirconium, iron, uranium, rare earths, beryllium, manganese, lime, and magnesia. Bismuth, lead, and copper should also be looked for.

(*a*) Simpson [2] fuses one portion in a nickel and another in a silver crucible; the first is used for the determination of tantalum, columbium, tungsten, tin, antimony, etc., the second for metals and bases (see tables).

First Portion.—

<table>
<tr><td colspan="6">Fuse 1 grm. with KOH (Ni crucible). Take up with dilute HCl, filter.</td></tr>
<tr><td colspan="4">R^1: extract hot with yellow $(NH_4)_2S$, filter.</td><td colspan="2">F^1: pass H_2S, filter.</td></tr>
<tr><td colspan="2">R^2: extract with dilute HCl, filter.</td><td colspan="2" rowspan="2">F^2: evaporate to dryness in porcelain crucible; oxidise with HNO_3, evaporate, fuse with KCN, leach, filter.</td><td>F^6: oxidise with HNO_3, ppte twice with NH_4OH.</td><td>P^6: test for Sb, Sn, add to R^5.</td></tr>
<tr><td>R^3: dissolve in HF, fume with H_2SO_4, neutralise with NH_4OH, boil 3 hours with salicylic acid, filter.</td><td>F^3: reject.</td><td rowspan="3">P^7: dissolve in HCl, neutralise, ppte with $Na_2S_2O_3$, ignite, add ppte from F^4, fuse with bisulphate, determine TiO_2.</td><td rowspan="3">F^7: reject.</td></tr>
<tr><td rowspan="2">F^4: ppte with NH_4OH, ignite ppte, fuse together with P^7.</td><td>R^4: ignite and weigh</td><td>R^5: determine Sb and Sn.</td><td>F^5: evaporate with HNO_3, add H_2O, filter, ignite, weigh WO_3.</td></tr>
<tr><td colspan="3">$Ta_2O_5+Cb_2O_5$. Dissolve in HF, apply Levy's or Marignac's method.</td></tr>
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[1] Simpson, *Bull. West Australia Geol. Soc.*, 1906, **23**, 71.

[2] *Loc. cit.*, § V, (*a*).

Second Portion.—

Fuse 1 grm. with KOH (Ag crucible), take up with dilute HCl, filter.

R^1 : digest with $(NH_4)_2CO_3$, filter.

R^2 : digest with $(NH_4)_2S$, filter.

F^2 : reject.

F^3 : reject.

R^3 : digest with dilute HNO_3, filter.

R^4 : ignite, weigh ; treat with $HF+H_2SO_4$, ignite with $(NH_4)_2CO_3$, weigh again ; loss = 1st silica.

F^4: reject.

F^1 : evaporate to dryness, take up with dilute HCl, filter.

F^5 : pass H_2S, filter.

R^5 : ignite and weigh 2nd silica.

P^6 : reject.

F^6 : oxidise with HNO_3, ppte with NH_4OH+Br, filter.

P^7 : dissolve in HCl, boil, add oxalic acid, filter.

F^7 : determine Ca, Mg.

F^8 : barely neutralise with NH_4OH, pour into excess of $(NH_4)_2CO_3$, add $(NH_4)_2S$, filter.

P^8 : rare earth oxalates (see Rare Earths, § VI.).

P^9 : determine Fe, Al, Mn. Separate and reject Ti (Titanium, § III, (*a*), (*d*)).

F^9 : acidify with HCl, boil, ppte with NaOH, filter.

P^{10} : dissolve in dilute H_2SO_4, adjust acidity to 1 per cent., add Na_2HPO_4 in excess, and H_2O_2. Filter next day.

F^{10} : acidify with HCl, ppte with NH_4OH, ignite, weigh BeO.

P^{11} : fuse with Na_2CO_3, extract with H_2O, fuse residue with bisulphate, dissolve, ppte with NH_4OH ; ignite, weigh ZrO_2.

F^{11} : boil to destroy H_2O_2, make alkaline with NH_4OH, acidify with H_2SO_4, add 5 grm. $Na_2S_2O_3$, boil, add 10 c.c. $CH_3CO_2NH_4$. Filter, ignite, weigh $(UO_2)_2P_2O_7$.

Third Portion : for Cu, Pb, Bi, if present.—Digest 1 grm. of slimed mineral with hot HCl. If much remains undecomposed, add a little HF. Evaporate with HNO_3 (in porcelain), expel bulk of acid, dilute, filter, reject residue. Pass H_2S, determine Cu, Pb, Bi in precipitate.

Fourth Portion : for S, if present.—Oxidise with HNO_3+KClO_3, evaporate with HCl, filter, treat filtrate as usual for SO_3.

(*b*) If the ore under investigation is monazite sand, see Rare Earths, § VII, (*a*).

CHAPTER VIII.

THE SIXTH GROUP.

SELENIUM—TELLURIUM—MOLYBDENUM—TUNGSTEN—URANIUM.

GENERALITIES.

THE sixth group contains five rarer elements, the constitution of whose highest stable oxides corresponds to the formula MO_3. Apart from this common property, their chemical behaviour justifies a subdivision into three sub-groups.

In the odd series, selenium and tellurium are closely related to each other and to sulphur. This is brought out, *inter alia*, in the similarity between sulphide, selenide, and telluride minerals. Selenium, like sulphur, is non-metallic and acid-forming. Tellurium is more metallic, and though the trioxide is the anhydride of a strong acid, the dioxide acts also as a weak base, giving unstable salts with nitric or sulphuric acid.

Molybdenum and tungsten are placed in the even series. Their trioxides are distinctly acidic, and readily dissolve in weak alkali even after ignition. They form with many other elements a large number of acid complexes, the most familiar of which is phosphomolybdic acid. In their relationship to each other molybdenum and tungsten are not unlike columbium and tantalum, their respective neighbours in the Table.

The properties of uranium assign to it a separate place. The trioxide has acidic properties, and combines with alkalies forming diuranates, which have the same formula as the dichromates; they are, however, insoluble in water. On the other hand, the trioxide behaves as a base in presence of acids, and in exchanging one atom of oxygen against an acid radicle gives rise to the most important series of uranium salts; these contain the bivalent radicle *uranyl* $(UO_2)''$, which is very stable. By reduction they are converted into uranous salts, in which the metal is quadrivalent.

SELENIUM.

§ I. Minerals.—(*a*) *Selenides.*—(1) *Clausthalite*, lead selenide, **PbSe**, is lead-grey, metallic, and resembles granular galena, with which it is isomorphous. Streak dark grey, cleavage cubic. H 3; sp. gr. 7·6–8·8. In *Naumannite*, silver predominates over lead.

(2) *Tiemannite*, mercury selenide, HgSe; dark grey, streak black; isometric. H 2·5; sp. gr. 8·2.

(3) *Guanajuatite* (*Frenzelite*), bismuth selenide, Bi_2Se_3; isomorphous with stibnite. Bluish-grey, shining grey streak. H 2·5; sp. gr. 6·2.

(4) *Berzelianite*, cuprous selenide, Cu_2Se. Silver-white, shining streak. Sp. gr. 6·7.

(5) *Crookesite*, $(Cu,Tl,Ag)_2Se$. See Thallium, § I.

(*b*) *Other Minerals.*—(1) *Chalcomenite*, hydrous cupric selenite, $CuSeO_3.2H_2O$. Bright blue transparent monoclinic crystals.

(2) *Selen-tellurium.* See Tellurium, § I.

(3) *Selen-sulphur* occurs in orange-red to brown crusts, containing the two elements in variable proportions. Native selenium, which is rare, contains a small proportion of sulphur, while native sulphur almost invariably contains minute amounts of selenium.

(4) Very small quantities of selenium occur in most sulphide minerals, such as pyrites and copper ores. The element is therefore found in by-products from metallurgical operations, such as flue-dusts, sulphuric acid-chamber mud, and electrolytic copper, etc., refinery sludge.

§ II. Properties and Compounds.—(*a*) The *element* is known in several allotropic modifications analogous to those of sulphur. The red, amorphous or colloidal, variety is produced by the reduction of selenious acid in the cold; it is soluble in carbon disulphide, as is also the vitreous form, obtained by rapid cooling from 217°. The solution in carbon disulphide deposits red crystalline selenium, which can be obtained in two modifications, both monoclinic, one of which is isomorphous with sulphur. Sp. gr. 4·47; M.P. 170°–180°. When fused it rapidly passes over into the black metallic variety, the temperature rising to 217°, the melting-point of the latter; sp. gr. 4·8; hexagonal, isomorphous with tellurium. B.P. 680°. The colour of the vapour is dark red, and its density, like that of sulphur vapour, decreases rapidly as the temperature increases. The metallic form conducts electricity, and its conductivity is transiently increased during exposure to light; in the dark, the resistance gradually returns to its former maximum. Nitric acid converts selenium into selenious acid.

(*b*) *Selenium dioxide*, SeO_2. Selenium burns in air or oxygen with a blue flame, when the dioxide is formed and can be collected in the form of a white sublimate. The crystals are needle-shaped, and are converted without melting into a greenish-yellow vapour at about 300°.

(*c*) *Selenious acid*, H_2SeO_3, formed by the action of nitric acid on the element, is a colourless solid soluble in water. The solution is reduced by sulphur dioxide, hydriodic acid, hydroxylamine, or ferrous sulphate, with precipitation of red selenium. Neutral and acid selenites are known.

(*d*) *Selenic acid*, H_2SeO_4, crystallises in colourless prisms, which melt at 58°. It has a great affinity for water, with which it forms a monohydrate (M.P. 25°). To prepare the acid, selenium or selenious acid is treated with chlorine in presence of water:

$H_2SeO_3+Cl_2+H_2O \rightleftharpoons H_2SeO_4+2HCl$. This reaction being reversible, selenic acid (as well as its salts) is reduced when heated with strong hydrochloric acid, but it is not affected by sulphur dioxide. The reduction to selenium must therefore be done in two stages.

(*e*) *Barium selenate*, $BaSeO_4$, bears a very close resemblance to barium sulphate; it is, however, reduced and rendered soluble by boiling with hydrochloric acid (*d*).

(*f*) *Selenosulphur trioxide*, $SeSO_3$. Selenium dissolves with green colour in strong sulphuric acid, the above compound being formed. The green solution upon addition of water is decolorised, and red selenium precipitated.

(*g*) *Hydrogen selenide*, H_2Se, prepared from iron or potassium selenide and hydrochloric acid, is a colourless, poisonous gas of most offensive odour. It precipitates selenides when passed through solutions of heavy metals. Decomposes at 150°.

(*h*) Although selenious acid yields a yellow precipitate with hydrogen sulphide, no definite sulphide of selenium appears to have been prepared. The precipitate, which is a mixture of selenium and sulphur, is soluble in alkaline sulphides.

(*i*) *Potassium selenocyanate*, KCNSe, is formed when amorphous selenium is dissolved in potassium cyanide solution, or by fusion of the element or its compounds with the salt in a hydrogen current. The aqueous solution is decomposed by hydrochloric acid, selenium being precipitated.

§ III. Quantitative Separation.—The separation of selenium from most elements is based upon the following properties: precipitation by sulphur dioxide or hydrogen sulphide; solubility of the element in cyanide solution or nitric acid, and its volatility in a chlorine current; formation of sodium selenate by fusion with carbonate and nitrate.

(*a*) *Separation from Gold.*—The elements precipitated by sulphur dioxide are boiled with dilute nitric acid, selenium dissolving; the filtrate is evaporated with hydrochloric acid and sodium or potassium chloride (to prevent loss of selenium by volatilisation), and again precipitated with sulphur dioxide.

(*b*) *Separation from Silver.*—The nitric acid solution is treated with a slight excess of hydrochloric acid to precipitate silver chloride; the filtrate is treated as under (*a*).

(*c*) *Separation from Arsenic, Antimony, and Tin.*—The chloride solution containing one-third of its volume of strong hydrochloric acid is precipitated with sulphur dioxide and the selenium collected on a tared filter. In presence of much antimony, the addition of tartaric acid is necessary.

(*d*) *Separation from Lead, Copper, and Alkaline Earths.*—The material is fused with a mixture consisting of two parts of sodium carbonate and one of nitrate; the filtered solution of the melt, containing sodium selenate, is evaporated with hydrochloric acid, and the selenite thus formed reduced to selenium by sulphur dioxide or sodium sulphite.

(*e*) *Separation from large quantities of Copper.*[1]—Small quantities of selenium (and tellurium) in presence of large amounts of copper are precipitated as ferric selenite (tellurite) by adding 0·25 grm. of iron, dissolved in nitric acid, to the nitrate solution, and precipitating hot with ammonia. The copper is removed by washing, followed by solution and re-precipitation. The ferric hydroxide is dissolved in hydrochloric and tartaric acids, the solution made alkaline with caustic potash, and precipitated with hydrogen sulphide. The filtrate is acidified with hydrochloric acid, and left in a warm place until hydrogen sulphide is expelled. The precipitate is dissolved in *aqua regia*, the liquid evaporated with hydrochloric acid after addition of a little sodium chloride, the residue taken up with 10 c.c. of hydrochloric acid (1·175) and 15 c.c. of water, and the solution saturated with sulphur dioxide. Selenium and tellurium are separated according to (*k*).

(*f*) *Separation from Bismuth.*—(1) The slightly acid chloride solution is diluted with water to precipitate bismuth oxychloride; the filtrate is concentrated and precipitated with sulphur dioxide. (2) The precipitated elements are digested with cyanide solution to extract selenium.

(*g*) *Separation from Mercury.*—By treating the strongly acid chloride solution with ferrous sulphate, selenium is precipitated.

(*h*) *Separation from Metals of the Ammonia and Alkaline Earth Groups.*—Hydrogen sulphide is passed through the solution acidified with hydrochloric acid. The precipitate is digested with cyanide, or dissolved in *aqua regia*, etc., as under (*e*).

(*i*) *Separation from non-Volatile Elements.*—In presence of large quantities of fixed compounds small amounts of selenium and tellurium are conveniently recovered by heating the material in a chlorine current and passing the gas into a receiver containing 20 c.c. of hydrochloric acid (1·175) and 30 of water. Chlorine is expelled by heating the liquid, which is then treated with sulphur dioxide.

(*j*) *Separation from Sulphur.*—The elements are oxidised with potassium chlorate and nitric acid, the resulting liquid being freed from nitric by evaporation with hydrochloric acid. Selenium is then precipitated by sulphur dioxide or potassium iodide. If the sulphur also is to be determined, the hydrochloric liquor containing sulphuric and selenious acid is precipitated with barium chloride as usual; the excess of barium in the filtrate is removed by sulphuric acid, after which selenium is precipitated as indicated above.

(*k*) *Separation from Tellurium.*—(1) The precipitated elements are digested for eight hours with potassium cyanide solution on a steam-bath to extract selenium. The bulk of the tellurium remains unaffected, but a small part goes into solution as tellurite. The filtered solution is treated with excess of hydrochloric acid and left to stand in a warm place, when the selenium is slowly deposited. The liquid should stand one to several days before filtering. The small quantity of dissolved tellurium is recovered by warming the filtrate from the selenium with

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[1] Whitehead, *Journ. Amer. Chem. Soc.*, 1895, **17**, 280.

sulphur dioxide and filtering after twenty-four hours; this precipitate is added to the insoluble residue from the cyanide treatment.[1]

The above process is more satisfactory than fusion with cyanide and precipitation of tellurium by the passage of air through the solution of the melt, as part of the tellurium is oxidised and escapes precipitation.

(2) The chloride solution, containing at least four-fifths its bulk of strong hydrochloric acid, is saturated with sulphur dioxide: selenium alone is precipitated.[2] The filtrate is diluted with an equal volume of water and again saturated with sulphur dioxide: tellurium is now thrown down. Each precipitate is collected on a tared filter, washed, dried and weighed.

(3) Another method, involving the use of more elaborate apparatus, is based upon the greater volatility of selenium tetrabromide over that of the tellurium compound.[3] The process is not so suitable for ore analysis as the two preceding.

§ IV. Gravimetric Determination.—Selenium is always weighed as the element; the weighing is carried out on a tared filter.

(*a*) If nitric acid is present in the solution to be precipitated it must be expelled by several evaporations with hydrochloric acid, the volatilisation of selenium being prevented by addition of alkali chloride. Selenic acid must first be reduced to selenious by the same treatment. The liquid, containing at least 30 per cent. of its bulk of hydrochloric acid (1·175), is treated with sulphur dioxide or sodium bisulphite at boiling heat (fifteen minutes), when the red precipitate is converted into the black modification, which is easier to filter and wash. The filtrate is again reduced to make sure that precipitation is complete.

(*b*) Reduction may also be accomplished by means of potassium iodide (3 grm. excess) in not less than 400 c.c. of solution acidified with hydrochloric acid.[4] The liquid is boiled ten to twenty minutes to expel iodine and effect the change to black selenium. Selenic acid is reduced by iodide on warming, hence for this compound the process is more rapid than the preceding.

(*c*) From solutions containing selenocyanate the element is precipitated by adding an excess of hydrochloric acid, heating for some time, and filtering after one to several days. When seleniferous material is fused with cyanide in hydrogen, the solution of the melt contains a little selenide in addition to selenocyanate. In this case the liquid is boiled for some time previous to acidification, whereby the selenide is converted into selenocyanate. Without this precaution, a small part of the selenium would escape as hydrogen selenide.

(*d*) The determination as barium selenate is not to be recommended. The precipitate is more soluble, and has greater adsorbtive power for salts, than barium sulphate.

§ V. Volumetric Determination.—(*a*) *Iodometric Determination of*

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[1] Crookes, *Select Methods*, 1905, 417.
[2] Keller, *Journ. Amer. Chem. Soc.*, 1897, **19**, 771.
[3] Gooch and Peirce, *Amer. Journ. Sci.*, 1896, **1**, 181.
[4] Peirce, *Amer. Journ. Sci.*, 1896, **1**, 416.

Selenious Acid.—(1) Selenious acid reacts with iodide in acid solution according to the equation $SeO_2+4HI=Se+2H_2O+4I$. The usual procedure (*i.e.* distillation of the liberated iodine) yields slightly low results, because a little iodine fails to volatilise. Hence Gooch and Peirce[1] allow a known excess of iodide to react on selenious acid in presence of more than sufficient arsenic acid to decompose the excess iodide: $H_3AsO_4+2HI=H_3AsO_3+H_2O+I_2$. After the iodine has been boiled off, the arsenious acid formed is determined by iodine solution: the balance of the iodine liberated by selenious acid is thus found by difference.

The process is carried out in a 300 c.c. conical flask; to the solution of selenious acid are added a measured volume of potassium iodide solution—a solution containing about 2 grm. of acid potassium arsenate, and 20 c.c. sulphuric acid (1 : 1). The liquid is boiled down from about 100 to 35 c.c., cooled, almost neutralised with caustic potash, made alkaline with excess of 20 c.c. of strong potassium bicarbonate solution, and titrated with N/10 iodine. An equal volume of the potassium iodide solution used in the determination is now titrated with N/10 thiosulphate in presence of excess of potassium arsenate and sulphuric acid. The difference between the second and the first titration gives the quantity of iodine (in terms of c.c. N/10 solution) liberated by the selenious acid. N/10 wt. of $SeO_2=0{\cdot}00278$ grm. per c.c.

(2) Norris and Fay[2] digest an acid solution of selenious acid with a known excess of thiosulphate, when one molecule of SeO_2 acts on four of $Na_2S_2O_3$, somewhat similarly to iodine:

$$H_2SeO_3+4Na_2S_2O_3+4HCl=Na_2S_4SeO_6+Na_2S_4O_6+4NaCl+3H_2O.$$

The excess of thiosulphate is measured with iodine.

The solution of selenious acid is diluted with ice-water, treated with 10 c.c. of hydrochloric acid (1·12) and a measured excess of N/10 thiosulphate solution, and left to stand for twenty-four hours. The liquid is then titrated with N/10 iodine solution. The iodide contained in the iodine solution must be free from iodate, and the thiosulphate solution free from sulphite: the latter must consume the same amount of iodine solution in acid as in neutral solution. The results obtained are highly concordant.

(*b*) *Determination of Selenic Acid.*—Selenic is first reduced to selenious acid, which latter is then titrated as explained before.

(1) In applying the method given under (*a*) (1), the solution of selenic acid must be boiled with 1 grm. of potassium bromide and 20 c.c. of sulphuric acid (1 : 1) until the volume has been reduced to about 35 c.c. and the liquid, after decoloration, again becomes coloured. The cooled solution is then treated with potassium iodide and arsenate, etc., as above. Selenious acid is more readily reduced, but selenic less so, by iodide than arsenic acid.

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[1] *Amer. Journ. Sci.*, 1896, **1**, 31.

[2] *Amer. Chem. Journ.*, 1896, **18**, 703; 1901, **23**, 119.

(2) For the determination of selenic acid by the thiosulphate method (*a*) (2), the solution containing 25 c.c. of strong hydrochloric acid and diluted to 100 c.c. is boiled for one hour, care being taken to keep the volume above 75 c.c. The solution is then cooled, diluted with ice-water, and digested with thiosulphate.

(*c*) *Simultaneous Determination of Selenious and Selenic Acids.*—Selenic acid is without action on thiosulphate, hence selenious acid can be determined in its presence according to (*a*) (2). Another portion of the solution is reduced as under (*b*) (2), giving total selenium in terms of SeO_2. The excess of SeO_2 found in the second titration is calculated to SeO_3.

§ **VI. Colorimetric Determination.**—Several processes are in use for determining selenium colorimetrically. They are based on the conversion of selenious acid into amorphous or colloidal selenium by means of various reducing agents (*e.g.* stannous chloride; see § VIII, (*c*)) and comparison of the reddish tint with that produced by a solution of selenious acid of known strength. The method of Meyer and von Garn,[1] described below, is the most sensitive, as the colour is intensified by the separation of iodine, which takes place when selenious and hydriodic acids interact (§ V, (*a*)). Five c.c. of the solution under investigation, and a similar volume of a standard solution, are transferred to Nessler tubes provided with a stopcock near the bottom. To each cylinder are added 70 c.c. of purest distilled water, one drop of protective colloid (gum arabic), and 5 c.c. of 5 per cent. hydrochloric acid. After making up to 99 c.c. and stirring well, 1 c.c. of 50 per cent. potassium iodide is mixed in, the tints being matched after five minutes' standing by withdrawing a suitable quantity of liquid from the tube in which the colour is strongest into a measuring cylinder. 0·0001 grm. of SeO_2 can thus be determined in 100 c.c. of solution.

§ **VII. Detection in Ores.**—(*a*) A particle of a mineral rich in selenium, heated on charcoal in the reducing flame, emits fumes of a penetrating odour, commonly compared to that of putrid horse-radish.

(*b*) The ore, or the portion of the hydrogen sulphide precipitate soluble in sodium sulphide, is fused with sodium carbonate and nitrite; the melt is dissolved in water, and the filtered solution boiled with an excess of hydrochloric acid to expel nitrous fumes and reduce the selenate to selenite. The cooled solution is saturated with sulphur dioxide, red selenium being precipitated. At the boiling-point of the liquid the black modification will separate, but selenium is soluble in strong sulphuric acid with green colour; this solution becomes colourless upon dilution, and selenium is precipitated in form of the red modification. (Distinction from tellurium.)

(*c*) The mineral (or the precipitate, as under (*b*)) is fused with potassium cyanide in a current of hydrogen. The filtered solution of the melt after addition of excess of hydrochloric acid gradually deposits a red precipitate.

(*d*) Ores poor in selenium may be heated in a chlorine current in a glass tube, the drawn-out end of which dips into dilute hydrochloric acid.

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[1] *Z. anal. Chem.*, 1913, **53**, 29.

The heat is applied for an hour, gently at first, later at dull redness, after which the acid solution is saturated with sulphur dioxide and left to stand overnight if necessary. A red precipitate proves presence of selenium.

(*e*) For the simultaneous detection of selenium and tellurium the precipitate produced by sulphur dioxide (see (*b*) and (*d*)) is digested with cyanide solution: selenium is dissolved, and re-precipitated from the filtrate by acid, as under (*c*); the black residue is tested for tellurium as explained under Tellurium, § VI, (*a*).

§ **VIII. Determination in Ores.**—(*a*) A method of general applicability consists in fusing the ore with sodium carbonate and nitrate, leaching, filtering, acidifying with hydrochloric acid, and evaporating to destroy nitrates and reduce selenates. The residue is taken up with hydrochloric acid (1 : 2 water), and the hot solution saturated with sulphur dioxide. By substituting sodium nitrite or peroxide for nitrate in the flux, the evaporation of the solution with hydrochloric acid is obviated: simple boiling with the latter suffices to destroy the oxidiser. In practice the usefulness of the method is limited, as it is not convenient for the determination of small quantities of selenium in common sulphide ores: a large amount of ore must be taken, and this requires considerable flux and a crucible of inconvenient size, while the concentration of sodium chloride in the solution to be reduced with sulphur dioxide is such that a bulky precipitate of this salt would be produced if the solution were acidified sufficiently to effect separation from tellurium (see § III, (*k*) (2)).

(*b*) For ores containing the selenium as selenide (*i.e.* the great majority of cases) the volatilisation method may be adopted. This consists in heating the ore, contained in a combustion tube, in a current of chlorine. The heat should not exceed dull redness; the treatment is continued for an hour. The gas is made to traverse two receivers placed in series, containing dilute hydrochloric acid (1 : 1), in which the selenium collects. The acid is then heated on a water-bath to expel chlorine, after which the acidity is adjusted so that the liquid contains four-fifths of its bulk of strong hydrochloric acid (§ III, (*k*) (2)). The hot liquor is saturated with sulphur dioxide (§ IV, (*a*)). Other elements are also (at least partly) volatilised as chlorides, chiefly arsenic, antimony, bismuth, iron, vanadium, sulphur: they do not interfere with the gravimetric estimation of selenium by precipitation with sulphur dioxide; neither does tellurium, which, though completely volatilised, is not reduced in the strongly acid liquor.

(*c*) *Determination of small quantities of Selenium in Pyrites.*—The determination of selenium in pyrites is the most frequent case in metallurgical analysis. The two methods given below have been proposed:—

(1) Method of Grabe and Petren.[1]—Ten grm. are dissolved in *aqua regia*; when the ore is decomposed, 15 grm. of anhydrous sodium carbonate are dissolved in the acid, which is then taken to dryness. The

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[1] *Kemi och Bergsvetenskap*, 1910; *Journ. Soc. Chem. Ind.*, 1910, **29**, 945.

residue is digested and evaporated with 50 c.c. of strong hydrochloric acid (several times if necessary) to destroy all the nitric acid, after which the solution is made up to 100 c.c. and filtered. Should the residue and filtrate show any indication of a red colour (due to free selenium), the assay must be again treated with nitric acid, and the latter destroyed as before. The filtrate is warmed to about 50°, reduced with a saturated solution of stannous chloride in strong hydrochloric acid, and digested on a water-bath for two hours. The precipitated selenium is filtered on a small plug of asbestos, washed with warm hydrochloric acid (1·06), and returned to the beaker, where it is dissolved in 10 c.c. of strong hydrochloric and two drops of nitric acid. The solution is then warmed to expel all chlorine, diluted to 150 c.c., and treated with a measured excess of thiosulphate solution; this is determined by iodine (§ V, (*a*) (2)). The latter is made of such strength that 1 c.c.=1 mgrm. Se (6·4 grm. per litre).

Instead of proceeding as described for the volumetric assay, the solution of selenious acid (obtained by dissolving the selenium in hydrochloric and two drops of nitric acid) is precipitated by stannous chloride in the cold; the red colour of the colloidal selenium is matched against a standard solution of selenious acid, treated in the same manner. (Tellurium interferes with the colorimetric determination.)

(2) According to Klason and Mellquist,[1] the ore is dissolved in hydrochloric acid and potassium chlorate. After eliminating free chlorine, the insoluble gangue is removed by filtration, and the iron reduced with zinc. More hydrochloric acid is added, and the selenium precipitated with stannous chloride at boiling heat. It is filtered on asbestos, washed with hydrochloric acid, dissolved in cyanide solution, and re-precipitated by adding hydrochloric acid and passing sulphur dioxide. Any arsenic is thus left in solution and separated from selenium. The latter is filtered on a plug of asbestos contained in a hard-glass filtering tube 28 cm. long. After washing, the tube and its contents are dried, a second asbestos plug inserted in the other end, and a slow current of oxygen passed through the tube while the selenium is gently heated and driven towards the other end. The oxygen current is then reversed, and the selenium again driven back by gentle heating; this operation is to be repeated until the sublimate shows a pure white colour. It is next dissolved in water (100–300 c.c.), the latter allowed to flow into a glass-stoppered flask, and two to ten drops of hydrochloric acid added, according to bulk. After warming on the water-bath the air is expelled from the flask by carbon dioxide, and potassium iodide (2–5 grm.) added. This is dissolved by shaking the stoppered flask, which is then cooled and left to stand an hour in the dark. The liberated iodine is titrated with N/100 thiosulphate (1 c.c.=0·000198 grm. Se). Tellurium does not interfere in this process, as the dioxide is insoluble in water and remains behind in the filtering tube.

§ IX. Complete Analysis of Ores.—See Tellurium, § VIII.

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[1] *Arkiv Kem., Min. Geol.*, 1911, 1912; *Journ. Soc. Chem. Ind.*, 1912, **31**, 331.

TELLURIUM.

§ I. Minerals.—(*a*) *Gold* (*Silver*) *Tellurides.*—(1) *Sylvanite* (graphic tellurium), $(Au,Ag)Te_2$, steel-grey to silver-white monoclinic crystals of metallic lustre. H 1·5–2 ; sp. gr. 7·9–8·3.

(2) *Calaverite* contains more gold than sylvanite. Pale yellow. H 2·5 ; sp. gr. 9.

(3) *Petzite*, $(Ag,Au)_2Te$, is iron-grey to black ; lustre metallic. H 2·5–3 ; sp. gr. 8·7–9·0. As the amount of gold decreases, it graduates into *hessite*, Ag_2Te.

(4) *Nagyagite*, perhaps $(Au,Pb)_2(Te,S,Sb)_3$; dark lead-grey colour and streak. H 1–1·5 ; sp. gr. 6·8–7·2.

(*b*) *Base-metal tellurides.*—(1) *Altaite*, lead telluride, PbTe, is tin-white, of metallic lustre, and cubic habit and cleavage. H 3 ; sp. gr. 8·2.

(2) *Coloradoite*, mercuric telluride, HgTe. Iron-black, metallic appearance. H 3 ; sp. gr. 8·6.

(3) *Tetradymite*, bismuth sulphotelluride, $Bi_2(Te,S)_3$. Steel-grey hexagonal crystals ; marks paper. H 1–2 ; sp. gr. 7·4.

(*c*) *Other Minerals.*—(1) *Tellurium* occurs native ; the crystals are hexagonal, of tin-white streak and colour. H 2–2·5 ; sp. gr. 6·2.

(2) *Selen-tellurium*, Te_3Se_2, is hexagonal, like the preceding. Dark grey, streak black.

(3) *Tellurite* (telluric ochre), impure TeO_2 ; yellowish, earthy.

(4) Tellurium is generally associated with gold, silver, and bismuth ores, but minute quantities are found, like selenium, in copper ores, and likewise find their way into the anode mud.

§ II. Properties and Compounds.—(*a*) The *element* may be obtained amorphous, by reduction of tellurous or telluric acid solutions, as a black precipitate. On heating, it changes into the crystalline variety, which is silver-white and of metallic appearance, but very brittle. Sp. gr. 6·27 ; M.P. 452°. It boils at about 1400°, giving a golden-yellow vapour. Insoluble in carbon disulphide, soluble in nitric (*c*) or strong sulphuric (*e*) acid.

(*b*) The *dioxide*, TeO_2, is formed when tellurium burns in the air ; it is a white crystalline mass, only very slightly soluble in water, which can be fused and sublimed.

(*c*) *Tellurous acid*, H_2TeO_3. The solution of tellurium in nitric acid contains an unstable nitrate and, when caused to crystallise out, deposits small octahedra of tellurium dioxide. If the nitric acid solution is poured into water, a voluminous white precipitate of tellurous acid is obtained. Its solubility in water is very slight. The solution is reduced by sulphur dioxide (but not by ferrous sulphate), tellurium being precipitated.

(*d*) *Telluric acid*, $H_2TeO_4.2H_2O$ or H_6TeO_6, is prepared by dissolving tellurium in a mixture of nitric and chromic acids, and purifying the crystalline mass by solution in water and re-precipitation with nitric acid. The crystals lose water at 160°, being converted into a white powder of allotelluric acid, $(H_2TeO_4)_n$. This is very slowly soluble in water, producing a solution of the hydrated acid. Sulphur dioxide or hydrogen sulphide reduce it to tellurium, hot hydrochloric acid to tellurous acid (*cf.* Selenic acid). Tellurates are formed by the action of chlorine on tellurite solutions.

(*e*) *Tellurium sulphoxide,* $TeSO_3$. Tellurium dissolves in warm strong sulphuric acid, forming a red solution which contains the above compound. On further heating this is oxidised with formation of a colourless unstable sulphate, but the addition of a little tin-foil restores the red colour. The red solution is decolorised by dilution with water, black tellurium being precipitated.

(*f*) *Hydrogen telluride,* H_2Te, is formed by the action of acids upon certain tellurides. Its properties are similar to those of hydrogen selenide, but it is much more unstable, decomposing at 0°.

(*g*) A definite sulphide of tellurium has not been isolated from the precipitate produced by hydrogen sulphide in solutions of tellurium compounds. The precipitate is soluble in alkaline sulphides.

(*h*) *Potassium telluride,* K_2Te, is present in the melt resulting from the fusion of tellurium with potassium cyanide. The solution in water has a reddish colour; when air is conducted through it, tellurium is precipitated. Unlike selenium, tellurium is insoluble in cyanide solution.

(*i*) The substance known as *radio-tellurium* is an isotope of tellurium, which has been identified as radium F (polonium).

§ III. Quantitative Separation.—The methods applicable to the separation of tellurium as well as selenium from the following elements have been discussed under Selenium, § III.: copper, arsenic, tin, sulphur, metals of the ammonia-ammonium sulphide and alkaline earth groups, and non-volatile elements. The separation from selenium is given in the same paragraph (*k*). Processes by which tellurium is separated from those elements with which it is ordinarily associated are given below.

(*a*) *Separation from Gold.*—(1) The elements precipitated by sulphur dioxide are digested with nitric acid, tellurium dissolving. (2) Gold alone is precipitated by ferrous sulphate or oxalic acid from the acid chloride solution free from nitric acid. The filtrate is reduced with sulphur dioxide to precipitate tellurium.

(*b*) *Separation from Silver.*—This metal is precipitated as chloride from the nitrate solution. Sufficient nitric acid must be present to prevent the precipitation of tellurous acid. For the treatment of the filtrate, see § IV, (*b*).

(*c*) *Separation from Antimony.*—Precipitation with sulphur dioxide yields tellurium contaminated with antimony. A good separation[1] is effected by passing hydrogen sulphide through the solution containing hydrochloric and tartaric acids, the gas being made to act for several hours. The precipitate is dissolved in a small excess of warm

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[1] Muthmann and Schröder, *Z. anorg. Chem.*, 1897, **14**, 433.

potassium sulphide, the solution poured into hot hydrochloric acid (sp. gr. 1·100) containing tartaric acid, and digested some time. The precipitate consisting of tellurium and sulphur is filtered off, and washed with 20 per cent. hydrochloric followed by tartaric acid. It is treated with fuming nitric acid, the tellurium being weighed as dioxide (§ IV, (*a*)).

(*d*) *Separation from Lead.*—The nitric acid solution is made alkaline with caustic soda, and precipitated with hydrogen sulphide. The filtrate from the lead sulphide is acidified, and left to settle for some time; the precipitate contains the tellurium mixed with sulphur, and antimony if the latter was originally present (see (*c*)).

(*e*) *Separation from Bismuth.*—(1) Bismuth is precipitated as oxychloride by diluting the hydrochloric acid solution with a sufficiency of water.

(2) The tellurium precipitate obtained by sulphur dioxide from a mixed solution (such as is obtained when minerals containing tellurium and bismuth are heated in a current of chlorine) is contaminated with bismuth, from which it can be freed by solution in nitric acid, evaporation with hydrochloric acid, and re-precipitation with sulphur dioxide.

(*f*) *Separation from Mercury.*—By the action of phosphorous acid on the cold dilute solution of the chlorides, the mercury is removed as mercurous chloride. The filtrate is treated with sulphur dioxide (IV, (*b*)).

§ IV. Gravimetric Determination.—(*a*) Tellurium is weighed either as such, after having been collected and dried on a tared filter; or as the dioxide, which is obtained by dissolving the sulphur dioxide or hydrogen sulphide precipitate in nitric acid (2 : 1 water) containing a few drops of sulphuric; this solution is evaporated to dryness and the residue gently ignited in a weighed porcelain dish or crucible.

(*b*) The precipitation of the element by sulphur dioxide must be preceded by evaporation with hydrochloric acid (with addition of alkali chloride if not already present) if any nitric acid is present in the solution. The residue is dissolved in dilute acid containing neither more than 50 nor less than 30 volumes of hydrochloric acid (1·175) per cent.[1] Small quantities of tellurium settle out after several days' standing. The precipitate is washed with sulphur dioxide solution, then water.

(*c*) Tellurium is also precipitated in the metallic state when an alkaline solution of tellurous acid is heated for about twenty minutes with pure glucose;[2] the precipitation takes less time than by the preceding method, but the glucose of commerce generally contains more or less calcium sulphate. A serviceable product may be obtained by inverting chemically pure cane-sugar.

§ V. Volumetric Determination.—(*a*) *Determination of Tellurous*

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[1] Keller, *loc. cit.*, p. 147.

[2] Stolba, *Z. anal. Chem.*, 1872, **11**, 437.

Acid.—(1) *Permanganate Methods.*—Tellurous is oxidised to telluric acid by permanganate, either in sulphuric acid or in alkaline solution. Chloride solutions must be evaporated with sulphuric acid on a steam-bath, then for a short time on a sand-bath.

(α) *In Acid Solution.*[1] —An excess (N c.c.) of N/10 permanganate is added to the cold solution acidified with sulphuric acid, followed by one-third to one-half the volume of permanganate in N/10 oxalic acid (x c.c.). On slight warming, decoloration occurs. The solution is then heated to 60°, and the excess of oxalic acid titrated with N/10 permanganate (n c.c.). The quantity of TeO_2 is calculated from the formula

$$N-(x-n)\frac{0\cdot007975}{1\cdot011},$$

in which the fraction represents the empirical value of 1 c.c. of N/10 permanganate, it having been found that a small, constant fraction of the oxygen takes no part in the reaction, but escapes as such.

(β) *In Alkaline Solution.*—Several modifications of this process have been worked out; they differ only in the manner in which the excess of permanganate is ascertained.

Brauner [2] adds excess of N/10 permanganate, acidifies with sulphuric acid, and decolorises by slight warming with N/10 oxalic acid (about one-half the volume of the added permanganate); the excess of oxalic acid is measured by N/10 permanganate at 60°. The calculation is made, using the same symbols as above (α), by means of the formula

$$N-(x-n)\frac{0\cdot007975}{1\cdot0035}.$$

The numerator is again the N/10 weight of TeO_2, and the denominator an empirical correction. By standardising the permanganate directly against pure tellurous acid no empirical factor is needed in the above processes.

Norris and Fay [3] direct adding an excess of 20 c.c. of 10 per cent. caustic soda to the tellurite solution, then a decided excess of N/10 permanganate. The liquor is diluted with 400 c.c. of ice-cold water and treated with 10 c.c. of 20 per cent. potassium iodide solution. Dilute sulphuric acid is then added until the solution just becomes clear, when it is titrated with N/10 thiosulphate. One c.c. N/10 permanganate $=0\cdot007975$ grm. TeO_2.

In the method elaborated by Gooch and Peters,[4] the iodine, liberated as in the preceding process, is titrated with arsenite solution, after the small amount of free sulphuric acid has been neutralised and a suitable excess of bicarbonate added. The end-point is marked by the disappearance of the yellow colour, no starch being added.

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[1] Brauner, *Monatshefte für Chemie*, 1892, **12**, 34.

[2] See preceding footnote.

[3] *Amer. Chem. Journ.*, 1898, **20**, 278.

[4] *Amer. Journ. Sci.*, 1899, **8**, 122.

(2) *Stannous Chloride Method.*[1]—Tellurous acid is reduced in hydrochloric acid solution by a measured volume of stannous chloride solution in excess: $TeCl_4+2SnCl_2=Te+2SnCl_4$; the latter is determined iodometrically.

The boiling hot acid solution contained in a 100 c.c. graduated flask is treated with stannous chloride until a further addition of the reagent fails to produce a precipitate and the liquid clears. The volume is made up with cold boiled water, a little bicarbonate being added to expel air from the neck of the flask. While the latter is being cooled in water, the stannous chloride solution is standardised against N/20 iodine. When cold, the volume is once more adjusted, and an aliquot part titrated with the iodine solution. If the finely divided tellurium does not settle, it must be filtered off. This is best done in a filtering tube containing carbon dioxide, the filtrate being received in a flask filled with the gas. As the stannous chloride undergoes oxidation to a slight extent during the operation, a blank assay is put through the whole process under identical conditions, and the difference between the standard and the blank added to the volume of iodine consumed by the excess stannous chloride. One c.c. N/20 iodine solution $=0{\cdot}001994$ grm. TeO_2.

(*b*) *Iodometric Determination of Telluric Acid.*[2]—The direct reduction of telluric acid by iodides does not give concordant results, but with bromides the reaction proceeds uniformly, thus: $TeO_3+2HBr=TeO_2+H_2O+Br_2$. The tellurate solution is distilled with 3 grm. of potassium bromide and 10 c.c. sulphuric acid (1 : 1) per 50 c.c. bulk. Two receivers placed in series contain a solution of 3 grm. of potassium iodide; the first is placed in cold water. The distillation is continued until the volume of the liquid has been reduced to 20 c.c.; the last of the bromine is expelled by a current of carbon dioxide. There should be no rubber connection between the distilling flask and the first receiver. The iodine in the distillate is titrated with N/10 thiosulphate, of which 1 c.c.$=0{\cdot}008775$ grm. TeO_3.

§ VI. Detection in Ores.—(*a*) Strong sulphuric acid when warmed with tellurium, or a picked particle of a telluride mineral, acquires a carmine colour. When the cold acid is diluted with water the colour is discharged and black tellurium precipitated (§ II, (*e*)). Oxidised tellurium minerals yield the same coloration if a small piece of tin-foil is added to the acid. Iron, if present, interferes with the test.

(*b*) The lead button obtained by crucible fusion, as in the gold-silver assay, is dissolved in dilute nitric acid. The solution is diluted and a bright strip of lead-foil inserted. Any black deposit is dried, rubbed off, and heated with sulphuric acid and tin-foil (see (*a*)). Alternatively, the acid solution is treated with enough ammonia to produce a slight precipitate. The latter, which contains the bulk of the tellurium, is heated with sulphuric acid and tin-foil.

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[1] Brauner, *Z. anal. Chem.*, 1891, **30**, 707.

[2] Gooch and Howland, *Z. anorg. Chem.*, 1894, **7**, 132.

(*c*) Ores poor in tellurium may be tested either by the preceding method or that given under Selenium, § VII, (*d*) (*i.e.* heating in a chlorine current). The dilute acid containing the volatilised chlorides is in this case nearly neutralised with soda or ammonia, saturated whilst warm with sulphur dioxide, and left to stand overnight. If a black precipitate has deposited, it is tested with sulphuric acid as under (*a*).

(*d*) *Simultaneous Detection of Tellurium and Selenium.*—Fusion of the ore (or the hydrogen sulphide precipitate) with sodium carbonate and nitrite is applicable to the detection of tellurium as well as selenium (Selenium, § VII, (*b*)); detection of both elements, *ibid.*, (*e*).

§ VII. Determination in Ores.—The first method here given effects a rapid separation of tellurium from heavy metals in complex rich telluride minerals, while the last is better adapted for the determination of very small quantities.

(*a*) 1–4 grm. of the finely ground ore is digested in a porcelain capsule with strong nitric acid. When decomposition is complete, the excess of acid is removed on a steam-bath. The dry mass is powdered, and digested for half an hour with strong caustic soda. Enough water is then added to prevent the tearing of the paper during filtration. The filtrate is boiled for twenty minutes with glucose, the tellurium being weighed as such or converted into TeO_2 [1] (see § IV.).

(*b*) *Fusion Method.*—The material is fused with alkaline carbonate, and nitrate or peroxide. If nitrate is used, the solution of the melt is to be evaporated to dryness two or three times with hydrochloric acid; with peroxide, boiling with the same acid suffices. The solution containing one-third its volume of hydrochloric acid (1·175) is precipitated with sulphur dioxide and left to stand one day or longer; the precipitate is filtered off and weighed on a tared paper. If selenium is also present, it must be extracted by boiling the precipitate with cyanide solution.

(*c*) The ore is attacked with *aqua regia*, and the nitric destroyed by evaporation with hydrochloric acid. The filtered solution containing one-third its volume of hydrochloric acid (1·175) is precipitated with sulphur dioxide, and the precipitate filtered off after thorough settling. It is dissolved in nitric acid, any residual gold being decanted off and washed. The clear liquor is evaporated to dryness, the residue taken up with a few drops of hydrochloric and tartaric acids, followed by a slight excess of caustic potash. This is saturated with hydrogen sulphide, and any insoluble bismuth sulphide filtered off. The filtrate is poured into strong hydrochloric acid (1·1) containing tartaric acid (§ III, (*c*)) and the liquid digested for some time. The precipitate is filtered off, washed first with hydrochloric acid, then with water, and extracted with cyanide solution to remove selenium. The residue is then converted into and weighed as TeO_2 (§ IV, (*a*)).

(*d*) *Volatilisation Method.*—This is carried out in a chlorine current,

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[1] Donath, *Z. angew. Chem.*, 1890, **3**, 216.

the ore being heated in a combustion tube. The temperature is kept low at first, then gradually raised to dull redness, and maintained there for an hour. The escaping gas is conducted through a receiver containing hydrochloric acid of the same strength as before (*b*) (*c*). When the tube has cooled down, any sublimate is taken up with the same acid, which is added to that from the receiver. The condensate is next freed from chlorine by boiling, and saturated hot with sulphur dioxide. The precipitate contains all the tellurium, and selenium if present; in addition, small quantities of bismuth and antimony may contaminate the precipitate, in which case it is worked up by solution in nitric acid, etc., as explained under (*c*); if these metals are absent, the precipitate is weighed or, if necessary, extracted with cyanide.

§ **VIII. Complete Analysis of Ores.**—The scheme here given is adapted to the analysis of complex mixtures of rich telluride or selenide minerals, and takes into account the possible presence of gold, silver, and thallium, as well as all the members of the hydrogen sulphide group except cadmium and tin. In the case of common sulphide ores, the complete analysis would be supplemented by a separate tellurium (selenium) determination on a more or less considerable quantity (*e.g.* 5–20 grm.) of the material.

First Portion.—

<table>
<tr><td colspan="6">1–2 grm. Decompose with $HCl+KClO_3$, boil off Cl, dilute, filter hot.</td></tr>
<tr><td colspan="2">R^1: digest with $(NH_4)_2CO_3$, filter.</td><td colspan="4" rowspan="3">F^1: adjust acidity so that solution contains one-third its bulk of HCl (1·175) (adding $C_4H_6O_6$ if necessary to keep up Sb). Saturate with SO_2, let stand till completely settled, filter, wash with dilute HCl.</td></tr>
<tr><td>R^2: extract with CH_3CO_2H, filter.</td><td>F^2: determine silver.</td></tr>
<tr><td>R^3: weigh insoluble gangue.</td><td>F^3: determine lead (see also P^{11}).</td></tr>
<tr><td colspan="2">P^4: digest with $HNO_3(+C_4H_6O_6)$, filter.</td><td colspan="4">F^4: warm to expel SO_2, add sufficient $C_4H_6O_6$ if not already present, excess of KOH, pass H_2S; filter.</td></tr>
<tr><td>R^5: weigh Au.</td><td>F^5: evaporate excess of HNO_3, add slight excess KOH, saturate with H_2S, filter.</td><td colspan="2">F^9: (Hg, As, Sb): boil with NH_4Cl, filter.</td><td colspan="2">P^9: dissolve in HNO_3, evaporate with H_2SO_4, dilute with 4 vols. of H_2O, filter.</td></tr>
<tr><td>P^6: pour into HCl (sp. gr. 1·1) containing a little $C_4H_6O_6$, digest hot till settled, filter.</td><td>P^6 (Bi): add to P^{12}.</td><td>P^{10}: determine Hg.</td><td>F^{10}: add F^7, determine As, Sb.</td><td>F^{11}: pass H_2S, filter.</td><td>P^{11}: $PbSO_4$ (test for Bi).</td></tr>
<tr><td>F^7 (Sb): add to F^{10}.</td><td>P^7: extract with KCN, filter.</td><td colspan="2">P^{12}: add P^6, determine Bi, Cu.</td><td colspan="2">F^{12}: boil off H_2S, neutralise, pass SO_2, add KI, filter.</td></tr>
<tr><td>R^8: weigh Te. Add small quantity of Te from F^8.</td><td>F^8: acidify with HCl, filter off and weigh Se. Recover small amount of Te from filtrate (Selenium, § III, (<i>k</i>)), add to R^8.</td><td colspan="2">P^{13}: TlI (see Thallium, § IV, (<i>a</i>)).</td><td colspan="2">F^{13}: determine Fe.</td></tr>
</table>

Second Portion.—Sulphur. See Selenium, § III, (*j*).

MOLYBDENUM.

§ I. Minerals.—(*a*) *Molybdenite*, the disulphide, MoS_2, is, up to the present, the only mineral of practical importance. It is readily identified by its physical properties, as it occurs in grey, soft, flexible scales which stain paper and are scratched by the finger nail. It bears a close resemblance to graphite, from which it is distinguished by its lighter colour and streak, but with greater certainty by its behaviour on heating, when it evolves sulphur dioxide and is converted into a yellow powder (trioxide). H 1–1½; sp. gr. 4·4–4·8.

(*b*) *Molybdine*, molybdic ochre, is usually described as molybdenum trioxide, but it generally contains iron, and is even regarded by some as a hydrated ferric molybdate. It does not occur independently, but accompanies molybdenite, from which it is derived by oxidation. It forms a yellowish powder or incrustations; sometimes it is fibrous or crystalline. Its colour is paler than that of tungstic ochre (*q.v.*); the latter, unlike molybdine, is insoluble in acids.

(*c*) *Wulfenite*, lead molybdate, $PbMoO_4$, will doubtless acquire economic importance. Soft, heavy, lustrous, of various shades of yellow, usually wax-yellow. Tetragonal; soluble in hydrochloric or nitric acid. H 3; sp. gr. 6–7.

(*d*) *Powellite* is calcium molybdate, tungsten partly replacing molybdenum: $Ca(Mo,W)O_4$. Isomorphous with wulfenite and scheelite, which it sometimes accompanies.

(*e*) Small quantities of molybdenum are sometimes found in iron and copper ores.

§ II. Properties and Compounds.—(*a*) The *metal* may be obtained by decomposing molybdenite in the electric furnace, or by reducing the trioxide with aluminium, hydrogen, or carbon. It is white, hard, and malleable; soluble in nitric or strong sulphuric acid. Sp. gr. 9·01; M.P. 2450°.

(*b*) *Sulphides.*—The *trisulphide*, MoS_3, is slowly precipitated by hydrogen sulphide in acid solution, the latter acquiring a blue colour. Precipitation is very incomplete when passing the gas in the usual manner, but it is readily accomplished by working under pressure. Dark brown powder, insoluble in dilute acids, soluble in alkaline sulphides. On gentle heating in a current of hydrogen it is converted into *disulphide*, MoS_2, which latter is reduced to metal at a higher temperature. On ignition in air, both sulphides furnish the trioxide.

(*c*) The *trioxide*, MoO_3, is an almost white powder, which becomes transiently yellow on heating. Unlike the corresponding tungsten compound, it is markedly volatile at the full heat of a Bunsen flame. It is soluble in ammonia and in caustic alkali. By boiling with potassium iodide and hydrochloric acid it is reduced to the *pentoxide*, Mo_2O_5, and a corresponding amount of iodine set free.

(*d*) *Molybdic acid*, H_2MoO_4, separates as a white precipitate when molybdate solutions are acidified; the precipitate is soluble in excess of acid as well as in alkali. The hydrochloric acid solution, when reduced with zinc, yields an oxide which corresponds approximately to the *sesquioxide*, Mo_2O_3. The yellow crystalline crusts which often deposit from the acid molybdate solution used for the determination of phosphoric acid consist of the monohydrate, $H_2MoO_4.H_2O$.

(*e*) *Ammonium Molybdates.*—The *normal salt*, $(NH_4)_2MoO_4$, is stable only in presence of an excess of ammonia, being decomposed by water into the *heptamolybdate*, $(NH_4)_6Mo_7O_{24}.4H_2O$. The latter forms large colourless crystals, and is the salt sold as "ammonium molybdate."

(*f*) *Lead molybdate*, $PbMoO_4$, precipitated from acetic acid solution by neutral lead acetate, is a cream-coloured crystalline powder, soluble in nitric, insoluble in dilute acetic acid. It remains unchanged on ignition.

(*g*) *Mercurous molybdate*, Hg_2MoO_4, is precipitated by mercurous nitrate from neutral molybdate solutions. It is white, soluble in nitric acid, and on ignition leaves molybdenum trioxide.

(*h*) *Ammonium phosphomolybdate*, $(NH_4)_3PO_4.12MoO_3$, is a bright yellow crystalline precipitate insoluble in nitric acid, formed when a large excess of ammonium molybdate solution acidified with nitric acid is added to a solution of an orthophosphate. The reaction cannot be applied to the quantitative determination of molybdenum, as excess of phosphate gives soluble complex compounds.

§ III. Quantitative Separation.—Molybdenum belongs to the hydrogen sulphide group, and the solubility of its sulphide in alkaline sulphide places it in the arsenic-antimony-tin sub-group. Hence it can be separated from elements of the next group (vanadium, chromium, phosphorus, etc.) by hydrogen sulphide under pressure (§ IV, (*a*)), and from the copper sub-group by sodium or ammonium sulphide. What remains to be considered is chiefly the separation of molybdenum from the members of its own sub-group.

(*a*) *Separation from Iron.*—(1) The following process is more convenient than separation by hydrogen sulphide. An acid solution of molybdic acid and ferric salt is nearly neutralised with caustic soda, and poured into hot 8–10 per cent. caustic soda solution (40–50 c.c. excess for 0·2 grm. of iron). The liquid is heated to boiling, the precipitate allowed to settle, filtered off, and thoroughly washed with hot water. With large quantities of either metal it is best to dissolve the ferric hydroxide in hydrochloric acid and repeat the precipitation. The alkaline filtrate is slightly acidified with hydrochloric acid, treated with ammonium acetate, and precipitated with lead acetate (§ IV, (*c*)).

(2) We have also applied double precipitation of small quantities of iron by means of ammonia with satisfactory results. If alkaline earths are also present, sodium carbonate is substituted for caustic soda or ammonia.

(*b*) *Separation from Sulphuric Acid.*—(1) The solution containing molybdate and sulphate is treated with enough hydrochloric acid to yield a 5 per cent. solution. This is heated to boiling and precipitated with 10 per cent. barium chloride solution added drop by drop. The precipitate is filtered off, and the filtrate boiled with sodium carbonate solution to eliminate the barium as carbonate; the filtrate from the latter is treated as under § IV, (*c*).

(2) The solution is treated for the direct precipitation of lead molybdate according to § IV, (*c*) (2).

(*c*) *Separation from Arsenic.*—(1) (Also applicable to phosphoric acid.) The solution containing molybdic and arsenic acids is made ammoniacal, precipitated with magnesia mixture (prepared from magnesium chloride) drop by drop whilst stirring, and allowed to stand twelve to forty-eight hours according to the quantity of arsenic present. The precipitate is filtered off, dissolved in acid, and the precipitation repeated once or twice more.[1] The combined filtrates are slightly acidified with acetic acid, and precipitated with lead acetate solution (§ IV, (*c*)).

(2) Arsenic is volatilised as trichloride by distillation with strong hydrochloric acid in presence of ferrous chloride or other reducing agent.[2]

(*d*) *Separation from Antimony.—Authors' Method.*—The chloride solution, free from nitrates or sulphates, and containing 20–25 c.c. of strong hydrochloric acid in a bulk of 100 c.c., is gently boiled with about 5 grm. of pure granulated or thin sheet lead for twenty to thirty minutes. The liquid first assumes a greenish-blue colour which gradually changes to brown, due to reduction of the molybdic acid, while the antimony is precipitated in the metallic state. When reduction is complete the liquid is diluted with boiling water and rapidly filtered, the paper being washed with hot water. The filtrate is boiled with a slight excess of nitric acid to re-oxidise the molybdenum, partially neutralised with ammonia, heated to boiling, and precipitated with 50 c.c. of strong ammonium acetate solution; the lead molybdate is ignited and weighed (§ IV, (*c*)). The precipitated antimony is dissolved, together with the lead, in nitric and tartaric acids, the lead removed as sulphate, and the antimony in the filtrate precipitated with hydrogen sulphide.

The results are very satisfactory for molybdenum; the antimony results are a trifle low, as is almost invariably the case where antimony is displaced from solution by another metal.[3]

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[1] Kehrmann, *Annalen*, 1888, **245**, 56; *Ber.*, 1887, **20**, 1813.

[2] Friedheim and Michaelis, *Ber.*, 1895, **28**, 1414, recommend methyl alcohol; Friedheim, Decker, and Diem, *Z. anal. Chem.*, 1905, **44**, 665, use potassium iodide and hydrochloric acid.

[3] Three test analyses gave the following results:—

No.	Taken.		Found.	
	MoO_3.	Sb_2O_3.	MoO_3.	Sb_2O_3.
1	0·0500	0·1500	0·0498	0·1472
2	0·1000	0·1000	0·0999	0·0985
3	0·1500	0·0500	0·1499	0·0495

(*e*) *Separation from Tin.*[1]—(1) This is accomplished by hydrogen sulphide (pressure precipitation) after addition of 15 grm. of oxalic acid per 100 c.c. of liquid : the tin is not precipitated under these conditions. The precipitated molybdenum sulphide is treated by one of the methods given in § IV, (*a*) or (*b*) (1).

(2) If the tin is present in an ore as cassiterite, the separation is effected by wet decomposition, tin remaining insoluble (§ VII, (*a*)).

(*f*) *Separation from Tungsten.*—(1) The alkaline solution containing molybdate and tungstate is acidified with 5 grm. of tartaric and sufficient sulphuric acid to produce a 10 per cent. solution, and precipitated with hydrogen sulphide under pressure (§ IV, (*a*)). Alternatively, the alkaline solution is first saturated with hydrogen sulphide and treated with 5 grm. of tartaric acid, sulphuric acid being added if necessary to acid reaction. The liquid is boiled till the molybdenum sulphide has coagulated. Tungsten is not precipitated.[2]

(2) The alkaline solution obtained by soda digestion or fusion is evaporated to dryness, taken to fumes with 5 c.c. excess of strong sulphuric acid, fumed for half an hour, and a few drops of nitric acid added to re-oxidise a small quantity of lower oxides formed. The cold mass is diluted with three times its volume of water ; the precipitated tungstic acid is left to settle, filtered off, and washed with dilute sulphuric acid followed by alcohol. The filtrate is treated with hydrogen sulphide under pressure.[3]

§ **IV. Gravimetric Determination.**—Molybdenum is weighed as disulphide or trioxide, but preferably as lead molybdate.

(*a*) *Determination as Disulphide.*[4]—The solution containing preferably sulphuric, but not nitric, acid is precipitated with hydrogen sulphide under pressure. This is done by saturating the cold liquid with hydrogen sulphide in a stout glass flask (a mineral-water bottle with screw-stopper is suitable). The flask is then almost completely filled with saturated hydrogen sulphide water, closed, and completely immersed by suspension in a deep cold water-bath, care being taken to prevent direct contact with the bottom of the bath. The latter is slowly heated to boiling and maintained at this temperature for two to three hours ; the loss by evaporation is made good by slowly pouring in boiling water. The flask must not be withdrawn until the bath has cooled to ordinary temperature.

The solution may also be made ammoniacal and treated with hydrogen or ammonium sulphide, digested on a steam-bath, the ammonium thiomolybdate decomposed with excess of dilute sulphuric acid, and the solution boiled until hydrogen sulphide is expelled.

In either case the precipitate is washed with acidulated and finally with pure water ; 50 per cent. alcohol is also used. The precipitate after drying is separated as completely as possible from the filter ; the

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[1] Clarke, *Amer. Journ. Sci.*, 1870, **49**, 48 ; *Chem. News*, 1870, **21**, 124.

[2] Rose, *Handbuch der analytischen Chemie*, 1871, 358.

[3] Hommel, Treadwell-Hall (1905), vol. ii. 225.

[4] See also Döhler, *Chem. Zeit.*, 1900, **24**, 537 ; Collet and Eckhardt, *ibid.*, 1909, **33**, 968.

latter is burned at very low temperature in a tared Rose crucible. The bulk of the precipitate is transferred to the crucible and the latter maintained a short time at a temperature below redness while a current of hydrogen is passing through it. If the temperature is too high or the ignition protracted, the disulphide begins to decompose into its elements; in fact, the whole of it can be thus reduced by using a blast lamp.[1]

(*b*) *Determination as Trioxide.*—(1) Instead of treating the sulphide precipitate as described above, it may be oxidised to trioxide. This operation must be conducted with care, as the temperature may rise to the point of incipient volatilisation of the trioxide.[2] Various schemes have been suggested to avoid loss from this cause. Thus, the wet filter and precipitate are placed in a tared crucible and dried at 100°. The covered crucible is then gently heated until volatile hydrocarbons have been driven off. The lid is removed, and the tarry matter around the inner sides burned off at very low temperature. The precipitate is then gently heated until the sulphur is driven off. After cooling, the mass is mixed with mercuric oxide emulsion, evaporated to dryness, and heated to expel the mercury.[3] Or, the roasted precipitate is digested with a few drops of nitric acid, the mass dissolved in ammonia, and re-acidified with nitric acid; the liquid is evaporated to dryness, the residue ignited gently, and weighed.[4] Alternatively, the sulphide may be mixed with anhydrous oxalic acid and heated until the latter is volatilised.

(2) The trioxide may also be obtained by ignition of mercurous molybdate at low temperature. The molybdate solution—free from tungstate, arsenate, chromate, vanadate, phosphate, sulphate, or silicate—is nearly neutralised with nitric acid; mercurous nitrate solution is added whilst stirring until further addition no longer produces a precipitate. The slight excess of sodium carbonate left in the liquid neutralises a small amount of free acid always present in the reagent. The solution is heated to boiling, the precipitate filtered off, washed with water containing 1 c.c. of saturated mercurous nitrate solution per litre, dried, and separated from the filter. The latter is replaced in the funnel, and washed with dilute nitric acid; the filtrate is evaporated in a tared crucible, after which the rest of the precipitate is added and heated very gently until the mercury is driven off.

(*c*) *Determination as Lead Molybdate.*—The preceding processes are liable to lead to errors unless care is exercised in regulating the temperature. The estimation as lead molybdate [5] is finding increased favour on account of its undeniable advantages. The precipitation is simpler than that of mercurous molybdate; the lead salt is stable at a high temperature and (unlike lead sulphate) not reduced by contact with glowing filter fibre; hence the incineration does not require any special

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[1] v. d. Pfordten, *Ber.*, 1884, **17**, 734.

[2] A temperature of 425° should not be exceeded (Wolf, *Z. angew. Chem.*, 1918, **31**, 140).

[3] Treadwell-Hall, vol. ii. 223.

[4] Binder, *Chem. Zeit.*, 1918, **42**, 225.

[5] Brearley and Ibbotson, *Analysis of Steel Works Materials*, 1902, 85, 273; Brearley, *Chem. News*, 1898, **78**, 203; 1899, **79**, 2, 14; 1900, **81**, 269.

precautions, and can even be carried out without separating the precipitate from the filter, provided the latter is charred at low temperature (by supporting the crucible on a wire gauze); finally, the molybdenum is weighed in combination with a metal of high atomic weight.

(1) The alkaline molybdate solution is acidified with 2 c.c. of acetic acid, treated with 5 grm. of ammonium chloride per 100 c.c. of liquid, and precipitated, whilst boiling, with a 4 per cent. lead acetate solution which is added slowly with constant stirring. The beaker is kept on a hot plate until the precipitate has settled, when it is filtered off on close-textured paper and washed with hot dilute ammonium acetate solution by decantation first, then on the filter until the washings fail to give a coloration with sodium sulphide solution. The moist filter is folded so that the portion containing the precipitate lies uppermost in the crucible. The drying is done in an air-oven or on an asbestos gauze; the paper is charred at a gentle heat, the carbon burnt off at low temperature, the precipitate heated for a short time to dull redness, cooled, and weighed.

(2) In the majority of cases the solution in which molybdenum is to be determined also contains sulphate, derived from the sulphur with which the metal was combined in the form of natural or precipitated sulphide. Its presence is known to lead to high results, due to co-precipitation of lead sulphate. Sulphates can be eliminated from the solution, previous to the precipitation of lead molybdate, according to § III, (*b*) (1), but the procedure is rather lengthy where a number of determinations have to be made. The usual practice in such cases consists in carrying out the precipitation in presence of ammonium chloride and a large excess (50 c.c.) of strong ammonium acetate solution; the precipitate is filtered off, dissolved in strong hydrochloric acid, and 100 c.c. of boiling water added to the clear solution followed by 5 grm. of ammonium chloride, and ammonia until a precipitate forms. The latter is re-dissolved in a small quantity of hydrochloric acid; a few drops of lead acetate solution are added, and, finally, 50 c.c. of strong ammonium acetate solution. The precipitate is left to settle, and treated as before.

By the use of the following modification we have obtained satisfactory results in presence of sulphate by means of a single precipitation. The solution of alkaline molybdate is acidified with an excess of 4 c.c. of 33 per cent. acetic acid; 10 grm. of ammonium chloride and 50 c.c. of 25 per cent. ammonium acetate solution are added. The liquid, now occupying a volume of 200 c.c., is precipitated while actually boiling, with a 4 per cent. lead acetate solution added drop by drop (from a burette). The further treatment of the precipitate is the same as described above.

The precipitation of lead molybdate can be carried out in presence of soluble salts of mercury, copper, cadmium, zinc, nickel, cobalt, manganese, and thus provides a method of separating molybdenum from these elements.

§ V. Volumetric Determination.—The methods for the volumetric estimation of molybdenum present no great advantage over the gravimetric determination as lead molybdate except where a number of assays are regularly made. A brief description of the volumetric methods will here be given. The last two are not well adapted for ore analysis, and while the permanganate method gives good results in practised hands, a gravimetric process is advisable where only an occasional determination is required. Titration with lead acetate is a useful method which is extensively used in practice; it presents the advantage that the precipitate obtained can be weighed as a check if desired.

(*a*) *Precipitation Method.*[1]—The molybdate solution is acidified with acetic acid, heated to boiling, and titrated with lead acetate solution (20 grm. per litre; 1 c.c. $=0{\cdot}005$ grm. Mo) until a drop of the solution fails to give a yellow tint with dilute tannin solution on a spot plate. This titration is the converse of Alexander's volumetric lead assay. The lead solution is standardised against pure molybdenum trioxide; this is dissolved in caustic alkali, the solution slightly acidified with acetic acid, heated to boiling, and titrated.

(*b*) *Permanganate Titration.*[2]—The purified sulphide is dissolved in *aqua regia* and the solution evaporated to fumes with sulphuric acid; it is diluted with water, heated to 75°, and run through a Jones' reductor (see Introduction). The reduced assay is at once titrated with permanganate, which latter is standardised against an approximately equal weight of pure trioxide reduced in exactly the same manner.

(*c*) *Iodometric Method.*[3]—Molybdenum trioxide, or a molybdate, boiled with potassium iodide and hydrochloric acid, is reduced as follows: $2MoO_3+2HI=Mo_2O_5+I_2+H_2O$. The determination is carried out in a small distillation flask in a current of carbon dioxide, and the liberated iodine titrated as usual. This process is used for the determination of molybdic acid in complex compounds such as silico- and phosphomolybdates. It is safest to standardise against pure molybdenum trioxide.

(*d*) *Acidimetric Method.*—Molybdenum trioxide is dissolved in N/2 sodium hydroxide, the excess of which is titrated back by N/2 acid in presence of phenolphthalein: $MoO_3+2NaOH=Na_2MoO_4+H_2O$. 1 c.c. N/2 NaOH $=0{\cdot}036$ grm. MoO_3.

§ VI. Detection in Ores.—Molybdenum minerals, fused with alkaline carbonate and nitrate, give a melt containing molybdate, which is identified by the following reactions:—

(*a*) The solution, strongly acidified with nitric acid, gives with one

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[1] Schindler, *Z. anal. Chem.*, 1888, **27**, 137.

[2] See also Mabee, *Engineering and Mining Journ.*, 1918, **105**, 836; Pisani, *Compt. Rend.*, 1864, **59**, 301; Rammelsberg, *Pogg. Ann.*, 1866, **127**, 281; Werneke, *Z. anal. Chem.*, 1875, **14**, 1; Bornträger, *ibid.*, 1898, **37**, 438. Randall, *Amer. Journ. Sci.*, 1907, **24**, 313, collects the reduced solution in phosphoric acid and ferric alum.

[3] Friedheim and Euler, *Ber.*, 1895, **28**, 2066; Hundeshagen, *Z. anal. Chem.*, 1889, **28**, 144, 171; Gooch and Norton, *Amer. Journ. Sci.*, 1898, **6**, 108. Gooch and Fairbanks, *ibid.*, 1896, **2**, 156, boil off the iodine, dilute with cold boiled water to 125 c.c., and add 1 grm. of tartaric acid, a slight excess of bicarbonate, and a known excess of standard iodine solution. After standing for two hours the excess of iodine is titrated with arsenite solution.

drop of sodium phosphate solution in presence of ammonium nitrate a bright yellow, crystalline precipitate. Stirring and warming favour the precipitation.

(*b*) Metallic zinc reduces the solution acidified with hydrochloric or sulphuric acid, with formation of coloured compounds. If the quantity of molybdenum predominates over that of the added acid, the liquid is coloured deep blue ; in presence of an excess of acid, however, it becomes at first reddish-yellow, then greenish-blue. Hence in applying the test it is advisable to add but little acid. Other elements which give coloured solutions or precipitates under the same conditions are tungsten, columbium, vanadium, and titanium (*q.v.*) ; the reduced molybdenum solution, however, gives with thiocyanate a deep red coloration.

(*c*) Tannin produces a deep orange coloration.

(*d*) A characteristic and sensitive test consists in heating a small quantity of the powdered mineral with a drop of strong sulphuric acid in a porcelain crucible until the acid is nearly driven off. On cooling a deep blue colour develops, more quickly when the test is breathed upon.

(*e*) Molybdic acid imparts a greenish colour to the Bunsen flame.

§ VII. Determination in Ores.—(*a*) *Ores free from Arsenic and Antimony.*—Molybdenum may be brought into solution by acid attack or by fusion. For low-grade siliceous material and for ores containing cassiterite the wet method of attack is preferable, because tin and silica are not thereby rendered soluble ; on the other hand, other metals present in the ore will accompany the molybdenum into solution. Fusion with carbonate and nitrate is especially adapted for high-grade, substantially pure molybdenite ores ; fusion with soda and sulphur answers well for the separation of large quantities of copper, iron, lead, bismuth, etc. (*i.e.* for iron, copper, and common sulphide ores).

(1) *Solution in Acids* (*generally aqua regia*).—The ore is decomposed by a suitable acid, and the liquor evaporated to fumes with 10 c.c. of sulphuric acid (1 : 1). The acid is diluted with three times its volume of water, and the insoluble portion filtered off and washed with dilute sulphuric acid. The filtrate is precipitated with hydrogen sulphide under pressure, and the precipitate digested with sodium sulphide and hydroxide ; the hot solution must be treated with hydrogen sulphide until it becomes deep red, when it is filtered and the filtrate boiled with a slight excess of sulphuric acid until hydrogen sulphide is expelled. The precipitate is filtered off, washed with water, dried, and gently ignited with the filter in a covered crucible. The cover is next removed, and the sulphur expelled as described in § IV, (*b*) (1) ; the residue after cooling is weighed as MoO_3.

(2) *Fusion with Carbonate-Nitrate Mixture* (8–10 parts) in an iron, nickel, or copper crucible.—Owing to the danger of loss by deflagration, it is advisable to gently roast high-grade ores before fusion until the smell of sulphur dioxide is no longer perceptible. The fused melt is leached with water and the solution freed from insoluble ferric and other

oxides by filtration. The residue is washed with 1 per cent. sodium carbonate solution ; the filtrate is treated with a slight excess of acetic acid, ammonium chloride, and lead acetate solution, as in § IV, (*c*).

If impure ores are treated in this manner, the alkaline molybdate solution may be contaminated with tungstate, stannate, vanadate, or chromate. It is boiled with excess of ammonium sulphate and filtered : the filtrate is saturated with hydrogen sulphide, acidified with 5 grm. of tartaric acid and sulphuric acid, and boiled till the precipitate has settled. This is filtered off, washed with hydrogen sulphide water, and dissolved in *aqua regia*. The acid liquor is evaporated to strong fumes with 15 c.c. of sulphuric acid (1 : 1), the acid cooled, diluted, and the solution precipitated with hydrogen sulphide under pressure. The precipitate is washed, dried, ignited gently, etc., as under (1).

(3) *Fusion with Soda and Sulphur* (6 parts) in a porcelain crucible, as for antimony ores.—The aqueous extract of the melt is boiled with excess of dilute sulphuric acid, or 15 grm. of oxalic acid if tin is present ; the precipitated sulphide is filtered off, ignited in a covered crucible, and the determination finished as under (1).

(*b*) *Arsenical and Antimonial Ores.*[1]—(1) When ores containing arsenic and antimony are treated according to one of the preceding methods the ignited molybdenum trioxide will be contaminated with oxides of these elements. It is digested with strong hydrochloric acid and a slight excess of saturated potassium iodide solution ; the liquid is transferred to a boiling flask, and repeatedly boiled down with strong hydrochloric acid over a free flame whereby arsenic is volatilised. The residue is taken up with 10 c.c. of strong hydrochloric acid, the latter diluted to 50 c.c. with water, and the solution reduced with lead for twenty to thirty minutes. The precipitated antimony is filtered off, washed with hot water, the filtrate oxidised with nitric acid, and the molybdenum precipitated by the addition of ammonia and ammonium acetate (§ III, (*d*)).

(2) If the hydrogen sulphide precipitate is small, it is dissolved, without previous ignition, in hydrochloric acid and bromine ; the excess of the latter is boiled off, potassium iodide solution added, and the determination finished as under (*b*) (1).

§ VIII. Determination of Impurities in Molybdenite Ores.—(*a*) *Copper, lead, and bismuth* may be determined in the residue from the extraction of the melt obtained by fusion with soda and sulphur (§ VII, (*a*) (3)). The thiomolybdate filtrate is boiled with sodium sulphite to recover the small quantity of copper dissolved by the polysulphide.

Lead alone may be determined by evaporation with *aqua regia* and sulphuric acid as usual, copper as thiocyanate ; bismuth, if small, is estimated by the colorimetric process described under Tungsten, § IX, (*c*).

(*b*) *Antimony* can be determined in the filtrate from the insoluble sulphides obtained by fusion with soda and sulphur (see (*a*)). The liquid is acidified with sulphuric acid, the precipitated sulphides dissolved in hydrochloric acid and bromine, the antimony precipitated

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[1] Authors' method.

with metallic iron, and filtered off; after solution in hydrochloric acid and bromine it is precipitated with hydrogen sulphide.

(*c*) *Arsenic.* The ore is dissolved in *aqua regia*, the nitric acid destroyed by two evaporations with hydrochloric acid, and the liquid distilled with ferrous chloride in the usual manner.

(*d*) *Tin*, if present as cassiterite, remains with the residue insoluble in *aqua regia*, in which it is determined by fusion with sodium peroxide followed by reduction and titration. If present as stannine, it must be separated from molybdenum by hydrogen sulphide and oxalic acid (§ III, (*e*)).

(*e*) *Calcium carbonate* is determined by attacking the ore with acetic acid. The solution thus obtained is precipitated with ammonium oxalate.

§ IX. Complete Analysis of Ores.—(*a*) *Molybdenite Ores.*—The gangue usually consists of quartz, muscovite, and felspars. A small quantity of copper pyrites is often found; pyrites and mispickel may also be present. Native bismuth is an important constituent of certain ores, in which it is often accompanied by galena. Wolfram, scheelite, and cassiterite should be looked for. Assuming an ore containing all the above minerals in addition to molybdenite and molybdine, the complete analysis will be carried out as follows:—

First Portion.—

<table>
<tr><td colspan="11">Boil 1 grm. of finely powdered ore with strong HCl to decompose tungstates, then with dilute HNO_3. Evaporate to small bulk, dilute, filter.</td></tr>
<tr><td colspan="6">R^1: warm with 1 per cent. NaOH, boil with excess of NH_4NO_3, filter.</td><td colspan="5">F^1: evaporate to dryness, take up with dilute HCl, filter.</td></tr>
<tr><td colspan="2">F^2: evaporate to fumes with H_2SO_4, dilute with 3 volumes of H_2O, filter, wash with dilute H_2SO_4.</td><td colspan="4">R^2: ignite, fuse with Na_2CO_3, take up with dilute HNO_3, evaporate to dryness, heat to 110° for 1 hour, take up with dilute HNO_3, filter, wash with 2 per cent. HNO_3.</td><td rowspan="4">R^7: 2nd SiO_2. Weigh.</td><td colspan="4">F^7: add F^3, ppte with H_2S under pressure, filter.</td></tr>
<tr><td rowspan="3">P^3: ignite, weigh WO_3.</td><td rowspan="3">F^3: add to F^7.</td><td rowspan="3">F^4: silicate bases. Add to F^8.</td><td colspan="3">R^4: ignite in Pt crucible, weigh. Treat with $HF+H_2SO_4$; ignite, weigh.</td><td rowspan="3">F^8: add F^4, determine Fe, Al, Ti, Mn, Ca, Mg.</td><td colspan="3">P^8: digest with Na_2S and NaOH, pass H_2S, filter, wash with dilute Na_2S.</td></tr>
<tr><td colspan="2">R^5: fuse with NaOH in Ag crucible, dissolve in HCl, pass H_2S, filter.</td><td rowspan="2">L^5: SiO_2.</td><td colspan="2">F^9: ppte with H_2SO_4, boil, filter, dissolve ppte in *aqua regia*. Add NH_4OH and magnesia mixture, filter, dissolve ppte, repeat pption, combine filtrates (§ III, (*c*)).</td><td rowspan="2">R^9: determine Pb, Bi, Cu.</td></tr>
<tr><td>P^6: SnS_2. Dissolve and titrate.</td><td>F^6: determine TiO_2.</td><td>F^{10}: acidify with CH_3CO_2H, ppte with $Pb(CH_3CO_2)_2$, weigh $PbMoO_4$.</td><td>P^{10}: $MgNH_4AsO_4$. Weigh as $Mg_2As_2O_7$, or titrate.</td></tr>
</table>

Second Portion: sulphur.—One grm. is digested with *aqua regia*, the nitric acid destroyed by two evaporations with hydrochloric acid, the residue taken up with dilute hydrochloric acid, and the solution precipitated with excess of ammonia. The filtrate is acidified with 5 per cent. excess of hydrochloric acid and precipitated with barium chloride (§ III, (*b*)).

Third Portion.—Molybdenum present as molybdine. 1–2 grm. of ore are digested with warm 2 per cent. caustic soda. The filtrate is acidified with sulphuric acid and precipitated with hydrogen sulphide under pressure, tartaric acid being added to keep up tungsten, if tungstic ochre is also present.

Fourth Portion: for alkalies, by L. Smith's method.

(*b*) *Wulfenite Ores.*—In addition to wulfenite, these may contain vanadinite (*q.v.*), mimetite ($3Pb_3As_2O_8.PbCl_2$), pyromorphite($3Pb_3P_2O_8.PbCl_2$), and crocoisite ($PbCrO_4$). The summarised procedure is as follows:—

First Portion.—

<table>
<tr><td colspan="5">Digest 1 grm. with strong HCl, and HNO_3 if required. Evaporate with H_2SO_4 to fumes. Cool, dilute with 3 volumes of H_2O; cool, filter, wash with dilute H_2SO_4.</td></tr>
<tr><td colspan="3">R^1: digest, hot, with $(NH_4)_2CO_3$, filter, wash with dilute $(NH_4)_2CO_3$.</td><td colspan="2">F^1: ppte with H_2S under pressure, filter.</td></tr>
<tr><td rowspan="2">F^2: evaporate to dryness, ignite, weigh WO_3.</td><td colspan="2">R^2: extract with HNO_3, filter.</td><td rowspan="2">F^4: oxidise with HNO_3, add 5 grm. of NH_4Cl, ppte with ammonia, filter. Dissolve ppte, repeat pption, combine filtrates.</td><td rowspan="2">P^4: treat like P^8 *et seq.* in preceding table (molybdenite).</td></tr>
<tr><td>R^3: SiO_2 (gangue). Weigh.</td><td>F^3: evaporate with H_2SO_4, weigh $PbSO_4$.</td></tr>
<tr><td>F^5: determine Ca, Mg.</td><td colspan="4">P^5: dissolve in HCl, ppte with NH_4OH and $(NH_4)_2S$, filter, wash with dilute $(NH_4)_2S$.</td></tr>
<tr><td colspan="2">F^6: boil with HCl, add HNO_3, take to fumes with H_2SO_4. Dilute, reduce with SO_2, titrate vanadium with $KMnO_4$. Reduce again, boil off SO_2, add NH_4NO_3 and molybdate reagent, determine P_2O_5.</td><td colspan="3">P^6: dissolve in H_2SO_4, boil, filter off sulphur. Add persulphate, boil, ppte with NH_4OH, filter. Dissolve ppte in H_2SO_4, repeat persulphate treatment and NH_4OH pption. Combine filtrates.</td></tr>
<tr><td colspan="4">P^7: treat with NaOH in porcelain basin; repeat treatment.</td><td rowspan="3">F^7: acidify with H_2SO_4, boil to destroy $H_2S_2O_8$, cool, titrate CrO_3.</td></tr>
<tr><td colspan="2">F^8: acidify with HNO_3, add NH_4NO_3 and molybdate reagent, filter.</td><td colspan="2" rowspan="2">P^8: determine Fe.</td></tr>
<tr><td>P^9: determine P_2O_5.</td><td>F^9: ppte with NH_4OH, filter, ignite ppte, weigh Al_2O_3.</td></tr>
</table>

Second Portion: for chlorine.—One grm. of the finely powdered ore is digested with dilute HNO_3 at a temperature not exceeding 50° to complete decomposition. Dilute considerably, filter, precipitate with $AgNO_3$, weigh AgCl.

(*c*) *Powellite.*—

<table>
<tr><td colspan="3">Digest 1 grm. with strong HCl, followed by HNO_3. Evaporate to strong fumes with H_2SO_4. Cool, dilute with three volumes of water, filter, wash with dilute H_2SO_4 to remove $CaSO_4$.</td></tr>
<tr><td rowspan="2">R^1: WO_3, $PbSO_4$, SiO_2: treat like R^1 *et seq.* in preceding table (*b*).</td><td colspan="2">F^1: treat with H_2S under pressure.</td></tr>
<tr><td>P^2: treat like P^8, (*a*), first portion.</td><td>F^2: determine Fe and Ca.</td></tr>
</table>

§ **X. Technical Methods.**—The following methods for assaying substantially pure molybdenite concentrates are used in technical work:—

(*a*) *Wet Method.*—0·5 to 2 grm. are attacked with *aqua regia.* The acid is evaporated just to dryness, the residue taken up with water, made alkaline with caustic soda, and re-acidified with hydrochloric acid. This solution is boiled, poured into hot 10 per cent. caustic soda, and after standing on a sand-bath for ten minutes the assay is filtered and the precipitate well washed with hot water. In presence of alkaline earths, sodium carbonate should be used instead of caustic soda. The filtrate is treated, for gravimetric or volumetric determination as lead molybdate, according to methods given in §§ IV, (*c*) or V, (*a*).

(*b*) *Fusion Method.*—0·625 grm. is gently roasted in a nickel crucible, and fused with 5 grm. of carbonate-nitrate mixture. The melt is taken up with water and the extract made up to 250 c.c.; 200 c.c. (equivalent to 0·5 grm.) are filtered off, and the assay finished as under (*a*).

In the volumetric process an ore of known molybdenum content is generally used as the standard; it is treated in the same manner as the assay.

TUNGSTEN.

§ **I. Minerals.**—(*a*) *Monoclinic Tungstates.*—(1) *Ferberite,* ferrous tungstate, $FeWO_4$.

(2) *Hübnerite,* manganous tungstate, $MnWO_4$.

(3) *Wolframite,* $(Fe,Mn)WO_4$, the most important ore of tungsten, may be regarded as an isomorphous mixture of the above two minerals. All three are similar in appearance and lustre (distinctly submetallic on fresh cleavage planes); they are brittle and give an uneven fracture. Streak red to chocolate-brown (distinction from cassiterite, with which it is generally found); colour brown to black. H 4·5–5·5; sp. gr. 6·8–7·5. Attracted by a strong electromagnet (*cf.* cassiterite). Finely powdered wolframite is soluble in hot strong hydrochloric, but scarcely attacked by nitric acid.

(*b*) *Tetragonal Tungstates.*—(1) *Scheelite,* calcium tungstate, $CaWO_4$, is a white, more or less opaque, heavy mineral. H 5; sp. gr. 6. An important ore of tungsten; it is often found with cassiterite. Hydrochloric acid dissolves powdered scheelite readily; nitric acid attacks it superficially, the particles becoming yellow through liberation of tungstic acid. It often contains a little molybdenum (*cf.* Powellite).

(2) *Cuproscheelite,* $(Ca,Cu)WO_4$, is a variety of the preceding in which copper partly replaces lime. Colour green, streak greenish-grey.

(3) *Stolzite,* lead tungstate, $PbWO_4$, is resinous, sub-translucent; colour grey, brown, or red. H 3; sp. gr. 8. Isomorphous with wulfenite (*q.v.*).

(4) *Reinite* has the same composition as ferberite, and appears to be a pseudomorph after scheelite. Unimportant.

(*c*) *Tungstic Ochre* is an alteration product of wolframite, to which the formula WO_3 is usually assigned; but it generally contains a little ferric oxide and water. Colour usually bright yellow, but sometimes light brown or even white. Amorphous soft powder or incrustations.

§ **II. Properties and Compounds.**—(*a*) The *element*, obtained by reduction of the trioxide with hydrogen at a bright red heat, is a very hard steel-grey metal of sp. gr. 18·7, melting above 3000°. It is insoluble in all acids, except a mixture of nitric and hydrofluoric. The powder dissolves in boiling caustic alkali, with formation of alkaline tungstate and liberation of hydrogen.

(*b*) *Tungsten trioxide*, WO_3, is a canary-yellow heavy powder, soluble in caustic alkalies or hydrofluoric, but insoluble in hydrochloric, nitric, or sulphuric acid.

(*c*) *Tungstic Acids.*—(1) A *hydrated acid*, $H_2WO_4.H_2O$, is a white amorphous precipitate formed by the addition of an acid to a cold solution of alkaline tungstate. It is slightly soluble in water.

(2) The *anhydrous acid*, H_2WO_4, precipitates as a yellow powder when hot tungstate solutions are treated with excess of acid. It is insoluble in water but tends to form a hydrosol ; soluble in ammonia (see (*d*) (2)).

(3) *Metatungstic acid*, $H_2W_4O_{13}.7H_2O$, forms yellow crystals readily soluble in water. Sodium metatungstate is formed by boiling a solution of sodium tungstate with insufficient hydrochloric acid to precipitate the normal acid. On boiling metatungstate with caustic alkali the normal tungstate is regenerated.

(*d*) *Tungstates.*—(1) *Sodium tungstate*, $Na_2WO_4.2H_2O$, obtained by fusing minerals with sodium carbonate. Soluble in four parts of cold water.

(2) *Ammonium tungstate*, $(NH_4)_2WO_4$, is obtained by dissolving precipitated tungstic acid in ammonia. The solution on evaporation deposits glittering plates of $(NH_4)_{10}W_{12}O_{41}.5H_2O$.

(3) *Mercurous tungstate*, Hg_2WO_4, flocculent white precipitate formed on mixing neutral solutions of alkaline tungstate and mercurous nitrate. Soluble in dilute nitric acid ; on ignition, tungsten trioxide remains.

(*e*) *Sulphides.*—When tungsten trioxide is dissolved in sodium sulphide a deep brown solution is obtained which contains the thiotungstate, Na_2WS_4, and which, on acidifying, yields a flocculent brown precipitate of tungsten trisulphide, WS_3. Tartaric or oxalic acid prevents the precipitation. The trisulphide is slightly soluble in water, giving a brown solution, and on ignition in an inert atmosphere yields the disulphide, WS_2. This bears a great resemblance to molybdenite (*q.v.*).

§ **III. Quantitative Separation.**—The separation of tungsten in mineral analysis is so closely related to the question of opening up its ores that the two operations will here be considered together.

The ore may be decomposed by one of the following processes : (*a*) acid attack ; (*b*) fusion with sodium carbonate or peroxide, or digestion with caustic soda ; (*c*) fusion with bisulphate.

(*a*) *Acid Attack.*—In this process, which is carried out as described in § VIII, (*a*), the insoluble residue may contain, in addition to tungstic acid: (1) antimonic; (2) silicic, columbic, tantalic, stannic, and titanic acids.

(1) *Separation from Antimonic Acid.*[1]—The unfiltered acid liquor resulting from the *aqua regia* attack is evaporated to dryness and the residue taken up with dilute nitric acid, which is again evaporated on the water-bath. The evaporation is repeated twice more. The residue is then taken up with dilute nitric and a little tartaric acid, and the residue containing the tungstic acid filtered off and washed with water containing a little nitric acid.

(2) *Separation from Silicic,*[2] *Columbic,*[3] *Tantalic, Stannic,*[4] and *Titanic*[5] *Acids.*—The residue from the *aqua regia* treatment (or from (1)) is rinsed back, boiled with dilute ammonia and a crystal of ammonium nitrate, and the residue filtered off and washed with 1 per cent. ammonium nitrate. The filtrate, containing the main part of the tungstic acid, is evaporated to dryness, and the residue ignited and weighed as WO_3.[6] It should be tested for silica by evaporation with hydrofluoric and sulphuric acids, but the amount thus found rarely exceeds 0·0005 grm. The residue from the ammonia extraction still contains a little tungstic acid; it is digested with hot 1 per cent. caustic soda, the solution boiled with 2 grm. of ammonium nitrate, and filtered. The filtrate, which contains all the tungstic acid and traces of silica, is neutralised, precipitated with mercurous nitrate (§ IV, (*b*)), and the precipitate ignited and weighed. (For purification, see (*d*).)

(*b*) *Fusion or Digestion with Alkali.*—Fusion of a complex ore with sodium carbonate, peroxide, or hydroxide results in a residue containing the metals as oxides or carbonates, and a solution of tungstate, molybdate, vanadate, arsenate, phosphate, chromate, and part or all of the following: silicate, aluminate, antimonate, stannate, tantalate, and columbate. Digestion with caustic soda results in at least partial solution of some of the above impurities. If the ore contains antimony, 5 grm. of tartaric acid are added to the solution of the melt, the liquid again made alkaline if necessary, saturated with hydrogen sulphide, and the determination finished as under (*c*). If no antimony is present, the separation is carried out as follows:—

(1) *Separation from Silicate, Stannate, Aluminate, Tantalate, Colum-*

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[1] Cobenzl, *Z. anal. Chem.*, 1882, **21**, 114.

[2] For methods based on volatilisation of the tungstic acid as chloride or oxychloride see Friedheim, Henderson, and Pinagel, *Z. anorg. Chem.*, 1905, **45**, 396; Bourion, *Compt. Rend.*, 1908, **146**, 1102; Defacqz, *ibid.*, 1319; Nicolardot, *ibid.*, 795.

[3] Another method is given by Bedford, *Journ. Amer. Chem. Soc.*, 1905, **27**, 1216.

[4] Other methods of separating tin: Rammelsberg, *Pogg. Ann.*, 1864, **120**, 66; *Chem. News*, 1864, **9**, 25 (volatilisation of stannic oxide by ammonium chloride); Donath and Müller, *Monatshefte f. Chem.*, 1887, **8**, 647 (fusion with zinc dust); Angenot, *Z. angew. Chem.*, 1906, **19**, 956 (fusion with sodium peroxide followed by precipitation of tungsten by zinc and hydrochloric acid); Travers, *Compt. Rend.*, 1917, **165**, 408 (fusion with sodium sulphite); Dittler and v. Graffenreid, *Chem. Zeit.*, 1916, **40**, 681.

[5] See also Defacqz, *Compt. Rend.*, 1896, **123**, 823.

[6] This separation is not absolutely exact (see (*d*)). For a discussion of the method see Wells and Metzger, *Journ. Amer. Chem. Soc.*, 1901, **23**, 356; de Benneville, *ibid.*, 1891, **19**, 377; Watts, *Chem. News*, 1907, **95**, 19; L. and G. Campredon, *Ann. Chim. anal.*, 1904, **9**, 41.

bate.[1]—The alkaline solution is boiled with sufficient ammonium nitrate to react with the excess of alkali, the precipitate allowed to settle, and filtered off; the filtrate, if free from impurities mentioned under (2) and (3), is ready for precipitation with nitric acid (§ IV, (*c*)), or mercurous nitrate after neutralisation (§ IV, (*b*)).[2] (Testing the weighed WO_3: see (*d*).)

(2) *Separation from Phosphate and Arsenate.*[1]—The filtrate from the last separation is treated with magnesia mixture free from sulphate or chloride (*i.e.* prepared from magnesium and ammonium nitrates).[3] After standing overnight the precipitate is filtered off, dissolved in nitric acid, and re-precipitated. If much phosphorus or arsenic is present the operation may have to be repeated three or four times. The combined filtrates are precipitated by one of the methods given in § IV., and the ignited tungstic acid tested as under (*d*).

(3) *Separation from Vanadate, Molybdate,*[4] *Chromate.*[5]—If vanadate, molybdate, and chromate are present, the filtrate from the precipitation with ammonium nitrate or magnesia mixture is acidified with acetic acid and precipitated hot with lead acetate solution.[6] The precipitate consisting of lead tungstate, molybdate, vanadate, and chromate is filtered off, gently ignited, dissolved in hydrochloric acid, and the liquor evaporated to dryness after addition of a few drops of nitric acid. The residue is taken up with 150 c.c. of hydrochloric acid (1 : 4), and the solution boiled and filtered; the residual tungstic acid is washed with dilute hydrochloric acid, ignited, and weighed.

(*c*) *Fusion with Bisulphate.*—If the bisulphate melt is leached with dilute sulphuric acid, the precipitate will contain the same compounds as if the ore had been opened up with *aqua regia*. If, however, the leaching is carried out with tartaric acid, the tungstic acid goes into solution with the metals.[7] A minute quantity of white flocculent tungstic acid may remain with the insoluble matter; it is recovered by warming with 1 per cent. caustic soda, filtering, boiling with 1–2 grm. of ammonium nitrate, again filtering, and precipitating with mercurous nitrate (§ IV, (*b*)).

The tartrate solution is made alkaline with caustic soda and saturated with hydrogen sulphide. The metals whose sulphides are insoluble in alkaline sulphides are thus precipitated. The precipitate is filtered off, washed with dilute ammonium sulphide, and the filtrate acidified with dilute sulphuric acid. The sulphides of molybdenum, arsenic,

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[1] *Cf.* Bullnheimer, *Chem. Zeit.*, 1901, **24**, 870, who performs operations (1) and (2) simultaneously.

[2] Hermann, *Z. anal. Chem.*, 1912, **51**, 736, states that the small amount of silica still left in solution after precipitation with ammonium nitrate tends to low results, due to the slight solubility of mercurous silicotungstate.

[3] Kehrmann, *Ber.*, 1887, **20**, 1811.

[4] Ibbotson and Brearley, *Chem. News*, 1900, **81**, 13.

[5] v. Knorre, *Z. anal. Chem.*, 1908, **47**, 337, reduces chromic acid with sulphur dioxide in faintly acid solution and precipitates tungstic acid with benzidine.

[6] Friedheim, *Ber.*, 1890, **23**, 353, recommends mercurous nitrate instead of lead acetate; procedure otherwise the same.

[7] Powell, *Journ. Soc. Chem. Ind.*, 1918, **37**, 285.

antimony, tin, and vanadium are now precipitated. After heating to coagulate the precipitate it is filtered off, and washed with acidulated hydrogen sulphide water.

The filtrate is evaporated to fumes with nitric and sulphuric acids. A little copper sulphate is then added and the mass heated until all organic matter is destroyed. After cooling it is boiled with water and a little nitric acid and the tungstic acid filtered off (§ IV, (*d*)). The solution contains alumina and titania. If columbic and tantalic acids are present, the precipitated tungstic acid should be extracted with dilute ammonia, or dilute caustic soda followed by boiling with ammonium nitrate (*a* (2)).

(*d*) *Testing Tungstic Acid after Weighing.*—If alkaline solutions of sodium tungstate are boiled with ammonium nitrate, the tungstic acid precipitated by mercurous nitrate is liable to contain small quantities of silica and alumina. To remove these the ignited tungstic acid is fused with three times its weight of sodium carbonate, and the solution of the melt boiled with 2–3 grm. of ammonium carbonate and filtered. The filtrate is again precipitated with mercurous nitrate.

Alternatively the moist mercurous tungstate obtained in the first precipitation is rinsed back into the beaker and evaporated nearly to dryness with *aqua regia.* The tungstic acid is filtered off, ignited, weighed, and treated with hydrofluoric and sulphuric acids; the dry residue is ignited and weighed as pure WO_3.

In the analysis of arsenical ores, the weighed tungstic acid may be tested for arsenic, if desired, by fusing it with sodium carbonate, saturating the solution of the melt with hydrogen sulphide, and acidifying with tartaric acid: if arsenic is present, a yellow precipitate of arsenic sulphide is thrown down. Antimony may be tested for in exactly the same manner; or the tungstic acid may be fused with potassium cyanide, giving potassium tungstate and a globule of metallic antimony.[1]

(*e*) *Separation from Silver.*—If argentiferous ores are treated with *aqua regia* (*a*), the mixed precipitate of silver chloride and tungstic acid is dissolved in ammonia, and the solution treated with ammonium sulphide; silver sulphide will be precipitated.

(*f*) *Separation from Molybdenum.*—See Molybdenum, § III, (*f*).

(*g*) *Separation from Vanadium.*—See Vanadium, § III, (*b*) (1).

§ **IV. Gravimetric Determination.**—Tungsten is weighed as trioxide, obtained as described below.

(*a*) *By Ignition of Ammonium Tungstate.*—A solution of ammonium tungstate free from other fixed constituents is evaporated to dryness in a tared porcelain or platinum dish and the residue ignited, gently at first, then more strongly, till pure yellow.

(*b*) *By Precipitation with Mercurous Nitrate.*[2]—To the ammoniacal

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[1] Hallopeau, *Bull. Soc. Chim.*, 1897, **17**, 170.

[2] Hutchin, *Analyst*, 1911, **36**, 398; Desvergnes, *Ann. Chim. anal.*, 1904, **9**, 321; Gibbs, *Proc. Amer. Acad.*, 1879, **16**, 134; *Amer. Chem. Journ.*, 1879, **1**, 219; v. d. Pfordten, *Z. anal. Chem.*, 1885, **24**, 92.

solution of ammonium tungstate a drop of methylorange is added and nitric acid till the solution is just acid; it is now rendered alkaline with an excess of two drops of 25 per cent. ammonium carbonate solution and a cold saturated nearly neutral solution of mercurous nitrate added drop by drop with constant stirring until the precipitate coagulates, leaving the supernatant liquid clear. Complete precipitation is tested for with a drop or two of mercurous nitrate. The contents of the beaker are heated nearly to boiling, left to settle, and filtered through a loose filter paper (Whatman No. 4). The precipitate is washed with hot water containing 1 c.c. of the mercurous nitrate solution per litre, ignited wet, and weighed as WO_3.[1]

(*c*) *By Precipitation with Nitric Acid.*[2]—The ammoniacal solution of ammonium tungstate is concentrated, if necessary, to 50 c.c., an equal volume of strong nitric acid added, and the solution boiled until the tungstic acid changes to pure yellow and settles well. The liquid is filtered, the precipitate decanted three times with nitric acid (sp. gr. 1·1), transferred to the filter, and washed free from sodium salts with the same acid, which is then displaced by ammonium nitrate. The filtrate, which always contains a little metatungstate, is evaporated to dryness, the residue moistened with strong ammonia, and again taken to dryness. The mass is taken up with a minimum of water, an equal volume of strong nitric acid added, and the solution boiled till the precipitate becomes pure yellow. It is collected on a small filter, washed as before, and ignited together with the first precipitate to WO_3.

(*d*) *By Precipitation with Sulphuric Acid.*[3]—The ammoniacal solution is evaporated as far as possible without separation of salts. An excess of 10–15 c.c. of strong sulphuric acid is added and the mixture evaporated to copious fumes whilst constantly stirring. Three c.c. of nitric acid are then added to re-oxidise any reduced tungstic acid. The mass is diluted with three times its bulk of water, the solution filtered, and the precipitate washed free from alkaline salts with very dilute sulphuric acid, then four times with alcohol. It is ignited wet and weighed as WO_3.[4]

§ **V. Volumetric Determination.**—No volumetric method for estimating tungstic acid has yet found a place in analytical practice, the gravimetric processes being more reliable. The volumetric methods are based on saturation or oxidation.

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[1] Tungsten trioxide is not volatile at the full heat of a Bunsen burner, but appreciable amounts will be lost if a blast is used. The ignited precipitate should be pure yellow; if it is tinged with green, the alkali has probably not been completely washed out.

[2] *E.g.* Philipp, *Ber.*, 1885, **15**, 501.

[3] Margueritte, *Erdmann's Journ.*, **35**, 249.

[4] Other precipitants which have been proposed are: (*a*) Lead acetate, Chatard, *Amer. Journ. Sci.*, 1871, **1**, 416; Brearley, *Chem. News*, 1899, **79**, 64; Ibbotson and Brearley, *ibid.*, 1899, **80**, 293; de Benneville, *Journ. Amer. Chem. Soc.*, 1897, **14**, 377. (*b*) Quinine acetate, Lefort, *Chem. News*, 1882, **45**, 57. (*c*) Cinchonine, Cremer, *Eng. Min. Journ.*, 1895, **59**, 345. (*d*) Benzidine, v. Knorre, *Ber.*, 1905, **38**, 783; *Z. anal. Chem.*, 1908, **47**, 37; Wdowiszewski, *Chem. Zeit.*, 1910, **34**, 1365. (*e*) α-naphthylamine, Tschilikin, *Ber.*, 1909, **42**, 1302. (*f*) "Nitron," Gutbier and Weise, *Z. anal. Chem.*, 1914, **53**, 426. (*g*) Stannous chloride, Mdiviani, *Bull. Soc. Chim.*, 1911, **9**, 122; Marbaker, *Journ. Amer. Chem. Soc.*, 1915, **37**, 86.

(*a*) *Acidimetric Method.*—The yellow precipitate of tungstic acid obtained by decomposition of tungstates with nitric acid is washed free from iron with dilute acid, then to neutral reaction with 5 per cent. sodium nitrate solution. It is dissolved in warm decinormal sodium hydroxide solution, the excess of which is determined by decinormal acid in presence of phenolphthalein.[1] Or it is dissolved in ethylamine and the excess titrated back with oxalic acid, using the same indicator. The latter process is stated to give good results in presence of silica, tantalic, and columbic acids.

(*b*) *Oxidation Method.*[2]—The strongly acid hydrochloric solution is vigorously reduced with zinc in an atmosphere of carbon dioxide. When all the zinc has dissolved, the blue liquor is titrated with iron alum in presence of thiocyanate. Repeated attempts on the part of the authors at using this method gave unreliable results.

§ **VI. Colorimetric Determination.**—The reduction of tungstic acid to the blue oxide has been made the basis of a colorimetric process for determining small quantities of the element. In Travers' method,[3] the sodium tungstate solution, occupying a bulk of about 60 c.c., and containing less than 1 mgrm. of tungsten per c.c., is exactly neutralised, then acidified with 2–4 c.c. of normal hydrochloric acid. A slight excess of titanous chloride solution (about 2 mgrm. Ti per c.c.) is added, and the colour matched against a standard prepared from pure sodium tungstate. With the above maximum concentration of tungsten the colloidal suspension is stated to keep for about thirty seconds, after which flocculation sets in. Vanadium, phosphorus, and molybdenum interfere; the coloration is also affected by a greater degree of acidity than corresponds to 10 c.c. of normal acid per 100 of solution.

We have suggested the addition of tartaric acid to the liquid before reduction in order to obtain a true solution of the blue oxide.[4]

§ **VII. Detection in Ores.**—(*a*) All tungsten minerals on fusion with sodium carbonate, hydroxide, or peroxide and extraction of the melt with water yield a solution of sodium tungstate which is tested as follows:—[5]

(1) Hydrochloric acid in the cold produces a white flocculent precipitate of hydrated tungstic acid (*q.v.*), which on boiling changes to the yellow anhydrous acid. Both precipitates are insoluble in acids but soluble in ammonia and alkalies (*cf.* Columbium). Phosphoric, arsenic, boric, tartaric, or oxalic acid prevents the precipitation.

(2) Addition of zinc and hydrochloric acid to a soluble tungstate produces a deep blue precipitate, or solution if phosphoric acid is present (*cf.* Molybdenum, Columbium, and Vanadium).

(*b*) A particle of a tungstate mineral boiled with strong hydro-

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[1] Mennicke, *op. cit.*, p. 118.

[2] Knecht and Hibbert, *Proc. Chem. Soc.*, 1909, 277.

[3] *Compt. Rend.*, 1918, **166**, 416.

[4] *Bull.* 166, *Inst. Min. Met.* (July 1918).

[5] Further tests are given by Torossian, *Amer. Journ. Sci.*, 1914, **38**, 537; Hartmann, *Chem. News*, 1916, **114**, 45; Defacqz, *Ann. Chim. Phys.*, 1901, **22**, 238; Frabot, *Ann. Chim. anal.*, 1904, **9**, 371.

chloric acid becomes coated with a bright yellow deposit of tungstic acid; the coating is soluble in ammonia or caustic soda.

§ **VIII. Determination in Ores.**—The determination of tungsten is subject to serious errors in presence of certain elements frequently found in its ores; in most cases their influence can be counteracted by applying a suitable method of decomposition.

Wolfram may be decomposed by any of the methods given below, whereas scheelite should not be treated by digestion with caustic soda, because the attack is not always complete and there is danger of precipitation of calcium tungstate on diluting the alkaline solution. If much mispickel is present there is a possibility of some tungstic acid escaping precipitation in the *aqua regia* method owing to the formation of complex acids. With such ores, bisulphate fusion should be resorted to. Mispickel can be separated from wolfram (but not from scheelite) by digestion with warm nitric acid (1·15). Phosphates interfere like arsenates, and ores containing them should be fused with alkali and the phosphorus removed as described in § III, (*b*) (2). If fluorides are present, the *aqua regia* method will often yield low results, tungstic acid being soluble in hydrofluoric acid; fusion with sodium carbonate or bisulphate should therefore be employed. Ores containing silicates decomposable by acid should be treated with hydrofluoric acid (see (*d*)).[1] Material rich in titanium is fused with sodium carbonate (*c*).[2]

(*a*) *Aqua Regia-Ammonium Tungstate Method.*[3] (Suitable for high-grade ores and concentrates.)—One grm. of the slimed ore is weighed into a 250 c.c. round flask, 100 c.c. of strong hydrochloric acid added, and the flask agitated till the ore is thoroughly mixed with the acid, leaving no unwetted particles. The acid is brought nearly to boiling, with occasional agitation to prevent the ore sticking to the bottom, and kept at that temperature until all the tungstate is dissolved. A white or brownish-white residue may be quartz or cassiterite, while a black, somewhat flocculent residue will probably consist of sulphides (pyrites). The acid is boiled down to about 10 c.c., 10 c.c. of strong nitric acid are added, the contents of the flask boiled down to about 5 c.c. and diluted with 50 c.c. of boiling water. The precipitate is left to settle, decanted through a close-textured paper (Whatman No. 5), and washed by decantation with water slightly acidified with hydrochloric acid until the washings are free from iron. The tungstic acid on the paper is rinsed back into the flask with a small quantity of water, and sufficient strong ammonia added to dissolve it, together with a tiny crystal of ammonium nitrate. The solution is boiled till any precipitate has coagulated and settled, then filtered through the same filter into a tared

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[1] See Guglialmelli and Hordh, *Anal. Soc. Quim. Argentina*, 1917, **5**, 81, for discussion on errors introduced into the assay by the presence of silica.

[2] Defacqz, *Compt. Rend.*, 1896, **123**, 823, recommends throwing the finely powdered ore (1 grm.) into 8 grm. of a mixture of eight parts of potassium nitrate and two parts of potassium carbonate heated just to fusion and fusing for twenty to thirty minutes, when all the tungstic acid is rendered soluble.

[3] Watts, *Chem. News*, 1907, **95**, 19; Hutchin, *Analyst*, 1911, **36**, 398; Hartmann, *Chem. News*, 1916, **114**, 27.

evaporating basin (80 c.c.), the flask and filter being washed with a solution containing 1 grm. of ammonium nitrate and 10 c.c. of strong ammonia per litre. The filtrate which now contains the greater part of the tungstic acid as ammonium tungstate is evaporated to dryness on the water-bath, the residue heated gently until all ammonium salts are driven off, then finally ignited over a Teclu burner and weighed as WO_3 (see § III, (*a*) (2)).

If any but transparent quartzy material remains in the flask it is advisable to repeat the treatment with about 20 c.c. of hydrochloric acid, although the tungsten minerals are readily soluble provided sliming has been thorough. If a further small quantity of tungstic acid is obtained, it is filtered off and washed on the paper previously used. In any case the latter as well as the residue in the flask must be treated with hot 10 per cent. caustic soda, the solution boiled with an excess of ammonium nitrate till the precipitate coagulates, filtered, and the filtrate neutralised and precipitated with mercurous nitrate as prescribed in § IV, (*b*). The small amount of tungsten trioxide thus obtained is added to the bulk; if not pure yellow it should be purified (§ III, (*d*)).

(*b*) *Aqua Regia-Mercurous Nitrate Method.* (Suitable for medium-grade tungsten ores and tin concentrates).[1]—The ore is attacked as in (*a*), the washed tungstic acid being dissolved directly in hot 1 per cent. caustic soda without previous ammonia treatment. The solution is boiled with 5 grm. of ammonium nitrate and filtered. The filtrate is neutralised with nitric acid and precipitated with mercurous nitrate (§ IV, (*b*)).

(*c*) *Fusion Method.*[2] (Best method for ores containing ilmenite or rutile).—0·5 grm. of ore is fused for half an hour with 3–4 grm. of sodium carbonate in platinum and the melt leached with water, the solution filtered and the residue washed with hot 1 per cent. sodium carbonate. The latter is treated with dilute hydrochloric acid and any undecomposed ore filtered off, ignited, and again fused. The solution containing the tungsten is boiled with an excess of ammonium nitrate, filtered, precipitated by one of the methods described under § IV, (*b*)–(*d*), and the tungstic acid purified if necessary.

(*d*) *Hydrofluoric Acid-Fusion Method.* (For low-grade ores and tailings.)—Five grm. of the finely powdered ore are evaporated with 40 to 50 c.c. of hydrofluoric acid in a platinum basin. When the mass becomes pasty, 5 c.c. of nitric acid are added and the whole evaporated to dryness. The dried residue is washed into a beaker with 40 c.c. of water and 5 c.c. of nitric acid, the solution heated to dissolve sulphides, diluted with 150 c.c. of hot water, and allowed to stand till the precipitate settles completely. It is then filtered off, washed with hot water, dried, ignited, and fused with sodium peroxide in an iron crucible. The melt is leached with hot water, the aqueous extract made up to 250 c.c., and 200 c.c. filtered through a dry paper after rejecting the first portion.

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[1] Hutchin, *loc. cit.*, p. 177.

[2] Hartmann, *loc. cit.*, p. 177; Low, *Technical Methods of Ore Analysis.*

The filtrate is boiled with an excess of ammonium nitrate, filtered if necessary, any precipitate being washed with 2 per cent. ammonium nitrate solution. The filtrate is nearly neutralised with nitric acid and the tungstic acid precipitated with mercurous nitrate (§ IV, (*b*)).

(*e*) *Caustic Soda Method.*[1] (For low-grade ores; inapplicable to ores containing scheelite.)—5–10 grm. of the finely powdered ore are heated for three-quarters of an hour with 20 c.c. of 25 per cent. solution of caustic soda in a porcelain basin. The solution is transferred to a 250 c.c. graduated flask and made up to the mark. 200 c.c. are poured through a dry filter, transferred to a beaker, and boiled with excess of ammonium nitrate. The precipitate is filtered off and washed with 2 per cent. ammonium nitrate; the filtrate is precipitated as usual with mercurous nitrate. More often than not the ignited tungstic acid requires purification.

(*f*) *Bisulphate Fusion.* (For impure ores containing mispickel and fluorspar; not suitable for phosphatic material.)—The fusion is described under § IX, (*a*) (2); the solution obtained by leaching the melt with 5 per cent. tartaric acid is filtered from the gangue and treated as under § III, (*c*).

§ IX. Determination of Impurities in Ores.—The most objectionable impurities commonly met with in tungsten ores are tin, arsenic, bismuth, copper, sulphur, and phosphorus; methods for their determination which the authors have found both rapid and accurate are described below.

(*a*) *Tin*, the most important impurity, is almost invariably present. While it is not so objectionable in wolfram ores, from which it can be eliminated by electromagnetic separation, it is a most harmful constituent of scheelite ores, as no commercial method for the satisfactory separation of the two minerals is known. The tin may occur as cassiterite or stannine, or both; the methods given below are applicable in every case.

(1) *Aqua Regia Method.*—The insoluble residue from the extraction of tungstic acid in the *aqua regia* method may be fused with sodium peroxide and the assay proceeded with according to Pearce's directions. If stannine is present, some tin will be found in the acid solution of the bases. This is recovered by adding ammonia to the liquid, filtering, igniting, and fusing the precipitate (ferric plus stannic oxide) together with the insoluble residue.

(2) *Bisulphate-Tartaric Acid Method.*[2]—One grm. of ore (-90 mesh) is fused with 5 grm. of dehydrated bisulphate in a silica crucible. About five minutes is generally sufficient. The melt is poured into a nickel crucible lid and, when cold, dropped into a beaker containing 50 c.c. of hot 5 per cent. tartaric acid solution, the crucible leached with the same solution, and the liquor and insoluble matter carefully transferred to the beaker. The assay is boiled until solution of the cake is complete. Hydrogen sulphide is then passed through the solution, for, even if no

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[1] Hutchin and Tonks, *Analyst*, 1909, **34**, 457; *Inst. Min. Met.*, 1909, **18**, 425.

[2] Powell, *Journ. Soc. Chem. Ind.*, 1918, **37**, 285.

stannine is present, a very small amount of tin (*i.e.* less than 1 mgrm.) is often rendered soluble in the fusion. The combined insoluble matter and sulphide precipitate are filtered off, washed thoroughly with very dilute ammonium acetate solution, ignited wet in an iron crucible (any arsenic sulphide is largely volatilised), and fused with peroxide as in Pearce's method. If copper or bismuth is present, the insoluble residue from the fusion is filtered off, the filtrate precipitated by hydrogen sulphide, and the precipitate extracted with sodium sulphide. The solution of thiostannate is precipitated with dilute sulphuric acid, the stannic sulphide filtered off, ignited, and fused together with the insoluble residue. By using this method one operator can complete twelve assays in three hours.

(3) *Sodium Peroxide Method.*[1]—2–5 grm. of ore are fused with 12 grm. of sodium peroxide in an iron crucible; the melt is taken up with hot water, the solution transferred to a 250 c.c. graduated flask, cooled, and filled up to the mark. 100 c.c. are filtered off, acidified with tartaric acid, 3 grm. in excess and a few drops of hydrochloric acid added, and the tin precipitated from the hot solution by hydrogen sulphide. If the colour of the precipitate proves arsenic to be present, the precipitate should be ignited and fused with peroxide as in the regular tin assay; otherwise it is dissolved at once in hydrochloric acid and potassium chlorate, the solution reduced, and titrated with iodine.

(*b*) *Arsenic* is next to tin the most frequent impurity. It occurs either as mispickel or as a ferric arsenate. The latter is very often insoluble in nitric, but soluble in hydrochloric, acid, and hence cannot be readily separated from wolfram by a selective attack. The first method here described is not applicable to ores containing arsenate.

(1) *Acid Attack.*[2]—From 1 to 20 grm. of ore, according to the arsenic content, are treated with 20 c.c. of strong nitric acid and 1 c.c. of bromine at 50° to 60° for about an hour. The acid is then boiled down to about 10 c.c., diluted with 50 c.c. of hot water, filtered, and the filtrate precipitated with an excess of ammonia. (If this does not produce a reasonably large precipitate of ferric hydroxide a little ferric chloride should be added to the acid solution, followed by an excess of ammonia.) The precipitate containing all the arsenic is filtered off, washed free from nitrates with 2 per cent. ammonium chloride, dissolved in hydrochloric acid, and the assay reduced with an excess of stannous chloride. Twice the volume of strong hydrochloric acid is added, the arsenic precipitated with hydrogen sulphide, the precipitate filtered and washed, first with 2 : 1 hydrochloric acid till free from tin, then with dilute sulphuric acid till free from chlorides. It is then dissolved in strong sulphuric acid, the solution neutralised with sodium bicarbonate, and the arsenious oxide titrated with weak iodine.

Alternatively, the ferric hydroxide precipitate may be distilled with concentrated hydrochloric acid and ferrous chloride, and the distillate titrated with potassium bromate in the presence of methylorange.

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[1] Powell, *loc. cit.*, p. 179.

[2] Authors' method.

(2) *Fusion Attack.*[1]—From 1·25 to 5 grm. of ore are fused with four to five times the weight in sodium peroxide; the cold melt is leached with hot water, the liquid transferred to a 250 c.c. flask, cooled, and made up to the mark. 100 or 200 c.c. are filtered off, saturated with hydrogen sulphide, and warmed with 5–10 grm. of tartaric and a large excess of hydrochloric acid. The precipitate is filtered off and treated as in the preceding method.

(*c*) *Bismuth* is usually present in very small quantities, in which case it is best determined colorimetrically.[2]

One grm. of ore is digested for ten to fifteen minutes with 10 c.c. 1 : 1 nitric acid, the acid boiled nearly to dryness, and the residue taken up with 50 c.c. 1 : 4 sulphuric acid. The solution is transferred by decantation to a 250 c.c. flask and diluted to the mark. 25 c.c. are filtered off into a Nessler tube, 3 c.c. of 50 per cent. potassium iodide added, and then a 0·5 per cent. solution of sodium sulphite drop by drop until the colour ceases to fade. The solution in the tube is then made up to the mark (50 c.c.) and compared with a standard tube containing known weights of bismuth. The standard is prepared with 50 c.c. of water containing 5 c.c. of 1 : 4 sulphuric acid, 3 c.c. of potassium iodide solution, and a few drops of the sodium sulphite solution. A bismuth solution, containing 0·1 grm. of bismuth per litre, is now added drop by drop to the standard tube till the tints match. One c.c. of standard solution is equivalent to 0·1 per cent. of bismuth on 0·1 grm. taken.

If much bismuth is present it is extracted from the ore by digestion with nitric acid, the insoluble residue filtered off, the filtrate diluted considerably, and the bismuth precipitated in the cold by hydrogen sulphide, the precipitate digested with sodium sulphide, then with sodium cyanide, dissolved in nitric acid, and the bismuth precipitated as oxychloride or phosphate.

(*d*) *Copper.*—The ore is digested with nitric acid, the wolfram filtered off, and the copper in the filtrate precipitated in the cold by hydrogen sulphide. The precipitate is ignited, dissolved in nitric acid, and the assay finished by any of the usual methods. If only small quantities are present ammonia is added without filtering off the wolfram and the copper determined colorimetrically in an aliquot portion of the filtrate.

(*e*) *Sulphur.*—The ore is digested with nitric acid and potassium chlorate until all the sulphur has dissolved. The unattacked wolfram is filtered off, the filtrate evaporated to dryness, the nitric acid destroyed by two evaporations with hydrochloric acid, the iron removed with ammonia, and the sulphur precipitated in the acidified filtrate with barium chloride in the usual manner.

(*f*) *Phosphorus.*[3]—2·5–5 grm. of slimed ore are decomposed with *aqua regia*, the tungstic acid is filtered off, and the filtrate evaporated

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[1] Authors' method; for distillation methods see Friedheim and Michaelis, *Ber.*, 1888, **28**, 56; Hilpert and Dieckmann, *ibid.*, 1913, **46**, 152.

[2] *Cf.* Beringer, *Textbook of Assaying.*

[3] See also Johnson, *Journ. Ind. Eng. Chem.*, 1913, **5**, 297.

with hydrochloric to expel nitric acid. The residue is taken up with dilute hydrochloric acid, the solution saturated whilst warm with hydrogen sulphide, allowed to stand overnight, and again treated with the gas. The filtered solution is boiled to expel hydrogen sulphide and evaporated to dryness with excess of nitric acid. The residue is taken up with dilute nitric acid and the solution treated with molybdate mixture as usual.

§ **X. Complete Analysis of Ores.**—The complete analysis of high-grade wolfram or scheelite concentrates is often required in connection with the manufacture of tungsten. The directions given below apply to such materials.

First Portion.—

1 grm. : *aqua regia* treatment (§ VIII, (*a*)).			
R^1 : extract with NH_4OH, then with 1 per cent. NaOH (§ III, (*a*) (2)).		F^1 : take to dryness, acidify, filter.	
R^2 : boil with salicylic acid (Columbium, § III, (*e*)), filter.	F^2 : WO_3 (§ IV.).	F^6 : pass H_2S, filter.	R^6 : 2nd SiO_2.
R^3 : ignite and weigh. Evaporate with $HF+H_2SO_4$, weigh again.	F^3 : TiO_2 (Cb, § III, (*e*)).	F^7 : oxidise with HNO_3; basic acetate separation.	P^7 : Pb, Bi, Cu, As, etc. (see Procedures 1 and 2).
R^4 : reduce in H current, extract with HCl.	L^4 : 1st SiO_2.	F^8 : boil with Br water and sodium acetate.	P^8 : determine Fe, Al, Ti.
R^5 : $Cb_2O_5 + Ta_2O_5$. Weigh.	F^5 : Sn. Titrate.	F^9 : determine Ca, Mg.	P^9 : MnO_2.

Notes.—R^5 : it is usually superfluous to separate the two earth acids.
P^7 : this will contain tin if stannine is present in the ore. In this case zinc should be looked for in F^9.

If the ore contains silicates, such as felspars, not decomposed by the acid treatment, the residue R^2 is fused with sodium carbonate, the melt evaporated to dryness with nitric acid, and taken up with nitric acid. The residue contains silicic, stannic, columbic, tantalic, and titanic acids, which are treated as detailed above. The acid filtrate containing the silicate bases is added to filtrate F^1.

Second Portion.—This is used for the determination of sulphur according to § IX, (*e*).

Third Portion.—For phosphorus determination, § IX, (*f*).

URANIUM.

§ **I. Minerals.**—All uranium minerals are radioactive.

(*a*) *Oxides, Carbonates.*—(1) *Uraninite*, uranoso-uranic oxide, U_3O_8, is a black pitch-like heavy mineral: sp. gr. 9·5 for the crystallised varieties, 6·4 for altered and massive varieties; H 5·5. Non-magnetic, brittle. Conchoidal fracture. It crystallises in the cubic system and is sometimes found as octahedra, but more often massive or botryoidal. Streak brown-black to olive-green and shining. There are many varieties of the mineral, of which *pitchblende* is the most important. This is a lighter (sp. gr. 6·5) amorphous, black mineral, which differs from uraninite in that it contains only traces of thorium and rare earths. *Gummite* is an orange to red-brown variety containing about 70 per cent. UO_3 : streak yellow. *Cleveite* contains about 10 per cent. of yttria earths ; *bröggerite* is a variety in which the ratio UO_3 to other bases is 1 : 1 ; *uranoniobite* contains up to 2·6 per cent. of nitrogen and rare gases.

(2) *Rutherfordine*, uranyl carbonate, UO_2CO_3, is a yellow, strongly radioactive alteration product of uraninite.

(3) *Uranothallite*, $U(CO_3)_2.2CaCO_3.10H_2O$, and *Liebigite*, $UO_2CO_3.CaCO_3.20H_2O$, are varieties of uranium calcium carbonate. They are both soft (H 2), green, translucent minerals having a vitreous to pearly fracture.

(*b*) *Silicates.*—(1) *Uranophane*, hydrous uranyl calcium silicate, $UO_3.CaO.2SiO_2.6H_2O$, occurs as minute acicular prisms in stellate or radiated aggregates, or massive with a fibrous structure. It is a honey-coloured, soft (H 2·5) mineral with a vitreous to pearly lustre. Sp. gr. 3·8.

(2) *Thorogummite*, $UO_3.3ThO_2.3SiO_2.6H_2O$, is a dull yellow-brown, hydrated silicate of uranyl and thoria crystallising in the tetragonal system ; the crystals resemble those of zircon (*q.v.*). H 4·5 ; sp. gr. 4·5.

(3) *Yttrogummite* is a translucent black mineral with a brilliant lustre and conchoidal fracture ; it consists of a silicate of uranyl, thoria, and yttria.

(*c*) *Phosphates and arsenates* of uranyl and copper, lime, or baryta ; general formula $R''O.2UO_3.P_2O_5.8H_2O$.

(1) *Torbernite* (copper uranite), copper uranyl phosphate (H 2·5 ; sp. gr. 3·5), is a brittle emerald-green mineral with a pearly to adamantine lustre and micaceous cleavage. Tetragonal, occurring in thin, transparent tablets or in micaceous aggregates.

(2) *Zeunerite* is the arsenic analogue of torbernite, which it closely resembles ; though the cleavage is perfect it is not micaceous.

(3) *Autunite* (lime uranite), calcium uranyl phosphate, occurs as thin tables or micaceous aggregates of a lemon-yellow colour giving a pale yellow streak. Perfect basal cleavage, and pearly lustre on cleavage faces. It is easily split up into brittle laminæ ; orthorhombic, usually transparent to translucent. H 2·5 ; sp. gr. 3·1.

(4) *Uranospinite*, the arsenic analogue of autunite, crystallises in green rectangular tables belonging to the orthorhombic system. H 2·5 ; sp. gr. 3·4. In other respects it resembles autunite.

(5) *Uranocircite* is autunite in which calcium is replaced by barium. Yellow-green mineral, sp. gr. 3·5 ; resembles autunite.

(*d*) *Other Phosphates and Arsenates.* — (1) *Phosphuranylite*,

$(UO_2)_3P_2O_8.6H_2O$, forms deep lemon-yellow incrustations consisting of minute rectangular crystals with a pearly lustre.

(2) *Trögerite*, $(UO_2)_3As_2O_8.12H_2O$, occurs as thin, yellow, monoclinic tables with a pearly lustre and perfect cleavage. Sp. gr. 3·3.

(3) *Walpurgite* is a yellow basic bismuth uranyl arsenate occurring in thin triclinic cleavable scales with a greasy lustre ; often twinned.

(*e*) *Other Minerals.*—(1) *Uranosphaerite* is a hydrated bismuth uranate found in greasy, orange, globular aggregates of radiated concentric crystals. Streak yellow. H 2 ; sp. gr. 6·4.

(2) Uranium is also found in minerals (*e.g. uranic ochre* and *zippeite*) consisting of basic uranyl sulphates with copper or lime or both, resulting from the decomposition of other uranium minerals, especially uraninite and its varieties.

(3) *Vanadates* (carnotite, etc.). See Vanadium, § I.

(4) Many titano-columbates, and minerals containing thoria and rare earths (*q.v.*), contain uranium.

§ II. Properties and Compounds.—(*a*) The *metal* is obtained by reducing the oxide, U_3O_8, with carbon in the electric furnace. It is white and readily combines with oxygen, the halogens, sulphur, and nitrogen. As a fine powder it decomposes cold water. The element and all its compounds are radioactive. Sp. gr. 18·7 ; M.P. 1500°.

(*b*) *Uranium dioxide*, UO_2, is a brown powder formed by heating the oxide, U_3O_8, in hydrogen. It has a sp. gr. of 10·15 and is soluble in strong sulphuric acid, giving uranous sulphate, $U(SO_4)_2.9H_2O$; strong nitric acid dissolves it to uranyl nitrate, $UO_2(NO_3)_2.6H_2O$; *aqua regia* converts it into uranyl chloride, $UO_2Cl_2.H_2O$. From fused borax it crystallises in black octahedra isomorphous with thoria (*q.v.*).

(*c*) *Uranoso-uranic oxide*, U_3O_8, is a satiny dark green powder formed by ignition of ammonium uranate, uranyl nitrate or carbonate, or any oxides of uranium in air. Sp. gr. 7·2. Soluble in strong nitric or sulphuric, more difficultly so in hydrochloric acid.

(*d*) *Ammonium diuranate*, $(NH_4)_2U_2O_7$, is an amorphous, deep yellow precipitate formed by adding ammonia to a uranyl salt. Soluble in acids. On ignition in air it leaves U_3O_8.

(*e*) *Sodium diuranate*, $Na_2U_2O_7$, is a yellow to orange precipitate produced by caustic soda in solutions of uranyl salts.

(*f*) *Uranyl nitrate*, $UO_2(NO_3)_2.6H_2O$, is formed by dissolving any oxide of uranium in nitric acid. It crystallises as lemon-yellow, fluorescent, rhombic prisms, readily soluble in water, alcohol, or ether.

(*g*) *Uranyl ammonium phosphate*, $UO_2NH_4PO_4$, is a greenish-yellow amorphous precipitate insoluble in acetic acid, obtained by mixing uranyl acetate with ammonium chloride and sodium phosphate solutions. On ignition it gives uranyl pyrophosphate, $(UO_2)_2P_2O_7$.

(*h*) *Uranyl ammonium carbonate*, $UO_2CO_3.2(NH_4)_2CO_3$, is very soluble in water, and is formed by adding excess of ammonium carbonate to solutions of uranyl salts. The corresponding sodium and potassium compounds are obtained in the same manner, and are also soluble in water.

(*i*) *Uranyl ferrocyanide.* See § VI, (*b*).

(*j*) *Uranyl sulphide*, UO_2S, is precipitated from neutral uranyl solutions by the addition of ammonium sulphide. It is a brown precipitate insoluble in ammonia (distinction from vanadium), but soluble in ammonium carbonate and in acids.

§ **III. Quantitative Separation.**[1]—In the general analytical procedure, uranium is found amongst the elements of the ammonia group. Advantage is taken of its solubility in solutions of alkali carbonates for separating it from many of the commoner metals. The following methods serve for the separation from most elements accompanying uranium in acid solution :—

(*a*) *Separation from Lead.*—This is best accomplished by precipitating lead as sulphate. The nitrate solution is evaporated with sulphuric acid to fumes as usual.

(*b*) *Separation from Metals of the Hydrogen Sulphide Group other than Lead.*—These are precipitated by hydrogen sulphide from a solution containing 5 per cent. of strong hydrochloric acid. It is sometimes advisable to dissolve the precipitate in acid and repeat the precipitation.

(*c*) *Separation from the Rare Earths.*[2]—The rare earths are precipitated from weakly acid solution with a small excess of oxalic acid ; the solution is warmed to 60° and allowed to stand overnight. The oxalate precipitate is filtered off and the solution evaporated to dryness ; the residue is gently ignited to destroy oxalates, and digested with hydrochloric acid, any insoluble material from this treatment being brought into solution by fusion with bisulphate.

(*d*) *Separation from Iron,*[3] *Titanium, Cobalt, Zinc, Manganese.*—The filtrate (100 c.c.) from the rare earth separation, or—if none of the latter were present—the solution of the ammonia precipitate in hydrochloric acid, is treated with excess of ammonia, 5 grm. of ammonium carbonate, and a sufficiency of ammonium sulphide.[4] The mixture is allowed to stand overnight in a corked flask, filtered, and the precipitate washed with water containing ammonium carbonate and sulphide. The filtrate is boiled, acidified with hydrochloric acid, again boiled to expel hydrogen sulphide, and the uranium precipitated with ammonia. The sulphide precipitate, if bulky, should be re-dissolved and re-precipitated as before. The uranium precipitate may contain beryllium, phosphoric acid, and small quantities of aluminium and zirconium. If nickel is present, the method given under (*e*) is preferable.

(*e*) *Separation from Iron,*[5] *Titanium,*[5] *Cobalt, Nickel, Manganese, Zinc, Beryllium, and Alkaline Earths.*—The boiling neutral solution (about 50 c.c.) is poured into 50 c.c. of hot water containing 3 grm.

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[1] Kern, *Journ. Amer. Chem. Soc.*, 1901, **23**, 685 ; Brearley, *The Analytical Chemistry of Uranium*, London, 1903.

[2] Hillebrand, *Bull. U.S. Geol. Survey*, No. 78 (1890), 43.

[3] See also Glaser, *Chem. Zeit.*, 1912, **36**, 1166.

[4] Rose, *Chem. News*, 1871, **24**, 233.

[5] Basic Acetate Separation, Rheineck, *Chem. News*, 1871, **24**, 233 ; Brearley, *op. cit.*, footnote [1].

of sodium carbonate.[1] After boiling for ten minutes the solution is diluted to 350 c.c. and boiled for another half hour. The precipitate is allowed to settle, filtered off, and washed with 1 per cent. sodium carbonate solution. The filtrate is boiled with hydrochloric acid to expel carbon dioxide and the uranium precipitated with ammonia. This precipitate may contain phosphoric acid and small amounts of aluminium.

(*f*) *Separation from Aluminium.*[2]—The ammonia precipitate obtained as under (*e*) is dissolved in nitric acid and the uranium and aluminium precipitated as phosphates according to § IV, (*c*). The washed precipitate is boiled with dilute nitric acid, the solution filtered and boiled with excess of sodium carbonate. Sufficient ammonium chloride is added to decompose the sodium carbonate, and the liquid allowed to stand for two hours. The aluminium phosphate is filtered off and washed with very dilute ammonium carbonate.

(*g*) *Separation from Zirconium.*—Zirconium is precipitated as phosphate from a solution containing hydrogen peroxide and 1 per cent. of free sulphuric acid. (See Titanium, § III, (*b*) (2).)

(*h*) *Separation from Vanadium.*[3]—(1) The best method consists in just acidifying the alkaline carbonate solution (from (*d*) or (*e*)) with nitric acid and adding excess of lead acetate, and ammonium acetate to replace the nitric acid; the vanadium is precipitated as lead vanadate; the uranium is in solution together with the excess of lead, which is removed by hydrogen sulphide, or preferably sulphuric acid.

(2) To the sulphuric acid solution of the uranium and vanadium, containing not more than 0·25 grm. of U_3O_8, 0·5 grm. of $(NH_4)_2HPO_4$ is added, the solution heated to boiling, and treated with an excess of ammonia. The uranium is precipitated as $UO_2NH_4PO_4$; the vanadium is in solution. If much vanadium is present the precipitate is dissolved in dilute nitric acid and re-precipitated with ammonia.[4] The precipitate should be washed with dilute ammonium sulphate solution.

(*i*) *Separation from Phosphoric* (*Arsenic*) *Acid.*[5]—The slightly acid (hydrochloric) solution is treated with an excess of potassium ferrocyanide and saturated with sodium chloride. The precipitate of uranyl ferrocyanide is filtered off and washed with cold saturated sodium chloride solution until the washings are free from ferrocyanide. The moist precipitate is digested in the cold with caustic potash, the potassium uranate filtered off, washed with ammonia and ammonium chloride till free from ferrocyanide, and dissolved in dilute hydrochloric acid. Any insoluble matter is filtered off and re-treated with caustic potash as above. The combined filtrates are treated according to (*b*) if copper is present; iron is next removed as under (*e*). If much

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[1] Patera, *Z. anal. Chem.*, 1866, **5**, 228; Low, *Technical Methods of Ore Analysis.*

[2] After Brearley (*op. cit.*, p. 185).

[3] Moore and Kithil, *Bull.* 70, *U.S. Bureau of Mines.*

[4] Finn, *Journ. Amer. Chem. Soc.*, 1906, **28**, 1443.

[5] Fresenius and Hintz, *Z. anal. Chem.*, 1895, **34**, 437.

arsenic acid is present, direct precipitation of uranium as ferrocyanide is preferable to removal of the arsenic as sulphide.

§ **IV. Gravimetric Determination.**—(*a*) *As Uranoso-uranic Oxide* (U_3O_8).[1]—The acid solution is treated with a small excess of ammonia (free from carbonate) and ammonium nitrate and heated to boiling. The yellow precipitate of ammonium uranate is allowed to settle, filtered off, washed with a hot 5 per cent. solution of ammonium nitrate, dried, ignited gently, and weighed as U_3O_8; this, if pure, should be of a dark green colour.

(*b*) *As Uranium Dioxide.*—The green oxide, U_3O_8, is heated to redness in a stream of pure hydrogen, whereby it is quantitatively changed to the pure brown dioxide, UO_2. After cooling in hydrogen it is weighed. This is the most accurate method of estimating uranium,[2] the composition of the green oxide never being quite constant.

(*c*) *By Precipitation as Uranyl Ammonium Phosphate and Ignition to Uranyl Pyrophosphate.*[3]—The acid solution is treated with microcosmic salt equal to at least ten times the weight of uranium present, and heated to boiling; ammonia is added drop by drop till a precipitate begins to form; this is cleared with a few drops of dilute nitric acid, after which 10 grm. of sodium thiosulphate are added and the solution boiled. After addition of 10 c.c. of 25 per cent. ammonium acetate solution (*i.e.* more than sufficient to replace the nitric by acetic acid) the solution is boiled ten minutes longer. The granular precipitate of uranyl ammonium phosphate and sulphur is ignited in a tared crucible, the greenish residue moistened with nitric acid, dried on the water-bath, and gently ignited. It is weighed as $(UO_2)_2P_2O_7$, which should be of a pure lemon-yellow colour.

(*d*) *As Sodium Diuranate,* $Na_2U_2O_7$.[4]—The acid solution of the pure uranium salt is precipitated by the addition of excess of caustic soda. The precipitate is filtered off, washed with hot water, dried, and brushed off the paper on to a watch-glass. The paper is burnt off in platinum, the rest of the precipitate added and strongly ignited. After cooling it is transferred to a small paper and well washed with hot water to remove alkali. The precipitate is again dried, ignited, and finally weighed as $Na_2U_2O_7$. As pure caustic soda is difficult to obtain the tendency is to get high results, but the method is useful as a rapid check.

§ **V. Volumetric Determination.**—(1) The solution containing the uranium as uranyl sulphate and 15 per cent. of sulphuric acid in a bulk of 100 to 150 c.c., is heated nearly to boiling and passed through the Jones' reductor, preceded by 200 c.c. of 15 per cent. sulphuric acid. The reducing column should be 18 in. long and charged with 20-mesh amalgamated zinc; gentle suction is used. The reductor is washed with 25 c.c. of the same acid, then with 250 c.c. of hot

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[1] Kern, *loc. cit.*, p. 185.

[2] Treadwell-Hall, vol. ii. p. 101; *cf.* Kern, *loc. cit.*

[3] Brearley, *op. cit.*, p. 185.

[4] Patera, *loc. cit.*, p. 186.

water. The contents of the receiver are poured slowly, with exposure to the air, into a capacious porcelain basin, diluted with 200 c.c. of hot water, and titrated with N/20 permanganate. During the reduction the zinc must always be kept covered with liquid; 0·3 grm. UO_3 requires half an hour for complete reduction. The solution is usually olive-green immediately after reduction, but on exposure to the air changes to sea-green, and the uranium is then all present in the tetravalent form.

(2) Instead of using the reductor,[1] the acid solution containing the uranium in 15 per cent. sulphuric acid may be treated with 10 grm. of granulated zinc[2] or strip aluminium,[3] and the action allowed to go on vigorously for half an hour, after which the zinc is filtered off on cotton-wool. The solution is titrated at 60° with N/20 permanganate (1 c.c=0·005955 grm. U, or 0·007022 grm. U_3O_8).

$$UO_2SO_4+2H_2SO_4+Zn=U(SO_4)_2+ZnSO_4+2H_2O$$
$$5U(SO_4)_2+2KMnO_4+2H_2O=5UO_2SO_4+2KHSO_4+2MnSO_4+H_2SO_4.$$

§ **VI. Detection in Ores.**—All uranium minerals are radioactive and affect a photographic plate (see Introduction). To detect uranium in an ore it is digested with nitric acid or fused with bisulphate, the solution evaporated to dryness, the residue digested with hydrochloric acid, and the heavy metals precipitated with hydrogen sulphide. The filtrate is oxidised with hydrogen peroxide and boiled with an excess of sodium carbonate. The uranium is in the solution, which is filtered, acidified with hydrochloric acid, and boiled to expel carbon dioxide, after which the following tests may be applied:—

(*a*) Ammonia produces a yellow precipitate, soluble in ammonium carbonate, re-precipitated on long boiling.

(*b*) Potassium ferrocyanide gives a brown precipitate which on digestion with caustic alkali is converted into yellow uranate.

(*c*) Reduction with zinc causes the yellow colour to change to deep green.

(*d*) Ammonium phosphate, in presence of excess of acetate, produces a greenish-white precipitate.

(*e*) Addition of ammonia and ammonium sulphide produces a brown precipitate soluble in ammonium carbonate.

(*f*) Caustic soda throws down a yellow to orange precipitate from the acid or sodium carbonate solution.

§ **VII. Determination in Ores.**[4]—(*a*) *Method for Ores free from Rare Earths. Applicable to Phosphate Ores.*—From 0·5 to 1 grm. of ore is boiled to complete decomposition with 10 c.c. nitric acid, using hydrochloric acid also if necessary, and finally evaporated to dryness to

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[1] Newton and Hughes, *Journ. Amer. Chem. Soc.*, 1915, **37**, 1711, reduce with titanous sulphate, add bismuth oxide to destroy the excess of titanous salt, and titrate the filtrate with permanganate.

[2] Ibbotson and Clarke, *Chem. News*, 1911, **103**, 146.

[3] Campbell and Griffin, *Journ. Ind. Eng. Chem.*, 1910, **1**, 455.

[4] After Moore and Kithil, *loc. cit.* (p. 186); Hillebrand, *loc. cit.* (p. 185); Low, *op. cit.* (p. 186).

remove silica. The residue is boiled with 3 c.c. of hydrochloric acid and 25 c.c. of water, the liquid filtered, the filtrate saturated with hydrogen sulphide (under pressure if molybdenum or arsenic is present), and filtered; the hydrogen sulphide is expelled from this filtrate and the iron oxidised with chlorate. The solution is now poured into 50 c.c. of water containing 5 grm. sodium carbonate, boiled, removed from the heat, treated with 5 grm. of ammonium chloride, and allowed to stand several hours. The precipitate is filtered off and washed with dilute ammonium carbonate; if large, it should be dissolved and re-precipitated. The filtrate is boiled to decompose ammonium carbonate, slightly acidified with nitric acid, and the carbon dioxide completely expelled by boiling. Microcosmic salt equal to ten times the uranium present is now added, and nitric acid drop by drop to clear any precipitate, followed by 10 grm. of thiosulphate and 25 c.c. of acetic acid. After boiling five minutes, 10 c.c. of 25 per cent. ammonium acetate are added and the boiling continued another ten minutes. The precipitate is allowed to settle, filtered off, washed thoroughly first by decantation, then on the filter with boiling water, and ignited wet in a porcelain crucible. The residue is moistened with nitric acid, the latter evaporated, the mass ignited, and weighed as $(UO_2)_2P_2O_7$.

(*b*) *Method for Ores containing Rare Earths, but free from Phosphoric Acid.*—Uraninite and oxide or silicate ores decomposed by acids are opened up as under (*a*). Titano-columbates and the like are fused with six times their weight in sodium bisulphate; the melt is extracted with cold dilute hydrochloric acid and the solution filtered. Either filtrate is treated with hydrogen sulphide, the precipitate filtered off, and the solution oxidised with nitric acid. It is then neutralised and treated with an excess of 3 grm. of sodium carbonate. After boiling and filtering, the precipitate is re-dissolved in dilute nitric acid and the solution again boiled with an excess of 3 grm. of sodium carbonate. The combined filtrates are acidified with hydrochloric acid, boiled to expel carbon dioxide, and precipitated with ammonia. The precipitate is washed with ammonium nitrate, dissolved in hydrochloric acid, and the solution treated with 20 c.c. of saturated ammonium oxalate solution followed by a few drops of hydrochloric acid. After boiling and allowing to stand overnight the precipitate of rare earth oxalates is filtered off, the filtrate evaporated to dryness, and the residue gently ignited. It is dissolved in nitric acid, an excess of ammonia and ammonium carbonate added, and the solution warmed. The small precipitate of alumina is filtered off, washed with ammonium carbonate water, re-dissolved in nitric acid, and re-precipitated with ammonium carbonate. The combined filtrates are boiled to destroy ammonium carbonate, the precipitated ammonium uranate dissolved in nitric acid and re-precipitated by ammonia, washed with 4 per cent. ammonium nitrate, ignited, and weighed as U_3O_8. The purity of this may be tested by reducing it to the dioxide in a stream of hydrogen, or by the following method (Hillebrand):—The weighed U_3O_8 is placed in a hard glass thick-walled tube with 10–15 c.c. of 1 : 6 sulphuric acid, the air displaced by carbon dioxide, and the tube sealed. It is heated to 150°–175° until all has dissolved to a clear green liquid. After cooling this is transferred to a beaker, diluted with 500 c.c. of cold water, and titrated with N/50 $KMnO_4$ (1 c.c.$=$0·008426 grm. U_3O_8).

$$U_3O_8+4H_2SO_4=2UO_2(SO_4)+U(SO_4)_2+4H_2O$$
$$2KMnO_4+5U(SO_4)_2+2H_2O=2KHSO_4+2MnSO_4+H_2SO_4+5UO_2SO_4.$$

(*c*) *Ores containing Phosphoric* (*Arsenic*) *Acid.*—The ore is dissolved in strong nitric acid, an excess of iron over that required to combine with all the P_2O_5 and As_2O_5 added, and the solution neutralised with ammonia, avoiding a permanent precipitate; 2 c.c. of acetic acid (sp. gr. 1·04) are added, the solution heated to boiling, and treated with 20 c.c. of 25 per cent. ammonium acetate. The precipitate of phosphate and arsenate of iron is filtered off, washed with dilute ammonium acetate, dissolved in nitric acid, and the precipitation repeated. The combined filtrates are treated with an excess of ammonia, the precipitate filtered, washed with 4 per cent. ammonium nitrate, dried, ignited, and weighed as U_3O_8. If much alkaline earths are present the precipitate should be re-dissolved in a minimum of nitric acid, and treated with a few c.c. of dilute sulphuric acid and an equal volume of alcohol. The precipitate is filtered off, washed with 40 per cent. alcohol, the filtrate boiled to expel the alcohol, traces of copper removed with hydrogen sulphide, the excess of which is boiled off and the uranium precipitated as above with ammonia. (See also § III, (*i*).)

(*d*) *Determination of Uranium in Carnotite.*—From 2 to 5 grm. of ore, according to the quantity of vanadium, uranium, and iron, are digested cold for fifteen minutes with 10 c.c. of strong hydrochloric acid with occasional shaking; 5 c.c. of nitric acid are added, the solution heated to boiling, and finally evaporated to dryness. The residue is taken up with 3 c.c, hydrochloric acid and 5 c.c. water, the solution heated on the steam-bath for five minutes, diluted with 25 c.c. hot water, and filtered. The residue, which may contain vanadium, is washed with warm water, ignited in a platinum dish, treated with 5 c.c. of hydrofluoric acid, and evaporated to dryness on the steam-bath, avoiding baking; it is taken up with 3 c.c. hydrochloric acid and again evaporated to dryness. The latter process is repeated once more to ensure complete expulsion of hydrofluoric acid, the final residue taken up with 5 c.c. 1 : 1 hydrochloric acid, warmed until any red crust has dissolved, and filtered into the main liquid, which is then saturated with hydrogen sulphide to remove heavy metals. The filtrate from the sulphides is boiled to expel hydrogen sulphide, oxidised with hydrogen peroxide, concentrated to 100 c.c., and neutralised with sodium carbonate. Three grm. excess are added, the solution boiled fifteen to twenty minutes, filtered, the precipitate washed with hot water, re-dissolved in a minimum of nitric acid, hydrogen peroxide added, and the same excess of sodium carbonate. The solution after boiling fifteen minutes is filtered into that from the first precipitation, the combined filtrates evaporated to 200 c.c., neutralised with nitric acid, and boiled to expel carbon dioxide. The solution is neutralised with ammonia and 4 c.c. nitric acid for each 100 c.c. of solution added, followed by 10 c.c. of 20 per cent. lead acetate solution and 25 c.c. of 25 per cent. ammonium acetate. The liquid is heated on the steam-bath for one hour, filtered through close-textured paper, the precipitate washed with warm water, and dissolved in a minimum of hot 1 : 5 nitric acid ; the solution is neutralised with ammonia, and 3 c.c. of nitric acid, 2 c.c. of lead acetate, and 15 c.c. ammonia acetate added. The precipitate is filtered and washed as before ; the filtrates are concentrated to 400 c.c., 10 c.c. of strong sulphuric acid added, and the lead sulphate filtered off and washed with cold water. The filtrate is neutralised with ammonia, an excess of ammonium sulphide added, and the solution heated on the water-bath till the precipitate settles. It is filtered off, washed slightly with warm water and dissolved in 1 : 2 nitric acid, which is taken to fumes with 5 c.c. of sulphuric acid. The cool mass is taken up with water, the solution boiled, and allowed to cool ; the small precipitate of lead sulphate is filtered and washed with dilute sulphuric acid. The filtrate is nearly neutralised with ammonia, cooled below 30°, treated with an excess of 2 grm. of ammonium carbonate, the precipitate allowed to settle, filtered, and washed with warm water. If large or of a yellowish colour it is dissolved in dilute sulphuric acid and re-precipitated with ammonium carbonate as before. The united filtrates are boiled with dilute sulphuric acid until all carbon dioxide is expelled, a small excess of ammonia added to the hot solution, and the whole allowed to stand until the precipitate of ammonium uranate collects and settles, when it is filtered, washed with 2 per cent. ammonium nitrate, ignited wet, and weighed as U_3O_8. It is advisable not to let the precipitate run dry on the paper after the first washing, and in all cases its purity should be tested by dissolving it in nitric acid and re-precipitating with ammonium carbonate to make sure it is quite free from alumina ; it should also be tested with hydrogen peroxide for vanadium.

The vanadium is determined in the lead precipitate by dissolving it in dilute nitric acid, evaporating to fumes with 10 c.c. of sulphuric acid, diluting, reducing with sulphur dioxide, and titrating with permanganate (see Vanadium, § V.). The iron precipitate after the second sodium carbonate extraction may contain vanadium. It is ignited in a platinum crucible and fused with sodium carbonate, the cold melt extracted with hot water, the solution filtered, acidified with dilute sulphuric acid, reduced, and titrated as usual.

§ VIII. Complete Analysis of Ores.—(*a*) *Oxides and Silicates.*—Mineral mixtures belonging to this class are likely to be of great complexity. Rare earths, zirconium, and selenium have to be taken into account in addition to the commoner metals of all the analytical groups. The scheme given below is fairly comprehensive, and includes the estimation of noble and other gases found in most radioactive minerals.

First Portion.—

Digest 1 grm. of finely crushed ore with acid (§ VII, (*a*)). Evaporate to dryness, take up with dilute HCl, filter.

R^1: extract with $CH_3CO_2NH_4$, filter.

R^2: fuse with Na_2CO_3. Leach, evaporate to dryness with HCl, take up in dilute HCl, filter.

F^2: ppte with H_2SO_4, add to P^8.

R^3: ignite, weigh. Treat with $HF+H_2SO_4$, ignite, weigh again.

F^3: add to F^1.

R^4: fuse with $NaHSO_4$. Leach with dilute H_2SO_4, filter.

L^4: SiO_2.

R^5: weigh $BaSO_4$.

F^5: ppte with NH_4OH, dissolve in HCl, add to F^1.

F^1: add F^3 and F^5; pass H_2S, filter.

P^6: extract with Na_2S, filter.

R^7: dissolve in HNO_3, evaporate with H_2SO_4, dilute with 4 vol. H_2O, filter.

P^8: add ppte from F^2, weigh $PbSO_4$.

F^8: pass H_2S, filter, reject filtrate, digest ppte with KCN, filter.

R^9: determine Bi.

F^9: boil with H_2SO_4, pass H_2S, filter off, ignite, weigh CuO.

F^7: ppte with CH_3CO_2H, pass H_2S, boil, filter, reject filtrate, dissolve ppte in $HCl+KClO_3$, boil off Cl, pass SO_2, filter next day.

F^{10}: add H_2O_2, NH_4OH, pass H_2S, acidify, pass H_2S, boil, filter, reject filtrate, treat ppte for As and Sb (Procedure 1).

P^{10}: Se, reject.

F^6: oxidise with HNO_3, add 5 grm. NH_4Cl, NH_4OH, pass H_2S, filter. Dissolve and reppte; combine filtrates.

P^{11}: dissolve in $HCl+HNO_3$, add 5 grm. NH_4Cl, excess NH_4OH, filter; repeat pption, combine filtrates.

F^{11}: Ca (Ba), Mg. See Procedure 9.

P^{12}: dissolve in HCl, adjust acidity to N/2, add saturated $C_2O_4H_2$ solution in slight excess, warm to 60°, let stand overnight, filter.

F^{12}: add F^{16}, determine Mn, Zn, Ni, Co (Procedure 6).

P^{13}: Th and rare earths. See Thorium, § III., and Rare Earths, § III, (*a*).

F^{13}: evaporate to fumes with H_2SO_4, dilute, neutralise with Na_2CO_3, add 3 grm. excess, boil, dilute to 200 c.c., boil again, filter. Dissolve ppte in HNO_3 or H_2SO_4; repeat pption, combine filtrates.

P^{14}: dissolve in HCl, add 1 grm. of $C_4H_6O_6$, make ammoniacal, pass H_2S, filter. Dissolve in HCl (a little NiS or CoS may remain undissolved), add 1 grm. $C_4H_6O_6$; repeat pption, combine filtrates.

F^{14}: acidify with H_2SO_4, boil to expel CO_2. Add NH_4OH, filter, wash with 2 per cent. NH_4NO_3, reject filtrate. Dissolve in hot dilute HNO_3, add 1 c.c. of saturated Na_2HPO_4 solution, pour into large excess of $(NH_4)_2CO_3$; warm, filter after 2 hours.

F^{15}: Al, Zr, Ti. See Ti, § III.

P^{15}: dissolve in *aqua regia*, ppte Fe as basic acetate, filter.

P^{16}: determine Fe.

F^{16}: add to F^{12}.

P^{17}: fuse with Na_2CO_3, leach, filter.

F^{17}: if much U is present, take aliquot portion containing less than 0·25 grm. U_3O_8, ppte as $UO_2NH_4PO_4$ (§ IV, (*c*)).

P^{18}: fuse with a little $NaHSO_4$, leach, adjust acidity to 1 per cent. H_2SO_4, add H_2O_2, 1 c.c. of Na_2HPO_4 solution, filter next day.

F^{18}: add to F^{19}.

P^{19}: ignite and weigh as zirconium phosphate containing 50 per cent. ZrO_2.

F^{19}: add F^{18}, acidify slightly, ppte with $Na_2S_2O_3$ and $CH_3CO_2NH_4$, filter, ignite and weigh $AlPO_4$.

Second Portion: selenium.—Heat ore in chlorine current (see Selenium, § VIII, (*b*)).

Third Portion: gases (helium, argon, nitrogen, hydrogen). Hillebrand's method.[1]—1–2 grm. of ore is mixed with six times its weight of fusion mixture in a platinum boat. The latter is completely surrounded by platinum-foil to prevent spattering on to the walls of the porcelain tube in which the fusion is carried out in a current of pure carbon dioxide. The latter must contain no gases unabsorbed by strong caustic potash solution. When the air in the apparatus is completely displaced by carbon dioxide the tube is heated gently, then to a bright red heat, and kept at that temperature until the volume of gas collected over strong caustic potash in a nitrometer ceases to increase (two to three hours). The gases are transferred to a tube filled with distilled water and the corrected volume ascertained in the usual manner. To convert the number of c.c. of gases per gramme of ore into per cent. by weight it is necessary to determine the specific gravity of the mixture by weighing the dried gas in a small gas pipette of known capacity.

Separate Portions for water (direct determination), carbon dioxide, sulphur, and sulphur trioxide.

(*b*) *Titanocolumbates.*—See Tantalum, § VII.

(*c*) *Phosphates* (*Arsenates*).—*First Portion.*—

<table>
<tr><td colspan="4">1 grm. ; dissolve in HCl, add HNO_3, evaporate to dryness, take up with HCl, filter.</td></tr>
<tr><td colspan="2">R^1 : extract w. $CH_3CO_2NH_4$, filter.</td><td colspan="2">F^1 : add F^3, pass H_2S, let stand overnight, again pass gas, filter.</td></tr>
<tr><td>R^2 : fuse with Na_2CO_3, evaporate with HCl, filter.</td><td>F^2 : add to Pb in P^4.</td><td rowspan="2">F^4 : add excess of 3 grm. Na_2CO_3, boil 10 minutes, filter. Re-dissolve and re-ppte as before, combine filtrates.</td><td rowspan="2">P^4 : determine As_2O_5, Cu, Bi, Pb (see also F^2).</td></tr>
<tr><td>R^3 : determine SiO_2 and $BaSO_4$.</td><td>F^3 : add to F^1.</td></tr>
<tr><td colspan="2">P^5 : dissolve in HCl, apply basic acetate separation.</td><td colspan="2">F^5 : add sufficient NH_4Cl to decompose Na_2CO_3, let stand two hours, filter.</td></tr>
<tr><td>F^7 : determine Ba, Ca.</td><td>P^7 : dissolve in minimum of HCl, pour into NaOH, filter, repeat treatment.</td><td>P^6 : dissolve in HCl, add to F^8.</td><td>F^6 : determine U with $Na_2S_2O_3$ and $NaNH_4HPO_4$ (§ IV.).</td></tr>
<tr><td colspan="3">F^8 : add solution from P^6, acidify with HCl, add 1 grm. Na_2HPO_4, ppte with $Na_2S_2O_3+CH_3CO_2NH_4$, ignite, weigh $AlPO_4$.</td><td>P^8 : titrate Fe.</td></tr>
</table>

Second Portion: phosphoric acid.—Dissolve as described above; remove all As by H_2S, evaporate filtrate with HNO_3 to expel HCl, proceed as usual for molybdate method.

Third Portion: combined water (Penfield's method).

(*d*) *Carnotite. First Portion.*—1 grm. of ore is treated in the same manner as a phosphate ore (see preceding table) up to the point where the treatment of F^4 with an excess of 3 grm. Na_2CO_3 results in a filtrate F^5 and a precipitate P^5. These are treated as follows :—

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[1] *Loc. cit.* (p. 185).

<table>
<tr><td colspan="2">P^5: ignite, fuse with 2–3 grm. Na_2CO_3, leach, filter.</td><td colspan="2">F^5: add F^6. Acidify with HNO_3, boil to expel CO_2, add $Pb(CH_3CO_2)_2$ and $CH_3CO_2NH_4$ (§ VII, (*d*)); repeat pption.</td></tr>
<tr><td>R^6: dissolve in HCl, apply basic acetate separation.</td><td>F^6: add to F^5.</td><td rowspan="2">F^8: add H_2SO_4, filter, reject ppte. Add NH_4OH and $(NH_4)_2S$, filter, reject filtrate. Dissolve ppte in HNO_3,</td><td rowspan="2">P^8: dissolve in HNO_3, evaporate with H_2SO_4, reduce with SO_2, titrate V_2O_5.</td></tr>
<tr><td>P^7: Fe, Ti, part of Al (Procedure 5).</td><td>F^7: Ba, Sr, Ca, Mg (Procedure 9).</td></tr>
<tr><td colspan="4">evaporate to fumes with H_2SO_4, dilute, filter, reject ppte. Ppte with $Na_2S_2O_3$, Na_2HPO_4, and $CH_3CO_2NH_4$ (§ IV.). Extract with dilute H_2SO_4, filter off sulphur, boil with excess of Na_2CO_3, add enough NH_4Cl to decompose Na_2CO_3, let stand two hours, filter.</td></tr>
<tr><td>P^9: ignite, weigh $AlPO_4$.</td><td colspan="3">F^9: acidify, boil, again ppte U as phosphate, ignite and weigh.</td></tr>
</table>

Second Portion: for alkalies by L. Smith's method; test for Li.

Third Portion: combined water.

Fourth Portion: for sulphur, if present.

§ **IX. Technical Methods.**—(*a*) *Gravimetric.*—(1) The ore is decomposed as described in § VII, (*a*). The filtrate from the silica is diluted to 100 c.c., nearly neutralised with ammonia, treated with 5 grm. of ammonium carbonate, heated to boiling, and filtered. The precipitate is dissolved in hydrochloric acid and the solution reprecipitated as before. The combined filtrates are boiled to decompose ammonium carbonate and acidified with hydrochloric acid, the solution treated with hydrogen sulphide, the filtrate oxidised with hydrogen peroxide, and the uranium precipitated as phosphate (§ VII, (*a*)). In this method vanadium interferes slightly by replacing part of the phosphorus in $(UO_2)_2P_2O_7$.

(2) 1–5 grm. of ore is digested with nitric acid, the dry residue taken up with dilute nitric acid, and the insoluble gangue filtered off. The solution is nearly neutralised with sodium carbonate and poured into a boiling solution of 10 grm. of sodium carbonate in 50 c.c. of water. After boiling a short time the precipitate is filtered off and washed with hot water. The filtrate is neutralised with hydrochloric acid, boiled to expel carbon dioxide, and treated with an excess of caustic soda, when all the uranium is thrown down as $Na_2U_2O_7$. This is filtered off, washed, dried, and ignited apart from the paper. The ignited residue is transferred to a filter and well washed with hot water to remove adsorbed sodium salts. The pure sodium diuranate is once more dried, ignited apart from the paper, and weighed. Copper leads to slightly high results; arsenates, vanadates, and phosphates must be absent.

(*b*) *Rapid Volumetric Method.*[1]—A quantity of ore containing not more than 0·25 grm. U_3O_8 is dissolved in sulphuric acid (1 : 5) and evaporated finally to fumes. The cool mass is taken up in water, the solution treated with an excess of sodium carbonate and well boiled; the precipitate is filtered off, washed with hot water, re-

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[1] Finn, *Journ. Amer. Chem. Soc.*, 1906, **28**, 1443.

dissolved in a minimum of sulphuric acid (1 : 5), and the precipitation with sodium carbonate repeated. The combined filtrates are acidified with sulphuric acid ; 0·5 grm. of ammonium phosphate is added, the solution heated to boiling, and made just alkaline with ammonia. After boiling a few minutes the precipitated uranyl ammonium phosphate is filtered, washed with 2 per cent. ammonium sulphate solution, dissolved in dilute sulphuric acid, and treated with 10–15 grm. of zinc to give a vigorous reduction for thirty minutes. The solution is then decanted through a plug of absorbent cotton-wool, and the flask and filter well washed with dilute sulphuric acid. The filtrate is titrated with N/20 permanganate at a temperature of 60°. Vanadium if present will be found in the filtrate from the phosphate precipitation, and may be estimated by any of the usual methods.

(*c*) *Electroscopic Method.*—This is based on the fact that the radioactivity of an ore is proportional to its uranium content, and is carried out in the Curie electroscope (see Introduction). The ore is crushed to pass a 30-mesh ; it need not be dry, and should not be dried by heat, as this would expel some of the emanation, and several days elapse before radioactive equilibrium is regained. The sample need not be weighed, but the area of the surface should be equal to that of the ore used as a standard, which is ensured by the use of shallow cylindrical containers of identical dimensions. The time taken by the gold leaf in traversing a certain number of divisions is ascertained by means of a stop-watch for the standard, and again over the same divisions for the ore. The air leak is determined by observing the fall of the leaf during five minutes. The rate of discharge per minute is calculated in each case ; the net rate of discharge (*i.e.* observed rate *minus* rate of leak) of the ore divided by that of the standard and multiplied by the percentage of uranium in the latter gives the percentage of uranium in the ore.

If the operator is skilled in the use of the instrument, the results are in fair agreement with those obtained by analysis. The ore and the standard should preferably belong to the same mineralogical species to ensure the same ratio of uranium to its degradation products (ionium, radium, its emanation and descendants), as the combined radioactive power of the latter is 3·62 times stronger than that of uranium (Rutherford). If, as is often done, pure uranium dioxide is used as a standard, the percentage of U_3O_8 found as above must be multiplied by $\frac{U_3O_8}{3UO_2 \times 4{\cdot}62}$, or 0·225.

CHAPTER IX.

THE EIGHTH GROUP.

RUTHENIUM—RHODIUM—PALLADIUM—OSMIUM—IRIDIUM—PLATINUM.

Generalities.

The six rarer elements of this group are those commonly called "platinum metals" because they occur together in native platinum, from which they were first isolated. They fall into two distinct sub-groups, viz. the lighter platinum metals (ruthenium group), and the heavier platinum metals (osmium group). Again, they may be grouped in three pairs according to their vertical arrangement in the Table. The members of each pair have certain features in common, although the six metals resemble each other more or less in some respects.

Perhaps the most gradual transition in chemical deportment may be observed if they are placed in the order indicated below :—

$$\begin{tikzcd}
\textit{Ruthenium group}: & \mathrm{Ru}\ (2) \arrow[r, dash] \arrow[d, dash] & \mathrm{Rh}\ (3) \arrow[d, dash] & \mathrm{Pd}\ (6). \arrow[d, dash] \\
\textit{Osmium group}: & \mathrm{Os}\ (1) & \mathrm{Ir}\ (4) \arrow[r, dash] & \mathrm{Pt}\ (5).
\end{tikzcd}$$

or, Os—Ru—Rh—Ir—Pt—Pd.

The two extremes of this series, linked together by the intermediate metals, exhibit greatest dissimilarity. Thus, osmium is rather non-metallic in habit : one of its most important compounds, osmic acid, gives well-defined salts. The element is characterised by the readiness with which it is converted into the volatile tetroxide. The compact metal is insoluble in all acids. Ruthenium closely resembles osmium in forming ruthenates and a volatile tetroxide ; the latter, however, is not so easily obtained and much more unstable, being readily reduced to trichloride by hydrochloric acid. The chief compounds of ruthenium are those in which it acts as a triad ; it shares this property with rhodium, which is uniformly trivalent in its salts. Iridium, intermediate between rhodium and platinum, gives two series of stable salts, derived from the sesquioxide and the dioxide : the sesquisulphate forms alums, like rhodium, but the tetrachloride bears a great resemblance to the corresponding platinum compound. Platinum is chiefly quadrivalent, but it also yields platinous salts, in which it is bivalent, like palladium. This element is rather easily soluble in acids, and of metallic character: it is readily precipitated as sulphide, iodide, or cyanide. The salient property of palladium is its power to absorb large quantities of hydrogen. The platinum metals yield soluble double nitrites of the following composition:—

$Ru(NO_2)_3.2NaNO_2$	$Rh(NO_2)_3.3NaNO_2$	$Pd(NO_2)_2.2NaNO_2$
$Os(NO_2)_3.2NaNO_2$	$Ir(NO_2)_3.3NaNO_2$	$Pt(NO_2)_2.2NaNO_2$

RUTHENIUM.

§ **I. Minerals.**—(*a*) *Laurite*, the sesquisulphide, is a very rare iron-black mineral crystallising in cubes or octahedra. It carries a little osmium. H 7·5; sp. gr. 7·0. Found in Borneo.

(*b*) *Osmiridium* (*q.v.*) sometimes contains up to 6 per cent. of ruthenium.

(*c*) Small quantities of ruthenium occur in native platinum.

§ **II. Properties and Compounds.**—(*a*) The *metal* melts at about

Page 196, last line;
For "gelatinous" *read* "platinous."

tion of alkali ruthenate or other soluble ruthenium compound mixed with excess of caustic alkali, is saturated with chlorine in a retort and gently heated, when the tetroxide volatilises as a yellow vapour and condenses in the form of yellow drops, which solidify to a crystalline mass, soluble in water. The solution is unstable and deposits a black precipitate. Organic substances readily reduce, and are blackened by, ruthenium tetroxide. It is not formed by distillation of solutions acidified with nitric acid, like osmium tetroxide.

(*c*) The *dioxide*, RuO_2, is obtained by direct union of the elements at high temperature, also by heating osmiridium (§ I, (*b*)) to 1000° in a current of air, or by ignition of the sulphide. The crystals, which exhibit a metallic lustre, are isomorphous with cassiterite.

(*d*) The *trihydroxide*, $Ru(OH)_3$, is a dark brown precipitate thrown down from the solution of the trichloride by caustic alkali; insoluble in excess, but soluble in acids with brown colour.

(*e*) *Potassium ruthenate*, $K_2RuO_4.H_2O$, is prepared as explained under (*a*). The crystals are red in transmitted and green in reflected light. By fusing the metal with sodium peroxide, sodium ruthenate is formed.

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(*b*) *Osmiridium* (*q.v.*) sometimes contains up to 6 per cent. of ruthenium.

(*c*) Small quantities of ruthenium occur in native platinum.

§ II. **Properties and Compounds.**—(*a*) The *metal* melts at about 2000°, and has a sp. gr. of 12·06. It is greyish-white, hard, and brittle, not attacked by acids or fused bisulphate. *Aqua regia* is almost without action upon it, but dissolves the precipitated unignited metal. By fusion with alkaline hydroxide and nitrate, chlorate, or peroxide it is converted into soluble ruthenate (*e*). At high temperature it combines directly with oxygen (*c*).

(*b*) The *tetroxide*, RuO_4, is the characteristic ruthenium compound, though more difficult to obtain and less stable than the corresponding oxide of osmium. Ruthenium tetroxide is a yellow solid which melts at 25·5° and sublimes at higher temperature, decomposing at 107° with a smoky flame and formation of dioxide; the vapour is explosive, poisonous, and of an offensive odour. To prepare the tetroxide, a solution of alkali ruthenate or other soluble ruthenium compound mixed with excess of caustic alkali, is saturated with chlorine in a retort and gently heated, when the tetroxide volatilises as a yellow vapour and condenses in the form of yellow drops, which solidify to a crystalline mass, soluble in water. The solution is unstable and deposits a black precipitate. Organic substances readily reduce, and are blackened by, ruthenium tetroxide. It is not formed by distillation of solutions acidified with nitric acid, like osmium tetroxide.

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(*f*) *Potassium perruthenate*, $KRuO_4.H_2O$, black crystals obtained on treating ruthenate solution with chlorine and subsequent evaporation. By saturating the solution with chlorine the tetroxide is formed (*cf.* (*b*)).

(*g*) The *trichloride*, $RuCl_3$, forms when a hydrochloric acid solution of the tetroxide is evaporated, chlorine being liberated. The solution has an orange-yellow colour, and gradually deposits a deep black, finely divided precipitate of oxychloride. This change takes place rapidly on heating and constitutes a delicate test for ruthenium. When the metal is heated in chlorine, incomplete combination takes place.

(*h*) *Sodium chlororuthenite*, Na_2RuCl_5, is obtained, together with varying proportions of chlororuthenate, Na_2RuCl_6, when the metal mixed with sodium chloride is heated in a current of chlorine. When the solution of the mass is treated with potassium chloride a crystalline glossy violet precipitate of potassium chlororuthenite, $K_2RuCl_5.H_2O$, is thrown down. This is also formed by adding potassium chloride to the trichloride solution.

(*i*) *Potassium chlororuthenate*, K_2RuCl_6, reddish-brown crystals sparingly soluble in water. Prepared by treating potassium ruthenate with dilute hydrochloric acid.

(*j*) *Sulphide.*—When hydrogen sulphide is conducted through ruthenium solutions, the liquid first assumes an azure-blue colour (probably due to the formation of $RuCl_2$), and after some time a dark brown precipitate is thrown down. It does not appear to be of definite composition.

§ III. Quantitative Separation.—The volatilisation of the tetroxide in a current of chlorine can be made the means of separating ruthenium from all other metals except osmium, which is also volatile under those conditions. Methods not involving the use of the distillation apparatus can also be used in cases enumerated below.

(*a*) *Separation from Silver.*—Ruthenium, if present in metallic silver, remains undissolved when the metal is attacked with dilute nitric acid.

(*b*) *Separation from Gold.*—The gold is precipitated from the solution of the mixed chlorides with sulphur dioxide, oxalic acid, ferrous sulphate, ferrous chloride, or hydroxylamine hydrochloride.

(*c*) *Separation from Rhodium.*—(1) The mixed metals are heated in a current of chlorine in presence of sodium chloride and the powdered mass extracted with alcohol, in which the rhodium salt is insoluble. The alcoholic filtrate is evaporated, the residue dissolved in water, and precipitated with magnesium (§ IV.).

(2) An approximate separation is effected by adding ammonium chloride in moderate excess to the aqueous extract of the mass obtained under (1): ammonium chlororuthenite is precipitated.

(3) The solution containing the two metals is treated with potassium carbonate till neutral or faintly alkaline and boiled with potassium nitrite.[1] The residue remaining after evaporation to dryness is powdered and warmed with alcohol, which extracts ruthenium. By once more boiling the residue with nitrite, evaporating and treating

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[1] Gibbs, *Amer. Journ. Sci.*, 1861, **31**, 63; 1862, **34**, 353.

with alcohol, the last traces of ruthenium are extracted. (4) See Iridium, § III, (*h*).

(*d*) *Separation from Palladium.*—(1) The palladium is extracted from a mixture of the two metals by nitric acid, dilute *aqua regia*, or fusion with bisulphate. (2) A solution of the chlorides is saturated with ammonium chloride; the precipitate consists of ammonium chlororuthenite. (3) Palladium is precipitated with mercuric cyanide (Palladium, § IV, (*c*)); the filtrate is evaporated, and the residue heated in coal-gas or hydrogen, leaving ruthenium.

(*e*) *Separation from Osmium.*—(1) The acid distillate obtained as directed under (*f*) (3)—except that no alcohol is added to the liquid in the receivers—is heated to 70° while a current of air is passing through it. The operation is carried out in the distillation apparatus described below; the first of the three receivers contains dilute hydrochloric acid (1 : 2), the others 12 per cent. caustic soda containing 2 per cent. of alcohol. A small amount of unaltered ruthenium tetroxide distils over along with osmium tetroxide. When the drops formed by condensation are no longer coloured the contents of the first receiver are returned to the distillation flask and replaced by caustic soda and alcohol. The distillation is now resumed with three receivers containing alcoholic lye, and one-half of the contents of the flask distilled over. The residual solution contains ruthenium, the distillate osmium.

(2) The acid distillate is precipitated with hydrogen sulphide, the precipitate filtered off on a tared filter, washed, dried in carbon dioxide, and weighed. It is then detached from the paper, weighed into a tared platinum boat, and ignited in a current of oxygen. Osmium is volatilised, and condensed in two receivers containing caustic soda and alcohol. The ruthenium dioxide in the boat is weighed as such, or preferably reduced in hydrogen, cooled in carbon dioxide, and weighed as metal.

(3) The solution of the chlorides is repeatedly distilled with small quantities of nitric acid, osmium volatilising. The presence of much free hydrochloric acid should be avoided. (4) See Osmium, § III, (*d*).

(*f*) *Separation from Iridium.*—(1) As in the case of rhodium, (*c*) (3), the solution is boiled with potassium carbonate and nitrite until the green colour disappears. The solution is evaporated, and the dry residue treated with alcohol to extract ruthenium.

(2) The solution is neutralised with sodium carbonate, and boiled with an excess of sodium nitrite; if green, more sodium nitrite must be added, also carbonate if necessary. A small excess of sodium sulphide is gradually added, and the liquid boiled for a few minutes. When quite cold it is carefully acidified with hydrochloric acid. The precipitated ruthenium sulphide is filtered off, washed with hot water, and ignited to dioxide.

(3) The finely divided metals are added to a fused mixture of twelve parts of potassium hydroxide and three of potassium nitrate (the sodium salts must not be used) in a gold crucible.[1] The latter, covered with a gold lid, is heated for three hours to 950°. The mass is

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[1] Deville and Stas, *De l'Analyse du Platine iridié*, Paris, 1878.

now leached with water, and the liquor poured through a funnel into a glass-stoppered 100 c.c. cylinder. The cylinder filled with solution is shaken, the insoluble residue left to settle, and the clear liquid carefully decanted. The cylinder is again filled, partly with dilute caustic soda, partly with hypochlorite or chlorine solution. The mixing, settling, and decanting are repeated; more hypochlorite is added to the residue, decanting each time, until the solution no longer assumes a yellow tinge. The residue is once more digested with hypochlorite while the next operation (volatilisation of the ruthenium) is in progress. The decanted solutions are transferred to a distilling flask provided with a tube for passing chlorine through the liquid, and a funnel with a glass tap, fused into a ground-glass stopper. Rubber must not be used in any part of the apparatus. The exit tube of the flask leads into two receivers placed in series and containing eighty parts of water, two of hydrochloric acid, and eighteen of alcohol free from fixed residue. A slow current of chlorine is passed in the cold until the colour of the gas above the liquid proves saturation to be complete; the temperature is then slowly raised to 70°–80°, and kept there until orange-coloured fumes are no longer disengaged, after which the liquid is boiled gently till the condensing drops are colourless. The flask is then left to cool, and emptied; the receivers are emptied, rinsed, and refilled; the hypochlorite liquor from the cylinder is decanted into the distilling flask, the residue being again left to digest with fresh hypochlorite solution. A second distillation in chlorine is now carried out in the same manner as the first. When the flask is cold, the liquid from the cylinder is once more added to its contents, and a third distillation made; the residue is submitted to a second fusion, followed by distillation, to extract the last of the ruthenium. 0·0005 grm. of ruthenium imparts a distinct yellow colour to 100 c.c. of acid liquid in the receiver. The distillates are evaporated in a tared porcelain crucible to dryness, the residue reduced in coal-gas, first at low temperature, then at a decided red heat, and weighed as ruthenium. This is washed with water, filtered off, dried, the particles brushed from the filter, and again weighed. This treatment removes a minute quantity of alkaline chloride which may have been carried over by the effervescence during distillation. The liquid in the distilling flask must remain alkaline during the operation; more alkali can be added through the funnel if necessary.

(*g*) *Separation from Platinum.*—(1) The mixed metals are digested with dilute *aqua regia* (1 : 5 water). A little ruthenium goes into solution; on the other hand a little platinum remains undissolved. By a compensation of errors, the results are fairly good.

(2) Potassium chloroplatinate and chlororuthenate are extracted with small quantities of moderately strong potassium chloride solution. Ruthenium dissolves, together with a little platinum. The filtrate may be boiled with potassium nitrite and evaporated to dryness; the powdered residue is extracted with boiling alcohol, giving a ruthenium solution free from platinum (*cf.* (*c*) (3)). The alcoholic filtrate is treated as in (*c*) (1). (3) See Iridium, § III, (*h*).

(*h*) *Separation from Platinum, Iridium, Palladium, Rhodium, etc.*—A solution of the metals in *aqua regia* is diluted so as to contain 1–2 per cent. of mixed metals, transferred to the distilling flask described above (*f*), and mixed with a large excess of caustic soda. A slow current of chlorine is then passed, and two to three successive distillations performed as described under (*f*) (3). The distillate is evaporated, the ignited metal washed with water, dried, and weighed. It is then digested with cold concentrated sodium hypochlorite solution, in which it dissolves, leaving a minute residue of the other metals carried over mechanically. The weight of the latter is subtracted from the original weight.

§ **IV. Gravimetric Determination.**—(*a*) Ruthenium is sometimes weighed as dioxide, in the manner described under § III, (*e*) (2), (*f*) (2). More generally, however, it is weighed in the metallic state, by evaporating to dryness the solution of the trichloride obtained by distillation, and heating the residue in coal-gas (§ III, (*f*) (3)).

(*b*) The determination may also be accomplished by evaporating the acid chloride solution, taking up the residue in water, and digesting with magnesium. The precipitated ruthenium is collected on a filter and washed with 5 per cent. sulphuric acid followed by water; the filter is dried, ashed separately, the metal added and ignited in coal-gas or hydrogen, and cooled in carbon dioxide.

§ **V. Detection in Ores.**—(*a*) The detection of ruthenium in alluvial deposits follows the lines indicated for osmium (*q.v.* § VI, (*a*)) and platinum (*q.v.* § VI, (*b*)). The particles to be tested are fused with sodium peroxide, the melt taken up in water, and the solution transferred to the distillation apparatus described above (§ III, (*f*)). Chlorine is passed in the cold to saturation, when the flask is gently heated, the vapour being received in dilute hydrochloric acid. Ruthenium tetroxide is evolved in the form of orange-yellow fumes condensing to orange-coloured drops, which impart a brownish-green tint to the acid. The latter is evaporated to dryness in a fume-cupboard to expel any osmium tetroxide present in the distillate. The residue taken up with water furnishes a deeply-coloured solution which decomposes on warming with separation of a black precipitate (§ II, (*g*)). The yellow solution, rendered ammoniacal and warmed with a little sodium thiosulphate, assumes an intense violet colour.

(*b*) The presence of ruthenium in a silver bead remaining after cupellation of the lead button obtained by crucible fusion is generally indicated by black spots, or a black crystalline deposit, on the bead. The silver, or preferably the lead button (see Iridium, § V, (*b*) (1)), is dissolved in dilute nitric acid, and the residue fused with a little sodium peroxide. The solution of the melt is distilled in chlorine, etc., as under (*a*).

§ **VI. Determination in Ores.**—(*a*) In osmiridium, platinum ore, and platinum ore residues, ruthenium is determined as explained under Osmium, § VIII.

(*b*) Dry assay. See Iridium, § V, (*b*) (1).

(*c*) A wet process of general applicability to ores may be carried out by concentrating the crushed material if necessary. The original ore or concentrate is digested with dilute nitric or hydrofluoric acids, or both in succession, according to the presence or absence of sulphides and silicates. The residue from this treatment is fused with potassium hydroxide and nitrate, or sodium peroxide, the melt dissolved in water, and the solution distilled in a current of chlorine. The distillation and treatment of the distillate are described in § III, (*f*) (3). If osmium is present, see § III, (*e*).

(*d*) *Analysis of Laurite.*—The mineral is opened up by fusion with potassium hydroxide and nitrate, with subsequent distillation of ruthenium and osmium in chlorine. The residual solution contains the sulphur as potassium sulphate and any other metals (rhodium) which may be present in the mineral.

RHODIUM.

§ I. Minerals.—(*a*) Rhodium is found chiefly in *native platinum*, of which it is a subordinate constituent; osmiridium, platiniridium, and laurite (*q.v.*) likewise contain small quantities of the metal.

(*b*) *Rhodium-gold*, containing as much as 43 per cent. of rhodium, has been found in Mexico; native gold occasionally carries a little rhodium.

(*c*) It has been detected in minute quantities in the Sudbury nickel-copper ores.

§ II. Properties and Compounds.—(*a*) The *metal* is white, ductile, and malleable at a red heat. It melts at about 2000°, and has a sp. gr. of 12·1. When precipitated from solution it is slightly soluble in nitric or hydrochloric acid in contact with air, and soluble in hot strong sulphuric acid or *aqua regia*. The compact or ignited metal is insoluble in all acids; if alloyed with relatively large quantities of lead, copper, bismuth, or platinum it is soluble in *aqua regia*. The metal is attacked by fused bisulphate, alkaline hydroxide and nitrate, peroxide, or sodium chloride in a current of chlorine.

(*b*) *Sulphides.*—Hydrogen sulphide produces a dark brown precipitate of hydrosulphide, $Rh(SH)_3$, complete precipitation requiring prolonged treatment of the boiling hot solution. The precipitate is insoluble in ammonium sulphide, soluble in *aqua regia* or hot strong nitric acid. The black sesquisulphide, Rh_2S_3, is obtained by heating the trichloride in a current of hydrogen sulphide.

(*c*) The *trichloride*, $RhCl_3$, may be prepared by heating the finely divided metal in a chlorine current. It is red, insoluble in water, and of much less practical importance than its derivative described under (*d*).

(*d*) *Sodium chlororhodite*, Na_3RhCl_6, is obtained anhydrous when the metal mixed with sodium chloride is heated in chlorine. It is insoluble in alcohol. On dissolving the mass in water a deep red solution is obtained, which contains the hydrate $Na_3RhCl_6.9H_2O$. Ammonium chlororhodite is soluble in water and in dilute ammonium chloride solution, but insoluble in a saturated solution of the latter salt.

(*e*) *Rhodium sulphate,* $Rh_2(SO_4)_3$, is formed by the action of fused bisulphate on the metal. The yellow solution of the salt turns red on the addition of hydrochloric acid. Rhodium alums have been prepared.

(*f*) *Oxides.*—When the metal is fused with alkaline hydroxide and nitrate the sesquioxide, Rh_2O_3, is obtained; this, by repeated fusion, is converted into dioxide, RhO_2. Both are grey powders, insoluble in acids. The sesquioxide is also obtained by adding excess of sodium carbonate to a solution of alkali chlororhodite, evaporating to dryness, igniting, and extracting the residue with water and hydrochloric acid.

(*g*) *The trihydroxide,* $Rh(OH)_3$, is a black precipitate, formed when alcohol is added drop by drop to the cold solution of rhodium chloride containing excess of caustic alkali.

(*h*) *Chloropentamminerhodium dichloride,* $[RhCl(NH_3)_5]Cl_2$, also known as Claus's salt, crystallises out in small, pale yellow crystals on evaporating and cooling an ammoniacal chloride solution. It is very stable, and dissolves in strong sulphuric acid without decomposition, but is reduced to metal by zinc. The ammoniacal rhodium compounds closely resemble those of cobalt.

§ III. Quantitative Separation.—(*a*) *Separation from Lead.*—The nitric acid solution is precipitated with sulphuric acid added very slowly whilst stirring; the liquid is heated to 100°, left to cool, and filtered. The precipitate is free from rhodium. The filtrate is evaporated to dryness, taken up with water, and again filtered; if the slight residue of lead sulphate shows a pink or buff colour it is washed on the filter with a saturated solution of ammonium carbonate, which extracts all the rhodium. The filtrate is evaporated to one-half its bulk, the lead carbonate filtered off, and the filtrate acidified with hydrochloric acid; the combined filtrates are precipitated with zinc or formic acid.

(*b*) *Separation from Silver.*—(1) The boiling nitrate or sulphate solution is precipitated, drop by drop, with very dilute hydrochloric acid until no further precipitate forms. The silver chloride is allowed to settle, filtered off, and washed as usual. The rhodium in the filtrate is precipitated with zinc or formic acid.

(2) The precipitated and ignited metals are digested with dilute nitric acid, silver dissolving. Compact silver containing rhodium is treated in the same manner; the filtrate containing silver may have to be tested for rhodium according to (1).

(*c*) *Separation from Gold.*—(1) See Ruthenium, § III, (*b*).

(2) The precipitated and ignited metals are digested with dilute *aqua regia*: the gold is dissolved.

(3) Rhodium-gold, if high in rhodium, is melted with lead, and the button dissolved in nitric acid; the lead nitrate solution is examined for rhodium according to (*a*). The residue is dissolved in *aqua regia*, the excess of acid evaporated, the residue taken up in water, and the noble metals precipitated with formic acid. The precipitate is strongly ignited and the gold extracted therefrom according to (2).

(*d*) *Separation from Ruthenium.*—See Ruthenium, § III, (*c*).

(*e*) *Separation from Palladium.*—(1) The metals mixed with sodium chloride are heated in a current of chlorine, the melt leached with water, the solution heated to expel chlorine, and precipitated with mercuric cyanide (Palladium, § III, (*j*)). The filtrate containing rhodium is evaporated to dryness and the residue heated in hydrogen or coal-gas.

(2) The solution is acidified with a few drops of hydrochloric acid and the palladium precipitated with dimethylglyoxime at boiling heat. The excess of reagent in the filtrate is destroyed by means of hydrochloric acid and sodium chlorate, the chlorine boiled off, and the solution digested with magnesium till colourless; the precipitated rhodium is washed with 5 per cent. sulphuric acid followed by water, the filter dried and ashed separately, the metal added, and the whole ignited in hydrogen.

(3) The roasted sulphides are digested hot with strong hydrochloric acid, or the precipitated ignited metals are treated with hot concentrated nitric acid; in both cases rhodium remains insoluble. (4) See Palladium, § III, (*j*) (2).

(*f*) *Separation from Osmium.*—See Osmium, § III, (*a*) and (*d*).

(*g*) *Separation from Iridium.*—(1) The separation of the mixed metals by fusion with bisulphate is unreliable.

(2) The solution of the mixed chlorides is treated with ammonium or potassium chloride with the same precautions as in the separation of rhodium from platinum, (*h*) (2). Iridium is precipitated as chloriridate.

(3) The dry mixed sodium chlororhodite and chloriridate are extracted with strong alcohol, iridium dissolving, (*h*) (3). (4) See Iridium, § III, (*h*).

(*h*) *Separation from Platinum.*—(1) The precipitated and ignited (unalloyed) metals are digested with dilute *aqua regia* (1 : 4 to 5 water) at 50°, platinum dissolving. The extraction is continued, using fresh acid if necessary, until the liquid remains colourless. The residual rhodium is ignited in hydrogen. The solution of the mixed chlorides may be evaporated to dryness with excess of sodium carbonate, the residue extracted with water and acid, and the insoluble rhodium sesquioxide plus platinum separated in the same manner.

(2) The solution containing sodium chlororhodite and chloroplatinate is precipitated with potassium or ammonium chloride, when platinum is thrown down; the solution must not be more than one-half saturated with the alkaline chloride, as otherwise part of the rhodium is also precipitated. The washing is conducted with one volume of saturated chloride solution to three of water, using no more than is strictly necessary on account of the slight solubility of the chloroplatinate.

(3) The same solution as in (2) is evaporated to dryness and the residue extracted with alcohol (sp. gr. 0·83): rhodium remains insoluble.

(4) The separation of the finely divided metals by fusion with bisulphate does not give good results unless the amount of rhodium is very small. The fusion should be repeated until the melt after ten minutes' fusion does not acquire a yellow colour. The dissolved rhodium is precipitated with formic acid, zinc, or magnesium.

§ IV. Gravimetric Determination.—(*a*) Rhodium is weighed in the metallic state after ignition in hydrogen or coal-gas; the metal is precipitated by means of magnesium or zinc.[1] In the first case the precipitate is washed with 5 per cent. sulphuric acid followed by water; in the second, it is digested with dilute nitric acid at a moderate heat for a few minutes before filtration. The metal may also be obtained by boiling its solutions with ammonium acetate and formic acid under reflux (see Platinum, § IV, (*e*)).

(*b*) Solutions containing chlororhodite or rhodium sulphate may be evaporated to dryness with excess of sodium carbonate, the residue ignited, extracted with water and washed with dilute hydrochloric acid, the residual sesquioxide strongly ignited in hydrogen, and weighed as metal.

§ V. Detection and Determination in Ores.—(*a*) *Detection.*—(1) The silver bead from the dry assay of an ore containing rhodium generally has a bluish colour. The bead, or the lead button obtained by melting the substance under investigation with granulated lead, is dissolved in dilute nitric acid (1 : 10), the residue strongly ignited in coal-gas, and extracted with dilute *aqua regia.* The residue from the last treatment is fused with bisulphate in a silica crucible and the yellow solution from the melt filtered if necessary; the colour turns pink on addition of a little hydrochloric acid. Addition of caustic alkali and alcohol causes formation of a black precipitate (§ II, (*g*)). The reactions of rhodium are much less pronounced than those of the other platinum metals; however, its insolubility in *aqua regia*, solubility in bisulphate, the red colour of sodium chlororhodite, and the insolubility of the latter in alcohol are sufficiently characteristic to prove its presence. (2) See Platinum, § VI, (*c*).

(*b*) *Determination.*—(1) *In sulphide ores.* See Platinum, § VII, (*b*) (3).

(2) *In rhodium-gold.* See § III, (*c*) (3).

(3) *In platinum ore and osmiridium.* See Platinum, § VIII.; Osmium, § VIII.

PALLADIUM.

§ I. Minerals.—(*a*) *Native palladium* has been found substantially pure in the form of grains, accompanying native platinum.

(*b*) *Native gold* is sometimes found alloyed with palladium and silver.

(*c*) Palladium is one of the minor constituents of native *platinum* (*q.v.*).

(*d*) It occurs in minute quantities in base metal ores, principally nickel-copper ores (Sudbury, Ontario). When these ores are smelted it passes into the matte.

§ II. Properties and Compounds.—(*a*) The *metal* melts at 1549° C., and has a sp. gr. of 11·9. It is silver-white, hard, and less ductile than platinum. The common acids when hot and concentrated dissolve the finely divided metal; in the compact state it is insoluble in hydrochloric, slightly soluble in sulphuric, and readily soluble in strong nitric acid or *aqua regia.* Fused bisulphate easily dissolves it; its alloys with silver or copper are soluble in nitric acid. Palladium has

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[1] For electrolytic determination see Langness, *Journ. Amer. Chem. Soc.*, 1907, **29**, 469.

the faculty of absorbing a large amount of hydrogen. All its compounds are decomposed by heat, leaving a residue of metal. It forms two series of salts corresponding to the types $PdCl_2$ and $PdCl_4$; of these the palladous salts are the more stable and important; their solutions undergo hydrolysis, with deposition of basic salts.

(*b*) *Palladous nitrate*, $Pd(NO_3)_2$, is formed when the metal is dissolved in fuming nitric acid. Brownish-yellow, deliquescent crystals.

(*c*) *Palladous sulphate*, $PdSO_4.H_2O$, obtained from the metal by fusion with bisulphate. Olive-green, deliquescent.

(*d*) *Palladous chloride*, $PdCl_2.2H_2O$, prepared by dissolving the metal in *aqua regia* and evaporating with hydrochloric acid. Reddish-brown crystals.

(*e*) *Potassium chloropalladite*, K_2PdCl_4, from the preceding and potassium chloride. Brownish-yellow crystals soluble in water, insoluble in strong alcohol.

(*f*) *Potassium chloropalladate*, K_2PdCl_6, is prepared by adding potassium chloride to the brown solution containing the unstable chloropalladic acid, H_2PdCl_6, obtained by dissolving the metal in excess of *aqua regia*. Red octahedra, insoluble in alcohol or potassium chloride solution.

(*g*) *Palladous sulphide*, PdS, is thrown down as a black precipitate when hydrogen sulphide is passed through acid or neutral palladium solutions. Insoluble in alkaline sulphides; soluble in hot strong hydrochloric or nitric acid, readily so in *aqua regia*.

(*h*) *Palladous iodide*, PdI_2, is a black flocculent precipitate obtained by adding hydriodic acid or potassium iodide to a palladium solution. It is soluble to a red liquid in potassium iodide, insoluble in hydrochloric acid. Alkaline thiocyanates also dissolve it with red colour, and it is not formed in their presence. Palladium, unlike platinum, is stained black by iodine.

(*i*) *Palladous cyanide*, $Pd(CN)_2$, yellowish-white gelatinous precipitate produced by mercuric or potassium cyanide in palladium solutions. It is slightly soluble in hydrochloric acid, readily in potassium cyanide or ammonia.

(*j*) *Diamminepalladous chloride*, $Pd(NH_3)_2Cl_2$, is precipitated as fine yellow needles when an ammoniacal solution of palladous chloride is acidified with hydrochloric acid. Two series of ammoniacal palladium salts are known; they are similar to the corresponding platinous compounds.

(*k*) *Palladium dimethylglyoxime*, $(CH_3)_2(C_2N_2O_2H)_2Pd$. See § IV.

(*l*) *Palladium nitroso-β-naphthol*, $(C_{10}H_6O.NO)_2Pd$. See § IV.

§ **III. Quantitative Separation.**—The precipitation as iodide or cyanide (§ IV.) enables palladium to be separated from all noble, as well as base, metals except silver, copper, and lead. The elimination of the latter, together with other methods of separating noble metals, will here be described.

(*a*) *Separation from Copper.*—(1) The copper is converted into cuprous thiocyanate in the usual manner; the filtrate is boiled to expel sulphur dioxide and the palladium precipitated by one of the methods given in § IV.

(2) The mixed sulphides are roasted, dissolved in *aqua regia*, the solution evaporated to dryness with potassium chloride, the residue taken up with 90 per cent. alcohol, the insoluble potassium chloropalladite filtered off and washed with alcohol. It is dried and ignited, the residue leached with hot water, filtered off, ignited again in hydrogen, and weighed as palladium.

(*b*) *Separation from Lead.*—(1) Lead is precipitated as sulphate in nitric acid solution; the palladium, in the filtrate, as cyanide.

(2) Palladium is precipitated as metal (Platinum, § IV, (*e*)).

(3) The mixed sulphides are boiled with 50 c.c. of potassium thiocarbonate solution[1] (made by digesting one part of sulphur, two of carbon disulphide, and fifteen of potassium hydroxide solution (1·13) for several days. The orange-coloured solution is decanted and the residue again treated with eight parts of potassium hydroxide solution). The reagent dissolves palladous sulphide. The solution is filtered, the filtrate acidified with hydrochloric acid, digested on a steam-bath, the palladous sulphide filtered off, washed, and dissolved in *aqua regia* or nitric and sulphuric acids.

(*c*) *Separation from Silver.*—(1) The only published method, as far as we know, is that of A. M. Smoot,[2] who directs precipitating the nitrate solution (*e.g.* parting acid) with hydrochloric acid. The silver chloride carries down some palladium, which colours it pink to brown. It is filtered off, cupelled with lead, the metallic button dissolved in nitric acid, and the solution re-precipitated with hydrochloric acid. This process may have to be repeated several times, *i.e.* until the silver chloride is pure white. The combined filtrates are precipitated with hydrogen sulphide or mercuric cyanide.

(2) We have found that silver chloride free from palladium can be obtained in one precipitation by converting the palladous salt into a diamminepalladous compound before precipitating with hydrochloric acid.[3] The separation is carried out as follows :—

(*a*) The hot solution of the nitrates or sulphates is treated with ammonia until the precipitate first formed re-dissolves and the solution becomes colourless. A small piece of litmus paper is dropped into the

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[1] Rosenbladt, *Z. anal. Chem.*, 1887, **26**, 15.

[2] *Eng. and Min. Journ.*, 1915, **99**, 700.

[3] Two test determinations gave the following results :—

No.	Ag taken.	Pd added.	Ag found.
1	0·1682	0·087	0·1679
2	0·1616	0·113	0·1619

The method has since been introduced into practice, and is applied in the analysis of gold-silver alloys containing palladium and platinum.

solution which is faintly acidified with acetic acid, and treated whilst hot with dilute hydrochloric acid drop by drop, with constant stirring, until no further precipitate forms, after which it is left in the dark till clear. The precipitate is filtered off by decantation and washed with very dilute nitric acid; the filtrate is evaporated with *aqua regia*, or precipitated with hydrogen sulphide, and the precipitate dissolved in nitric and sulphuric acids.

(β) When dealing with a precipitate of silver chloride containing palladium the procedure is as follows: The precipitate is dissolved in a small excess of ammonia and the hot solution slightly acidified with acetic acid: the silver is precipitated as chloride free from palladium.

(γ) In the separation of palladium from other platinum metals by silver iodide (see (*j*) (2)), a precipitate is obtained which contains palladium and silver iodides. Orlow,[1] to whom this method is due, states that palladium may be extracted from the mixed precipitate by potassium iodide or thiocyanate solution, or by "heating and subsequent treatment with *aqua regia*." Our attempts at separating palladium from silver by any of these reagents were unsuccessful; either the extraction of palladium was incomplete, or a more or less considerable quantity of silver went into solution. We therefore proceed as follows for the recovery of palladium from the mixed iodide precipitate: Ammonia and ammonium chloride solution are added until the precipitate is pale yellow, followed by ammonium sulphide. The liquid is heated on the water-bath until the precipitate has settled; the latter is filtered off, washed with hot water containing a little ammonium sulphide, and dissolved in nitric and sulphuric acids. The excess of acid is then expelled by evaporation and the diluted solution treated as under (*a*).

(*d*) *Separation from Gold*.—(1) The slightly acid solution of the chlorides is digested on the water-bath with excess of sulphurous acid until the liquid is clear; the solution should smell of sulphur dioxide. Gold alone is precipitated. Sulphurous acid effects a better separation than ferrous sulphate or oxalic acid.

(2) Palladium may be extracted from the mixed precipitate of the metals by fusion with bisulphate in a silica crucible.

(*e*) *Separation from Ruthenium*.—See Ruthenium, § III, (*d*), (*h*).

(*f*) *Separation from Rhodium*.—See Rhodium, § III, (*e*).

(*g*) *Separation from Osmium*.—See Osmium, § III, (*a*) and (*d*).

(*h*) *Separation from Iridium*.—(1) The precipitated metals are strongly ignited in a current of hydrogen and digested with dilute *aqua regia* (1 : 3 water) at a temperature below 80°, or they are fused with bisulphate in a silica crucible. In both cases palladium is rendered soluble.

(2) See Iridium, § III, (*h*).

(3) By dimethylglyoxime, as for rhodium (*q.v.* § III, (*e*) (2)).

(*i*) *Separation from Platinum*.[2]—The solution containing platinic

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[1] *Chem. Zeit.*, 1906, **30**, 714.

[2] By acetylene: see Erdmann and Makowka, *Z. anal. Chem.*, 1907, **46**, 146.

and palladous chlorides and freed from nitric acid by repeated evaporation with hydrochloric acid, is saturated with potassium or ammonium chloride (see Platinum, § IV, (*c*)). Platinum and iridium may be precipitated together by this method.

(*j*) *Separation from all the Platinum Metals.*—(1) Palladium is precipitated as cyanide (§ IV.).

(2) The solution of the mixed chlorides, free from nitric acid, is digested at ordinary temperature with a moderate excess of freshly precipitated silver iodide. Palladous iodide is precipitated; it is filtered off, washed, and the palladium separated from silver as shown under (*c*) (2) (γ).

§ IV. Gravimetric Determination.—Palladium is weighed in the metallic state,[1] in which it is obtained by ignition of the cyanide, iodide, or the other compounds enumerated below. The metal oxidises superficially during ignition; it should therefore be strongly heated in a current of hydrogen, the gas current turned off and displaced by carbon dioxide before the heat is withdrawn. Alternatively a flow of coal-gas may be brought in contact with the hot metallic sponge after ignition in air, or the ignited metal is boiled with 20 per cent. formic acid and dried before weighing.

(*a*) *Precipitation as Metal.*—As for platinum (*q.v.* § IV, (*e*)).

(*b*) *Precipitation as Sulphide.*—Palladium is readily precipitated by hydrogen sulphide, but the precipitate does not part with the whole of its sulphur on ignition and the impure metal runs into one or several globules. The sulphide precipitate should be dissolved in nitric and sulphuric acids and the solution precipitated with mercuric cyanide (*c*).

(*c*) *Precipitation as Cyanide.*—The chloride solution is almost neutralised with sodium carbonate; it must remain faintly but distinctly acid. An excess of mercuric cyanide solution is then added, and the liquid gently warmed till the free hydrocyanic acid is expelled and the precipitate has settled. With minute quantities of palladium the solution should be allowed to stand for at least twenty-four hours. The clear liquid is decanted through a filter, the precipitate washed in the beaker, then on the filter, after which it is dried, ignited, and reduced. Nitrate or sulphate solutions need not be neutralised with sodium carbonate before precipitation with mercuric cyanide.

(*d*) *Precipitation as Iodide.*—The usual directions prescribe precipitation by hydriodic acid in a dilute solution of the nitrate free from alkaline salts. According to M. Schwitter,[2] complete precipitation is ensured by the use of potassium iodide, a 10 per cent. solution of which is added, a few drops at a time, to the palladium solution containing one-fifth its volume of strong hydrochloric acid until no further precipitate is produced. The liquid is heated nearly to boiling, cooled, filtered, the precipitate washed with dilute hydrochloric acid, dried, ignited, and reduced.

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[1] Precipitation by electrolysis: see Amberg, *Z. Elektrochemie*, 1904, **10**, 386, 853; Langness, *Journ. Amer. Chem. Soc.*, 1907, **29**, 459.

[2] *Engineering and Mining Journ.*, 1914, **97**, 1249.

(*e*) *Precipitation with Dimethylglyoxime.*[1]—The acidified solution of palladous chloride is precipitated with a 1 per cent. solution of the reagent in 2 per cent. hydrochloric acid and left half an hour on the water-bath. The bulky orange-yellow precipitate is washed with hot water, dried, and ignited to metal as before. The precipitate may also be weighed on a tared filter or in a Gooch crucible after drying at 110°.

(*f*) *Precipitation with Nitroso-β-Naphthol.*[2]—The acid solution of the chloride, containing less than 0·05 grm. of palladium, is precipitated at boiling heat with a solution of the reagent in 50 per cent. acetic acid. The voluminous reddish-brown precipitate is filtered off while the liquid is hot, washed with hot 5 per cent. hydrochloric acid, then hot water, dried, and heated in a crucible on an asbestos wire-gauze. When the paper has charred the mass is heated very strongly. The addition of a few crystals of oxalic acid facilitates ashing. The ignited metal is reduced and weighed.

(*g*) *Precipitation as Potassium* (*Ammonium*) *Chloropalladate.*[3]—A solution of potassium chloropalladite (*e.g.* the filtrate from potassium chloroplatinate, § III, (*h*)), is saturated with chlorine, or slowly evaporated on the water-bath with excess of nitric acid. (If insufficient nitric acid is present a brown basic salt separates.) The red crystalline precipitate is filtered off, washed with strong potassium chloride solution containing nitric acid, and treated like the corresponding platinum compound (Platinum, § IV, (*d*)).

§ V. Detection and Determination in Ores.—(*a*) *Detection.*—In the dry assay for gold and silver the whole of the palladium present in an ore will be found in the silver button left after cupellation. When this is parted with nitric or sulphuric acid most of the palladium goes into solution, colouring the liquid pale yellow to orange. On adding dilute potassium iodide solution to the parting acid yellow silver iodide will be thrown down first, then black palladous iodide. If much silver is present, fractional precipitation may be employed. The mixed iodide precipitate may be digested with warm thiocyanate solution, which will acquire a pink or reddish colour; on filtration and evaporation of the filtrate with *aqua regia* a deep orange-red liquor is obtained, from which potassium iodide throws down a black precipitate.

(*b*) *Determination.*—(1) *In platinum ore:* see Platinum, § VIII.

(2) *In sulphide ores:* see Platinum, § VII, (*b*) (3). In parting with nitric acid, palladium is completely dissolved if the amount of silver is more than three times that of the palladium; in doubtful cases, the residue from the parting is again alloyed with a suitable proportion of silver and the parting repeated.

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[1] Wunder and Thüringer, *Z. anal. Chem.*, 1913, **52**, 101.

[2] *Ibid.*, 737.

[3] Cohn and Fleissner, *Z. anal. Chem.*, 1897, **36**, 796.

OSMIUM.

§ I. Minerals.—(*a*) *Osmiridium*, or iridosmine, consists of an alloy containing varying quantities of iridium and osmium, the former generally predominating, and subordinate amounts of ruthenium and rhodium (*e.g.* Ir 53·5, Os 43·4, Rh 2·6, and Ru 0·5 per cent.). It is found in hard, flattened grains or pellets, sometimes in hexagonal prisms, of white or grey colour. H 6–7; sp. gr. 19·3–21·1. Its occurrence is the same as that of native platinum, *i.e.* in alluvial deposits resulting from the disintegration of basic igneous rocks. It almost invariably accompanies platinum, often in considerable proportion, and, as it is unacted on by *aqua regia*, remains behind with the sand when the concentrate is worked up for platinum. Occasionally native gold is accompanied by osmiridium. The mineral also occurs independently in several localities, principally New South Wales and Tasmania.

(*b*) *Laurite* (*q.v.*) contains about 3 per cent. of osmium.

§ II. Properties and Compounds.—(*a*) The *metal* is the heaviest known substance, of sp. gr. 22·47; its melting-point lies about 2500°. When finely divided it is dissolved by fuming nitric acid and, though less readily, by *aqua regia*. The compact metal, which is bluish-white, is insoluble in all acids, but may be rendered soluble by fusion with sodium peroxide, or hydroxide and nitrate or chlorate. When strongly ignited in air it is oxidised to the volatile tetroxide.

(*b*) *Oxides.*—The *tetroxide*, OsO_4, is the most important and characteristic compound. It forms colourless, transparent needles which melt at about 40° and begin to sublime at a moderate heat; the liquid boils at 100°, giving a colourless vapour. The latter has a very penetrating odour, recalling that of chlorine, and acts as a violent poison on the lungs and eyes; it is reduced to the metallic state in contact with the tissues, and the metallic film deposited on the cornea produces permanent injury to the eyesight. In the same manner the crystals stain the skin black and cause painful sores. The tetroxide is formed when the metal is heated in air or oxygen, or when a soluble osmium compound or the finely divided metal is heated with nitric acid or *aqua regia*, or, like ruthenium tetroxide, by distillation of osmate solutions in chlorine. In all cases the tetroxide is evolved in the state of vapour. It is soluble in water to a colourless liquid devoid of acid reaction, and emitting the characteristic smell of the compound. By the action of reducing agents it is converted into metal or lower oxides, such as the *dioxide*, OsO_2, and the *sesquioxide*, Os_2O_3. The latter two are non-volatile.

(*c*) *Potassium osmate*, $K_2OsO_4.2H_2O$, is obtained when the solid or gaseous tetroxide acts on potassium hydroxide in presence of a reducing agent (*e.g.* alcohol), the solution assuming a red colour. The solid salt forms deep red octahedra; its aqueous solution decomposes into tetroxide and lower oxides. Free osmic acid, H_2OsO_4, is also known.

(*d*) *Osmium tetrachloride*, $OsCl_4$.—The action of dry chlorine on heated osmium gives ill-defined products, and the attack is not complete. A small quantity of brownish-black dichloride, $OsCl_2$, is formed, and a red sublimate of tetrachloride. The latter is soluble in water, and the solution decomposes into hydrochloric acid, osmium tetroxide, and lower oxides.

(*e*) *Chlorosmates.*—When a mixture of osmium and dehydrated powdered sodium chloride is heated in dry chlorine at a dark red heat the metal is completely converted into *sodium chlorosmate.* This salt crystallises from aqueous solution in orange-red crystals, $Na_2OsCl_6.2H_2O$, easily soluble in water and alcohol. When solid ammonium chloride is added to the solution a red crystalline precipitate of *ammonium chlorosmate,* $(NH_4)_2OsCl_6$, separates. The *potassium* salt, K_2OsCl_6, may be obtained by evaporation of a solution of osmium tetroxide and potassium chloride in hydrochloric acid, or by heating a mixture of potassium chloride and osmium in chlorine. If in the latter operation the temperature be raised above dark red heat, *potassium chlorosmite* is formed, the solution of which is dark red and deposits $K_3OsCl_6.3H_2O$. The chlorosmate crystallises in dark brown octahedra, like the corresponding platinum, iridium, and palladium compounds. It is soluble in water with yellow colour; alcohol precipitates it from the solution in form of a red crystalline powder. On heating it evolves chlorine and leaves a mixture of potassium chloride and osmium.

Osmiridium mixed with sodium chloride is attacked by dry chlorine at a moderate heat, with formation of chloriridate and chlorosmate; if moist chlorine be used, the bulk of the osmium will volatilise as tetroxide: $2OsCl_4+4H_2O=OsO_4+8HCl+Os$, and $Os+4H_2O+4Cl_2=OsO_4+8HCl$.

(*f*) *Sulphides.*—The *tetrasulphide,* OsS_4, is precipitated as a brown powder when hydrogen sulphide is conducted through an acid solution of the tetroxide; insoluble in alkaline sulphides. The *disulphide,* OsS_2, is a dark brown precipitate produced by hydrogen sulphide in a solution of chlorosmate. It is also formed when an alkaline solution of the tetroxide is treated with thiosulphate, neutralised, and acidified with one-fifth of its bulk of hydrochloric acid (1·12).

(*g*) *Osmyltetrammine chloride,* $OsO_2(NH_3)_4Cl_2$, is a yellow crystalline precipitate, from potassium osmate and excess of strong ammonium chloride solution: $K_2OsO_4+4NH_4Cl=OsO_2(NH_3)_4Cl_2+2KCl+2H_2O$.

(*h*) *Osmiamic acid,* $OsO_3:NH$.—Potassium osmiamate is formed by addition of ammonia and potassium hydroxide to a solution of osmium tetroxide; orange-yellow crystals.

(*i*) *Osmium sulphite,* $OsSO_3$.—Made by conducting sulphur dioxide through a solution of the tetroxide, the liquid turning blue. The solid salt, which is precipitated by addition of sodium sulphate, is very stable.

§ **III. Quantitative Separation.**—(*a*) The property of forming a volatile oxide by boiling solutions of its compounds with nitric acid allows osmium to be separated from all other metals. The apparatus used consists of a retort or distilling flask provided with a glass-stoppered funnel and two or three absorption flasks, all connected by well-fitting ground-glass joints; rubber joints must not be used. The absorption flasks, which contain 12 per cent. caustic soda mixed with 2 per cent. of alcohol, are cooled with running water. The osmium solution is poured into the distilling vessel, followed by a small excess of nitric acid. Heat is applied gently at first; the solution is then boiled, and one-half of the liquid distilled over. The distillate will acquire a reddish colour, due to the formation of osmate; it is treated for the determination of osmium as explained in § IV. To ensure complete volatilisation the retort is allowed to cool, the receivers emptied and washed, again filled with caustic soda and alcohol, and the distillation repeated after addition of more nitric acid. This should always be done.

Distillation with *aqua regia* is less satisfactory. The presence of an undue amount of hydrochloric acid prevents the complete volatilisation of osmium as tetroxide (*cf.* also Ruthenium, § III, (*e*) (3)).

(*b*) *Separation from Iridium.*—Compounds insoluble in acids (*e.g.* osmiridium) must be opened up by one of the following methods before the separation of osmium by distillation can be applied:

(1) Fusion with barium peroxide and nitrate (Deville and Debray).[1] The material (2 grm.) mixed with six times its weight in pure zinc is heated in a graphite crucible enclosed in a larger crucible for half an hour at a red heat, then two hours at white heat, to drive off the zinc. The spongy residue is heated with three parts of barium peroxide and one of barium nitrate in a well-covered silver crucible. The mass is rinsed into the retort or distilling flask, the liquid acidified with hydrochloric acid poured through the funnel, and distilled with nitric acid.

(2) Fusion with sodium hydroxide and nitrate in an iron crucible. The nitrate is melted first, the hydroxide added next, then gradually the osmiridium. The melt is taken up with water, and the solution distilled with hydrochloric and nitric acids; any heavy residue remaining in the retort is again fused till decomposition is complete.

(3) Fusion with sodium peroxide in a nickel crucible.[2] Pounding in a diamond steel mortar is advisable. The material mixed with four times its weight in sodium peroxide is added gradually to one part of fused sodium hydroxide and fused for half an hour. The crucible should be frequently rotated, or the mass stirred with a nickel rod. The melt is taken up in water, the solution acidified and distilled.

(4) Opening up with sodium chloride in a chlorine current.[3] By carrying out the process with moist chlorine the osmium is evolved as tetroxide, which is absorbed in suitable receivers (see (*a*)). The residue in the porcelain boat is dissolved in water and distilled with a little nitric acid to drive off the last of the osmium. The residual liquor is poured into a basin, and any heavy metallic residue again opened up in chlorine. This method obviates contamination by fusion, but it is more tedious than the peroxide process except for small quantities.

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[1] *Loc. cit.*, p. 216.

[2] Leidié and Quennessen, *Bull. Soc. Chim.*, 1902, **27**, 181.

[3] Wöhler, *Pogg. Annalen*, 1834, **31**, 161.

(*c*) *Separation from Ruthenium.*—See Ruthenium, § III, (*e*).

(*d*) *Separation from Platinum, Iridium, Ruthenium, Rhodium.*—The metals precipitated by formic acid, zinc, or magnesium are digested with hydrogen peroxide, which converts osmium into tetroxide, the other metals remaining unaffected.[1]

§ IV. Gravimetric Determination.—The quantitative estimation of osmium is much more difficult than that of the other platinum metals. In nearly every case the determination has to be carried out in an alkaline solution of sodium osmate, obtained by absorbing the tetroxide in caustic soda solution containing alcohol.

(*a*) As a technical method, the precipitation as sulphide has been found sufficiently accurate for materials containing subordinate quantities of osmium. The cold osmate solution is slightly acidified with dilute hydrochloric acid and saturated with hydrogen sulphide. The flask is stoppered and left to stand till the precipitate has settled ; the latter is filtered off on a Gooch crucible, washed, cautiously dried, and strongly ignited in hydrogen. Or the alkaline solution is treated with yellow ammonium sulphide and left overnight in a warm place. The clear liquid is decanted, the precipitate washed, dried, and ignited in hydrogen as before.

Paal and Amberger[2] nearly neutralise the cold liquid with dilute hydrochloric acid and pass hydrogen sulphide for fifteen minutes; the solution is now acidified, and again treated with the gas whilst being heated on a steam-bath. The precipitate is filtered on hardened paper, washed with water, alcohol, carbon bisulphide, dried *in vacuo*, and quantitatively detached from the paper. It is then gently heated in a tared Rose crucible in a current of hydrogen ; the heat is gradually increased, the crucible being finally ignited over a blast burner for one hour.

The osmium obtained by ignition of the sulphide in hydrogen still retains alkali and a little sulphur ; in addition, it may be contaminated with iron, alumina, and silica, resulting from the action of the alkali on the glass. It is therefore treated with dilute hydrochloric and hydrofluoric acids, and the residue from the evaporation taken up with dilute hydrochloric acid, which is then filtered through a Gooch crucible or hardened filter ; the osmium is washed, dried, and weighed ; it is next dissolved in *aqua regia* and the solution evaporated, or distilled if it is intended to recover the osmium. The residual liquor is tested with barium chloride, and any sulphur thus found deducted from the weight of the osmium.

Where doubt exists as to the complete recovery of the osmium as sulphide, it is advisable to evaporate the filtrate to dryness, ignite the residue in hydrogen, and extract the sodium salts with dilute hydrochloric acid. Any black residue is weighed, and tested as explained above.

Aqueous solutions of osmium tetroxide may be evaporated with

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[1] Orlow, *Chem. Zeit.*, 1906, **30**, 714.

[2] *Ber.*, 1907, **40**, 1378.

ammonium sulphide in a tared porcelain crucible; the dry residue is covered with sulphur, and the crucible placed in a covered graphite crucible and strongly ignited.[1]

(*b*) The method of Leidié and Quennessen,[2] which consists in precipitating the alkaline osmate solution with aluminium-foil, has been adversely criticised by Paal and Amberger,[3] who found that a quantitative precipitation could not thereby be effected. For the same reason they reject precipitation by strong ammonium chloride solution [4] (see § II, (*g*)) and by hydrazine.

(*c*) The best method is probably that used by Ruff and Bornemann.[5] The alkaline solution containing alcohol is heated on a water-bath and exactly neutralised with 2N-sulphuric acid in presence of phenolphthalein, so that the solution remains colourless after prolonged heating. When the precipitate has settled the liquid is heated for six hours more, and filtered through a tared tube containing asbestos; the precipitate is well washed, dried at 150° in a current of carbon dioxide charged with alcohol vapour, then heated to 250° and cooled in carbon dioxide, and weighed as OsO_2. The dioxide may also be ignited in hydrogen and the metal weighed; as a check, the dioxide or metal is ignited in oxygen and any fixed residue deducted.

(*d*) Makowka [6] precipitates the alkaline osmate solution by means of an acetylene current; the reduction to metallic osmium is stated to be complete after twenty to thirty minutes. The precipitate is ignited, at first gently, then strongly, in a current of hydrogen. The purity of the metal may be ascertained by a subsequent ignition in oxygen.

(*e*) On account of the volatility of the tetroxide and the difficulties attaching to the exact determination of the element, the osmium content of high-grade materials such as osmiridium has been frequently, if not generally, reported by difference.

Note.—Before and after ignition of osmium precipitates in hydrogen it is necessary to pass a current of carbon dioxide over the metal to prevent catalytic action, which sometimes takes place with explosive violence.

§ V. Volumetric Determination.[7]—Osmium tetroxide can be determined iodometrically in a solution free from nitric acid, which may be obtained by first precipitating a solution of alkaline osmate as directed in § IV, (*c*) or (*d*). The precipitated metal or dioxide is filtered off on asbestos, washed, and heated with chromic and strong sulphuric acids to 120° in a current of oxygen. The usual distillation apparatus is employed, and the tetroxide received in caustic alkali. The cold distillate is carefully neutralised with sulphuric acid; an excess of

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[1] Deville and Debray, *loc. cit.* (p. 216).

[2] *Bull. Soc. Chim.*, 1903, **29**, 805.

[3] *Loc. cit.*, p. 214.

[4] Frémy, *Ann. Chim. Phys.*, 1844, **12**, 521.

[5] *Z. anorg. Chem.*, 1910, **65**, 429.

[6] *Z. anal. Chem.*, 1907, **46**, 147.

[7] Klobbie, *Chem. Centralbl.*, 1898, **11**, 65; Ruff and Bornemann, *Z. anorg. Chem* **1910**, **65**, 429.

potassium iodide is added, and the liquid titrated with thiosulphate: $OsO_4+4KI+2H_2SO_4=OsO_2+2K_2SO_4+4I+2H_2O$. 1 c.c. N/10 $Na_2S_2O_3$ $=0{\cdot}0063725$ grm. OsO_4. Starch paper is used as an outside indicator, as the dark green colour of the solution masks the end-point if starch solution be added.

§ VI. Detection in Ores.—(*a*) The detection of osmium in ores involves, as a rule, the isolation and identification of osmiridium. For alluvial sands the procedure is the same as for platinum (*q.v.* § VI, (*b*)). The metallic particles obtained by mineralogical analysis are digested with *aqua regia* to dissolve platinum, gold, etc.; the osmiridium in the residue may be identified by its mineralogical characters, and by the smell of osmium tetroxide on strong ignition in air. For a chemical test the metallic particles are fused with peroxide (§ III, (*b*) (3)), the melt leached with water, and the solution distilled with *aqua regia* into a well-cooled receiver containing water. The distillate, which has a penetrating smell, yields a brown precipitate on acidification and treatment with hydrogen sulphide; a drop of oil, in contact with it or the vapour, becomes black; when heated with caustic alkali and alcohol it acquires a purple colour. A Bunsen flame becomes luminous when held in the vapour.

(*b*) If an ore or rock in lump form is to be tested for osmium the procedure used for platinum, palladium, and rhodium is not applicable, as the whole of the osmium may be volatilised during cupellation. In such a case the material may be fused as described in § VIII, (*a*), or under Iridium, § V, (*b*) (1). The residue from the nitric acid treatment of the lead button is fused with peroxide and the solution of the melt distilled with *aqua regia*, etc., as under (*a*). A wet method for isolating osmium is given under Ruthenium, § VI, (*c*).

§ VII. Determination in Ores.—(*a*) The determination in osmiridium, and platinum ore and residues, will be found in § VIII.

(*b*) The determination in sulphide or other ores, or materials containing small quantities of osmium, is conducted like that in platinum ore residues (§ VIII, (*a*)), or as directed for iridium (*q.v.* § V, (*b*) (1)), or ruthenium (*q.v.* § VI, (*c*)).

§ VIII. Complete Analysis.—(*a*) *Platinum Ore Residues.*—These consist chiefly of osmiridium and sand. They are mixed with three to four parts of litharge; the mixture is poured into a crucible containing one to two parts of fused lead.[1] The mass is covered with litharge and fused for half an hour, being stirred from time to time with a pipeclay stem. When cold the crucible is broken, the button freed from litharge with acetic acid, cleaned by brushing, and dissolved in dilute nitric acid (see F[1]). The solution is filtered, the residue well washed with nitric acid followed by water, and dried; it is brushed off the filter, the latter ashed, and the residue and ash weighed (see R[1]).

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[1] Deville and Debray, *Ann. Chim. Phys.*, 1859, **56**, 463.

<table>
<tr><td colspan="2">F^1: ppte with small excess of H_2SO_4, filter, wash.</td><td colspan="2">R^1: digest with *aqua regia*, filter, wash.</td></tr>
<tr><td>P^2: $PbSO_4$; reject.</td><td>F^2: evaporate almost to dryness, take up with water, filter, ppte filtrate with $Hg(CN)_2$; ignite, weigh Pd.</td><td>R^3: dry and weigh as OsIr. Analysis: see (*b*).</td><td>F^3: evaporate with a few drops of H_2SO_4, dilute, filter off and reject $PbSO_4$, evaporate filtrate, add NH_4Cl (Rhodium, § III, (*h*) (2)). Let stand and filter.</td></tr>
<tr><td colspan="3">F^4: evaporate again, filter, wash with ammonium chloride solution.</td><td rowspan="2">P^4: add P^5; ignite gently, weigh Pt+Ir, Separation: Iridium, § III, (*g*).</td></tr>
<tr><td colspan="2">F^5: ppte with HCO_2H, ignite and weigh Rh.</td><td>P^5: add to P^4.</td></tr>
</table>

The difference between the original weight and that of the residue R^1 *plus* Pd (F^2) is sand.

(*b*) *Osmiridium* (see (*a*), R^3). (After Leidié and Quennessen.[1])

<table>
<tr><td colspan="5">1–2 grm.; fuse with 1 part NaOH and 4 of Na_2O_2 in Ni crucible for ½ hour, stirring continuously with Ni spatula and keeping mixture in pasty condition. Pour, leach melt with water, transfer to glass-stoppered decantation flask. Decant clear liquid into distillation flask, digest residue with NaOCl, wash by decantation.</td></tr>
<tr><td colspan="2">S^1: distil in Cl current (Ruthenium, § III, (*f*)) into three receivers cooled in ice and filled to two-thirds with HCl (1 : 2 H_2O).</td><td colspan="3">R^1: dissolve in hot dilute HCl, filter.</td></tr>
<tr><td>S^2: acidify with HCl; add to F^4.</td><td>D^2: return to distillation flask after emptying the latter. Pass current of air, heat to 70°, receive distillate in three condensers, the first containing HCl, the others 12 per cent. NaOH and alcohol. When condensed drops are no longer coloured, return contents of first condenser to distilling flask, fill first condenser with NaOH and C_2H_5OH, distil half the contents of the flask.</td><td>R^4: OsIr. If small, dry, weigh, subtract from original weight; if large, again fuse and distil.</td><td colspan="2">F^4: add S^2. Treat with $NaNO_2$ followed by Na_2CO_3. Boil some time, filter.</td></tr>
<tr><td rowspan="2">D^3: see Osmium, § IV, (*c*).</td><td rowspan="2">S^3: see Ruthenium, § IV, (*b*).</td><td rowspan="2">F^5: warm with HCl, saturate with HCl gas, filter, reject NaCl, evaporate filtrate, dilute with H_2O, gradually add Mg till colourless. Filter, wash with 5 per cent. H_2SO_4, then H_2O, dry, ash filter, ignite in H, cool in CO_2, weigh Ir+small amounts of Pt, Pd, and Rh. Fuse with Pb, and proceed as directed under Iridium, § III, (*h*), for determination of Pt, Pd, and Rh. Ir is found by difference.</td><td colspan="2">P^5: extract with dilute HCl, filter.</td></tr>
<tr><td>R^6: Au.</td><td>F^6: Cu, Fe.</td></tr>
</table>

(*c*) *Native osmiridium* is analysed like platinum ore (fusion with silver, etc.: Platinum, § VIII.) or platinum ore residues (see (*a*)). The portion insoluble in *aqua regia* is treated as above (*b*).

IRIDIUM.

§ I. Minerals.—(*a*) *Platiniridium*, chiefly platinum and iridium in varying proportions; either may predominate. Occurs together with native platinum in form of white metallic grains or pellets, insoluble in *aqua regia*. H 6–7; sp. gr. 22.

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[1] *Comptes Rendus*, 1903, **136**, 1399; *Bull. Soc. Chim.*, 1901, **25**, 840. See also Martius, *Annalen*, 1860, **117**, 357; Lea, *Chem. News*, 1864, **10**, 279, 301; Pirngruber, *Eng. Min. Journ.*, 1888, **44**, 256; Leidié, *Bull. Soc. Chim.*, 1901, **25**, 9.

(*b*) *Osmiridium.*—See Osmium, § I.

(*c*) *Native platinum* contains a subordinate amount of iridium.

(*d*) Iridium is occasionally found in minute quantity in some base metal ores.

§ **II. Properties and Compounds.**—(*a*) The *metal* is white, hard, and brittle. Sp. gr. 22·4; M.P. 2300°. Compact, it is insoluble in all acids and in *aqua regia*; the latter attacks the finely divided metal, though slowly. If in the compact state it may be brought to a fine state of subdivision by fusion with ten to twenty times its weight of zinc, the surface of which is kept bright by frequent additions of small quantities of ammonium chloride; the heating is continued until the zinc is entirely volatilised.[1] Fused bisulphate oxidises, but does not dissolve it; similarly, fusion with sodium hydroxide and nitrate converts it into sesquioxide, insoluble in water, but soluble in *aqua regia.* The metal is also rendered soluble by ignition with sodium chloride in a current of chlorine. It alloys with platinum, but not with gold; the platinum alloy is soluble in *aqua regia* provided the iridium content does not exceed 30 per cent.

(*b*) *Iridium sesquisulphide*, Ir_2S_3, is precipitated by hydrogen sulphide from the solution of the trichloride or the tetrachloride; the latter first undergoes reduction to the former, with separation of sulphur. The brown precipitate is soluble in ammonium sulphide.

(*c*) The *tetrachloride*, $IrCl_4$, is obtained as a black residue by evaporating a solution of *chloriridic acid*, H_2IrCl_6. The latter is prepared by dissolving the tetrahydroxide in hydrochloric acid, or the finely divided metal or the sesquioxide in *aqua regia.*

(*d*) *Potassium chloriridate*, K_2IrCl_6, blackish-red octahedra, from potassium chloride and chloriridic acid or its sodium salt; insoluble in alcohol and in saturated potassium chloride solution. One part of iridium in 500 of platinum can be detected by the reddish tinge of the chloroplatinate precipitate, due to admixture of chloriridate; the colour deepens with increase in the proportion of iridium.

(*e*) *Ammonium chloriridate*, $(NH_4)_2IrCl_6$, from ammonium chloride and chloriridic acid or the sodium salt; same properties and appearance as the preceding.

(*f*) *Sodium chloriridate*, Na_2IrCl_6, is formed when a mixture of sodium chloride and iridium is heated in chlorine. Reddish-black crystals very soluble in water and in alcohol.

(*g*) The *trichloride*, $IrCl_3$, is obtained by reducing the solution of the tetrachloride with ferrous sulphate, oxalic acid, stannous chloride, hydroxylamine, sulphur dioxide, or sodium nitrite; the colour of the liquid changes from orange-brown to green. The solid salt is olive-green. *Aqua regia* converts it into tetrachloride.

(*h*) *Potassium chloriridite*, $K_3IrCl_6.3H_2O$, from potassium chloride and the preceding, or from the chloriridate by reduction with one of the reagents enumerated under (*g*); soluble green crystals.

(*i*) The *sesquioxide*, Ir_2O_3, is formed when the metal is fused with

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[1] Deville and Debray, *Ann. Chim. Phys.*, 1859, **56**, 474.

alkaline hydroxide and nitrate. Black powder soluble in *aqua regia* (see (*c*)); decomposes at 1000°.

(*j*) The *tetrahydroxide*, $Ir(OH)_4$, is a blue precipitate formed when caustic alkali is added to tetrachloride solutions. It dissolves slowly in hydrochloric acid. Ignition in a current of carbon dioxide converts it into the black *dioxide*, IrO_2, insoluble in acids.

(*k*) *Sulphates.*—The *sesquisulphate*, $Ir_2(SO_4)_3.xH_2O$, from the trihydroxide and sulphuric acid, forms alums crystallising in yellow octahedra. *Iridic sulphate*, $Ir(SO_4)_2$, has also been prepared.

§ **III. Quantitative Separation.**—(*a*) *Separation from Silver.*—When silver containing iridium is dissolved in nitric or sulphuric acid the latter metal remains insoluble.

(*b*) *Separation from Gold.*—(1) The metals are parted with dilute *aqua regia*, which dissolves the gold.

(2) Oxalic acid, ferrous chloride, or sulphur dioxide reduce auric chloride to metal, while converting iridium tetrachloride into trichloride.

(3) Iridium present as or oxidised to tetrachloride is precipitated with potassium or ammonium chloride, like platinum (*q.v.* § III, (*e*)).

(*c*) *Separation from Ruthenium.*
(*d*) *Separation from Rhodium.*
(*e*) *Separation from Palladium.*
(*f*) *Separation from Osmium.*
See these metals, § III.

(*g*) *Separation from Platinum.*—(1) The mixed precipitate of ammonium chloriridate and chloroplatinate is cautiously heated (see Platinum, § IV, (*c*)) until all volatile matter is driven off; it is then strongly ignited in hydrogen, and the metallic residue (consisting of unalloyed iridium and platinum) digested at 50° with dilute *aqua regia* (1 : 4 to 5 water). The extraction is repeated, using fresh acid each time, until the liquid no longer becomes coloured. The iridium remains insoluble; it is filtered off, ignited in hydrogen, and weighed. The filtrate is evaporated to dryness, the residue ignited and weighed as platinum.[1]

(2) The mixed precipitate of the double chlorides is dissolved in 20–25 times its weight of hot water, and a few crystals of oxalic acid are added.[2] When effervescence has ceased, more oxalic acid is added until reduction of iridium to the trichloride is complete. After boiling for a few minutes one-half of the amount of ammonium chloride necessary for saturation is added. After two to three days' standing the precipitate of chloroplatinate is filtered off. The filtrate is boiled with *aqua regia* and saturated with ammonium chloride, when the chloriridate is precipitated.

(3) Alloys of platinum and iridium containing less than 30 per cent. of the latter metal are dissolved in *aqua regia*; the solution is freed from nitric acid by evaporation with hydrochloric, the residue dissolved in water, and the solution precipitated with ammonium chloride. The precipitate is treated as under (1) or (2). Metal containing more than 30 per cent. of iridium (*e.g.* platiniridium) is fused with zinc (§ II, (*a*)) if necessary and the comminuted material opened up by ignition with an equal weight of sodium chloride in a current of chlorine.

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[1] Deville and Debray, see p. 229.

[2] Lea, *loc. cit.* (p. 217).

The solution of the melt is precipitated with ammonium chloride. In the case of native platiniridium, the filtrate from the mixed precipitate contains rhodium, palladium, copper, and iron (*cf.* Platinum, § VIII, *A* (*f*) and (*g*)).

(*h*) *Separation of Iridium, Ruthenium, Platinum, Rhodium, and Palladium by Fusion with Lead* (after Deville and Stas [1]).—When an alloy or sponge containing the above platinum metals is heated with ten times its weight of lead to 1000° for two hours the lead alloys with platinum, palladium, and rhodium, but not with iridium and ruthenium. When cold the crucible is broken, the button cleaned, dissolved in nitric acid (1 : 10 water), and the solution filtered; the residue is washed with hot water. The further treatment of the residue and filtrate is tabulated below.

F^1: ppte cold with slight excess of dilute H_2SO_4, heat, let stand, filter when cold, wash and reject $PbSO_4$. Evaporate filtrate, together with F^4 and F^5, to expel HNO_3. Dilute, add excess of $CH_3CO_2NH_4$, boil with HCO_2H under reflux, filter, reject filtrate after testing for complete pption. Dissolve ppte in *aqua regia*, evaporate with HCl to destroy HNO_3, leaving residue slightly acid with HCl. Dilute, add freshly ppted AgI, digest, filter.

P^2: determine Pd.

F^2: evaporate to dryness with slight excess of NaCl, extract powdered residue with strong alcohol, filter, wash with alcohol.

F^3: evaporate to dryness, add a little H_2O and excess of Na_2CO_3 solution, evaporate, ignite gently, extract with H_2O, filter, wash with dilute HCl, ignite, weigh Pt.

R^3: dissolve in H_2O, evaporate to dryness with excess of Na_2CO_3 solution, ignite gently, extract with H_2O, filter, wash with dilute HCl, ignite, weigh Rh.

R^1: boil with strong H_2SO_4, dilute, filter, wash with $CH_3CO_2NH_4$.

F^4: add to F^1.

R^4: boil with dilute *aqua regia* (1 : 10 H_2O), filter.

R^5: fuse with one part NaOH and four of Na_2O_2 in Ni crucible, leach, decant, digest residue with NaOCl, decant washings.

F^5: add to F^1.

R^6: add to S^7.

S^6: transfer decanted liquid and washings to distillation flask; distil in chlorine current.

D^7: ppte with Mg, filter, wash with dilute HCl, ignite, weigh Ru.

S^7: add R^6, dissolve in dilute HCl, avoiding excess. Ppte with Mg, wash with dilute HCl, ignite, weigh Ir.

Note.—Previous to weighing the platinum metals must be ignited in hydrogen and cooled in carbon dioxide.

§ IV. Gravimetric Determination.—(*a*) Iridium is always weighed in the metallic state after ignition in hydrogen (*cf.* § III, (*g*)).

(*b*) The solution containing iridium is evaporated with *aqua regia* to convert all of the iridium into tetrachloride; the evaporation must be done at low temperature on the water-bath, or the dry residue evaporated once more with a little *aqua regia*. It is then dissolved in very little water, the solution precipitated with potassium or ammonium chloride, and the determination conducted like that of platinum (*q.v.* § IV, (*c*) or (*d*)), except that the metal must be ignited in hydrogen.

(*c*) The solution, free from other platinum metals, is evaporated to dryness with excess of sodium carbonate, the dry residue gently ignited,

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[1] *Op. cit.*, p. 199.

extracted with water, digested and washed with dilute hydrochloric acid, reduced by ignition in hydrogen, and weighed.

§ **V. Detection and Determination in Ores.**—(*a*) *Detection.*—(1) The black residue from the parting of a silver bead (in the fire assay for gold and silver) or from the solution of a lead button (see (*b*) (1)) in nitric acid is extracted with dilute *aqua regia*, and the residue from that treatment mixed with sodium chloride and heated in chlorine. The melt is taken up in a minimum of water and treated with potassium chloride, giving a reddish-black crystalline precipitate. For a further test, this precipitate may be dissolved in hot water and the solution boiled with sodium nitrite, when the colour will change to green—or treated with excess of caustic potash: the green solution thus obtained turns paler on heating, then pink, violet, and lastly, the blue hydroxide is precipitated.

(2) Detection in osmiridium: the mineral is fused with sodium peroxide (Osmium, § VI, (*a*)) and the solution of the melt evaporated with *aqua regia* under a hood to expel osmium; the residue is taken up with *aqua regia* and the solution precipitated with potassium chloride.

(3) Detection in platiniridium: this is opened up as in § III, (*g*) (3). The resulting solution is boiled with oxalic acid, cooled, and precipitated with ammonium chloride: a yellow precipitate of chloroplatinate will be obtained. The green filtrate is boiled with *aqua regia* and saturated with ammonium chloride, when a dark red precipitate is formed. (4) See Platinum, § VI, (*c*).

(*b*) *Determination.*—(1) *Sulphide and Base Metal Ores.*—When an ore containing iridium, ruthenium, or osmiridium is submitted to crucible fusion with litharge and suitable fluxes these metals will collect in the lead button, but unlike platinum, palladium, and rhodium they only sink through the fluid lead without alloying with it. Hence in pouring the charge there is risk of leaving some of the heavy particles in the crucible. Further, in cupelling the button the iridium, etc., may not wholly concentrate in the silver bead but partly remain on the cupel, while at least part, sometimes the whole, of the osmium will be volatilised. To carry out a dry assay for iridium, ruthenium, or osmiridium the ore is smelted with appropriate fluxes to obtain a fairly large lead button. When fusion is tranquil the crucible is withdrawn from the fire without agitating its contents and left to cool. It is then broken, and the lead button separated from the slag and cleaned without hammering. Acetic and dilute hydrofluoric acids may be used. The clean metal is dissolved in dilute nitric acid (1 : 10) and the solution of lead nitrate filtered from the heavy black residue. This is treated with dilute *aqua regia* to extract lead, gold, platinum, or rhodium, filtered off and washed, the paper dried and ashed separately, and the weighed residue fused with peroxide, as described under Osmium, § III, (*b*) (3). The solution of the melt is treated for the determination of iridium, ruthenium, and osmium, as described for osmiridium (see Osmium, § VIII, (*b*)).

(2) *Platinum Ore.*—See Platinum, § VIII.

(3) *Osmiridium.*—See Osmium, § VIII, (*b*).

PLATINUM.

§ I. Minerals.—(*a*) *Platinum* is found native, in the form of an alloy containing more or less subordinate quantities of the other platinum metals, iron, and copper. It occurs in small, whitish steel-grey, flattened grains or pellets of sp. gr. 16–19, more rarely in nuggets, in alluvial deposits resulting from the disintegration of basic igneous rocks (*e.g.* peridotite, norite, gabbro) and their alteration product, serpentine. The gravels consist mainly of chromite, magnetite, ilmenite, spinel, corundum, zircon, and quartz; besides platinum, they usually carry osmiridium (*q.v.*) and gold. The most important deposits are found in the Ural Mountains, where 100 tons of placer yield about 1 lb. of concentrate termed " platinum ore "; this contains 70–80 per cent. of platinum and about 10 per cent. of other platinum metals. The sands of some rivers carry platinum.

(*b*) Very small quantities of platinum, palladium, rhodium, etc., exist in sulphide ores such as pyrrhotine and nickel-copper ores, especially in Ontario and some American localities. Platinum has also been found in tetrahedrite. The noble metals accompany the copper in the smelting processes and finally pass over into the electrolytic refinery sludge.

(*c*) *Sperrylite*, the diarsenide, $PtAs_2$, is the only compound of platinum found in Nature. It is met with in the nickel-copper ores of Ontario.

§ II. Properties and Compounds.—(*a*) The *metal* is white, soft, and malleable, melts at 1755°, and can be welded at a white heat. Sp. gr. 21·45. *Aqua regia* readily dissolves it, sulphuric acid very slightly at high temperature, while hydrochloric, hydrofluoric, or nitric acid are without action. It is soluble in nitric acid when alloyed with much silver, copper, or lead. The metal is appreciably attacked by fusion with alkaline hydroxide, peroxide, nitrate, or cyanide, less so by bisulphate. Fused lead, bismuth, antimony, or arsenic combine with platinum, forming easily fusible alloys. It also alloys with gold and the other platinum metals. All its compounds are decomposed on ignition, leaving a residue of spongy platinum.

(*b*) *Platinum disulphide*, PtS_2, is a black precipitate which falls when hydrogen sulphide is passed through hot solutions of platinic salts; it forms more slowly in the cold. Contrary to the usual statements it is practically insoluble in alkaline sulphides, but more or less soluble in presence of sulphides of the base metals. Soluble in *aqua regia*. Sometimes the precipitate produced by hydrogen sulphide is brown in colour; this is hydrogen platinum sulphide.

(*c*) *Chloroplatinic acid*, $H_2PtCl_6.6H_2O$, is formed by solution of the metal in *aqua regia* and evaporation with hydrochloric acid. Reddish deliquescent crystals very soluble in water and in alcohol.

(*d*) *Ammonium chloroplatinate*, $(NH_4)_2PtCl_6$, crystalline precipitate consisting of microscopic octahedra, formed by addition of ammonium salts to chloroplatinic acid solutions. When produced in the cold it is pale yellow, but if precipitated from hot solutions its colour is orange. Sparingly soluble in water (100 parts dissolve 0·66 part at ordinary temperature), insoluble in alcohol and in saturated ammonium chloride solution. When ignited it leaves a residue of spongy platinum.

(*e*) *Potassium chloroplatinate*, K_2PtCl_6, isomorphous with and indistinguishable from the preceding; ignition, however, converts it into a mixture of potassium chloride and platinum. From chloroplatinic acid and potassium salts. 100 parts of cold water dissolve 0·9 part. Insoluble in alcohol and in saturated potassium chloride solution.

(*f*) *Sodium chloroplatinate*, $Na_2PtCl_6.6H_2O$, red crystals very soluble in water and in alcohol. The anhydrous salt may be obtained by heating common salt and finely divided platinum in chlorine.

(*g*) *Tetrammineplatinous chloroplatinite* $[Pt(NH_3)_4][PtCl_4]$—Magnus's green salt—is of great scientific interest as being the starting-point for the preparation of the twelve series of ammoniacal platinum compounds, analogous to those of cobalt and chromium.

(*h*) *Barium platinocyanide*, $BaPt(CN)_4.4H_2O$.—The rhombic crystals are dichroic, transmitting green light in the direction of the primary axis, and yellow light at right angles thereto. Becomes luminous when exposed to Röntgen rays.

§ **III. Quantitative Separation.**—(*a*) *Separation from Base Metals.*—From members of the ammonia-ammonium sulphide group, platinum is separated by precipitation with zinc or hydrogen sulphide; from metals of the hydrogen sulphide group by precipitation with formic acid and ammonium acetate (§ IV, (*e*)). In each case the precipitate is ignited and weighed as platinum.

(*b*) *Separation from Lead, Bismuth, Copper, Cadmium.*—The alloy is boiled with sulphuric acid (9 : 1 water); platinum remains insoluble. In the case of lead, the residual metal should be boiled with ammonium acetate solution.

(*c*) *Separation from Lead.*—When a lead button containing platinum is cupelled, the metal sets before all the lead has been absorbed by the cupel; the button is dissolved in *aqua regia* and the solution treated as under (*a*), or re-cupelled with excess of silver and lead, and the silver bead treated as under (*d*) (1) below.

(*d*) *Separation from Silver.*—(1) Alloys rich in silver (*i.e.* more than ten times the amount of platinum) are parted with sulphuric acid. The metal, in the form of thin sheet or fine filings, is boiled with slightly diluted sulphuric acid (9 : 1 water) and the boiling continued for a few minutes after the evolution of sulphur dioxide has ceased. The silver is converted into sulphate; platinum is unattacked. The latter is filtered off, thoroughly washed with boiling water, ignited, and weighed. If the proportion of platinum is higher than that indicated above, the alloy must be cupelled with lead and sufficient silver to obtain the desired ratio. Or the alloy is first parted with sulphuric acid and the residue treated with *aqua regia* (see (2)).

(2) Alloys containing less than 15 per cent. of silver can be parted with dilute *aqua regia* (1 : 1 water). Silver is converted into chloride,

platinum into chloroplatinic acid. The excess of acid is almost expelled by evaporation, the residue taken up with water, the silver chloride left to settle, filtered off, and washed with acidulated water. If not pure white, or if much platinum is present, the precipitate is dissolved in a minimum of ammonia, the hot solution faintly acidified with acetic acid, and left in the dark till clear.[1] The combined filtrates are evaporated to dryness, the residue taken up with hydrochloric acid, which is again evaporated to expel nitric acid prior to precipitation of the platinum with ammonium chloride.

(3) [1] The nitric acid solution of the two metals (resulting from solution of silver-rich alloys) is precipitated hot with a slight excess of hydrochloric acid. The silver chloride is left to settle in a dark cupboard, filtered off, washed, and the filtrate evaporated to dryness. The silver precipitate almost invariably contains minute quantities of platinum which may impart to it a very pale flesh colour. It is dissolved in a minimum of ammonia and the solution acidified with acetic acid as under (2). If the absolute quantity of silver is very large, the ammoniacal solution of the chloride is preferably evaporated on a water-bath until the bulk of the ammonia has been driven off; the last of the silver in the filtered liquid is then precipitated by acidification with acetic acid. The filtrate from the re-precipitated silver chloride is treated with a small excess of ammonia and ammonium sulphide, heated, acidified, and boiled. The precipitate is filtered off, ignited, and dissolved in *aqua regia*; the solution is added to the evaporated filtrate containing the bulk of the platinum, the nitric acid expelled as usual, and the platinum precipitated with ammonium chloride. Alternatively, the silver chloride containing a little platinum may be reduced with zinc, the sponge washed, dried, and boiled with sulphuric acid as under (1).

(*e*) *Separation from Gold.*—(1) The concentrated solution of the chlorides is treated with excess of ammonium chloride (§ IV, (*c*)): the gold remains in solution.

(2) The weakly acid chloride solution is heated with oxalic acid, or ferrous chloride or sulphate, until the precipitated gold has settled. The filtrate is heated to boiling and the platinum precipitated with hydrogen sulphide. If oxalic acid is used, the filtrate may also be evaporated to dryness and the residue cautiously ignited.

(3) The acid solution of the chlorides is shaken with ether in a separator, the operation being repeated two to three times with fresh ether. The gold is in the ethereal, platinum in the aqueous layer.

(*f*) *Separation from the other Platinum Metals.*—This is discussed under each individual metal (§ III.).

§ **IV. Gravimetric Determination.**—Platinum is always weighed in the metallic state.[2]

(*a*) Solutions containing no other fixed constituents are evaporated to dryness in a tared porcelain crucible. The residue is ignited (in hydrogen if considerable) and weighed.

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[1] Authors' method.

[2] Electrolysis: see Classen, *Berichte*, 1884, **17**, 2467; *Z. anal. Chem.*, 1885, **24**, 250.

(*b*) If no other heavy metals are present, the boiling-hot solution, free from nitric acid, may be precipitated with hydrogen sulphide. The precipitate is filtered off, washed with dilute acid, ignited, and weighed.

In order to produce a sulphide precipitate which settles well and gives a clear filtrate Gaze[1] recommends adding mercuric chloride (5–10 per cent. of the platinum present) to the solution prior to passing hydrogen sulphide, the mercury being volatilised in the subsequent ignition. Ivanov[2] brings about flocculation by adding 5 grm. of magnesium chloride per 100 c.c. of solution, saturating with hydrogen sulphide, and boiling till all the gas is expelled.

In the authors' experience, precipitation of very dilute platinum solutions acidified with hydrochloric acid is successfully accomplished by saturating the liquid with the gas and keeping it on a boiling water-bath till quite clear.

(*c*) *Precipitation as ammonium chloroplatinate:* the concentrated, weakly acid solution is saturated whilst hot with solid ammonium chloride, or a hot saturated solution of the same salt, and left to stand overnight. The precipitate is filtered off and washed with saturated ammonium chloride solution. The precipitation may also be carried out in a solution to which two to three volumes of alcohol have been added, the precipitate being washed with 80 per cent. alcohol. The precipitate is wrapped in the filter paper, dried, and heated very gradually in a covered crucible tared with its lid. The ammonium salt should volatilise without evolution of visible fumes; the larger the amount of precipitate the more cautiously should the heating proceed, otherwise minute particles of platinum will be carried away by the gases. The tarry matter is finally burned off, the residue strongly ignited for a few minutes, and weighed. Large quantities should be ignited in hydrogen after the removal of the carbonaceous matter.

(*d*) *Precipitation as potassium chloroplatinate* is carried out like the preceding. Ignition of the precipitate gives a residue containing potassium chloride; this is extracted from the ignited mass with hot water; the platinum is filtered off, washed, ignited, and weighed.

The potassium or ammonium precipitate may also be dissolved in hot dilute hydrochloric acid, the boiling solution precipitated with hydrogen sulphide (see (*b*)), and the precipitate ignited and weighed. Another method, suitable for bulky precipitates, consists in transferring the dried precipitate to a small porcelain basin and removing the last particles adhering to the paper by means of hot water. The washings are added to the dish containing the precipitate, and the whole evaporated to dryness with excess of sodium carbonate solution. The dry residue is gently ignited, cooled, and extracted with water; the metallic residue is filtered off, washed with dilute hydrochloric acid, ignited, and weighed.

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[1] *Journ. Chem. Soc.*, 1913, **104**, ii. 440.

[2] *Ibid.*, 1917, **111**, ii. 154.

(*e*) *Precipitation with formic acid.* The solution, free from nitrates, and containing but little acid (*i.e.* nearly neutralised with ammonia), is boiled under reflux with excess of formic acid and ammonium acetate. After several hours' boiling the precipitate of metallic platinum is filtered off, washed with dilute hydrochloric acid, ignited, and weighed. The filtrate should always be boiled again for some hours to make sure that the whole of the platinum has been precipitated.

Palladium, iridium, and rhodium are also precipitated, and may be determined, by this method.

§ **V. Volumetric Determination.**—Platinum may be determined iodometrically by pouring the chloroplatinate solution into a cold concentrated potassium iodide solution.[1] Iodine is liberated, and measured by very dilute sodium thiosulphate: $PtCl_4+4KI=PtI_2+4KCl+I_2$. 1 c.c. of N/1000 thiosulphate = 0·0976 mgrm. Pt.

Gold reacts in the same manner as platinum: $AuCl_3+3KI=AuI+3KCl+I_2$.

§ **VI. Detection in Ores.**—The procedure adopted depends upon the character of the material. This may be (*a*) a base metal ore (oxide, sulphide, or matte); (*b*) an alluvial.

(*a*) The ore is subjected to crucible fusion as in the dry assay of gold and silver. If the silver button (or the residue from the parting) is very small, a number of fusions must be made and the lead buttons scorified into one, so as to collect sufficient metal for a reliable test. The cleaned and flattened silver bead is boiled with strong sulphuric acid until the silver is dissolved, the acid cooled and decanted off. The residue is washed with hot water, dissolved in *aqua regia*, the acid expelled on the water-bath, the residue evaporated with hydrochloric acid and taken up with a few drops of water. Enough solid ammonium chloride is added to saturate the solution, which is stirred with a glass rod. A yellow crystalline precipitate consisting of octahedra when viewed through a microscope proves platinum to be present.

(*b*) The alluvial is screened through sieves of suitable aperture to eliminate coarse material. The undersize is submitted to the operations of mineralogical analysis (Chapter I.) to obtain a concentrate which will contain the platinum. If the sample is apparently low-grade, it is first concentrated by panning; the concentrate is dried and extracted with the weak power of an electromagnet to remove ilmenite, chromite, or other iron minerals. Care has to be exercised, however, in the use of the electromagnet, as some varieties of native platinum are said to be strongly magnetic. Both the magnetic and the non-magnetic fraction should therefore be examined. The magnetic portion may be submitted to fractional magnetic separation, and the non-magnetic treated with bromoform; the heavy material and the magnetic fractions are examined with a pocket lens. Particles of metallic appearance are picked out, treated with *aqua regia*, and the solution thus obtained further examined as under (*a*).

(*c*) When platinum has been detected in an ore, the presence of

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[1] Peterson, *Z. anorg. Chem.*, 1899, **19**, 63.

one or several other platinum metals is at least probable. Thus the yellow or orange colour of the parting acid indicates palladium. A black or metallic-looking residue insoluble in dilute *aqua regia* may contain iridium, rhodium, ruthenium, or osmiridium. In view of the scarcity of these precious metals, active search is being made for new sources of supply in ores other than alluvials. The procedure for the detection and separation of the platinum metals given in Chapter I. (Qualitative Chemical Analysis, Table III.), whilst suitable for rich alluvial material and concentrates, is not well adapted for the examination of base metal ores or rocks suspected to contain small quantities of platinum metals. The general scheme outlined below, which is applicable to sulphide ores as well as non-metallic mineral mixtures, summarises the directions found elsewhere in this chapter.

<table>
<tr><td colspan="5">Fuse with litharge and fluxes (see Iridium, § V, (*b*). Cool and break crucible, clean button, dissolve in HNO_3 (1 : 10) ; filter.</td></tr>
<tr><td colspan="2">F^1 : ppte with H_2SO_4, filter, reject ppte, treat filtrate with a little HCl ; filter.</td><td colspan="3">R^1 : warm with dilute *aqua regia*, filter.</td></tr>
<tr><td>P^2 : AgCl.</td><td>F^2 : evaporate to fumes, filter off and reject small amount of $PbSO_4$, treat filtrate with freshly ppted AgI, or a drop of dilute KI solution, for Pd (*q.v.* § V, (*a*)).</td><td>R^3 :</td><td colspan="2">F^3 : evaporate with HCl, take up with very little water, nearly saturate with NH_4Cl ; let stand, filter.</td></tr>
<tr><td colspan="3">Fuse with $KOH+KNO_3$ in Ag crucible, leach melt, decant clear solution into distilling flask, wash residue.</td><td>P^4 : yellow, crystalline : Pt.</td><td>F^4 : boil with oxalic acid, filter.</td></tr>
<tr><td colspan="2">S^6 : acidify with HCl, distil with a little HNO_3 into KOH.</td><td rowspan="2">R^6 : extract with dilute HNO_3 ; heat residue with NaCl in Cl current. Dissolve in little H_2O, saturate with NH_4Cl ; reddish-black ppte=Ir.</td><td rowspan="2">F^5 : add H_2SO_4, reject any $PbSO_4$, ppte filtrate with Zn, heat ppte with NaCl in Cl current ; add drop of water to melt. Rose-red colour =Rh.</td><td rowspan="2">P^5: Au.</td></tr>
<tr><td>D^7 : test for Os with C_2H_5OH (Osmium, § VI, (*a*)).</td><td>S^7 : test for Ru with $Na_2S_2O_3$ (Ruthenium, § V, (*a*)).</td></tr>
</table>

Note to R^3.—The fusion of R^3 may also be carried out with NaOH and Na_2O_2 in a nickel crucible. In this case the residue R^6 from the decantation is dissolved in hot dilute HCl, the solution treated with $NaNO_2+Na_2CO_3$, the filtrate from the Ni precipitate evaporated with HCl, and tested with NH_4Cl for iridium.

§ VII. Determination in Ores.—(*a*) *In Platinum Ore.*—See § VIII.

(*b*) *In Base Metal Ores, Matte, etc.*—The actual separation and determination of platinum is preceded by crucible fusion of the ore, as in the fire assay for gold and silver, in order to obtain a button containing the noble metals. If several portions of the ore are smelted to obtain sufficient material, the lead buttons so obtained are scorified into one, which is cupelled. To prevent solidification of the button before the lead is almost wholly eliminated the quantity of silver should be more than ten times that of the platinum, and if the ore is deficient in silver, the requisite amount should be added. Very low-grade ores or sands require a preliminary concentration by panning.

(1) The method used for materials comparatively rich in platinum aims at obtaining a button in which the silver-gold-platinum ratio is 33 : 10 : 1, by adding the necessary amount of gold and silver after having determined the three metals by a preliminary assay. The silver button is flattened and parted by boiling with slightly diluted sulphuric acid (9 : 1 water), which dissolves the silver. The residue of gold *plus* platinum is washed with hot water, annealed, and weighed, then wrapped in sheet lead with three times its weight in silver, and cupelled. The resulting bead is now parted with nitric acid of sp. gr. 1·1, and again with stronger acid (1·3). Platinum and silver dissolve; the gold is annealed and weighed, and the platinum found by difference. If the residual gold after annealing is not of a pure yellow colour, inquartation and parting with nitric acid should be repeated. In this method a quantity of pure platinum equal to that found in the preliminary assay is generally used as a standard. It is cupelled with ten parts of gold and thirty-three of silver, and the silver button treated exactly like the assay. Any variation in the weight of the standard is allowed for in the assay.

(2) Where the quantity of platinum is very small, it should be determined direct. This can be done by Dewey's method.[1] The silver button is parted with weak and strong nitric acid as before, the platinum going into solution. The combined parting acids and washings are treated with very dilute hydrogen sulphide water (1 of saturated solution in twenty of water), drop by drop, whilst stirring, to precipitate all the platinum and three to five times as much silver. The precipitate is allowed to coagulate overnight, filtered off, ignited, wrapped in sheet lead, and cupelled; the resulting button is parted with sulphuric acid, the residue washed with hot water, annealed, and weighed.

(3) The determination by chemical methods must be resorted to if other platinum metals are also present. The method described below effects the estimation of silver, gold, platinum, palladium, and rhodium in a bead obtained by cupellation.

<table>
<tr><td colspan="4">Part silver bead with HNO_3 of sp. gr. 1·1, then with acid of sp. gr. 1·3. Decant; wash.</td></tr>
<tr><td colspan="2">R^1: extract with dilute <i>aqua regia</i>, destroy HNO_3 with HCl, dilute, filter.</td><td colspan="2">F^1: ppte with small excess HCl, let stand in the dark till settled, filter, wash.</td></tr>
<tr><td>R^2: add to residue from F^6.</td><td>F^2: boil with oxalic acid, filter, wash.</td><td rowspan="2">P^4: dissolve in minimum of ammonia, add bit of litmus paper, acidify slightly with acetic acid, let stand in the dark till settled; filter and wash.</td><td rowspan="2">F^4: evaporate to dryness: see F^5.</td></tr>
<tr><td>F^3: add to residue from F^6.</td><td>P^3: ignite, weigh Au.</td></tr>
<tr><td colspan="3">F^5: add to residue of F^4, evaporate to dryness, take up with water and a few drops of HCl, boil with HCO_2H and $CH_3CO_2NH_4$ to eliminate a small quantity of Pb and Cu. Filter, reject filtrate after again boiling with above reagents to test for complete pption. Dissolve residue in <i>aqua regia</i>, evaporate excess of acid, dilute, ppte with $Hg(CN)_2$. Filter next day.</td><td>P^5: AgCl. Ignite and weigh, or cupel.</td></tr>
</table>

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[1] *Trans. Amer. Inst. Min. Eng.*, 1912, **43**, 578.

P^6 : ignite, weigh Pd.

F^6 : evaporate to dryness in small porcelain crucible, ignite gently ; add R^2 and F^3, again evaporate and ignite. Thoroughly mix residue with dry NaCl, ignite in Cl current. Extract with alcohol, filter. (If not completely attacked, repeat ignition in Cl.)

R^7 : dissolve in H_2O, ppte with Zn or HCO_2H, ignite, weigh Rh.

F^7 : evaporate to dryness, ignite gently, extract with dilute HCl, ignite strongly in H, weigh. Dissolve in dilute *aqua regia* (1 : 5) : if completely soluble, and evaporated *aqua regia* solution gives yellow ppte with NH_4Cl, the weight represents Pt ; if a residue is obtained, filter it off, ignite and weigh ; test evaporated filtrate with NH_4Cl ; Pt is obtained by difference.

Note.—It is assumed that the quantity of silver is more than three times that of the palladium.

§ **VIII. Complete Analysis of Platinum Ore.**[1]—The analysis of platinum ore (*i.e.* the concentrate from alluvial deposits) involves the determination of noble and base metals soluble in *aqua regia*, and that of the insoluble portion containing osmiridium and non-metallic matter termed " sand." The latter consists of some of the minerals enumerated in § I, (*a*). In the metallurgy of platinum, the osmiridium and sand form a by-product called " platinum ore residues " (see Osmium, § VIII, (*a*)).

Method A (after Deville and Debray [2]).—(*a*) *Sand.*—Two grm. of ore and 7–10 grm. of pure silver (exactly weighed) are placed in an annealing pot or small crucible glazed inside with borax, and covered with about 10 grm. of borax glass. The crucible is heated above the melting-point of silver in a muffle for twenty-five minutes, allowed to cool, broken, the silver button cleaned with hydrochloric and dilute hydrofluoric acids, and weighed. The increase over the weight of the silver represents the metallic portion of the ore ; the sand is found by difference.

(*b*) *Osmiridium.*—The silver button is dissolved in dilute nitric acid, the residue filtered off, dried, and weighed, then treated with small portions of *aqua regia* (2 vol. HCl : 1 vol. HNO_3) at 70° in a retort provided with a cooled, well-fitting condenser ; the acid is distilled off every other day, the soluble portion of the residue decanted, and the insoluble again digested until the acid leaves no saline residue on distillation. The operation takes ten to fifteen days. The decanted liquors are filtered, and the metallic residue from the retort collected on the same paper, which is dried ; the residue is brushed off, the filter burned, and the ash added to the bulk of the insoluble. This is weighed as osmiridium.

(*c*) *Silver Nitrate Solution.*—If the weight of the residue from the nitric acid treatment is smaller than that of the silver button *minus* the added silver, the fraction rendered soluble during the fusion must be recovered from the silver nitrate solution. This is done by precipitating

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[1] See also Mylius and Förster, *Ber.*, 1892, **25**, 665 ; Wunder and Thüringer, *Z. anal. Chem.*, 1913, **52**, 740 ; Duparc and Holtz, *Chem. Zeit.*, 1911, **35**, 765 ; Bunsen, *Annalen*, 1868, **146**, 265 ; Claus, *Beiträge zur Chemie der Platinmetalle*, Dorpat, 1854 ; Gibbs, *Amer. Journ. Sci.*, 1861, **31**, 63 ; 1862, **34**, 353 ; Schwitter, *loc. cit.* (p. 209).

[2] *Ann. Chim. Phys.*, 1859, **56**, 439.

the silver as chloride and evaporating the filtrate to dryness. The silver chloride containing a small quantity of platinum (palladium) is dissolved in ammonia and the solution treated as under § III, (*d*) (3); the small amount of metal obtained by ignition of the sulphide precipitate is dissolved in *aqua regia,* the solution added to the evaporated filtrate from the silver chloride, and the whole added to the main solution (*e*).

(*d*) *Osmium.*—A small amount of osmium is often found in the acid distillates obtained in (*b*). The latter are poured into excess of caustic soda containing alcohol, and the solution treated as under Osmium, § IV, (*c*).

(*e*) *Platinum and Iridium.*—The filtrate from the osmiridium is evaporated at low temperature, the residue evaporated with hydrochloric acid, and taken up in a little water. Twice the volume of alcohol and a slight excess of solid ammonium chloride are added; the liquid is warmed to dissolve most of the salt, and left to stand twenty-four hours. The precipitate is filtered off, washed with 75 per cent. alcohol, incinerated at low temperature, then ignited in hydrogen to constant weight, and weighed as $Pt+Ir$.

The filtrate from the ammonium chloride precipitate is evaporated to crystallising point and left to stand overnight, when a further small quantity of iridium and platinum precipitate is obtained. This is added to the main portion. The metals are separated by digestion with dilute *aqua regia* (Iridium, § III, (*g*)).

(*f*) *Palladium, Copper, and Iron.*—The filtrate is concentrated to expel alcohol, digested with strong nitric acid to destroy the ammonium chloride, and evaporated to dryness in a glazed Rose crucible. A few c.c. of ammonium sulphide and 2–3 grm. of pure sulphur are added to the residue. After again evaporating to dryness the mass is ignited, gently at first, then to redness, in a current of hydrogen sulphide. It is then digested for some time with strong nitric acid at 70°, the residue of gold and rhodium (see (*g*)) filtered off and washed, the filtrate evaporated to dryness, and the residue ignited. The latter is treated with moderately strong hydrochloric acid to dissolve iron and copper, which are estimated as usual; palladium, which remains insoluble, is ignited in hydrogen and weighed.

(*g*) *Rhodium and Gold.*—This residue (see (*f*)) is digested with very dilute *aqua regia,* which dissolves gold. The residual rhodium is weighed after ignition in hydrogen.

Method B (E. V. Koukline).[1]—

<table>
<tr><td colspan="4">Proceed as in Method A, (*a*) to (*d*). The filtrate from OsIr, freed from HNO_3 (*e*), is treated with C_2H_2 for 45 minutes at 90°–95°. Filter.</td></tr>
<tr><td colspan="2">P^1: moisten filter with NH_4NO_3, ignite, dissolve in *aqua regia*, evaporate, take up with H_2O and one drop HCl; ppte with $Hg(CN)_2$, let stand, filter.</td><td colspan="2">F^1: add F^2, evaporate nearly to dryness, dilute with H_2O, heat to 70°, add concentrated $NaNO_2$ solution to convert metals into double nitrites, then Na_2CO_3 solution, boil 45 minutes, filter into distillation flask.</td></tr>
<tr><td>P^2</td><td>F^2</td><td>F^3</td><td>P^3</td></tr>
</table>

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[1] *Revue de Métallurgie,* 1912, **9,** 815.

P^2: ignite, reduce in H, cool in CO_2, weigh Pd.

F^2: evaporate, ignite residue, dissolve in *aqua regia*, expel HNO_3, add to F^1.

F^3: add NaOH, pass Cl current, heat to 70°–80°, distil into HCl.

P^3: wash on filter with dilute HCl.

R^4: ignite, weigh Au.

F^4: Cu, Fe, and common metals.

D^5: evaporate to syrup, dilute with H_2O, ppte with Mg added a little at a time. Filter off, wash with H_2O, 5 per cent. H_2SO_4, and H_2O, dry, ignite in air at low temperature, then in H, cool in CO_2, weigh Ru.

S^5: neutralise with HCl, evaporate partly, reconvert into double nitrites with $NaNO_2$; add KNO_2 and KCl, filter, wash with 5 per cent. KNO_2 solution.

P^6: dissolve in *aqua regia*, expel all HNO_3, add slight excess of Mg; filter, wash with dilute HCl, ignite in H; treat with dilute H_2SO_4, wash with H_2O, heat to incipient redness in H, cool in CO_2, weigh Ir+Rh. Fuse with fifty times the weight of pure Pb in porcelain crucible under KCN for 2 hours, stirring occasionally with glass rod. Dissolve KCN in H_2O, Pb in dilute HNO_3, treat residue with hot *aqua regia*, filter.

F^6: evaporate to dryness with HCl, take up with H_2O, make slightly alkaline with NaOH, boil with HCOH, filter, ignite, weigh Pt.

R^7: Dry, ignite, reduce in H, weigh Ir.

F^7: Rh. Reject, take Rh by difference.

INTERNATIONAL ATOMIC WEIGHTS (1917).

Aluminium	27·1	Holmium	163·5	Rhodium	102·9
Antimony	120·2	Hydrogen	1·008	Rubidium	85·45
Argon	39·88	Indium	114·8	Ruthenium	101·7
Arsenic	74·96	Iodine	126·92	Samarium	150·4
Barium	137·37	Iridium	193·1	Scandium	44·1
Beryllium	9·1	Iron	55·84	Selenium	79·2
Bismuth	208·0	Krypton	82·9	Silicon	28·3
Boron	11·0	Lanthanum	139·0	Silver	107·88
Bromine	79·92	Lead	207·20	Sodium	23·00
Cadmium	112·40	Lithium	6·94	Strontium	87·63
Cæsium	132·81	Lutecium	175·0	Sulphur	32·06
Calcium	40·07	Magnesium	24·32	Tantalum	181·5
Carbon	12·005	Manganese	54·93	Tellurium	127·5
Cerium	140·25	Mercury	200·6	Terbium	159·2
Chlorine	35·46	Molybdenum	96·0	Thallium	204·0
Chromium	52·0	Neodymium	144·3	Thorium	232·4
Cobalt	58·97	Neon	20·2	Thulium	168·5
Columbium	93·1	Nickel	58·68	Tin	118·7
Copper	63·57	Niton	222·4	Titanium	48·1
Dysprosium	162·5	Nitrogen	14·01	Tungsten	184·0
Erbium	167·7	Osmium	190·9	Uranium	238·2
Europium	152·0	Oxygen	16·00	Vanadium	51·0
Fluorine	19·0	Palladium	106·7	Xenon	130·2
Gadolinium	157·3	Phosphorus	31·04	Ytterbium	173·5
Gallium	69·9	Platinum	195·2	Yttrium	88·7
Germanium	72·5	Potassium	39·10	Zinc	65·37
Gold	197·2	Praseodymium	140·9	Zirconium	90·6
Helium	4·00	Radium	226·0		

GRAVIMETRIC FACTORS.

Element.	Atomic Weight, 1917.	Known.	Required.	Factor.	Log. (Mantissa).
Beryllium . .	9·1	BeO	Be	0·3626	·55937
Cæsium . . .	132·81	Cs_2O	Cs	0·9432	·97460
		CsCl	Cs_2O	0·8368	·92262
		Cs_2SO_4	Cs_2O	0·7786	·89132
		Cs_2PtCl_6	Cs_2O	0·4181	·62127
		Cs_2PtCl_6	CsCl	0·4996	·69865
Cerium . . .	140·25	CeO_2	Ce	0·8142	·91074
		CeO_2	Ce_2O_3	0·9536	·97935
Columbium . .	93·1	Cb_2O_5	Cb	0·6995	·84477
		FeO	$Fe(CbO_3)_2$	4·7055	·67260
		MnO	$Mn(CbO_3)_2$	4·7530	·67697
Gallium . . .	69·9	Ga_2O_3	Ga	0·7444	·87181
Germanium . .	72·5	GeO_2	Ge	0·6938	·84121
		GeS_2	Ge	0·5306	·72482
Indium . . .	114·8	In_2O_3	In	0·8271	·91755
Lithium . . .	6·94	Li_2O	Li	0·4645	·66701
		LiCl	Li_2O	0·3524	·54698
		LiF	Li_2O	0·5759	·76038
		Li_2SO_4	Li_2O	0·2718	·43422
		Li_3PO_4	Li_2O	0·3868	·58754
Molybdenum . .	96·0	Mo	MoO_3	1·5000	·17609
		Mo	MoS_2	1·6679	·22218
		MoO_3	Mo	0·6667	·82391
		MoO_3	MoS_2	1·1120	·04609
		MoS_2	Mo	0·5995	·77782
		$PbMoO_4$	Mo	0·2614	·41737
		$PbMoO_4$	MoO_3	0·3922	·59346
		$PbMoO_4$	MoS_2	0·4361	·63955
Osmium . . .	190·9	OsO_2	Os	0·8564	·93270
		OsO_4	Os	0·7489	·87443
Palladium . .	106·7	PdI_2	Pd	0·2959	·47121
		$(C_4H_7N_2O_2)_2Pd$	Pd	0·3167	·50067
Platinum . .	195·2	K_2PtCl_6	Pt	0·4015	·60370
		$(NH_4)_2PtCl_6$	Pt	0·4396	·64306
Rubidium . .	85·45	Rb_2O	Rb	0·9144	·96113
		RbCl	Rb_2O	0·7729	·88812
		Rb_2SO_4	Rb_2O	0·7001	·84515
		Rb_2PtCl_6	Rb_2O	0·3229	·50903
		Rb_2PtCl_6	RbCl	0·4178	·62092
Ruthenium . .	101·7	RuO_2	Ru	0·7607	·88119
Scandium . .	44·1	Sc_2O_3	Sc	0·6476	·81129

Element.	Atomic Weight, 1917.	Known.	Required.	Factor.	Log. (Mantissa).
Selenium . .	79·2	Se	SeO_2	1·4040	·14737
		Se	SeO_3	1·6060	·20576
		SeO_2	SeO_3	1·1439	·05839
Tantalum . .	181·5	Ta_2O_5	Ta	0·8194	·91351
		FeO	$Fe(TaO_3)_2$	7·1667	·85531
		MnO	$Mn(TaO_3)_2$	7·2457	·86008
Tellurium .	127·5	Te	TeO_2	1·2510	·09725
		Te	TeO_3	1·3765	·13877
		TeO_2	Te	0·7994	·90275
		TeO_2	TeO_3	1·1003	·04152
Thallium . . .	204·0	Tl	Tl_2O	1·0392	·01671
		Tl_2O_3	Tl	0·8947	·95170
		Tl_2O_3	Tl_2O	0·9298	·96841
		TlI	Tl	0·6165	·78991
		Tl_2PtCl_6	Tl	0·5000	·69900
		Tl_2CrO_4	Tl	0·7786	·89133
		Tl_4SnS_4	Tl	0·7677	·88518
Thorium . . .	232·4	ThO_2	Th	0·8790	·94398
		$Th(SO_4)_2$	ThO_2	0·6228	·79436
Titanium . .	48·1	TiO_2	Ti	0·6005	·77852
		TiO_2	K_2TiF_6	3·0000	·47712
Tungsten . .	184·0	W	WO_3	1·2609	·10067
		WO_3	W	0·7931	·89933
		$FeWO_4$	WO_3	0·7636	·88285
		$MnWO_4$	WO_3	0·7658	·88414
		$CaWO_4$	WO_3	0·8054	·90599
		$PbWO_4$	WO_3	0·5097	·70729
		FeO	$FeWO_4$	4·2293	·62627
		MnO	$MnWO_4$	4·2708	·63051
		CaO	$CaWO_4$	5·1377	·71077
Uranium . .	238·2	UO_2	U	0·8816	·94526
		UO_2	U_3O_8	1·0395	·01682
		UO_2	UO_3	1·0592	·02498
		U_3O_8	U	0·8481	·92844
		U_3O_8	UO_3	1·0190	·00817
		$Na_2U_2O_7$	U	0·7509	·87561
		$Na_2U_2O_7$	U_3O_8	0·8855	·94717
		$Na_2U_2O_7$	UO_3	0·9023	·95533
		$(UO_2)_2P_2O_7$	U	0·6668	·82398
		$(UO_2)_2P_2O_7$	U_3O_8	0·7862	·89555
		$(UO_2)_2P_2O_7$	UO_3	0·8011	·90370
Vanadium . .	51·0	V_2O_5	V	0·5604	·74853
		V_2O_5	V_2O_3	0·8242	·91602
		$AgVO_3$	V_2O_5	0·4399	·64332
		NH_4VO_3	V_2O_5	0·7775	·89071
Zirconium . .	90·6	ZrO_2	Zr	0·7390	·86864

MELTING-POINTS.

After the proofs of this book had been completed, a Commercial Report, dated 16th January 1919, was issued by the U.S. Bureau of Standards, giving the melting-points of elements according to the most accurate determinations available. The data for the elements here discussed are reproduced below; the melting-points of rare-earth metals other than those shown in this table have not yet been determined.

First Group.		*Fourth Group.*	
Lithium	186°	Titanium	1800°
Rubidium	38°	Zirconium	1700° ?
Cæsium	26°	Thorium	>1700° <Mo
		Germanium	958°
Second Group.		*Fifth Group.*	
Beryllium	1280°	Vanadium	1720°
Radium	700°	Columbium	1700° ?
		Tantalum	2900°
Third Group.		*Sixth Group.*	
Gallium	30°	Selenium	217°–220°
Indium	155°	Tellurium	452°
Thallium	302°	Molybdenum	2550°
		Tungsten	3400°
		Uranium	<1850°
Rare-Earth Group.		*Eighth Group.*	
Cerium	640°	Ruthenium	2450° ?
Lanthanum	810° ?	Rhodium	1950°
Praseodymium	940°	Palladium	1549°
Neodymium	840° ?	Osmium	2700° ?
Samarium	1300°–1400°	Iridium	2350° ?
Yttrium	1490°	Platinum	1755°

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