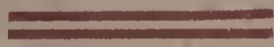


The Assay-book



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The
ASSAY-BOOK

FOR

STUDENTS

BY

JOHN HOWARD APPLETON, Sc. D.

Professor of Chemistry in Brown University



Providence, R. I.
Remington Printing Company
1906

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ZINC

Principal Ores of Zinc

	Smithsonite, (Dana, 279), Zinc carbonate, ZnCO ₃ .		Calamine, (Dana, 546), Hydrous silicate of zinc, Zn ₂ SiO ₄ ·H ₂ O
CO ₂	35.2		SiO ₂ 25.0
ZnO	64.88 (Zn, 52.1)		ZnO 67.5 (Zn, 54.2).
	—————		H ₂ O 7.5
	100.		100.

	Blende, black-jack, (Dana 59), Zinc sulphide, ZnS.		Franklinite, (Dana, 227), Metallic oxides, (Fe, Zn, Mn) O. (Fe, Mn) ₂ O ₃
S	33.		Fe ₂ O ₃ 60.52
Zn	67.		Mn ₂ O ₃ 6.79
	—————		ZnO 19.44 (Zn, 15.6)
	100.		MnO 12.81
			99.56

	Zincite, (Dana, 208), Zinc oxide, ZnO.
O	19.7
Zn	80.3
	—————
	100.

Zinc—Synopsis of Methods

Gravimetric Methods

1. Zinc oxide. Fresenius, 1: 286.
 - a. By precipitation as zinc carbonate.
Precipitate from a boiling solution with sodium carbonate.
Wash, dry, and ignite. Weigh as ZnO.
 - b. By precipitation as zinc sulphide.
Make the solution alkaline with ammonia and add ammonium chloride.
Precipitate as sulphide with colorless ammonium sulphide.
Dissolve in hydrochloric acid and re-precipitate as carbonate.
Weigh as ZnO.
 - c. By direct ignition.
Heat the compound in a weighed platinum crucible, raising the temperature gradually to a very intense heat. Weigh as ZnO.

2. Zinc sulphide, Fresenius, 1: 289.
Precipitate as sulphide from an ammoniacal solution.
Heat in a weighed crucible in a current of hydrogen, or of hydrogen sulphide, (or illuminating gas). Weigh as ZnS.
3. Zinc ammonium phosphate, Talbot, 55.
Precipitate with *neutral* ammonium phosphate in a neutral solution.
Weigh, after drying at 105° C.

Volametric Methods

1. Indirect method. Mann's method. Fresenius, 2: 444.
Precipitate the zinc as hydrated sulphide.
Decompose the zinc sulphide with moist silver chloride.
To the zinc chloride (thus formed) add a definite volume of standard silver solution—but an excess.
Determine the excess with standard ammonium sulphocyanate, using a ferric indicator. (Volhard's method.)
Subtract the excess from the whole amount of silver solution, and from the difference compute the amount of zinc chloride, and thence of zinc itself.
2. Sulphide method. Schwarz's method. Sutton 377.
Precipitate the zinc as sulphide from an ammoniacal solution.
Digest the precipitate with ferric sulphate and sulphuric acid, until only a slight yellow color from undecomposed ferric salt remains.
Titrate the reduced iron compound with a standard permanganate solution (2 atoms of iron represent 1 atom of zinc).
3. Ferrocyanide method. Sutton, 382.
 - a. In acetic acid solution (without removal of iron), Galetti's method.
Convert the zinc into a soluble acetate.
Titrate with standard ferrocyanide, using uranium acetate as indicator.
 - b. In hydrochloric acid solution (requiring removal of iron). Fahlberg's method.
Titrate with ferrocyanide solution, using uranium acetate as indicator.

Dry Methods

Since metallic zinc is volatile at comparatively low temperatures, it is hardly practicable to use dry processes.

Zinc—Assay of Calamine

- A.—The stock solution.
- B.—Gravimetric test: oxide method, with preliminary precipitation as sulphide.
- C.—Volumetric test: ferrocyanide method.
(No dry process.)

A.—The Stock Solution

The intention is to produce, from 10 gms. of ore, one stock solution of the volume of 1 litre. Next it is intended to use separate parts of this solution for separate gravimetric and volumetric tests.

Outline of the Process

- a. Treat the powdered ore with potassium chlorate and nitric acid. This action is intended to be solvent for zinc compounds and oxidizing for sulphides. Evaporate the solution to remove oxides of nitrogen and chlorine.
- b. Next treat with hydrochloric acid to dissolve zinc and to liberate silicic acid.
Evaporate again and dry thoroughly to produce insoluble silicic oxide.
- c. Filter to remove silicic oxide.

The Process

1. *Weighing and dissolving.*—Weigh ten g. of the finely powdered ore.

Transfer it to a No. 4 beaker. Add 50 cc. of water, and 5 g. of potassium chlorate. Next add 10 cc. of nitric acid. Cover the beaker. Warm the mixture for 30 minutes on an iron plate.

Evaporate to dryness, in the beaker, and on the plate.

To the residue, add 20 cc. of water and 30 cc. of hydrochloric acid.

2. *Removing silicic oxide.*—Evaporate again upon the plate to complete dryness (in order to change the gelatinous silicic acid to insoluble silicic oxide).

Cool the dry mass; then add to it 50 cc. of water and 10 cc. of hydrochloric acid. Warm the mixture, to dissolve the zinc (but leaving silicic anhydride insoluble). Heat the mixture to boiling.

Filter with the filter-pump and wash. (Dry and ignite the paper and contents; weigh the residue as silica.)

3. *Completing the stock solution.*—Transfer the filtrate from the preceding process to a litre flask; dilute the whole to 1000 cc.; 100 cc. of it represents 1 g. of the original ore.

B.—Gravimetric Method for Zinc.

Oxide method, with preliminary precipitation as sulphide.

Beringer, 217.

Outline of the Process

Precipitate the zinc first as sulphide, then as basic carbonate.
Weigh as zinc oxide, ZnO.

Supplies

Apparatus for generating hydrogen sulphide.

The Process

1. *Drawing the sample.*—Draw from the stock solution 100 cc. (It represents 1 g. of ore.) To this, add 100 cc. of water.

2. *Removing copper, etc.*—Saturate the solution with hydrogen sulphide; filter; wash with water acidulated with hydrochloric acid. Boil to expel hydrogen sulphide; add a few drops of nitric acid. Cool.

3. *Removing iron and aluminium.*—Add caustic soda (about 10 cc.) until the acid is nearly neutralized and then sodium acetate (10 g. in 20 cc. of water) until the color of the solution is no longer darkened. Boil. Filter.

4. *Separating zinc.*—To the filtrate add ammonia (about 10 cc.) until the solution is alkaline; then pass hydrogen sulphide in. Allow the precipitate to subside; decant upon a filter.

Remove the filter paper with the precipitate to a beaker and add 20 cc. of concentrated hydrochloric acid and 20 cc. of water. Boil to free from hydrogen sulphide and evaporate, if necessary, to get rid of excess of acid.

The solution should contain the zinc (together with any manganese the ore contained) and perhaps traces of cobalt and nickel. Evaporate this solution to dryness; re-dissolve the residue, using 2 cc. of hydrochloric acid and 50 cc. of water.

5. *Precipitating basic zinc carbonate.*—Cautiously add sodium carbonate (15 cc. of a 10% solution) to the hot, moderately dilute solution, until the liquid is distinctly alkaline; then bring the mixture to boiling.

Allow the precipitate to subside, decant on a filter, and wash with hot water.

6. *Changing zinc carbonate to zinc oxide.*—Dry the precipitate. Separate it as far as possible from the filter paper. Burn the paper in a porcelain crucible. To the ashes add the zinc carbonate; ignite, and weigh. The substance weighed is zinc oxide, ZnO. (It contains 80.34% of the metal.)

Remarks

In certain cases, manganese, as Mn_2O_3 , may be present with the zinc oxide.

In such cases, dissolve the contents of the crucible in dilute hydrochloric acid. Boil with excess of sodium hydroxide. The oxide of manganese should be precipitated, ignited, and weighed as Mn_3O_4 . Its weight, multiplied by 1.035, must be subtracted from the weight of the mixture with oxide of zinc previously obtained.

C.—Volumetric Method for Zinc.

Ferrocyanide Method with Uranium Indicator

Cairns, 185, 188.

Hiorns, 321, 440.

Crookes' Select Methods, 145E.

Ricketts & Miller, 153.

Outline of the Process

Titrate the zinc in a hydrochloric acid solution with standard potassium ferrocyanide solution, using uranium acetate (in concentrated solution) in spots on a porcelain plate, as an indicator.

Supplies

1. Uranium acetate, a few cc. of a saturated solution.
2. Pure zinc, 5 g. dissolved in 33 cc. of hydrochloric acid and diluted to 500 cc. (or some other convenient weight of zinc, dissolved in its proper amount of water). 1 cc. corresponds to 10 mg. of metallic zinc.
3. Potassium ferrocyanide, 21.6 g. dissolved in 500 cc. of water. 1 cc. correspond to 0.010 g. of metallic zinc.

Standardize this solution by the zinc solution (No. 2 above) as follows:

Draw 50 cc. of the zinc solution; to it add 2 cc. of concentrated hydrochloric acid and about 150 cc. of water.

Heat the mixture to incipient boiling and keep the solution hot.

Into the warm solution, slowly add the ferrocyanide solution from a burette, spotting from time to time upon drops of uranium acetate upon the porcelain plate.

From the number of cc. required, compute the exact value of each cc. of the ferrocyanide solution, in terms of metallic zinc.

The Process

1. *Drawing the sample.*—Draw from the stock solution 100 cc. (It represents 1 g. of ore.) Heat to boiling.

2. *Removing iron.*—To the solution add about 15 cc. of concentrated ammonia to precipitate iron, etc., and to dissolve zinc.

Filter, using the pump.

Re-dissolve the precipitate of ferric and aluminium oxides in 5 cc. of concentrated hydrochloric acid; re-precipitate with 6 cc. of concentrated ammonia and refilter (to secure zinc which at first went down with ferric oxide, etc.); add this filtrate to the foregoing filtrate. Make the solution to the volume of 200 cc.

3. *Titration.*—Place the prepared solution in a casserole. To it add 15 cc. of hydrochloric acid. Heat to incipient boiling. Keep the solution hot. Titrate carefully and rather slowly with the standard ferrocyanide solution, spotting from time to time upon uranium solution. (As described, each cc. of ferrocyanide solution represents about 1% of metallic zinc.)

Remarks

Copper and iron are objectionable.

Potassium chloride appears to be unobjectionable.

Zinc sulphate gives only fairly good results.

Excess of hydrochloric acid seems objectionable in titration, but distinct acid reaction with hydrochloric acid is desirable.

Zinc fluoride is insoluble in ammonia; this seems to forbid immediate use of hydrofluoric acid on the sample.

Silica does not appear to carry down zinc.

Iron appears to carry down about $\frac{3}{10}\%$ of zinc in the first precipitation—this is recovered in the second precipitation.

LEAD

Principal Ores of Lead

Galena, (Dana, 48), Lead Sulphide, PbS.		Cerussite, (Dana, 286), Lead carbonate, PbCO ₃ .	
S	13.4	CO ₂	16.5
Pb	86.6	PbO	83.5 (Pb, 77.50)
<hr/>		<hr/>	
100.00		100.00	
Anglesite, (Dana, 907), Lead sulphate, PbSO ₄		Pyromorphite, (Dana, 770), Lead phosphate 3Pb ₃ P ₂ O ₈ .PbCl ₂	
SO ₃	26.4	P ₂ O ₅	15.7
PbO	73.6 (Pb, 68.31)	PbO	82.2 (Pb, 76.29)
		Cl	2.6
<hr/>		<hr/>	
100.00		100.5	

Lead—Synopsis of Methods

Gravimetric Methods. Fresenius, 1: 358.

1. Metallic lead.
 - a. Potassium cyanide method.
Reduce by fusion with potassium cyanide.
Wash, dry and weigh.
Dissolve in nitric acid and subtract the weight of the residue from the first weight.
 - b. By metallic zinc or metallic cadmium.
2. Lead oxide.
 - a. By precipitation.
Precipitate with ammonium carbonate.
Ignite and weigh as PbO.
 - b. By ignition.
Heat the compound in a weighed crucible.
Weigh as PbO.
3. Lead sulphate.
 - a. By precipitation.
Precipitate with dilute sulphuric acid. Wash with alcohol.
Weigh as lead sulphate, PbSO₄.
 - b. By evaporation.
Treat the compound in a weighed dish with sulphuric acid.
4. Lead chromate.
Precipitate with potassium dichromate in acetic acid solution.
Weigh as lead chromate, PbCrO₄.
5. Lead chloride. Olsen, 136.
Precipitate by hydrochloric acid in the presence of a mixture of alcohol and ether.
Weigh as lead chloride, on a balanced filter.

Volumetric Methods

1. Potassium sulphate method. Schimpf, 270.
Titrate with the sulphate solution until a drop of the mixture fails to produce a yellow color upon a paper saturated with potassium iodide and sodium thiosulphate.
2. Potassium chromate method. Beringer, 174.
Add an excess of potassium chromate to the solution.
Determine the excess colorimetrically.
3. Potassium dichromate method. Sutton, 253.
Titrate with the dichromate solution until a drop of the mixture fails to produce a precipitate with silver nitrate.

Dry Methods

1. Metallic lead. Brown; Hiorns; Beringer; Ricketts.
Fuse in a crucible or scorifier with fluxes and reducing agents.
Weigh as metallic lead.

Lead—Assay of Galena

- A.—Gravimetric test, sulphate method, by precipitation.
B.—Volumetric test, chromate method with silver indicator.
C.—Dry process for galena, using iron rods.

A.—Gravimetric Test—Sulphate Method—Fresenius 2 : 574

Outline of the Process

Oxidize lead sulphide to lead sulphate and weigh as such. (But separate gangue, removing lead sulphate by dissolving it in ammonium acetate.)

The Process

1. *Weighing and oxidizing.*—Weigh 2 g. of the finely powdered galena. Transfer it to a No. 4 beaker provided with a glass cover.

Add 10 cc. of fuming nitric acid. Place the beaker on a hot plate. Heat gently for about 30 minutes. Now remove the glass cover; evaporate to dryness on the same plate. To the residue add 50 cc. of water, then carefully add 3 cc. of concentrated sulphuric acid. Boil the mixture for a few minutes.

2. *Filtering, drying, etc.*—Filter; wash the precipitate with water acidulated with sulphuric acid; then wash with alcohol.

Dry the paper and contents. Remove the precipitate to a piece of glazed paper. Ignite the filter paper in a porcelain crucible. To the ash, add 5 drops of dilute nitric acid; warm the mixture; then evaporate to dryness.

Transfer the precipitate to the crucible containing the filter ash, etc. Add 5 drops of dilute sulphuric acid. Carefully evaporate the mixture to dryness. Ignite gently.

3. *Weighing*.—Weigh as lead sulphate and gangue.

4. *Separating lead sulphate from gangue*.—Transfer dry the contents of the crucible to a dry beaker. Add 25 g. of solid ammonium acetate; then 50 cc. of water; then 2 cc. of ammonium hydroxide; then boil the whole until it is judged that all of the lead sulphate is dissolved.

5. *Filtering, etc.*—Finally transfer everything to a filter; wash with hot water, dry, ignite.

6. *Weighing*.—Weigh the residue as gangue. Subtract this weight found from that of the original residue (gangue and lead sulphate). The difference is the weight of the lead sulphate.

B.—Volumetric Test—Chromate Method

Sutton, 253; Beringer, 173

Outline of the Process

Boil the galena in hydrochloric acid. From the solution, precipitate metallic lead by means of a zinc rod. Strip the metallic lead from the zinc.

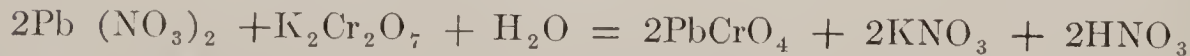
Titrate the lead in an acetic acid solution with a standard solution of potassium dichromate, using silver nitrate as an indicator.

Supplies

1. Silver nitrate, saturated solution.
2. Pure zinc rods.
3. Potassium dichromate, at the rate of 7.117 g. per litre; 1 cc. represents 0.010 g. lead.

Compute the amount of dichromate per litre necessary to precipitate the lead, so that 1 cc. of dichromate will be equivalent to exactly 0.010 g. of lead.

Pb(NO ₃) ₂		K ₂ Cr ₂ O ₇	
Pb	206.9 × 2 = 413.8	K ₂	78.30
2N	28.08	Cr ₂	104.2
2O ₃	96.	O ₇	112.
	<hr/>		<hr/>
	330.98 × 2 = 661.96		294.50



$$413.8 : 294.5 :: 10 \text{ g.} : x \text{ the wt. of K}_2\text{Cr}_2\text{O}_7. \quad x = 7.117\text{g.}$$

Standardizing.—Weigh $\frac{1}{2}$ the quantity (3.5585 g.) of the dichromate; dissolve it in water and dilute the solution to 500 cc.

Weigh 2 g. of pure metallic lead. Place this amount in a No. 4 beaker. Add 50 cc. of dilute nitric acid. Warm the mixture until the lead is dissolved. Neutralize the solution with about 50 cc. of ammonia. Add a considerable excess of acetic acid. Dilute the whole to a volume of 500 cc.

For each test take 100 cc. of this solution (equals 0.400 g. of metallic lead).

Boil the solution; then add a measured quantity of the dichromate solution until nearly all the lead has been precipitated. Boil the mixture again until the precipitate becomes orange-colored.

Finish the titration by carefully adding dichromate, as needed, to the hot solution. Determine the end-point by bringing small portions of the solution in contact with drops of silver nitrate placed upon a white porcelain tile.

Compute the exact value of 1 cc. of the dichromate solution in terms of metallic lead.

The Process

1. *Weighing and dissolving.*—Place 2.5 g. of the finely powdered ore in a No. 4 beaker, with a glass cover; add 50 cc. of dilute hydrochloric acid. Heat the mixture until the evolution of hydrogen sulphide almost ceases. Add water if necessary.

Introduce a piece of a zinc rod. Continue the heating until all the sulphide has been dissolved and all the lead has been precipitated in metallic form.

Decant the liquid; then wash the metallic residue twice with cold water.

Strip off the precipitated lead and clean the zinc. Cover the lead with 25 cc. of water and about 12 cc. of nitric acid. Heat gently until all the metallic lead is dissolved.

Dilute the solution to a volume of 250 cc. Use for each test 50 cc. of this solution (equivalent to 0.500 g. of ore).

Neutralize the 50 cc. with ammonia (2 or 3 cc.), then add a considerable excess of acetic acid (about 15 cc.).

(The solution thus prepared is such that it will, in the subsequent titration, require from 30 to 43 cc. of dichromate solution, representing from 60% to 86% of metallic lead in the ore.)

2. *Titrating.*—Boil the solution. Then add the standard solution of potassium dichromate as in standardizing. Determine the end-point as before.

3. *Computing.*—From the number of cc. used and the strength of the dichromate solution, determined in the preliminary standardizing, compute the amount of lead in the sample taken. (As described, each cc. of dichromate solution represents about 2 % of metallic lead.)

C—Crucible Method for Lead in Galena

Brown, 186, 189, 190; Hiorns (*Assaying*), 208; Beringer, 171

Outline of the Process

Mix the ore with proper fluxes. These should be reducing (as the alkaline carbonates, carbon, etc.) and desulphurizing (iron).

Fuse the charge.

Weigh the metallic lead.

Supplies

Crucible. Wedgwood mortar. Sodium bicarbonate. Argols. Salt. Borax.

Iron rods. Each is rod to be about $\frac{3}{8}$ in. in diameter, 6 in. long; at one end a portion of 2 in. to be bent over so that the whole assumes the shape of an L.

The Process

1. *Preparing the charge.*—Weigh the materials :

ore	30 g.
sodium bicarbonate,	30 g.
borax,	30 g.
argol,	10 g.

Transfer them to a wedgwood mortar. Grind the mixture with a pestle so as to thoroughly intermingle the substances.

2. *Charging the crucible.*—Transfer the mixture to a piece of paper and thence to the crucible.

Into the same mortar introduce 10 g. of common salt. With a pestle stir this around, thus rinsing the mortar. Transfer the salt to the crucible so as to form a cover on the top of the principal portion of the charge.

Place 4 iron rods in the crucible in such a way that they reach through the charge to the bottom.

3. *Fusing.*—Place the crucible in a moderately hot fire; cover it. Fuse for about 30 minutes, or until the mass is red-hot, and in quiet fusion.

When the charge is in a liquid condition, remove the cover. Draw out one of the iron rods; examine it and replace it.

Stir the molten mass thoroughly with the iron rods. Then continue quiet fusion for 15 minutes longer.

Withdraw the iron rods one by one and slowly (the purpose is to allow any adhering globules of metallic lead to run from the rods into the melted charge).

Withdraw the crucible. Tap it gently with a pair of tongs (the purpose is to help scattered globules of lead to sink to the bottom of the crucible).

4. *Cooling and weighing.*—Cool the crucible (over night if convenient). Break the crucible with a hammer. Break away the slag from the button of lead. Hammer this button into a little cube (by this means small portions of slag are more effectually removed).

Weigh the button of metallic lead, and make the necessary computation.

Experiments on the Fusion of Lead and Lead Oxide in Presence of Silicon Dioxide (or Silicates)

1. Lead oxide in a crucible.—In a small sand crucible, place about 150 g. of lead oxide, PbO, also called litharge. Place crucible and contents

in a good coal fire. Continue the experiment until (first) the lead oxide is in fusion; (second) it makes a hole in the crucible, and runs away.

Withdraw the crucible; cool it; examine it; break it and examine it again.

The oxide easily fuses; it forms an easily fusible lead silicate. Thus the *silicious matter of the walls of the crucible* may be dissolved by the melted lead oxide.

(Lead oxide is used, with other substances, especially soda ash—sodium carbonate—and sand in making flint glass. The fusible lead silicate formed blends with other silicates, making an easily fusible glass. Moreover, the density of the lead silicate is so great that glass containing it refracts light strongly—thus the glass has a more brilliant appearance.)

2. Lead in a crucible.—In a small sand crucible, place about 400 g. of ordinary metallic lead. Then place the crucible and contents in a good coal fire. Continue the heating for about 1 hour.

Withdraw the crucible; pour the melted lead—if any remains—into some proper receptacle.

Cool the crucible; examine it, breaking it if necessary for inspection.

ANTIMONY

Principal Ore of Antimony

Stibnite, (Dana 36),
Antimony trisulphide

	Sb_2S_3 .	
S		28.6
Sb		71.4
		<hr/>
		100.

Antimony—Synopsis of Methods

Gravimetric Methods

1. Antimony tetroxide. Fresenius, 1: 398.
 - a. By direct ignition. (In case of compounds containing easily volatilized acids.)
 - b. By previous precipitation as antimonious sulphide.
Heat the dried sulphide, in a covered crucible, with fuming nitric acid.
2. Antimonious sulphide. Fresenius, 1: 395.
Precipitate the antimony with sulphuretted hydrogen; dry and weigh the product.
Correct the result (1) by heating a weighed portion of the sulphide in a porcelain boat in a current of carbon dioxide or (2) by acting on a weight portion of the sulphide with fuming nitric acid—thus producing antimony tetroxide.

Volumetric Methods

1. Iodine method. Mohr's method. Fresenius, 1: 400.
Dissolve the antimonious compound in presence of tartaric acid; neutralize the solution with sodium bicarbonate; titrate with a standard solution of iodine, using starch-water as an indicator.
$$\text{Sb}_2\text{O}_3 + 4\text{I} + 4\text{HNaCO}_3 = \text{Sb}_2\text{O}_5 + 4\text{NaI} + 2\text{H}_2\text{O} + 4\text{CO}_2$$
2. Dichromate method. Kessler's method. Sutton, 162.
(Tartaric acid is not admissible.)
Titrate with slight excess of potassium dichromate (previously standardized by arsenious oxide) using standard solution of ferrous sulphate as an opposite balancing solution, and employing potassium ferricyanide as an indicator. (Potassium permanganate may be substituted for dichromate as the oxidizing agent.)
Compute the amount of antimony from the amount of arsenious oxide.
0.005 g. As_2O_3 corresponds to 0.007253 g. Sb_2O_3 .
3. Hydrogen sulphide method. Schneider's method. Sutton, 163.
Turn the antimony into sulphide.

Decompose this antimony sulphide (either form) by boiling in hydrochloric acid in a special apparatus, absorbing the expelled gas in an excess and alkaline arsenite.

Titrate the excess of arsenious oxide with standard solution of iodine, using starch-water as indicator.

Compute the amount of hydrogen sulphide and thence the amount of antimony. 3 equivalents of H_2S correspond to 1 equivalent of Sb.

Dry Methods

There are certain objections to dry methods (though the latter are sometimes used.) The antimony after reduction is volatile at furnace heat; moreover, in the process of reduction other metals tend to go into the antimony button. (When metallic iron is used to separate sulphur from antimony, there is this difficulty: an alloy of iron and antimony may form.)

Antimony—Assay of Stibnite—Gravimetric Method

Outline of the Process

- (a.) Treat the ore with hydrochloric acid, noting the amount of insoluble matter.
- (b.) Precipitate the antimony as sulphide, $Sb_2S_3 + nS$.
- (c.) Make the proper corrections for the irregular amount of sulphur.

Supplies

Balanced filters,
Sulphuretted hydrogen water.

The Process

1. *Weighing and dissolving.*—Weigh .500 g. of the very finely powdered ore. Transfer it to a No. 2 beaker provided with a glass cover. Add 6 cc. concentrated hydrochloric acid, sp. g. 1.20.

Warm the mixture to expel sulphuretted hydrogen (but keep the solution below the boiling point, to avoid loss of volatile chlorides of antimony).

Add 1 g. of tartaric acid, then carefully add water—5 cc. at a time—until the volume of the solution is about 100 cc. (It is intended to prevent precipitation of oxychlorides.)

2.—*Determining the insoluble part.*—Filter the solution. (Save the filtrate.)

Wash the precipitate with water containing a little hydrochloric acid and a little tartaric acid (to prevent precipitation of oxychloride).

Add the washings to the rest of the filtrate.

Dry and ignite the precipitate and weigh it as insoluble matter.

3. *Determining the antimony.*—In the united filtrate and washings precipitate the antimony with clean sulphuretted hydrogen gas and continue the process as described in Appleton's Quantitative Analysis, pages 53 to 56.

Antimony—Assay of Stibnite—Volumetric Method by Iodine

Outline of the Process

- (a.) Prepare the starch-water.
- (b.) Prepare solution of hydrosodium carbonate.
- (c.) Prepare the iodine solution.
- (d.) Prepare the thiosulphate solution; compare this with the iodine solution.
- (e.) Prepare the arsenious solution; standardize the iodine solution by means of this one.
- (f.) Prepare the potassium iodate solution; standardize the iodine solution by means of this one.
- (g.) Determine antimony in the sample of stibnite.

Supplies

Iodine. Sodium thiosulphate. Arsenious oxide. Sodium bicarbonate. Potassium iodide. Potassium iodate. Starch.
Burettes.

The Standard Solutions

1. The starch-water; the indicator.—Mix 1 g. starch with 5 cc. cold water, add 150 cc. boiling water; allow the solution to stand; filter.

2. Hydrosodium carbonate solution.—Dissolve 6 g. hydrosodium carbonate, HNaCO_3 , in 200 cc. of water.

3. The iodine solution.—Weigh 13 g. iodine and 18 g. potassium iodide; triturate both in a mortar with small portions of water, until all is dissolved. Dilute the whole to 1000 cc.

4. The thiosulphate solution.—Weigh 25 g. sodium thiosulphate, dissolve in water, and dilute to 1000 cc.

(The purpose in mind is this: To use the thiosulphate solution as an intermediary and balancing solution—not as a basal standard. Its numerical relations to the iodine solution must be definitely learned; then if in subsequent work too much iodine has been inadvertently added when titrating, such excess may be counterbalanced by addition of thiosulphate, the latter's relation to iodine being known.)

5. Comparing the solutions 3 and 4.—From a burette, draw 40 cc. of thiosulphate solution into a casserole; add about 100 cc. of water and 5 cc. of starch-water.

From another burette, cautiously draw iodine solution until permanent appearance of the blue of the iodo-starch.

Compute and record the ratio of the iodine solution to the thiosulphate solution.

6. The arsenious solutions.—Weigh about 5 g. of hydro-sodium carbonate. Dissolve in 50 cc. of water. If the salt does not completely dissolve, use the clear solution.

Weigh two portions each .200 g. of pure arsenious acid. Treat each as follows: Dissolve the weighed portion, with stirring, in 10 cc. sodium hydroxide; then dilute to 150 cc. Add hydrochloric acid until slightly in excess; then neutralize with a concentrated solution of the bicarbonate. Add to each, 5 cc. of the starch solution.

7. Arsenious standardizing of the iodine solution.—Draw cautiously the iodine solution first into one, then into the other arsenious solution (taking care not to pass the end-point) until the permanent appearance of the blue. Record the amount of iodine solution used in each case.

From the corrected volume of the iodine solution used, compute the quantity of iodine in each cc. of the iodine solution.

(The purpose in mind is this: Since the iodine used is not perfectly pure, it must be tested by some substance that may be accepted as pure; such a substance is arsenious oxide. In this case, then, the real and true amount of iodine is determined by means of arsenious oxide—which latter is assumed to be pure.)

8. The iodate solutions.—Weigh two portions each .150 g. of potassium iodate. Treat each as follows: Place the weighed portion in a beaker and dissolve in 50 cc. of water. Add a solution of potassium iodide containing 3 g. of the salt.

Add to the mixture 10 cc. dilute sulphuric acid. Allow the whole to stand for three minutes. Dilute to 150 cc.

9. Iodate standardizing of the iodine solution.—Draw from a burette into each iodate (now iodine) solution a measured volume of thiosulphate until the color of the iodine is nearly destroyed.

Add 5 cc. starch solution; then add more thiosulphate, cautiously, until the blue color disappears. Finally, add iodine solution (from the main original standard) until the blue color is just restored.

(Make a blank test on the potassium iodide for potassium iodate: The latter is usually present in small but variable proportions in commercial iodide.) Weigh two portions, 3 g. each, of potassium iodide such as has been previously used.

Dissolve the weighed portions; add sulphuric acid; dilute to 150 cc.; then add starch and thiosulphate solutions till the blue color just disappears.

(Make the proper computations.) These are three: First, from the number of cc. of thiosulphate used for iodate and iodide, subtract that used for iodide alone; the difference is the amount of thiosulphate referable to the action of the iodate weighed. Second, compute the true amount of iodine referable to the iodate weighed, and thence the amount of iodine neutralizable by 1 cc. of thiosulphate. Third, from the true amount of iodine just found as referable to each cc. of thiosulphate solution, compute the amount of iodine in the amount of iodine solution, described in 3 above.

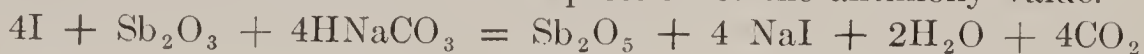
(The purpose of this work with iodate is this: Since the iodine used is not perfectly pure, it must be tested by some substance that may be accepted as pure; such a substance is potassium iodate.)

This iodate experiment amounts to a second test, in addition to the arsenious test, of the amount of real iodine in the standard iodine solution.

Two tests are given in order to afford more certain results and also in order to instruct the pupil.

10. Computing the antimony value of the iodine solution.—The tests already described have led to a correct estimate of the true iodine value of the iodine solution.

This must be transformed into an expression of the antimony value.



Then	Value in I	Value in Sb
4×126.97	2×120.2	of 1 cc. iodine sol.
487.88	240.4	of 1 cc. iodine sol.
:	::	x :
		y

The Process

1. *Weighing and dissolving.*—Weigh .400 g. of finely powdered stibnite. Place the powder in a dry beaker, No. 2, with a cover. Add 5 cc. concentrated hydrochloric acid, sp. g. 1.20. Warm the mixture gently; for, first, all sulphuretted hydrogen must be expelled; second, the liquid must not be boiled lest volatile antimonious chloride be driven off.

When the residue is white, add 1 g. of solid tartaric acid. Cautiously add, in quantities of 5 cc. at a time, 120 cc. of water.

If white oxychloride is produced, discard all the material, and start the experiment again.

If at any time red sulphide of antimony appears (showing incomplete expulsion of sulphuretted hydrogen), warm the solution (before adding more water) until it becomes colorless; so continue until, after addition of all the water, a clear and colorless solution has been obtained. Cool this solution.

2. *Neutralizing.*—Carefully pour the solution, little by little, into the sodium carbonate solution (avoiding loss by violent effervescence).

3. *Titrating.*—To the solution add 2 cc. of starch-water. Titrate with the standard iodine solution until the blue color appears—avoiding much excess of iodine.

(If much excess of iodine is accidentally added, thiosulphate solution may be run back, and afterwards allowed for.)

4. *Computing.*—From the value in antimony of the iodine solution compute the quantity of antimony in the ore examined, and thence the percent.

TIN

Principal ores of Tin

	Cassiterite, (Dana, 234), Tin dioxide, SnO ₂ .		Stannite, (Dana, 83), Tin sulphide, Cu ₂ S.FeS.SnS ₂ .
		S	29.9
		Sn	27.5
O	21.4	Cu	29.5
Sn	78.6	Fe	13.1
	<hr/>		<hr/>
	100.00		100.00

Tin—Synopsis of Methods

Gravimetric Methods

- Stannic oxide. Fresenius, 1: 405.
 - By treatment with nitric acid.
Oxidize the tin with concentrated pure nitric acid.
Dry, ignite, and weigh as stannic oxide.
 - By precipitation as stannic (or metastannic) acid.
Oxidize all the solution of tin to the stannic form.
Precipitate with ammonium nitrate or sodium sulphate.
Dry, ignite, and weigh as stannic oxide.

$$\text{SnCl}_4 + 4\text{Na}_2\text{SO}_4 + 3\text{H}_2\text{O} = \text{H}_2\text{SnO}_3 + 4\text{NaCl} + 4\text{HNaSO}_4$$

$$\text{SnCl}_4 + 4\text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O} = \text{H}_2\text{SnO}_3 + 4\text{NH}_4\text{Cl} + 4\text{HNO}_3$$
 - By precipitation as sulphides, -ous or -ic.
Precipitate in moderately acid solution with hydrogen sulphide.
Filter and wash the precipitate with the aid of a salt solution.
Dry and heat, in the presence of air, to drive off the sulphur.
Finally ignite strongly with ammonium carbonate until the weight is constant.

Volumetric Methods

- By iodine in alkaline solution. Lenssen's method, Fresenius, 1: 408.
Dissolve the substance in hydrochloric acid.
Reduce to the stannous form.
Add sodium potassium tartrate and then sodium bicarbonate in excess. Add starch solution. Titrate with a standard iodine solution.
- Ferric chloride method. Lowenthal's method, Sutton, 373.
Reduce the tin to the stannous form.
Treat with a concentrated solution of ferric chloride.
Titrate the reduced ferrous chloride with a standard solution of potassium permanganate.

$$\text{SnCl}_2 + \text{Fe}_2\text{Cl}_6 = \text{SnCl}_4 + 2\text{FeCl}_2$$

Dry Methods

1. Cornish method. Beringer, 232.
Reduce the oxide with carbon (anthracite).
Weigh the metallic tin.
2. Cyanide method.
Dissolve impurities in the ore with hydrochloric acid.
Oxidize with nitric acid.
Reduce the oxide by fusion with carbon and potassium cyanide.
Weigh the metallic button of tin.
 $\text{SnO}_2 + 2\text{KCN} = \text{Sn} + 2\text{KCNO}$.

Volumetric Method for Tin—Dichromate Method

Outline of the Process

Treat the ore with acid to remove iron and reducible substances.
Heat the residue in a current of hydrogen or other reducing gas to produce metallic tin.
Dissolve the metallic tin in hydrochloric acid.
Titrate with standard potassium dichromate.

Supplies

1. Pure metallic tin.
2. Glass combustion tube with porcelain boat.
3. Hydrogen generator.
4. Starch-Iodide mixture. Place in a casserole.

powdered starch,	1 g.
potassium iodide,	3 g.
water,	100 cc.

Boil the mixture with constant stirring, then allow the whole to cool before use.

5. Standard solution of potassium dichromate.—Dissolve 4.125 g. of the pure dry salt in about 50 cc. of hot water. Dilute this solution to the volume of 500 cc. 1 cc. is intended to represent 10 mg. of metallic tin.

Standardizing.—Weigh 5 g. of pure metallic tin. Place it in a small platinum dish. Place the latter, with its contents, in a casserole. Cover the tin with hydrochloric acid (150 cc. of concentrated acid with 50 cc. of water). Cover the casserole with a large watch glass and boil the acid. (It may require three or four hours to dissolve all the tin.) Add more hydrochloric acid if necessary.

When the tin is dissolved, dilute its solution to 500 cc. The solution contains stannous chloride, SnCl_2 . Each cc. contains the equivalent of 10 mg. of metallic tin.

(In some cases, it is better to dissolve only a part of the 5 g. of tin. In this case, proceed as follows: Remove the platinum dish with its undissolved tin. Wash the latter. Dry dish and contents. Weigh the undissolved tin; subtract this weight from 5 g. Dilute the solution to a volume such that 1 cc. of it will represent 10 mg. of metallic tin.)

Into a casserole draw 50 cc. of the tin solution. To it, add 5 cc. of pure concentrated hydrochloric acid and 5 cc. of the starch-iodide mixture. Titrate this stannous solution with the dichromate solution.

From the results of titration, compute the exact value of potassium dichromate solution in terms of metallic tin. 1 cc. of the dichromate solution is intended to represent 10 mg. of metallic tin.

The Process

1. *Weighing and washing.*—Weigh 1 g. of the finely powdered ore. Transfer it to a No. 4 beaker.

To the ore add 30 cc. of hydrochloric acid and 10 cc. of nitric acid. Warm the mixture; later boil it; finally remove the cover and evaporate the whole to dryness.

Cool the residue; add 50 cc. of water, and 10 cc. of hydrochloric acid; warm the mixture for 30 minutes.

Filter the mixture. Discard the filtrate which may contain iron, copper, and certain other substances. Dry and ignite the residue.

2. *Reducing stannic oxide.*—Transfer the residue, which contains stannic oxide, SnO_2 , to a porcelain boat. Ignite the boat and contents gently; then weigh the whole. Next place the whole in a glass combustion tube. Through the tube conduct a current of hydrogen gas. Heat the boat, etc., to a low red heat for one hour. Continue the current of gas while the boat is cooling.

3. *Trial Weighing.*—Weigh the boat and contents. The loss of weight may be considered as principally oxygen from the stannic oxide. From the amount of this loss compute the amount of tin it represents. Of course the result is only approximate.

(It is well to heat the material in hydrogen a second time, again noting the loss of weight.)

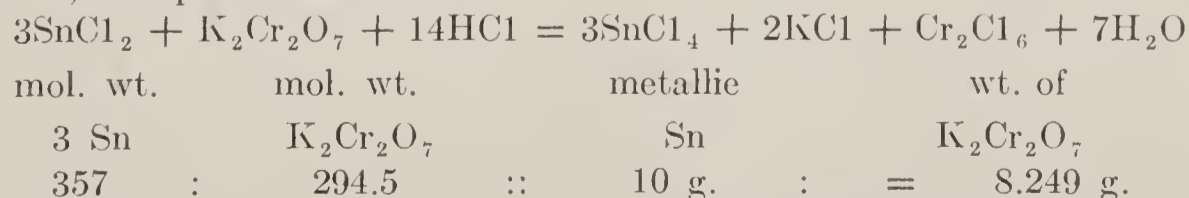
4. *Dissolving the tin.*—Transfer the contents of the boat to an erlenmeyer flask provided with a funnel. Add 10 cc. of water and 10 cc. of hydrochloric acid. Boil for at least an hour in order to dissolve the metallic tin.

5. *Titration.*—To the mixture in the erlenmeyer, add 5 cc. of hydrochloric acid and 5 cc. of the starch-iodide mixture. Then titrate with potassium dichromate.

(As described, each cc. of the potassium dichromate represents 1 % of metallic tin.)

Note

The action of potassium dichromate upon stannous chloride, in acid solution, is expressed as follows:



(This amount, 8.249 g. of $\text{K}_2\text{Cr}_2\text{O}_7$, dissolved to the volume of 1 litre, represents 10 g. of metallic tin; and 1 cc. represents 10 mg. of metallic tin.)

Dry Method for Tin—Cyanide Method. Beringer, 234

Outline of the Process

Dissolve the impurities from the ore with hydrochloric acid.
Reduce the stannic oxide by fusion with potassium cyanide and charcoal.

Supplies

Hydrochloric acid. Nitric acid. Potassium cyanide. Charcoal.

The Process

1. *Dissolving impurities.*—Weigh 10 g. of the finely powdered ore. Transfer to a No. 4 beaker.

Add to the ore 50 cc. of dilute hydrochloric acid and 3 cc. of concentrated nitric acid. Digest the mixture on a hot plate for thirty minutes or until the iron and other oxides are entirely dissolved.

Filter off the solution; wash the remaining mass, SnO_2 , with hot water, and dry thoroughly.

2. *Reducing the stannic oxide.*—Place the filter paper and its contents in a crucible and ignite to burn off the paper and to drive off the last traces of moisture.

Mix the residue from above with 10 g. of finely powdered potassium cyanide and 2.5 g. of powdered charcoal; place the mixture in a crucible; cover the charge with another 10 g. of potassium cyanide.

Fuse at a dull red heat for half an hour. Remove the crucible and allow it to cool. Break the crucible; detach and clean the button.

Weigh the button of metallic tin.

COPPER

Classification of Ores of Copper

- a. Those containing the uncombined metal.
Native copper.
- b. Those practically free from sulphur (chiefly oxides and carbonates).
Cuprite, Cu_2O ,
Melaconite, CuO ,
Malachite, $\text{CuCO}_3 \cdot \text{CuO}_2 \cdot \text{H}_2\text{O}$,
Azurite, $2\text{CuCO}_3 \cdot \text{CuO}_2 \cdot \text{H}_2\text{O}$.
- c. Non-arsenical sulphur ores, generally containing iron.
Copper glance, Cu_2S ,
Chalcopyrite, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$,
Bornite (Erubescite), $3\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$.
- d. Arsenical sulphur ores, often very complex.
Tetrahedrite (gray ore, fahl ore).
 $4 (\text{Cu}_2\text{S} \cdot \text{FeS} \cdot \text{ZnS} \cdot \text{AgS} \cdot \text{PbS}) (\text{Sb}_2\text{S}_3 \cdot \text{As}_2\text{S}_3)$

Principal Ores of Copper

<p>Cuprite, (Dana, 206), Cuprous oxide, Cu_2O.</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%;"></td> <td style="width: 40%; text-align: center;">O</td> <td style="width: 50%; text-align: center;">11.2</td> </tr> <tr> <td></td> <td style="text-align: center;">Cu</td> <td style="text-align: center;">88.8</td> </tr> <tr> <td></td> <td></td> <td style="text-align: center;"><hr style="width: 20%; margin: 0 auto;"/>100.</td> </tr> </table>		O	11.2		Cu	88.8			<hr style="width: 20%; margin: 0 auto;"/> 100.	<p>Melaconite, (Dana, 209), Cupric oxide, CuO.</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%;"></td> <td style="width: 40%; text-align: center;">O</td> <td style="width: 50%; text-align: center;">20.2</td> </tr> <tr> <td></td> <td style="text-align: center;">Cu</td> <td style="text-align: center;">79.8</td> </tr> <tr> <td></td> <td></td> <td style="text-align: center;"><hr style="width: 20%; margin: 0 auto;"/>100.</td> </tr> </table>		O	20.2		Cu	79.8			<hr style="width: 20%; margin: 0 auto;"/> 100.						
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<p>Chalcocite, copper glance, (Dana 55) Cuprous sulphide, Cu_2S.</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%;"></td> <td style="width: 40%; text-align: center;">S</td> <td style="width: 50%; text-align: center;">20.2</td> </tr> <tr> <td></td> <td style="text-align: center;">Cu</td> <td style="text-align: center;">79.8</td> </tr> <tr> <td></td> <td></td> <td style="text-align: center;"><hr style="width: 20%; margin: 0 auto;"/>100.</td> </tr> </table>		S	20.2		Cu	79.8			<hr style="width: 20%; margin: 0 auto;"/> 100.	<p>Chalcopyrite, (Dana, 80), Sulphide of copper and iron, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$.</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%;"></td> <td style="width: 40%; text-align: center;">S</td> <td style="width: 50%; text-align: center;">35.</td> </tr> <tr> <td></td> <td style="text-align: center;">Cu</td> <td style="text-align: center;">34.5</td> </tr> <tr> <td></td> <td style="text-align: center;">Fe</td> <td style="text-align: center;">30.5</td> </tr> <tr> <td></td> <td></td> <td style="text-align: center;"><hr style="width: 20%; margin: 0 auto;"/>100.</td> </tr> </table>		S	35.		Cu	34.5		Fe	30.5			<hr style="width: 20%; margin: 0 auto;"/> 100.			
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Copper—Synopsis of Methods

Gravimetric Methods

1. Cupric oxide. Fresenius, 1: 371.
 - a. By direct precipitation.
Precipitate from a boiling solution with sodium hydroxide or potassium hydroxide.
Ignite and weigh as CuO.
 - b. By ignition.
Heat the compound in a weighed crucible.
Weigh as CuO.
2. Metallic copper.
 - a. By metallic zinc or metallic iron.
 - b. By electricity.
3. Cuprous sulphide.
 - a. By precipitation as cupric sulphide.
Precipitate from a boiling solution with hydrogen sulphide.
Dry and transfer to a weighed crucible.
Reduce by strongly igniting in the presence of sulphur and a current of hydrogen or of illuminating gas.
Weigh as cuprous sulphide, Cu₂S.
 - b. By precipitation as cuprous sulphocyanate.
Precipitate by potassium sulphocyanate, KSCN, in the presence of sulphurous acid.
Reduce the dried cuprous sulphocyanate with sulphur and hydrogen as in a.
Weigh as cuprous sulphide, Cu₂S.

Volumetric Methods

1. Potassium iodide method, DeHaen's method: Sutton, 201; Schimpf, 264.
Titrate with potassium iodide in excess.
Determine the free iodine with sodium thiosulphate.
$$2\text{CuSO}_4 + 4\text{KI} = 2\text{K}_2\text{SO}_4 + \text{Cu}_2\text{I}_2 + \text{I}_2$$

1 at. wt. of iodine = 1 at. wt. copper.
2. Potassium cyanide method, Parkes' method; Sutton, 204.
Make the copper solution ammoniacal.
Titrate with the cyanide until the blue color is discharged.
3. Sodium sulphide in alkaline solution; Sutton, 206.
Titrate with the sulphide until the blue color is discharged.
4. Steinbeck's method (especially for copper ores).
Standardize the cyanide solution.
Separate the copper from the ore by aqua regia.
Separate the copper from the other metals by precipitation upon a zinc-platinum couple.
Dissolve the copper in nitric acid and neutralize with ammonia.
Titrate with the standard cyanide, as in Parkes' method.

Dry Methods

1. Cornish method; Beringer, 136.
 - Concentrate the ore to a regulus.
 - Separate the sulphur by calcining.
 - Reduce the copper by fusion.
 - Refine the copper obtained.

Copper—Assay of Chalcopyrite

- A.—The stock solution.
- B.—Gravimetric electrolytic test.
- C.—Gravimetric test producing cuprous sulphide.
- D.—Gravimetric test producing cupric oxide.
- E.—Volumetric test by potassium cyanide.
- F.—Dry process.

A.—The Stock Solution

The intention is to produce, from 10 g. of the ore, one stock solution of the volume of 1 litre. Next it is intended to use separate parts of this solution for separate gravimetric and volumetric tests. (But of course independent portions of ore must be used for the dry assays.)

Supplies

Nitric acid, 10 cc. (sp. g. 1.20), diluted with water to 50 cc.
Hydrochloric acid, 50 cc. (sp. g. 1.16).

Outline of the Process

Treat the powdered ore with aqua regia. Evaporate this solution to dryness.

Add hydrochloric acid and boil the mixture.

Filter the solution; burn the insoluble part to remove sulphur, etc.

Redissolve the ashes from this process, adding their solution to that previously obtained.

The Process

1. *Treating with aqua regia.*—Weigh 10 g. of the finely powdered ore. Transfer it to a No. 4 beaker. Add 50 cc. of hydrochloric acid. Boil the mixture about 30 minutes on a hot plate. Then add carefully 50 cc. of nitric acid (mentioned above.) Evaporate the mixture to dryness on the hot plate. Cool the beaker and contents.

2. *Treating with hydrochloric acid.*—To the cool mixture add 50 cc. of water and 10 cc. of concentrated hydrochloric acid. Boil the mixture again on the hot plate.

Filter the solution; with water wash the residue on the paper.

3. *Second treating of the insoluble part.*—Dry the insoluble residue, and when dry, burn the paper and contents in a porcelain crucible. Return the ashes to the same beaker used for dissolving before.

To the ashes in the beaker, add 2 cc. of hydrochloric acid and 1cc. of nitric acid, both concentrated. Place the beaker and its contents on a hot plate and evaporate the material to dryness.

To the cool and dry residue add 25 cc. of water and 2 cc. of hydrochloric acid. Boil the mixture again.

Filter the solution, washing the precipitate.

(It is always well, before final dilution to 1000 cc. as described below, to treat the insoluble matter yet again with acids and to test a portion of the new filtrate for copper. The purpose is to make sure that the preceding operations have extracted all the copper from the ore.)

The filtrate is now supposed to have taken out the last traces of copper. Return this filtrate to the preceding copper solution.

4. *Completing the stock solution.*—Make this solution to the volume of 1000 cc.; 100 cc. of it represents 1 g. of the original ore.

B.—Gravimetric Method for Copper—Electrolytic Method

Brown, 211; Olsen, 193, 206

Remark.—The electrolytic method is to be recommended in most cases. It is especially useful in industrial laboratories, in which large numbers of assays must be made.

But this method faces difficulties in presence of arsenic, antimony or bismuth.

Outline of the Process

Dissolve the copper from the ore.

From the solution, precipitate the copper electrically upon a platinum electrode.

Supplies

Two selected small beakers, appropriate for receiving the platinum electrodes.

The galvanic battery (or other source of electric current), with voltmeter and ammeter.

The platinum electrodes. (Before use, clean the electrodes with sand-soap and water—then with dilute nitric acid. Finally rinse the negative electrode—the cathode—with ethyl alcohol. Before the alcohol dries, set it on fire. Cool the cathode in a desiccator and then weigh it.

The Process

1. *Preparing the solutions.*—Prepare two solutions, just alike, as follows: From the stock solution measure into a small evaporating dish 50 cc.; it represents .500 g. of ore. To it add 5 cc. of concentrated sulphuric acid;

then evaporate the solution nearly to dryness (or until white fumes of sulphuric acid begin to escape.)

To the residue add 50 cc. of water; decant the clear solution into one of the selected small beakers. To any undissolved residue add *aqua regia*, drop by drop, heating meanwhile. (The purpose is to dissolve all of the copper, but to introduce as little *aqua regia* as possible.)

Add the *aqua-regia* solution to the preceding sulphuric acid solution. To the whole add about 1 g. of ammonium nitrate. Now the small beaker has the solution ready for deposition of metallic copper.

2. *Depositing the metallic copper.*—In the solution place the proper platinum pieces—anode (the spiral); cathode (the cylinder). Connect with the battery so that the cathode is attached to the terminal wire from the zinc battery-plate: i.e., with the negative pole.

Allow the current (about 2—5 volts, and about .2—.3 amperes) to act until apparently all the copper is out of the solution—perhaps 12 to 24 hours, or, in some cases, more time may be required.

Remove the electrodes and save the solution.

3. *Washing and weighing the coated cathode.*—Rinse the cathode with water and then with ethyl alcohol. Set the alcohol on fire. (The heat afforded dries the coated cathode, under reducing conditions.)

Place the cathode in a desiccator to cool; weigh it.

(Subsequently place the cathode in a small beaker containing moderately concentrated nitric acid; the copper should dissolve. Wash the cathode with water.)

4. *Testing the solution.*—To the solution, after deposition of the copper, add about 5 cc. of ammonia (or enough to render the solution alkaline); if the solution does not become blue, practically all copper has been removed.

(In some industrial works, any such solution becoming blue is compared with several already prepared blue solutions, each one of which contains a different, small, known amount of metallic copper. If the blue solution, afforded by the assay, matches color with one of the standards, then the numerical amount previously obtained is enlarged by adding an amount corresponding to that represented by the matched blue standard.)

Notes on the Electrolytic Precipitation of Copper

Introduction

An alternating current cannot be used. One of its impulses would throw copper ions upon the platinum electrode; at the next reversed impulse the ions would be thrown back into the solution.

The direct current separates the copper continuously.

Dynamo Currents and Galvanic Currents

Within certain limits either current may be used.

The dynamo direct current.—If this current is of low voltage, say 50 volts or lower, it can be conveniently used. Practically all that is necessary is to

introduce resistance in the form of a single lamp in the circuit. The lamp usually reduces the voltage sufficiently for our purposes.

At the present time many laboratories are supplied with a direct current from a dynamo. But this current is often of 250 volts. So high a pressure is entirely unnecessary—indeed, unless carefully employed, it may work injury to the experimenter. With proper care, such a current may be passed through a single lamp as a resistance and then into the solution to be tested; notwithstanding the resistance, there is still sufficient pressure for the purpose. Observe, however, that these high pressure currents are always “grounded”: If, then, the experimenter connects himself with the ground by means of a metallic water-faucet, he is in danger of getting a 250 volt charge through his person.

A second difficulty may be mentioned: When the volt-meter is attached to his appliances, the experimenter may, in a moment of forgetfulness, remove his solution while the current is flowing; then the high-pressure current flows through the volt-meter, whose fine wires may be melted or even vaporized—with a destruction of the contrivance or under some circumstances with its explosion.

The galvanic current.—This current is generated by a galvanic battery. The general principle of the battery is such that it demands a suitable vessel and three substances. One is usually a solution of an acid or salt; one is a comparatively inert metal (or maybe carbon); one is a metal (often zinc) which is acted upon by the solution with greater chemical energy than is the other metal (or carbon). Evidently this general description allows use of a great variety of substances; it is thus that the great variety of batteries is accounted for.

It must be noted that the three substances in a battery must absolutely be conductors of the electricity. Sometimes one or more of them being a poor conductor gives rise to what is called internal resistance in the cell.

Several cells may be used together. They may then be arranged in series or in multiples (or in a combination).

The series arrangement increases the voltage (provided the internal resistance of each cell is not too great).

The multiple arrangement gives no more voltage than a single cell; it practically produces a larger cell and thus increases the amperage.

The gravity battery.—The simplest gravity battery consists of a jar containing (first) two water solutions, (second) a piece of copper with its connecting wire (third) a piece of zinc with its connecting wire.

The lower water solution is a saturated solution of copper sulphate, and in it is placed the piece of copper, its wire leading upward and out.

The upper solution is a water solution of zinc sulphate, and in it is suspended the piece of zinc with its conducting wire leading upward and out.

As the upper solution is lighter in weight than the lower solution, it sometimes is allowed merely to float upon the other. In some cases, however, it is more convenient to keep the upper solution, with its piece of zinc, in a porous cup, the latter and its contents hanging in the upper part of the copper sulphate solution.

In galvanic batteries, generally, there is but little chemical action when the leading wires are disconnected. The moment the leading wires are brought into terminal contact, chemical action commences in the cell and an electric current flows through the wires.

In the gravity battery described, when the terminal wires are connected, the action is *approximately* as follows:

The SO_4 ions of the copper sulphate attack the metallic zinc, form zinc sulphate, and at the same time they liberate their electric charges, the latter flowing through the wire.

The Cu ions of the copper sulphate deposit upon the metallic copper and liberate their electric charges.

It is these electric charges repeatedly delivered which constitute the current.

A Few Electrical Units

The volt.—The volt is the unit of electro-motive force; it is the force needed to drive one ampere through the resistance of one ohm.

It is *approximately* the electro-motive force of one galvanic cell.

Voltage may be compared to the pressure of water in a pipe.

The ampere.—The ampere is the unit of electric current (in quantity); it is the quantity of current that may be driven through the resistance of one ohm by the pressure of one volt.

An ampere is the quantity of current that deposits

about 18,302,400 grains (1.186 g.) of copper per hour

about .305,040 grains (.020 g.) of copper per minute

about .005,084 grains (.000,329 g.) of copper per second.

Amperage may be compared to the quantity of water passing through a pipe.

The coulomb.—The coulomb is the unit of electric quantity (in time). It represents one ampere-second.

It has been found that 96,540 coulombs of electricity sent through a circuit will decompose, under proper conditions, the *grammes-equivalent* of any conducting compound:

96,540 coulombs will decompose 58.50 g. NaCl

96,540 coulombs will decompose 169.97 g. AgNO_3

96,540 coulombs will decompose 79.83 g. Cu SO_4

Hence under proper conditions, one ampere in one second (one coulomb) will liberate as follows:

1 coulomb will liberate .000 367 g. Cl

1 coulomb will liberate .000 117 g. Ag

1 coulomb will liberate .000 329 g. Cu

These numbers are obtained by dividing the number of grammes representing the proper molecular equivalent by 96,540.

The coulomb may be compared to the amount of water delivered from some contrivance in a *unit of time*.

The ohm.—The ohm is the unit of electrical resistance; it is the resistance of about 106.3 c.m. of mercury (1 m. m. square section) at 0°C .

(It is approximately the resistance offered to a current of electricity by a wire of pure silver or copper whose diameter is 1 millimetre and whose

length is 48.61 metres, the test being made at 18.3 degrees C. 65 degrees F.

It may be roughly compared to the friction experienced by water in flowing through a pipe.)

Resistance of Copper Wire at 20° C

No. 1—8,083 ft. = 1 ohm.

No. 6—2,535 ft. = 1 ohm.

No. 12— 800 ft. = 1 ohm.

No. 16— 249 ft. = 1 ohm.

No. 27— 78 ft. = 1 ohm.

C.—Gravimetric Method for Copper—Cuprous Sulphide

Fresenius, 1: 375

Outline of the Process

Precipitate the copper as cupric sulphide with hydrogen sulphide.

Reduce the cupric sulphide by ignition with sulphur and sulphuretted hydrogen.

Weigh as cuprous sulphide, Cu_2S .

Supplies

Hydrogen sulphide generator. Rose's crucible.

The Process

1. *The solution.*—Draw 100 cc. of the stock solution of copper. Evaporate to dryness upon a water bath.

Dissolve the residue in a few cc. of dilute hydrochloric acid; again evaporate to dryness to remove the last traces of nitric acid.

Finally dissolve the residue in 10 cc. of dilute hydrochloric acid, adding a drop or two of nitric acid, if necessary, to clear the solution. Dilute the whole to 200 cc.; heat to boiling.

2. *Precipitating the copper.*—Into the boiling solution pass the hydrogen sulphide gas for half an hour, keeping the mixture warm upon a hot plate.

Allow the precipitate to subside; add 25 cc. of strong hydrogen sulphide water to make sure of thorough precipitation. (If no color or precipitate appears, proceed with the filtering, etc. but if the solution is at all colored, again pass hydrogen sulphide through the mixture for 30 minutes and test as before.)

When thoroughly precipitated, filter the cupric sulphide quickly; wash with hydrogen sulphide water continuously; then dry the filter paper, etc. quickly.

3. *Reducing the cupric sulphide.*—Transfer the dried filter, etc., to a weighed Rose porcelain crucible.

Add 1 g. of pure powdered sulphur.

Adjust the sulphuretted hydrogen apparatus and pass the gas into the crucible in a moderate stream.

Heat the crucible at first gently for 30 minutes; then raise the temperature to intense redness for 5 minutes. Finally allow the crucible to cool with a continued transmission of the gas.

4. *Weighing.*—Weigh the precipitate as cuprous sulphide, Cu_2S .

D.—Gravimetric Method for Copper—Oxide Method

Outline of the Process

- a. Precipitating as sulphide.
 1. Dissolve the copper from the ore as above.
 2. Precipitate the copper as sulphide by sulphuretted hydrogen.
- b. Separating from other metals.
 1. From the copper sulphide remove sulphides of arsenic, antimony, and tin by the use of sodium sulphide.
 2. Dry the copper sulphide left after the treatment with sodium sulphide. Separate from the paper; burn the latter, and add the ashes to the mass of copper sulphide.
 3. Dissolve the sulphide in nitric acid and remove the sulphur, which should be pure yellow in color.
- c. Precipitating as hydroxide.
 1. Precipitate the copper as cupric hydroxide by the use of sodium hydroxide.
 2. Finish the analysis as usual in this case.

E.—Volumetric Method—Potassium Cyanide Method

Sutton, 204, 210. Beringer, 154

Outline of the Process

Dissolve the copper from the ore by aqua regia.

Separate copper from other metals by a zinc-platinum couple.

Titrate with standard potassium cyanide in an ammoniacal solution.

Supplies

1. Nitric acid, 1 pt. water and 1 pt. nitric acid (1.20 sp. g.).
2. Ammonium hydroxide, 0.90 sp. g.
3. Pure copper.

Dissolve 2.0 g. of pure copper (electrolytically precipitated) in 100 cc. of the nitric acid. Boil to expel nitrous fumes.

Dilute the copper solution and cool. Neutralize with sodium hydroxide; and when just neutral add 5 cc. of strong ammonia. Make the solution to 500 cc.

4. Pure zinc.
5. Platinum foil.

6. Potassium cyanide, (at the rate of 42 g. per litre. 1 cc. corresponds to 0.010 g. of metallic copper).

Standardizing.—Dissolve 21 g. of potassium cyanide in water and dilute the solution to 500 cc.

Standardize this solution by means of the copper solution.

Place in a beaker 100 cc. of the copper solution (.400 g. metallic copper). From a burette draw into the blue solution sufficient potassium cyanide solution to accomplish the decolorizing.

From the number of cc. required compute the exact value of the cyanide solution in terms of metallic copper.

The Process

1. *The solution.*—Draw 100 cc. from the stock solution. (It represents one gram of ore.)

2. *Separating the copper from other metals.*—Place in the beaker a rod of metallic zinc weighing about 50 g. and fastened to a piece of stout platinum foil.

Allow the precipitation of the copper to proceed for several hours or over night. After the operation has proceeded for about two hours, add 5 cc. of hydrochloric acid. (Finally test with hydrogen sulphide to make sure of thorough precipitation.)

(If the beaker is placed on a steam radiator, on a warm iron plate, or in a warm water-bath, about 2 hours suffices for complete precipitation of the copper. If there is a deficiency of acid present there is danger of precipitation of an iron compound, perhaps hydroxide.)

Remove the excess of zinc but leave the platinum foil. Wash the copper repeatedly and carefully with fresh water.

To the spongy copper in the beaker, add 20 cc. of the special nitric acid. Heat moderately until the copper is dissolved; allow the solution to cool.

3. *Titration.*—Just before titration, neutralize the solution with sodium hydroxide and when neutral, add 1 cc. of ammonium hydroxide. Dilute the solution to 500 cc. For each test, use 100 cc. (representing 1 g. of ore.)

Titrate with the standard cyanide as described above.

(As described, each cc. of the cyanide solution represents about 1% of metallic copper.)

F.—Dry Method—German Method—Hiorns, Mett., 201

Outline of the Process

Roast the ore to oxidize the copper and to remove volatile impurities, especially sulphur.

Reduce the oxidized copper to metallic copper.

Refine the crude copper obtained above.

Supplies

Anthracite. Argols. Glass, powdered. Sodium bicarbonate. Borax. Salt. Charcoal.

The Process

1. *Roasting*.—Weigh 30 g. of the finely powdered ore. Place it in a roasting dish.

Introduce the dish and contents into the red-hot furnace. Heat the ore with stirring until sulphur dioxide ceases to be evolved.

Remove the roasted mass from the dish and mix with 15 g. of anthracite. Roast again for 15 minutes.

2. *Reducing*.—Remove the roasted mass a second time; mix with 10 g. of argols; replace in the crucible.

Mix 30 g. sodium bicarbonate, 15 g. of powdered glass, and 10 g. of borax; place the mixture on top of the first portion of the charge.

Cover the whole with 10 g. of salt and add a piece of charcoal.

Place the crucible in a furnace; raise the temperature to a very bright red heat; then continue the heating for half an hour.

Remove the crucible and allow it to cool. Break the crucible and free the metallic button from any crust of slag, etc.

3. *Refining*.—Wrap the coarse copper in a piece of paper with an equal weight of borax. Place the whole in a small red-hot scorifier.

When the oxides of other metals have passed off and the copper button sinks beneath the borax, remove the vessel with its contents.

Cool the mass and detach the button from the slag.

Weigh the metallic copper.

IRON

Classification of Ores of Iron

Anhydrous oxides.

Sesquioxides.

Hematite, Fe_2O_3 , (specular, red ocherous, clay iron stone).

Ilmenite, an iron and titanium oxide, FeTiO_3

Intermediate.

Magnetite, iron sesquioxide and iron protoxide, $\text{FeO}.\text{Fe}_2\text{O}_3$

Hydrous oxides.

Limonite, hydrous iron sesquioxide, $2\text{Fe}_2\text{O}_3.3\text{H}_2\text{O}$, (brown hematite, compact, ocherous, bog ore, brown clay iron stone).

Sulphides.

Pyrites, iron disulphide, FeS_2

Carbonates.

Siderite, iron protocarbonate, FeCO_3 (Spathic iron ore).

Principal Ores of Iron

Hematite, (Dana, 213), iron sesquioxide, Fe_2O_3 .		Ilmenite, (Dana, 217), an iron and titanium oxide, FeTiO_3 , (or sometimes $\text{Fe}_2\text{Ti}_2\text{O}_3$).	
O	30	O	31.6
Fe	70	Ti	31.6
		Fe	36.8
	100.		100.
Magnetite, (Dana, 224), Iron sesquioxide and protoxide, $\text{FeO}.\text{Fe}_2\text{O}_3$.		Limonite, (Dana, 250), Hydrous iron sesquioxide, $2\text{Fe}_2\text{O}_3.3\text{H}_2\text{O}$	
O	27.6	O	25.7
Fe	72.4	Fe	59.8
		H_2O	14.5
	100.		100.
Pyrites, (Dana, 85) Iron disulphide, FeS_2 .		Siderite, (Dana, 276), Iron protocarbonate, FeCO_3 .	
S	53.4	CO_2	37.9
Fe	46.6	FeO	62.1 (Fe, 48.2)
	100.		100.

Iron—Synopsis of Methods

Remarks

1. In some cases it is necessary to learn the total amount of iron irrespective of its ferrous or ferric condition.

Now steps may be taken to turn all the iron to the ferrous form and thereupon to determine it by processes appropriate to this condition.

Again, steps may be taken to turn all the iron to the ferric form and thereupon to determine it by processes appropriate to this condition.

2. In some cases it is necessary to learn what amount of iron was originally present in the ferrous form, irrespective of anything else present.

Now (supposing other reducing substances to be absent) processes suitable for determining only ferrous iron may be employed.

3. In some cases it is necessary to learn what amount of iron was originally present in the ferric form, irrespective of anything else present.

Now (supposing other oxidizing substances to be absent) processes suitable for determining only ferric iron may be employed.

Gravimetric Methods

(Gravimetric methods are almost entirely supplanted by volumetric methods or are employed in conjunction with them.)

Ferrous Compounds. Fresenius, 1: 310

1. Convert the ferrous compound into ferric iron and determine as such. (Oxidize by use of chlorine or bromine, or nitric acid or potassium permanganate.)

Then treat the ferric compound as under the next title.

2. Sulphide method.

Precipitate as sulphide. Weigh as such.

3. Gold method.

Treat with gold trichloride. Weigh the reduced gold.

Ferric Compounds, Fresenius, 1: 322

1. Ferric oxide.

- a. By precipitation as ferric hydroxide.

Precipitate with ammonium hydroxide. Weigh as Fe_2O_3 .

- b. By precipitation as ferrous sulphide.

Precipitate with ammonium sulphide. Change to chloride.

Re-precipitate as ferric hydroxide. Weigh as Fe_2O_3 .

- e. By ignition.

Heat in a weighed crucible to constant weight. Weigh as Fe_2O_3

2. Ferrous sulphide.

Precipitate as sulphide. Heat in a Rose's crucible in a current of hydrogen. Weigh as FeS .

For Either Ferrous Compounds or Ferric Compounds or Mixtures of Them

1. Copper method. Fuchs's method. Fresenius, 2: 499.

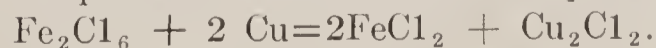
Dissolve the ore in hydrochloric acid.

Oxidize with potassium chlorate.

Reduce by a weighed piece of pure copper.

Weigh the remaining copper.

1 equivalent of Cu reduces 1 equivalent of Fe.



2. Modified method. (In presence of considerable amounts of titanitic acid.) Fresenius, 2:501.

Volumetric Methods

Ferrous Compounds

1. Permanganate method. Marguerite's method. Fresenius, 1: 312.
Into the ferrous solution, draw standard solution of potassium permanganate from a burette until permanent color appears.
2. Potassium dichromate method. Penny's method. Fresenius, 1: 319.
Into the ferrous solution, draw standard solution of potassium dichromate from a burette; to determine the end-point, take from time to time a drop of the mixture and apply it to a spot of solution of potassium ferricyanide on a porcelain plate.

Ferric Compounds

1. Stannous chloride method. Fresenius's method. Fresenius, 1: 327.
To the ferric solution add a measured but slight excess of standard solution of stannous chloride. To the solution, now colorless, add a little starch-water. Next add standard solution of iodine until the permanent blue color of starch-iodide appears.
(But in some cases sufficiently accurate results are obtained by carefully noting the point at which stannous chloride produces decolorization—without subsequent estimation of the excess of stannous chloride.)
2. Potassium iodide method. Fresenius, 1: 331.
Reduce the ferric compound by adding slight excess of potassium iodide solution. Iodine is liberated; titrate the amount liberated with standard solution of sodium thiosulphate.
3. Sodium thiosulphate method. Oudemans' method. Fresenius, 1: 332.
To the ferric solution add a small amount of solution of cupric sulphate and also of potassium sulphocyanate—these act as indicators. To the solution so prepared, add a slight but known excess of standard solution of sodium thiosulphate. Titrate the excess of thiosulphate by corresponding standard solution of iodine.

For Either Ferrous Compounds or Ferric Compounds or Mixtures of Them

- A. Reduce the material (by zinc, by sulphur dioxide, by sulphuretted hydrogen, or otherwise).
 1. Employ the permanganate method. (mentioned above under *ferrous compounds*).
 2. Employ the dichromate method. (mentioned above under *ferrous compounds*).

- B. Oxidize the material (by potassium chlorate, by nitric acid, by hydrogen peroxide, or otherwise).
1. Employ the stannous chloride method (mentioned above under *ferric compounds*).
 2. Employ the potassium iodide method (mentioned above under *ferric compounds*).
 3. Employ the sodium thiosulphate method (mentioned above under *ferric compounds*).

Dry Methods

Dry methods, while possible, are little used at present. Volumetric methods are almost exclusively employed for the determination of iron. (In complete analysis of iron ores, combinations of gravimetric with volumetric tests are employed.)

Iron—Assay of Limonite

- A.—The stock solution.
- B.—Gravimetric test for iron and aluminium.
- C.—Volumetric test by permanganate.
- D.—Volumetric test by dichromate.
- E.—Volumetric test by stannous chloride.

A—The Stock Solution

The intention is to produce from 5 g. of ore one stock solution of the volume of 500 cc. Next it is intended to use separate parts of this solution for separate gravimetric and volumetric tests.

Outline of the Process

(a) Roast the powdered ore, to destroy organic matter (if undestroyed, this will consume potassium permanganate, and thus count as iron).

(b) Treat the cooled, roasted ore, first with hydrochloric acid. Then fuse the insoluble portion with sodium carbonate. Add the second soluble product, containing iron, to the soluble product previously obtained.

(Incidentally determine the amount of matter insoluble in hydrochloric acid; also the amount of silicic oxide in the ore.)

(c) Make the stock solution, from the soluble substances, to 500 cc.

The Process

1. *Roasting the ore.*—Weigh 5 g. of the finely powdered limonite. Heat the weighed portion to dull redness for ten minutes; do not overheat the ore (there is danger of diminishing the solubility of the oxides).

2. *Treating with hydrochloric acid.*—Transfer it to a No. 4 beaker, provided with a suitable glass cover. Add 20 cc. concentrated hydrochloric acid, then 20 cc. of water. Boil the whole for at least two hours.

Filter, with suction, using a platinum cone.

The filtrate. Treat this first solution as described below. (3).

The insoluble part. Treat this as described in paragraph (4).

3. *Evaporating the first solution.*—While in its No. 4 beaker placed on a hot plate, evaporate this solution to complete dryness. Later add to this residue the second solution (4).

4. *Fusing the insoluble part.*—Dry this material. Transfer it to a small platinum dish. Heat it to burn away the paper. To the residue add what is judged to be about four times its weight of pure sodium carbonate. Fuse the mixture (by this process it is proposed to turn silica into a soluble sodium silicate; to disintegrate the iron oxide so that later it may be dissolved in acid).

Place the cooled crucible with its contents in a No. 4 beaker. Add about 50 cc. of water. Boil the whole for some time or until the melted mass separates from the crucible and softens into pulp. Now carefully remove the platinum dish.

Heat the mixture longer if necessary, carefully breaking lumps of melted material with a glass rod.

Cover the beaker with a glass cover. While the cover is only partially removed, carefully add dilute pure hydrochloric acid, heating gently at the same time (this hydrochloric acid should dissolve all iron and other dark material; at the same time there should be produced silicic acid, partly soluble and partly insoluble).

Transfer the whole of the material thus produced to the beaker which contains the first acid solution from the ore, and which is now either partly or wholly evaporated. (2 and 3, above).

Continue the evaporation of the mixture, carrying it to complete dryness.

Next place the beaker and its contents in the oven and heat the whole, maintaining the temperature at about 130° C. (The purpose is to completely dehydrate the silicic acid, turning it into silicic oxide, SiO_2).

5. *Determining silica.*—To the residue in the beaker (consisting mainly of silica and compounds of iron), add water and an amount of hydrochloric acid, added gradually and in small quantities, sufficient while the solution is hot to dissolve everything but silica.

Filter.

The filtrate. Save this for the preparation of the stock solution, as described below (6).

The insoluble part. Dry this material. Ignite it in a platinum dish. Weigh the residue. (This residue contains silica, but it may also contain insoluble mineral matters that have not yielded to the dissolving operation).

6.—*The stock solution.*—Dilute this solution to 500 cc. Of this solution 100 cc. represents 1 g. of the original ore; of course 50 cc. represents .500 g.

B.—Gravimetric Test for Iron and Aluminium

Outline of the Process

Precipitate iron and aluminium together with ammonium acetate (this leaves manganese in solution). Filter.

Re-dissolve the precipitated acetates, then precipitate with ammonium hydroxide. (This affords a precipitate of ferric hydroxide and aluminic hydroxide.) Ignite and weigh iron and aluminium together as oxides.

The Process

1. *Oxidizing and evaporating.*—Draw 25 cc. from the stock solution (representing .250 g. of ore), and place this portion in a No. 4 beaker. Add about 1 cc. of nitric acid (to oxidize the iron). Evaporate the solution on an iron plate. Dissolve the residue in about 10 cc. of water, to which a drop or two of hydrochloric acid are added; a complete solution must be produced, but the acid added must be the smallest possible amount.

Dilute the solution slightly with water. Then nearly neutralize the acid by use of solution of ammonium carbonate.

2. *Adding ammonium acetate.*—Dilute the solution approximately to the volume of 250 cc. Bring the mixture to the boiling point.

Dissolve about 1 g. of solid ammonium acetate in about 10 cc. of water. Add this to the boiling solution containing iron, etc.

Allow the bulky precipitate to subside and filter as soon as possible (if solutions at this stage become cold, the precipitated basic acetates tend to re-dissolve).

3. *Dissolving the basic acetates.*—Through the moist precipitate pour warm dilute hydrochloric acid. (It should quickly dissolve the precipitate.) Wash the filter paper with boiling water.

4. *Precipitating the hydroxides.*—To the filtrate add ammonium hydroxide. This should precipitate iron and aluminium together as hydroxide.

5. *Filtering, etc.*—Filter the precipitate, wash, dry, incinerate, weigh. The result gives the amount of iron oxide and aluminum oxide together.

C.—Volumetric Test by Permanganate

Outline of the Process

(a) Prepare a standard solution of potassium permanganate.

(b) Prepare a standard solution of ferrous ammonium sulphate which shall balance the permanganate solution (or nearly so).

(c) Standardize the permanganate solution by iron wire, using the Jones reductor.

(d) Determine the iron in a specimen of limonite (using a portion of the stock solution already prepared).

Supplies

Amalgamated zinc. Potassium permanganate. Ferrous ammonium sulphate. Iron wire. Jones reductor.

The Standard Solutions

1. The permanganate solution. Dissolve 1.625 grams of potassium permanganate crystals in 200 cc. water with warming. Filter through asbestos; cool; dilute to 500 cc.; then mix thoroughly.

2. The ferrous solution. Pulverize 20 g. ferrous ammonium sulphate; dissolve the salt in water; add 5 cc. concentrated pure sulphuric acid; dilute to 500 cc.

3. Comparing the balanced solutions. From a burette draw 40 cc. of the ferrous solution; add 10 cc. of dilute sulphuric acid; dilute to the volume of 100 cc.

From another burette cautiously draw in the permanganate solution until a slight permanent pink color is established.

Compute (first) the ratio of 1 cc. of permanganate solution to ferrous ammonium sulphate solution; (second) the value of 1 cc. permanganate solution in mg. of metallic iron, according to the foregoing experiment.

4. Standardizing permanganate by metallic iron. Weigh two portions, each .250 g., of fine iron wire. Treat each as follows:—

Place the wire in a beaker and to it add 100 cc. of water and 5 cc. of concentrated sulphuric acid; warm the mixture to promote solution.

Prepare the Jones reductor for use (it is practically an air-tight tube containing amalgamated zinc).

Pour the iron solution while hot through the reductor at a rate of about 50 cc. a minute. Follow the iron solution without interruption (without air admission) with 175 cc. warm dilute sulphuric acid and next with 75 cc. of water.

Cool the bottle containing the iron solution (now ferrous) under the water tap.

To the cooled solution add 10 cc. dilute sulphuric acid and then draw into it, from a burette, the standard permanganate solution until a very slight permanent pink color is established; in case the end-point is over-stepped, add a measured quantity of the balanced ferrous ammonium sulphate solution; and, if desired, again add permanganate until again pink color is established.

From the data thus obtained, compute the value of each cc. of permanganate solution in terms of milligrams of metallic iron.

The Process

1. *Drawing the solution.*—From the stock solution draw 50 cc. (corresponding to .500 g. of the original ore) into a casserole. Cautiously add 5 cc. concentrated sulphuric acid; evaporate the mixture on a water-bath until it is nearly dry.

Carefully complete the evaporation by heating over the lamp flame until the heavy white fumes of sulphur trioxide begin to appear. (The purpose is to expel chlorine, since it is liable to decompose permanganate and so give rise to an incorrect inference as to the amount of iron present.)

Cool the casserole; to the residue add 100 cc. of water; boil the mixture until ferric sulphate is dissolved.

2. *Reducing.*—Pass the warm solution through the Jones reductor, as previously described.

3. *Titrating.*—Titrate this solution with permanganate, in a manner similar to that already described above under standardizing permanganate.

4. *Computing.*—From the number of cc. of the permanganate solution demanded (knowing already its value per cc. in metallic iron), compute the amount of iron in the portion of stock solution tested, and thence the per cent of iron in the original ore.

D.—Volumetric Test by Dichromate

Outline of the Process

- (a) Prepare a standard solution of potassium dichromate.
- (b) Prepare a standard solution of ferrous ammonium sulphate (which may be a mere intermediary solution with a recorded ratio to the dichromate solution).
- (c) Standardize the dichromate solution by iron wire, using a slight excess of stannous chloride as a reducing agent (and subsequently using mercuric chloride to neutralize the excess of stannous chloride).
- (d) Determine the iron in a specimen of limonite (using a portion of the stock solution already prepared).

Supplies

Ferrous ammonium sulphate. Stannous chloride. Mercuric chloride. Potassium ferricyanide. Hydrochloric acid, sp. g. 1.12. Iron wire. Porcelain tile.

The Standard Solutions

1. The dichromate solution.—Pulverize a little more than $2\frac{1}{2}$ g. potassium dichromate. Dissolve exactly 2.500 g. in 500 cc. of water.
2. The ferrous solution.—Pulverize 20 g. ferrous ammonium sulphate; dissolve in water, dilute to 500 cc. and add 5 cc. concentrated pure sulphuric acid.
3. The stannous solution.—Dissolve about 5 g. pure stannous chloride in pure concentrated hydrochloric acid. Dilute the solution to 500 cc.
4. The mercuric solution.—Dissolve 25 g. mercuric chloride in 500 cc. water; boil the mixture at first, but cool it before use.
5. The ferricyanide solution: the indicator. Dissolve a crystal of potassium ferricyanide (the size of a pin-head) in 25 cc. water.
6. Comparing the balanced solutions.—From a burette, draw 40 cc. of the ferrous solution, add 15 cc. hydrochloric acid, dilute to 150 cc. Next from another burette, cautiously draw the dichromate solution into the ferrous solution.

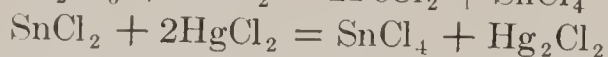
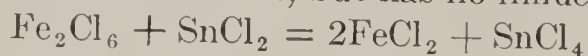
Remove a small drop of the mixed solutions on the end of a stirring rod and add it to a drop of the ferricyanide on the porcelain tile. Add the dichromate solution to the ferrous solution until it no longer affords a blue color with the indicator.

From the corrected volumes of the solutions used, compute (first) the value of the dichromate solution in terms of metallic iron, (second) compute the value of the ferrous solution in terms of the dichromate solution.

7. *Standardizing the dichromate solution by iron wire.*—Weigh two portions each .250 g. of iron wire free from rust. Treat each as follows:

Place each piece in a covered beaker; to it add 30 cc. of hydrochloric acid; warm the whole. (The solution contains chiefly ferrous chloride—necessarily so because hydrogen, a reducing agent, is liberated.)

To the hot solution, add solution of stannous chloride until the iron solution becomes colorless; avoid having stannous chloride in an excess of more than one or two drops. Dilute the solution by adding 150 cc. of water; then cool it. Next add rapidly 30 cc. mercuric chloride solution; allow the solution produced to stand for three minutes. (The mercuric chloride takes up excess of stannous chloride, but has no influence on the stannic chloride.)



Titrate with dichromate solution and determine the end-point as in 6.

Compute the value of each cc. of the dichromate solution in terms of metallic iron.

The Process

1. *Drawing the solution.*—From the stock solution, draw 50 cc. (corresponding to .500 g. of the original ore); transfer this portion to a casserole. Heat the solution to boiling.

2. *Reducing, etc.*—To the hot solution, add carefully stannous chloride solution until the disappearance of any yellow color indicates complete reduction of ferric compounds. (Avoid an excess of more than a few drops of stannous solution.)

Cool the reduced solution. Add about 30 cc. of mercuric solution.

3. *Titration.*—Titrate with standard dichromate solution, spotting on ferricyanide drops, just as in standardizing already described.

4. *Computing.*—From the number of cc. of dichromate solution required (knowing already its value per cc. in metallic iron), compute the amount of iron, and thence its per cent in the limonite.

E—Volumetric Test for Iron—Stannous Chloride Test

Outline of the Process

(a) Prepare the standard solutions required. Make a tabular statement, showing how many milligrammes of metallic iron are represented by one cubic centimetre of each of the standard solutions used.

(b) Oxidize the iron to be tested to the ferric form; then heat the solution to boiling.

(c) Into the hot solution, which has a deep yellow color, draw a *slight* excess of standard stannous chloride solution from a burette.

(d) Cool the colorless solution produced by (c), and add a few cubic centimetres of starch-water.

(e) By means of the solution of iodine, estimate the excess of tin solution added.

(f) Make the necessary computations.

The Standard Solutions

Prepare solutions as follows:

1. *The Ferric Solution.*—This is a standard solution of ammonio-ferric sulphate, iron alum, $(\text{NH}_4)_2 \text{SO}_4 \cdot \text{Fe}_2 (\text{SO}_4)_3 \cdot 24 \text{H}_2 \text{O}$. Dissolve 10.775

grams of the crystallized salt in a small amount of hot water, adding a little hydrochloric acid if necessary; dilute the solution to the volume of 250 cubic centimetres. One cubic centimetre of this solution contains the equivalent of 5 milligrams of metallic iron.

2. *The Stannous Solution.*—This is a solution of stannous chloride, tin crystals, ($\text{Sn Cl}_2 + 2 \text{H}_2 \text{O}$). Dissolve about 2.5 grams of the crystals in pure hydrochloric acid; dilute the solution to the volume of 500 cc.

When tin crystals are added to water, there sometimes appears a basic salt of tin, which is almost completely insoluble in water and difficultly soluble even in dilute hydrochloric acid. The formation of this salt is prevented by dissolving the tin crystals at once in boiling pure concentrated hydrochloric acid and afterward diluting the solution with warm water.

It must be remembered that the tin solution is not permanent, consequently it must be tested afresh from time to time.

3. *The Iodine Solution.*—Weigh about 500 milligrams of the purified iodine; dissolve it in water by aid of a few crystals of potassium iodide; dilute the solution to the volume of 250 cubic centimetres.

4. *Starch-Water.*—Prepare this by softening about 3 grams of starch in 100 cubic centimetres of boiling water; allow the mixture to cool.

The Value of the Iodine Solution

Determine the relation between the tin solution and the iodine solution. Proceed as follows: Draw from a burette, into a clean casserole or beaker, 10 cubic centimetres of the tin solution; add 5 cubic centimetres of the starch paste; into the mixture draw iodine solution from another burette until the blue color produced remains permanent after stirring. Form the number of cubic centimetres of iodine solution used, the value of one cubic centimetre of it, in terms of the tin solution, may be calculated.



The Value of the Stannous Solution

Take 20 cubic centimetres of the standard ferric solution (prepared as above described); place them in a casserole with 20 cubic centimetres of pure concentrated hydrochloric acid, and boil; while the solution is boiling, run in, from a burette, the stannous chloride solution until the yellow color of the iron solution is wholly destroyed.



Place the casserole, with its contents, in a basin of cold water to cool. When cold, add 5 cubic centimetres of the starch-water, and run in the iodine solution until the blue color is produced.

Knowing the value of the iodine solution in terms of the tin solution, the exact number of cubic centimetres of the tin solution required for 20 cubic centimetres of the ferric solution may be calculated.

Repeat the operation with three different portions, of 20 cubic centimetres each, of the ferric solution.

From the average number of cubic centimetres of the tin solution used, find the value of one cubic centimetre of the tin solution in terms of iron

solution, and from that, by calculation, its value in terms of metallic iron. Work out the necessary figures for filling the blanks in the following table:

Results of Standardizing

10 cc. Sn Cl₂ solution = cc. Iodine solution.
 . . cc. Sn Cl₂ solution = 1 cc. Iodine solution.

20 cc. Iron solution = . . . cc. Sn Cl₂ solution.

Subtract cc. Sn Cl₂ solution,)
 the equivalent of cc. Iodine solution)
 run back.

20 cc. Iron solution = *net* . . . cc. Sn Cl₂ solution.

SUMMARY

but 20 cc. iron solution = 100 milligrams of iron.
 hence 1 cc. Sn Cl₂ solution = . . . milligrams of iron.
 1 cc. iodine solution = . . . milligrams of iron.

The Process

The Titration.—Place in a casserole 50. cubic centimetres of the stock solution; this represents .500 g. of ore. Add 20 cubic centimetres of pure concentrated hydrochloric acid, and boil the whole. While boiling, run in the tin solution from a burette until the iron solution becomes colorless. Now cool the colorless solution; when it is cold, estimate the *excess* of tin solution as follows:

Add to the colorless solution 5 cubic centimetres of starch paste; then draw from a burette the iodine solution, drop by drop, until the blue color of iodine and starch appears.

Computing.—Find, as above directed, the average number of cubic centimetres of the tin solution actually needed for the iron. Knowing the value of one cubic centimetre of the tin solution in terms of metallic iron, the number of milligrams of metallic iron in 100 cubic centimetres of the iron solution tested may be obtained.

Notes

1. The strength of the standard iron alum solution should be such that one cubic centimetre contains 5 milligrams of metallic iron. The amount of the crystallized salt needed to furnish this amount of iron in a solution of 250 cubic centimetres is found by the following proportion:

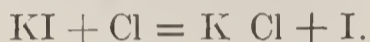
Molecular weight		Molecular weight		Grams		Grams
of iron	:	of iron alum	::	of iron	::	of iron alum
111.8		964.57		1.250		10.775

2. To ascertain that all the iron is oxidized to the ferric form, it is sufficient to show that ferrous iron is no longer present. For this purpose test the liquid by placing a drop of it in a drop of solution of potassium ferricyanide; no blue color should appear, for the reagent gives only a brown color with ferric salts, while it gives a deep blue precipitate (a variety of Prussian blue) with ferrous salts. But the solution of potassium ferricyanide must be freshly prepared, as it decomposes upon keeping.

3. Iodine is constantly evolving vapors which corrode the metal work of the balances. The weighing should therefore be quickly performed and the balance-case aired afterwards.

Pure iodine is not absolutely necessary in this analysis. Iodine may be purified, when desired, as follows:

Take about 3 grams of iodine, rub it in a mortar with a few crystals of potassium iodide, KI. Place the mixture between two watch-glasses, and gently heat so as to vaporize the iodine. Allow the glasses to cool, and when cold, scrape off the resublimed iodine from the upper glass. The potassium iodide purifies the iodine from chlorine and bromine.



4. Heat destroys the blue color of the iodide of starch, hence the solution must be cooled before adding the iodine.

GOLD AND SILVER

General Introduction

In the majority of cases, a quantitative test for one of these metals involves a similar test for the other.

The reason is to be found in the facts (first) that ores in which gold is the chief constituent usually contain also silver; (second) that ores in which silver is the chief constituent usually contain gold—sometimes in only minute amount; (third) that the various kinds of bullion—a term employed in a somewhat general way to designate almost any metal which contains larger or smaller quantities of gold or silver, or both at once, alloyed with it—are either produced directly or indirectly from ores manifesting the peculiarities mentioned, or else are so made up as to contain gold and silver at once.

A gold coin, or a piece of gold jewelry, generally contains copper or silver, or both, in addition to the gold.

A silver coin, or a piece of silver ware, usually contains copper alloyed with the silver. But in accordance with a preceding statement, it should be noted that there is also a minute quantity of gold present.

In the statement of analyses following, in certain cases methods are given for determining gold alone by an appropriate process, and in certain cases methods are given for determining silver alone by an appropriate process; but in some cases reference is made to a process involving the determination of both metals consecutively.

The student ought to study carefully, at the outset, the *Remarks* which appear after the description of the dry assay of ores of gold and silver by the crucible process.

GOLD

Principal Ores of Gold

In the majority of rocks of the earth's surface, especially silicious rock, gold exists—yet in most cases the amount present is so small that the metal cannot be extracted with profit.

It is a general assumption that the gold generally exists in the metallic condition, called native gold (not the pure metal, but alloyed with metallic silver, and it may be other metals).

But gold exists, sometimes in only minute quantity, in iron pyrites, and other so-called sulphurets—in such cases it is sometimes assumed that the gold itself is a sulphide.

Gold—Synopsis of Methods

Gravimetric Methods

1. Metallic gold. Fresenius, 1:391.
 - a. By ignition.
 - b. By precipitation as metallic gold.
Free the solution from nitric acid by evaporation.
Precipitate with ferrous sulphate, oxalic acid, or zinc, cadmium, etc.
 - c. By precipitation as auric sulphide.
Precipitate by sulphuretted hydrogen in the presence of hydrochloric acid.
Wash, dry, and ignite. Weigh as metallic gold.

Volumetric Methods

1. Oxalic acid method. Sutton, 229.
Add an excess of oxalic acid to precipitate the gold.
Determine the excess by titration with standard permanganate solution.
2. Iodine and thiosulphate method. Gooch and Morley's method. Sutton, 229.
Add a slight excess of potassium iodide to reduce the auric gold.
Add starch paste.
Titrate the solution with thiosulphate solution to the disappearance of the blue. Then add standard iodine until a faint rose color appears.

Dry Methods

(These are applicable to bullion and to ores.)

They are discussed more at length, further on, under the title Gold and Silver.

SILVER

Classification of Ores of Silver

- a. Those containing the uncombined metal.
Native silver.
- b. One practically free from sulphur.
Keragyrite (horn silver), AgCl .
- c. Sulphuretted ores, some of them arsenical.
Argentite (silver glance), Ag_2S .
Stromeyerite (silver copper glance), $(\text{AgCu})_2\text{S}$.
Pyrargyrite, (ruby silver), Ag_2SbS_3 .
Stephanite, Ag_5SbS_4 .
Polybasite, $(\text{AgCu})_9(\text{SbAs})\text{S}_6$.
- d. Those containing large quantities of lead.
Galena (lead sulphide), PbS .
Cerussite (lead carbonate).

Principal Ores of Silver

<p>Keragyrite, horn silver, (Dana, 158) Silver chloride, AgCl.</p> <table border="0"> <tr><td>Cl</td><td>24.7</td></tr> <tr><td>Ag</td><td>75.3</td></tr> <tr><td colspan="2"><hr/></td></tr> <tr><td></td><td>100.</td></tr> </table> <p>Stromeyerite, (Dana, 56), Sulphide of silver and copper, $\text{Ag}_2\text{S.Cu}_2\text{S}$.</p> <table border="0"> <tr><td>S</td><td>15.8</td></tr> <tr><td>Ag</td><td>53.1</td></tr> <tr><td>Cu</td><td>31.1</td></tr> <tr><td colspan="2"><hr/></td></tr> <tr><td></td><td>100.</td></tr> </table> <p>Stephanite, (Dana, 143), A sulphide of silver and antimony, $5\text{Ag}_2\text{S.Sb}_2\text{S}_3$.</p> <table border="0"> <tr><td>S</td><td>16.3</td></tr> <tr><td>Sb</td><td>15.2</td></tr> <tr><td>Ag</td><td>68.5</td></tr> <tr><td colspan="2"><hr/></td></tr> <tr><td></td><td>100.</td></tr> </table>	Cl	24.7	Ag	75.3	<hr/>			100.	S	15.8	Ag	53.1	Cu	31.1	<hr/>			100.	S	16.3	Sb	15.2	Ag	68.5	<hr/>			100.	<p>Argentite, silver glance, (Dana, 46) Silver sulphide, Ag_2S.</p> <table border="0"> <tr><td>S</td><td>12.9</td></tr> <tr><td>Ag</td><td>87.1</td></tr> <tr><td colspan="2"><hr/></td></tr> <tr><td></td><td>100.</td></tr> </table> <p>Pyrargyrite, ruby silver, (Dana, 131) Sulphide of silver and antimony, $3\text{Ag}_2\text{S.Sb}_2\text{S}_3$.</p> <table border="0"> <tr><td>S</td><td>17.8</td></tr> <tr><td>Sb</td><td>22.3</td></tr> <tr><td>Ag</td><td>59.9</td></tr> <tr><td colspan="2"><hr/></td></tr> <tr><td></td><td>100.</td></tr> </table> <p>Polybasite, (Dana, 146), A sulphide of silver and antimony $9\text{Ag}_2\text{S.Sb}_2\text{S}_3$.</p> <table border="0"> <tr><td>S</td><td>15.</td></tr> <tr><td>Sb</td><td>9.4</td></tr> <tr><td>Ag</td><td>75.6</td></tr> <tr><td colspan="2"><hr/></td></tr> <tr><td></td><td>100.</td></tr> </table>	S	12.9	Ag	87.1	<hr/>			100.	S	17.8	Sb	22.3	Ag	59.9	<hr/>			100.	S	15.	Sb	9.4	Ag	75.6	<hr/>			100.
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Silver—Synopsis of Methods

Gravimetric Methods

1. Silver chloride. Fresenius, 1:337.
 - a. Wet method.

Precipitate the silver as chloride with hydrochloric acid, in the presence of nitric acid.
Weigh as AgCl.
 - b. Dry method. Fresenius, 1:339.

Fuse the substance in a weighed glass tube.
Convert it into silver chloride by passing a current of chlorine gas over the fused mass.
Repeat this process until the weight of the tube, plus that of the chloride, is constant.
2. Silver sulphide.

Precipitate as sulphide with hydrogen sulphide gas in the presence of an alkaline nitrate.
Collect on a weighed filter, wash, and dry at 100°.
Weigh as silver sulphide, Ag₂S.
Dissolve the sulphur (contained in the precipitate) with carbon disulphide.
Wash, dry, and weigh again.
Subtract the second weight from the first and compute.
3. Silver cyanide. Fresenius, 1:341.

Neutralize any free acid with potassium carbonate.
Precipitate as cyanide with potassium cyanide in the presence of nitric acid.
Collect the precipitate on a weighed filter, wash, and dry at 100°.
Weigh as silver cyanide, AgCN.
4. Metallic silver.
 - a. Dry method.
 - (1) Reduce the salt, by direct ignition in a weighed porcelain crucible.
 - (2) Reduce the salt, by heating in a current of pure hydrogen.
 - b. Wet method.

Convert the silver to silver sulphate by treatment with sulphuric acid.
Reduce to metallic silver by metallic cadmium.
Wash the precipitated silver, dry, and ignite. Weigh as Ag.

Volumetric Methods

1. Sodium chloride methods. Sutton, 325.
 - a. With chromate indicator. Mohr's method. Sutton, 152.

Precipitate the silver as chloride until red silver chromate appears.
 - b. Gay-Lussac's method. Sutton, 327.

Precipitate the silver as chloride with a strong standard solution of sodium chloride (called "the unit solution") until nearly all the silver is precipitated.

Finish the titration with a weak standard solution of salt (called "the decimal solution"—it is of one-tenth of the strength of the unit solution).

Make sure of the end-point by use of a decimal solution of silver.

2. Starch-iodide method. Pisani's method. Sutton, 326.

Add a solution of blue starch-iodide to a neutral silver solution until the blue color is just permanent.

3. Ammonium sulphocyanate method. Volhard's method. Sutton, 155.

Add a standard ammonium sulphocyanate solution, using a ferric indicator, until the appearance of red ferric sulphocyanate.

Dry Methods

1. For solutions.

Evaporate the solution to dryness. Treat the residue as described further on for ores.

2. For alloys.

Wrap a portion of the alloy in pure lead, (it may be with addition of pure silver), and then separate the silver by cupellation, as described later under the title Gold and Silver.

3. For ores.

Subject the ore to fusion, cupellation and quartation, as described later under the title Gold and Silver.

Silver—Gravimetric Test—Chloride Method

Outline of the Process

- (a) Roll the coin into a thin ribbon.
- (b) Dissolve the bullion in nitric acid.
- (c) Precipitate the silver with hydrochloric acid.
- (d) Weigh the metal as chloride.

This is the ordinary, and well-known, process of gravimetric determination of silver: therefore its detailed description need not be repeated at length here.

Silver—Volumetric Process—Gay-Lussac's Method

This is the approved process employed in the government assay offices of most of the great nations of the world. From time to time it has been carefully studied and subjected to slight modifications to promote its speed and accuracy.

In government offices, the analyst has usually the great advantage of knowing in advance very nearly the exact amount of silver in the bullion tested.

If the approximate amount of silver in a given specimen of bullion is not known by the investigator, it may be learned by a preliminary test.

Outline of the Process

- (a) Prepare a standard solution of common salt (1 cc. corresponds to 10 mg. metallic silver). This may be called "the unit solution."

(b) Prepare a "decimal" solution of common salt (1 cc. represents 1 mg. of metallic silver).

(c) Prepare a "decimal" solution of silver nitrate (1 cc. corresponds to 1 mg. of metallic silver).

(d) Dissolve the bullion in a test bottle.

(e) Titrate the bullion solution, using as described the two salt solutions and the "decimal" silver solution.

The Standard Solutions

(a) *The unit salt solution.*—Weigh about 6 g. of pure chloride of sodium. Heat the salt carefully to expel moisture; but do not carry the heating to the point of fusion of salt.

Weigh of this dried salt 5.4207 g. Dissolve this quantity in distilled water and make the solution to the volume of 1 liter.

This solution is intended to be of such a strength that 1 cc. corresponds to 10 mg. of metallic silver.

(b) *The decimal salt solution.*—From the unit salt solution draw 50 cc.; then dilute this quantity to the volume of 500 cc.

This solution is intended to be of such a strength that 1 cc. corresponds to 1 mg. of metallic silver.

(c) *The decimal silver solution.*—Weigh as exactly as possible .500 g. of fine silver. Dissolve this quantity in from 2 to 3 cc. of concentrated nitric acid, 1.20 sp. g. Dilute this solution to the volume of 500 cc.

If this solution is correctly made, 1 cc. of it contains exactly 1 mg. of metallic silver.

The Standardizing

Note.—Although the unit salt solution is intended to have the exact relation to pure silver stated above, its real working power must be found by experiment.

Testing the unit salt solution.—Weigh as exactly as possible 1.003 g. of fine silver; place the metal in a test bottle with 5 cc. of pure nitric acid, 1.20 sp. g.; heat the mixture gently on a hot plate until the metal is completely dissolved; by means of a glass tube, blow nitrous vapors from the bottle; allow the bottle to cool to the temperature of the air.

To the silver solution add exactly, from a pipette, 100 cc. of unit salt solution.

Place the glass stopper in the bottle; place the whole in the black bag; shake the whole thoroughly, to coagulate the silver chloride; remove the bottle from the bag; carefully lift the stopper, washing down the solution and precipitate, with distilled water. The liquid above the precipitate should be as clear as water.

From the proper burette draw decimal salt solution to the extent of .5 cc.; it should produce a slight cloud of silver chloride. Shake the bottle in its bag. Repeat additions of decimal salt solution, .5 cc. at first, and later one or two drops at a time until, after the various shakings, the point is reached at which addition of one or two drops has given no milkiness.

Consider these final two drops as an excess of decimal salt solution, and take as the reading the number of cc. used, the two drops being subtracted.

If for any reason the proper point has been passed, draw in exactly 2 or 3 cc. of the decimal silver solution—at all events, a slight, but known, excess. Now go back and titrate again with decimal salt solution until the true point is reached.

Compute the value of unit salt solution in terms of metallic silver as follows:

First—to the amount of silver originally weighed, add an amount represented by the quantity of decimal silver solution run back.

Second—divide by 10 the number of cc. of decimal salt solution used. Add the result to the number of cc. of unit salt solution employed, that is 100.

Third—divide the total weight of silver involved, by the number of cc. of unit salt solution employed; the quotient represents the real working value of the unit salt solution per cc. expressed in terms of metallic silver.

The Process

1.—*Weighing the bullion* (previously rolled).—Compute as nearly as possible on the basis of information what weight of bullion represents 1 g. of pure silver; then weigh exactly this amount.

If the analyst has not satisfactory information as to the amount of silver present in the bullion tested, he may make a quick direct test with unit salt solution; upon the results of this test he may compute how much bullion to employ to yield very nearly 1 g. of pure silver.

2. *Dissolving*.—Place the weighed bullion in a test bottle with 5 cc. of pure nitric acid 1.20 sp. g.; heat the mixture gently on a hot plate until the metal is completely dissolved; by means of a glass tube, blow nitrous vapors from the bottle; allow the bottle to cool to the temperature of the air.

Continue the operation exactly as described above under “Standardizing,” that is, add 100 cc. of unit salt solution; shake; add decimal salt solution; if necessary, add decimal silver solution; again add decimal salt solution until the end-point is determined.

3. *Computing*.—Compute the amount of silver in the bullion, not in terms of per cent, but in terms of per thousand. (For example, if a portion of bullion shows 92.5 per cent of silver, report it as 925. thousandths).

Notes

In titrations such as those described, there may be reached a stage called by Mulder “the neutral point”; at this point, if the clear solution is divided into two halves, the one half will give milkiness upon addition of decimal salt, and the other half will give milkiness upon addition of decimal silver solution (at this stage the solution contains silver chloride dissolved in sodium nitrate—or at all events there exists some kind of equilibrium of the several salts present).

But the ordinary analyst rarely hits this condition—practically, he intends to introduce a slight excess of salt and make allowance for it. Fresenius, 1:343.

Silver—Volumetric Process—Potassium Sulphocyanate Method

Outline of the Process

- (a) Prepare a standard solution of potassium sulphocyanate.
- (b) Prepare a ferric solution (for use as an indicator).
- (c) Prepare a standard solution of silver nitrate from fine silver.
- (d) Dissolve the bullion to be tested and then titrate it by the standard potassium sulphocyanate solution, using the ferric solution as an indicator.

Supplies

Silver bullion. Fine silver. Potassium sulphocyanate. Nitric acid. Ferric alum. Burettes.

The Standard Solutions

1. *The sulphocyanate solution.*—Weigh 5 g. of the potassium sulphocyanate; dissolve in water; then dilute to 1000 cc.

2. *The ferric solution.*—Dissolve 10 g. ferric alum in 30 cc. water. Add to the solution 5 cc. nitric acid.

3. *The silver nitrate solution.*—Weigh two portions of “fine” silver, each about .250 g. Treat each as follows: dissolve the metal in about 2 cc. concentrated nitric acid, diluted with about 5 cc. of water. After solution, add 10 cc. concentrated nitric acid, sp. g. 1.20. Boil the solution until fumes of nitrous compounds are expelled.

Add 5 cc. of the ferric solution, (as the indicator).

4. *Standardizing the sulphocyanate solution.*—Treat each silver solution further as follows: Draw from a burette into it sulphocyanate solution until a faint red tinge can be detected.

5. *Computing.*—Compute the value of the solution in terms of metallic silver per cc.

The Process

1. *Weighing the bullion.* (previously rolled).—Weigh two portions, each .250 g. of the bullion to be tested. Treat each as follows:

2. *Dissolving.*—Dissolve the weighed portion in 5 cc. nitric acid; boil the solution until all the nitrous fumes are expelled; cool the liquid; then dilute to 50 cc.

3. *Titrating.*—Add 5 cc. of the ferric solution, as an indicator, and then draw in sulphocyanate solution to the appearance of the red tinge.

4. *Computing.*—Make the proper computations expressing the amount of silver as thousandths of the original bullion

Note

This process is practicable in presence of copper in quantity below 70 per cent; if the amount of copper is greater, its *relative* quantity may be reduced by addition of fine silver in known amount.

Silver—Dry Process—Cupellation Process

This process is applicable to known alloys containing silver and it may be other base metals, but containing very little gold. If considerable gold is present (33 per cent and upwards), silver must be added and a parting process must be employed as described.

The student should carefully examine the Remarks which appear further on under the title Gold and Silver together—Crucible Process, page 60. In these remarks the details of the chemical changes associated with cupellation and parting are discussed at some length.

Outline of the Process

Wrap a weighed portion of the ribbon in pure metallic lead and cupel the mixture. The cupellation removes the lead and leaves the silver as a "prill"—a small button. (But there may be a minute amount of gold present.)

Part the prill with nitric acid. Weigh the gold, if any. (Prove that the residual material is gold—first, by inspecting it under the microscope; second, by the purple of Cassius test.)

The Process

1. *Weighing, etc.*—Weigh about .200 g. of the rolled bullion. Wrap this in about 5 g. of assay-lead. (But the amount of lead ought to be about 20 times the amount of copper believed to be present.)

2. *Cupelling.*—Select a cupel whose weight is approximately that of the lead button.

Heat the cupel thoroughly in a muffle.

Wrap the lead button in a piece of filter paper; then place it in the heated cupel, and place over it and near it a somewhat large piece of charcoal. The lead should soon fuse; and the charcoal and the carbon of the filter paper should not only help to heat the button, but should reduce the oxide on its surface.

When the button appears to be red hot and to display a clean metallic surface, remove the charcoal.

Allow the operation to continue, regulating the fire from time to time, so that the button may neither become too hot nor too cold, and so that the current of air may be sufficient to oxidize the lead (which is, in a proper sense, burning), but not sufficient to chill the surface of the button and so stop oxidizing.

Watch the gradual diminution in size of the button.

When the button has so far reduced that only a prill is left, watch for the brightening of the prill (this sudden brightening is followed by a duller appearance and sometimes a display of prismatic colors on the surface).

Carefully remove the cupel from the furnace. Allow the whole to cool.

When the cupel is cool, remove the prill with a pair of tweezers or with the point of a knife blade. Remove any adhering bone-ash from the prill (sometimes this is best done by fusing the prill on a piece of charcoal before the blow-pipe).

Weigh the prill.

3. *Parting the prill.*—Place the prill in a 6-inch test-tube. Add 2 cc. of dilute nitric acid. Warm the mixture gently, so as to dissolve silver. But the solution must not proceed too rapidly.

Carry the process of dissolving silver to completion, using repeated portions of dilute nitric acid; decanting the silver nitrate formed; toward the end using concentrated nitric acid, to remove the last portions of silver; finally washing the residual gold, even though its amount be very small, with water.

4. *Weighing the gold.*—(The operation next described has for its purpose the transfer of even minute quantities of gold without loss to a porcelain crucible in which the gold is to be heated.)

Provide a casserole full of water. Provide a small porcelain crucible.

Fill with water to the very top the test-tube containing the gold; cover the test-tube with the little crucible as with a cap; quickly invert this system so that the crucible is in the downward position and the test-tube is in the upward position, as of a bell-glass nearly full of water; now the gold should fall through the water into the crucible. Transfer the system to the casserole so that the little crucible is at the bottom of the casserole and the junction of crucible and test-tube is under water; raise the test-tube slightly; pass it—its mouth still under water—to one side; then lift the porcelain crucible—still full of water and with the gold at the bottom—out of the casserole. Carefully pour away the water in the crucible so as not to disturb the gold. Carefully dry the gold in the crucible and finally heat it to a red heat. Cool the crucible and contents.

Weigh the gold.

5. *Testing the gold.*—After weighing the gold, examine it under a microscope.

Transfer the gold to a small porcelain crucible; to it add 1 or two drops of aqua regia; add the drops of solution carefully and without agitation to a test-solution containing the proper iron and tin salts for this purpose; the gold should give a coloration or precipitate of purple of Cassius.

GOLD AND SILVER TOGETHER

Gold and Silver in Bullion—Synopsis of Methods

Gravimetric Method

1. Nitric acid method.

Treat an alloy with nitric acid to dissolve all metals (in certain cases including silver), leaving gold unattacked.

Wash the residue, ignite it, and weight it as metallic gold (if necessary, test the weighed residue for silver).

Dry Methods

1. Cupellation method.

Alloy the bullion with a computed amount of silver.

Wrap the alloy with assay-lead and cupel.

Part the prill.

Alloys containing gold may contain beside the gold:

1st. Base metals which are easily oxidizable, as lead, copper, etc.

2nd. Noble metals which are not easily oxidizable, as silver, and also platinum and the platinum metals, so-called.

Under certain conditions, treatment with nitric acid may remove the base metals (except, perhaps, antimony and tin), and even silver, but will leave gold, platinum, and some of the platinum metals undissolved.

The cupellation process, if properly conducted, removes the base metals, leaving an alloy of gold, silver and platinum and, it may be, the platinum metals.

Gold and Silver in an Ore—Synopsis of Methods

1. Crucible method. Brown, 170.

Fuse the ore in a crucible with the proper fluxes, including litharge (lead oxide), intended to furnish metallic lead, which shall, in the fusion, collect the gold and silver in the ore, and then form a button. Cupel the lead button, thus removing the lead and leaving a smaller button or "prill" containing gold and silver.

Alloy the prill with a computed amount of pure silver. (Alloys containing 33 per cent of gold and upwards do not permit of complete removal of silver by nitric acid.)

Part the new prill with nitric acid.

Weigh the gold left.

(The weight of the first prill has been learned; the weight of the gold has been learned; the difference between these weights is the weight of the silver.)

2. Scorification method. Brown, 139.
Scorify the ore with metallic lead, borax-glass, or other fluxes.
Cupel the lead button.
Part the prill.
3. Chlorination method. Brown, 234. Ricketts, 194. Kustel, Extraction of gold by chlorination, 136.
Pass chlorine gas through the moistened ore (soluble chloride of gold is formed.)
With water, wash the chloride of gold from the gangue.
By means of ferrous sulphate, precipitate metallic gold from its solution.
Wrap the gold in assay-lead and cupel the product.
4. Amalgamation method. Brown, 221.
Grind the ore with water, potassium cyanide and mercury. Strain out the mercury, now containing gold. Scorify and cupel the gold amalgam.
5. Pan test. Brown, 225.
Weigh from 3. k. to 15. k. of ore; pulverize it.
Wash it in a current of water, using a large pan (the purpose is to wash away lighter portions of ore, but to retain the gold).
Scorify the residual gold with assay-lead.
Cupel.

NOTE.—Certain gold ores may contain gold in the form of scales, which can be removed from the powdered ore by sifting.

In such cases, the scales are tested as bullion; the powdered ore is tested as an ore.

Gold and Silver—Test of Gold Bullion—Wet Process

Outline of the Process

- (a) Make a preliminary test for silver.
- (b) Alloy the bullion with the silver if necessary.
- (c) Treat a portion of bullion with nitric acid.
- (d) Weigh the metallic gold.

The Process

1. *Preliminary test.*—Weigh about .100 g. of thin bullion; to it add 3 cc. of aqua regia (about 1 cc. of nitric acid, and 2 cc. hydrochloric acid). Gently warm the mixture.

When the bullion is completely dissolved or completely disintegrated, dilute the solution with water. If silver is present, in considerable quantity, it will appear as silver chloride.

Filter the mixture and learn the weight of silver chloride as usual; from this weight, compute the per cent of silver in the bullion.

Compute how much silver, if any, must be added in order to make the amount of silver and base metal together equal to twice the weight of gold.

2. *Adding silver.*—Weigh about .200 g. of thin bullion; place it on charcoal together with the required quantity of silver; fuse the two; roll the alloy to a thin ribbon.

3. *Parting.*—To the ribbon, in a test-tube, add 1 cc. of water and 1 cc. of concentrated nitric acid; warm the mixture. When action has practically ceased, decant the solution. Then, to the gold, add 2 cc. of concentrated nitric acid, and warm again—hoping thus to remove the last traces of silver.

Wash the gold several times with water.

4. *Drying and weighing the gold.*—Transfer the gold to a porcelain crucible; dry the whole and then ignite it gently; cool the crucible and contents.

Weigh the gold as accurately as possible.

5. *Computing.*—Compute the gold as thousandths of the bullion.

Gold and Silver—Test of Gold Bullion—Cupellation Process

Outline of the Process

- (a) Alloy the bullion with a computed amount of silver.
- (b) Wrap the alloy with assay-lead and cupel.
- (c) "Part" the "prill."

The Process

1. *Adding silver.*—Weigh about .200 g. of the bullion. Compute the probable amount of silver to be added (so as to give an alloy containing two parts silver to one part gold); alloy the bullion on charcoal, before the blowpipe, with the exactly weighed amount of fine silver.

2. *Cupelling.*—Wrap the alloy in a portion of assay-lead judged to be about 20 times the weight of copper believed to be present.

Cupel the mass; weigh the prill; flatten it on a clean anvil.

3. *Parting.*—To the prill in a test-tube add a few cc. of dilute nitric acid; warm the mixture. When action has practically ceased, decant the solution. Then, to the gold, add 2 cc. of concentrated nitric acid, and warm again—hoping thus to remove the last traces of silver.

Wash the gold several times with water.

4. *Drying and weighing the gold.*—Transfer the gold to a porcelain crucible; dry the whole and then ignite it gently; cool the crucible and contents.

Weigh the gold as accurately as possible.

5. *Computing.*—Compute the gold as thousandths of the bullion.

From the weight of the prill, subtract the weight of added silver; the difference is the weight of gold and silver in the bullion.

From the total weight of bullion, subtract the weight of gold and silver; the difference is the weight of base metal in the bullion.

From the weight of gold and silver in the bullion, subtract the weight of gold; the difference is the weight of silver in the bullion; compute it in thousandths.

Gold and Silver—Test of an Ore—Crucible Process

Brown, 170

Outline of the Process

- (a) Make the necessary preliminary tests. These are:
 - Test the reducing power of argol or other reducing agent.
 - Test the litharge for silver and gold.
 - Test the assay-lead for silver and gold.
- (b) Pulverize the ore.
- (c) Fuse the ore in a crucible with the proper fluxes.
Cool the crucible; then break it, and secure the lead button.
- (d) Cupel the lead button.
- (e) Part the prill.

Supplies

Hessian or Battersea sand crucibles. Cupels.

Litharge. Sodium carbonate or hydro-sodium carbonate. Borax. Argol. Common salt. Pure assay-lead. Fine silver.

The Preliminary Tests—the Blank Tests

1. *The reducing power of argol.*—Brown, 98, 121. Weigh the following substances:

Sodium bicarbonate,	30 g.
Litharge,	30 g.
Argol,	2 g.
Salt,	10 g.

Mix all the substances, except the salt, in a wedgwood mortar or on a piece of paper. Place the mixture in a sand crucible of proper size. Place the salt on top of the mixture, and pack the whole down with a wedgwood pestle.

Place the crucible and contents in a hot fire. Cover the crucible with an iron cover. When the mixture is thoroughly fused (requiring 15 or 20 minutes) place the hot crucible in a larger crucible to cool.

When the smaller crucible is thoroughly cooled, break it with a hammer, detach the lead button from the slag. Weigh the lead button. Since 2 g. of argol were used, and since an excess of litharge was present, the reducing power of 1 g. of argol is apparent.

The reducing power of other agents may be determined in similar manner.

2. *Testing litharge for silver and gold.*—Brown, 116. Weigh the following substances:

Sodium bicarbonate,	120 g.
Potassium carbonate,	5 g.
Litharge,	120 g.
Argol,	4 g.
Salt,	20 g.

Place the charge in the crucible, and conduct the fusion; then remove the lead button, exactly as described in the process of testing the reducing power of argol, above.

Cupel the lead button as described below in the process for testing an ore. Later, weigh the prill and part it, exactly as described below in the process for testing an ore.

3. *Testing assay-lead for silver and gold.*—Brown, 118. Weigh 60 g. of the assay-lead. Place the metal in a scorifier, and cover it with a few fragments of borax glass. Scorify the whole by a process described later, the purpose being to reduce the weight of the lead to a quantity suitable for cupellation.

Remove the lead from the scorifier; cupel it; part the prill.

The Process

1. *Pulverizing the ore.*—Weigh approximately 200 g. of ore. If the latter is in lumps, carefully select such as are fairly representative of the whole lot supplied. It is of the utmost importance that the portion tested shall be a just sample of the material furnished.

Break the lumps down to as fine a powder as practicable, in an iron mortar; then reduce the whole to a still finer powder in a wedgwood mortar.

2. *Preparing the charge.*—Weigh the following substances:

Powdered ore	30 g. (or 29.166 g.)
Sodium carbonate	30 g.
Litharge	60 g.
Borax	30 g.
Argol	4 g.
Common salt	20 g.

Place all the materials except the salt in a wedgwood mortar and mix them carefully. Transfer the mixture to a suitable sand crucible. Grind the salt in the same wedgwood mortar (so as to rinse the mortar); then put the salt in the crucible on top of the other materials. By means of a wedgwood pestle, pack the whole charge in a somewhat compact form in the crucible.

3. *Fusing.*—Place the crucible in the fire; cover it with an iron cover; continue the fusion for 15 or 20 minutes, or until the whole mass is red-hot, thoroughly liquid, and has ceased to give off any considerable quantity of gas or vapor in the form of bubbles.

When the fusion is judged to be completed, remove the crucible and contents, placing the whole on an iron plate to cool.

When the crucible and its contents have thoroughly cooled so that the whole may be handled, break the crucible with a hammer and examine the contents. These should be practically three: (First) on top, a layer of salt; generally distinct from the other materials. (Second) the slag; this is generally dark in color but it should be uniformly glassy in appearance—should be free from lumps of unassimilated material. (Third) the lead button; this should be a well rounded disc-like piece, regular in form.

There should be no small globules of lead distributed through the slag.

The button should not have lying above it either a brilliant layer (looking like lead but separating from the button), nor yet a dark, brittle, granular layer of so-called "regulus."

Hammer the button, on a clean anvil, into a more or less rectangular form. (The principal purpose of the hammering is to detach fragments of slag, which latter are brittle.)

The button should be soft and malleable. Brittleness in the button may indicate presence of sulphur or of some other substance, as arsenic, antimony, or something else.

In any event, weigh the button. (It may advantageously weigh from 15 to 30 g.)

4.—*Cupelling the lead button.*—Select a cupel whose weight is approximately that of the lead button.

Cupel the lead button as already described, page 52.

Weigh the prill.

5.—*Parting the prill.*—If the prill is believed to have less than 33 per cent of gold, part it immediately with nitric acid.

If the prill has 33 per cent and upwards of gold, alloy it with a computed amount of fine silver, so as to reduce the relative amount of gold to about 30 per cent. Then part this prill with nitric acid, as usual.

REMARKS

1. *Alloys of gold and silver.*—Native gold of California is said to average from 875 to 885 thousandths fine; that of Australia is said to average from 960 to 966 thousandths fine.

Fine gold (that is, gold which is perfectly pure) is nearly as soft as lead; hence, it is rarely, if ever, used for coin or jewelry—it is usually alloyed with copper or silver, or both.

An alloy containing gold in considerable amount and copper in small amount, is at once harder than pure gold, and more easily fusible.

An alloy containing gold in large amount and antimony or lead in small amount, is brittle.

The proportion of gold in an alloy is usually expressed in thousandths; it is also often expressed in twenty-fourths called carats (but the carat system may express so small a fraction as 1-768th, for each carat is divided into four assay grains and each assay grain into 8 eighths; thus pure gold may be called 24 carats fine, or 96 grains fine, or 768 eighths fine.)

The gold coin of Great Britain contains 11 parts of gold to 1 part of copper; hence it is 22 carats fine or 916.66 thousandths fine.

The gold coin of the United States and of France contains 9 parts of gold and 1 part of copper; hence it is 21 carats $2\frac{3}{8}$ grains fine or 900 thousandths fine.

Pure silver is too soft to resist much wear; hence it is rarely, if ever, used for coin or jewelry—it is usually alloyed with copper.

An alloy containing silver in considerable amount and copper in small amount, is at once harder than pure silver and it retains practically the whiteness of the latter.

The silver coins of Great Britain contain 92 5-10 per cent of silver and 7 5-10 per cent of copper; hence the alloy is 925 thousandths fine. (It is called sterling silver.)

The silver coins of the United States and of France contain 90 per cent of silver and 10 per cent of copper; hence they are 900 thousandths fine.

The term "coin" with respect to silver is applied only to pieces of the higher denominations; pieces of lower denominations, as well as those consisting largely of copper, or of bronze, or of nickel, are called "tokens."

The proportion of silver in an alloy is usually expressed in thousandths; the term carat and its congeners are not applied to alloys of silver.

2. *The assay ton.*—Ores are often weighed by the avoirdupois ton of 2000 pounds, while gold and silver are weighed by the troy ounce. Now 2000 pounds of 7000 grains each equal 14,000,000. grains. But 1 ounce troy equals 480 grains. $14,000,000. \div 480 = 29,166.$ Hence 1 part of noble metal in 29,166. parts of ore, represents 1 troy ounce of noble metal in 1 avoirdupois ton of ore; therefore 1 milligram of gold or silver in 29.166 grams of ore, represents 1 ounce of noble metal to the ton of ore. Thus it has risen, that a weight representing 29.166 g. is called 1 assay ton; and of course from 1 assay ton a weight of 1 milligram may be called 1 assay ounce.

3. *Substances used in the fusion assay.*—The commonest substances employed are litharge (lead oxide, PbO), sodium carbonate, argol (an impure mixture containing potassium tartrate), borax, common salt.

Litharge is used for three reasons:

First, it is a valuable flux by itself, because it fuses readily; second, it forms an easily fusible silicate with silicon dioxide, an important constituent of most ores; third, in the process of fusion, with reducing agents like argol, it liberates metallic lead in very fine particles. These particles of lead, in a molten condition, fall through the fused mass in a kind of shower; they very readily alloy themselves with gold and silver in the charge; together they fall to the bottom of the crucible, forming there a button of lead. (This button is subsequently cupelled.)

Litharge should be pure to the extent of being free from everything but gold and silver; it is difficult to obtain litharge entirely free from these metals; their amounts in the sample of litharge used must be determined by a blank test and subsequently allowed for.

Sodium carbonate acts in a manner somewhat similar to litharge; that is, it forms a fusible silicate with silicious matter of the ore.

Of course, in forming the silicate, carbon dioxide is liberated. It manifests itself in bubbles of gas which escape from the "melt." While escaping, these bubbles help to agitate the melt—and in so doing they advantageously mix the various materials together. But they ought to be completely expelled before the crucible is removed from the furnace.

Borax is used sometimes in the form of powder derived from the crystallized substance, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; sometimes in the form of borax glass (the latter is borax from which the water of crystallization has been expelled).

Borax, when in a state of fusion, is able to dissolve metallic oxides; the so-called bases. When the crucible charge is melting, the borax dissolves those oxides which are in the ore, forming with them double borates of varying constitution, but fusible. Among the most important of these oxides are those of iron, aluminium and calcium. The following may be accepted, in a general way, as a typical equation:



If borax is used, the heat drives off its water of crystallization; in this process, the melt sometimes froths; but after complete expulsion of water, the melt subsides into a thin liquid mass.

Litharge and sodium carbonate may be looked upon as basic fluxes: they combine with acid material, principally silicic oxide, of the ore. Borax may be looked upon as an *acid flux*; it combines with basic materials of the ore, as already described. If a given ore is largely silicious, it may be necessary to increase the relative amount of basic fluxes; if an ore is largely basic it may be necessary to increase the relative amount of acid flux.

Argol or argols is an impure potassium tartrate. It may be a mixture of tartrates, or it may be a calcium-potassium tartrate. It is obtained from wine—settling as a deposit at the bottom of the casks. Its precipitation from solution is incidental to the formation of alcohol by fermentation.

Argol is used as a reducing agent; when heated in the melt it liberates carbon in a finely divided condition. (It also forms potassium carbonate.) The carbon reduces the litharge, setting free metallic lead, as already stated.

Salt is placed upon the top of the charge before melting. During the melting, the salt fuses; but it usually retains its place above the other materials and without considerably diffusing among them. Although some of the salt is vaporized at the high temperature of the process, the most of it is found as a layer above the slag after the crucible has cooled. The salt appears to act during fusion as a kind of cover, which keeps the melt at a higher temperature than it would otherwise attain. Further, it is believed to prevent loss of silver by volatilization.

4. *Scorification* is an oxidizing process—in the main. It is usually performed in a shallow earthen dish; but the clay of which the scorifier is made must be carefully selected as one which powerfully resists fluxes.

Scorification may be applied to a lead button for the purpose of diminishing the quantity of lead preliminary to cupellation. Of course the process must not be carried on too long—there is danger of diminishing the lead unduly, and there is danger of perforating the scorifier by reason of the fusible lead silicate formed.

Scorification may be applied to an ore mixed with metallic lead. In this case volatile materials of the ore, like sulphur, arsenic, antimony, etc., may be oxidized and vaporized; the oxide of lead formed combines with silicious substances to form a fusible slag; unoxidized lead combines with gold and silver to form a button suitable for cupellation.

5. *Cupellation* is a very ancient process, whose purpose is to remove the base metals of a specimen of bullion, and to leave a prill of gold and silver in a form such that it may be removed and weighed.

Cupellation is performed in a cupel made of bone-ash. The bone-ash does not melt at high temperature nor does it combine with oxide of lead to form a slag; on the contrary it allows the melted oxide of lead to sink into its minute pores. At the same time the oxide of lead may carry into the cupel with it a moderate amount of oxide of copper (about 1-20 of its weight) but it does not usually carry all the copper in—a small portion called the “surecharge” is left in the prill.

In cupellation, about 2 or 3 per cent of the metallic lead vaporizes *as such*; the lead vapor is usually oxidized in the air above the cupel.

Cupellation is usually conducted in an arched clay chamber, called a “muffle,” surrounded by burning fuel, except at the front. The heat reflected or radiated from the roof of the muffle, is an important factor in keeping the upper portions of the button at a high temperature, and so favoring cupellation.

If the temperature of the muffle, and thence of the button, falls to a certain point, the button may become coated with oxide of lead which thus no longer fuses; now the operation of cupellation stops. But it may be renewed, by increasing the heat of the fire and at the same time by placing a small piece of charcoal directly upon the button in the cupel. Now the charcoal burns; its combustion raises the temperature of the button; the

carbon itself reduces the oxide of lead which has formed a film on the button. When these results have been secured, the charcoal may be removed, and the operation of cupellation may proceed.

The end of the process is reached when the lead and other base metals have been completely removed—being volatilized into the air or else oxidized and absorbed as oxides into the cupel.

The end-point is determined by the so-called “brightening” of the silver.

Pure silver, when melted in air, dissolves about 22 times its volume of oxygen gas. When such silver begins to cool in the air, an exterior crust is first formed. Soon the general lowering of temperature leads to the expulsion of the oxygen gas; the latter escapes through the outer crust with violence, carrying with it some molten silver from the interior; this silver cools in filaments. The button is said to have “sprouted” or “vegetated.”

6. *Parting*, that is, separating gold and silver by acid, is usually accomplished by nitric acid. The acid acts best on bullion containing 2 1-2 to 3 parts of silver to 1 part of gold (30 per cent to 25 per cent of gold); if less silver is present, it is not completely dissolved by the acid; if more silver is present, the gold is liable to be left in so spongy a condition that it easily breaks into fragments, of which some are liable to be lost (it is always preferable, in parting, to have the gold left in a completely coherent ribbon or plate).

Instead of the term parting, the terms “quartation” or “inquartation” are sometimes used.

7. *Errors incidental to the processes described*. Like all other practical operations, the processes described are more or less imperfect.

In fusing in the crucible, minute quantities of silver and gold are volatilized in the heating operation of the crucible assay. The amount of loss from this source is of no consequence. (The fact of such loss is proved by an examination of the dust found in the chimney flues.)

In cupelling, there may be a loss of silver by reason of the absorption of a minute amount of it—with oxide of lead into the cupel.

There may be an *apparent gain of silver*, by reason of a small amount of copper remaining in the prill (this copper incidentally being reckoned later as silver).

In parting, there may be a minute loss of gold by its solution (this danger is the greater, if the nitric acid contains chlorine).

There may be an *apparent gain of gold*, by reason of the fact that invariably a small amount of silver—about 2 one-thousandths of the silver present—fails to dissolve in the parting operation. This amount is called the “surcharge”; it is usually “allowed for.”

It is eustomary in government assaying establishments (and in others also) to learn what “allowances” should be made for gains or losses incidental to a particular method of assaying; this is accomplished by conducting a precisely similar set of processes upon weighed amounts of pure silver, or of pure gold, or of known alloys of them

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