CIRCULAR

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 14

ANALYZED IRONS AND STEELS— METHODS OF ANALYSIS

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Used at the Bureau of Standards

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I. INTRODUCTION

General information regarding standard samples, including descriptions of the methods used in their preparation, is published in Circular No. 25. The information and methods given in the present circular have special reference to the irons and steels listed in Circular No. 25. Former editions of Circular 14 gave outlines of the methods of analysis used at the

Bureau of Standards for the earlier samples. Some of those methods have undergone modification from time to time and as herein given apply mainly to the irons and steels recently issued.

The earlier samples were analyzed usually only by the rapid technical methods used more or less generally by the steel trade. The analyses made by the other cooperating chemists were mostly of the same type. The object on the one hand was to indicate the order of agreement which might be expected from careful analysis, using these methods and working on a homogeneous material, and on the other hand to supply samples whose composition was known within the limits of error indicated by the results published on the certificates. It is therefore emphasized here that the Bureau's analyzed irons and steels are "standardized" only in this sense. In other words, the figures on the certificates are perhaps to be regarded as a criterion of the existing state of the analytical chemistry of this class of materials, and of methods, and they no doubt represent fairly well the result which may be expected by attempting to fix the composition of such materials in this way. It should be remembered, however, that the composition so determined is not necessarily the absolute or correct one, and that judgment should be used in the application of the data afforded by the certificates. An illustration will make this clear.

Scrutiny of all the iron and steel certificates thus far issued shows that the color method for manganese has furnished results over 5 per cent higher on the average than were obtained by the other methods combined. Without raising the question whether the average of the color results or that of the others is nearer the truth, it is clear that both can not be correct and that their "general average" must probably be in error. Hence, an analyst, using the samples, is justified in rejecting the "general average" if experience has convinced him that the average for any particular one of the methods tabulated is worthy of greater credence. Further, for instance, it would be manifestly wrong to use any one of the general averages for manganese (possibly in error by one or more per cent of the manganese) for the standardization of a volumetric solution that is to be used for a ferromanganese alloy or a manganese ore.

No doubt the above cautions will be found applicable to some of the other elements as well as to manganese, but, owing to the much smaller percentages of most of those others, their errors are not as a rule so immediately apparent nor so amenable to the corrective study which the Bureau hopes to take up in time.

Closer approximation to the truth might be obtained through determinations by a greater variety of technical methods, or with better promise of success by the longer and perhaps more exact methods not generally used for technical work or by correcting for some more or less obvious sources of error often overlooked by the technical analyst. The amount of work to be thus expended on a given sample must be regulated by the importance of higher accuracy to those who use it. The Bureau endeavors to have the results by its own chemists well within the limits of error permissible in

practical work. These in turn are governed by such factors as the degree of segregation in ingots, castings, etc., the difficulties of sampling large lots of metal, etc. At present it is believed that in the steel and iron industry most of the technical analytical methods are capable of yielding results quite up to if not in advance of the requirements of practice. However, as already intimated, the Bureau will, when opportunity offers, investigate sources of error in present analytical methods and endeavor to devise new ones. The amount of such work which can be undertaken at present is limited.

It follows from what has been said that sometimes a method used by the Bureau to secure a somewhat higher degree of accuracy is too cumbersome or slow for technical needs and this fact should be borne in mind by those employed at works.

A further caution is called for with respect to the methods detailed in the pages that follow. It should not be inferred in the absence of a direct implication or statement to that effect that the Bureau regards them as superior to others that might have been selected.

II. METHODS FOR IRONS AND ORDINARY STEELS

1. TOTAL CARBON

(*a*) **In irons.**—Two grams of iron are mixed with about twice the weight of purified ferric oxide. The mixture is placed in a platinum boat, which is lined with a suitable bed material, and is burned in a current of oxygen, using an electric resistance furnace wound with "nichrome" at a temperature of 1000° to 1100° C. Porcelain combustion tubes are used.

(*b*) **In steels.**—The method is the same as for irons with omission of the ferric oxide admixture.

(*c*) **Sources of error.**—Many sources of error may be met in the direct-combustion method for carbon in irons and steels. One of the chief of these is the defective character of much of the material that is used for lining the boat in which the combustion is made. It behooves the analyst to test his material most carefully.

Alumina as prepared from the sulphate or from alum may not be free from sulphate or alkali, both of which have given serious trouble at the Bureau. The alkali may not manifest itself by an alkaline reaction until after one or two combustions have been made, using the same bed material. Even the ordinary white "alundum" on the market carries a few hundredths of 1 per cent of alkali. A special grade free from this impurity is now obtainable.

Iron oxide has been tried and when pure should, apparently, give good service. As yet, however, it has been difficult to obtain or prepare acceptable material for use with steels.

Quartz sand gives rise to a fusible slag which, melting before combustion is complete, incloses bubbles of carbon dioxide gas. (Personal communication from Mr. George M. Berry of the Halcomb Steel Co.) This defect would probably inhere in any other material of an acid character.

Mr. Berry has also occasionally noted the presence in the silica bed after combustion of crystals which appear to be carborundum.

There is much greater difficulty in securing constant conditions when weighing absorption tubes than is usually considered to be the case. Electrical effects, caused by wiping as a preliminary to weighing, may occasionally cause errors in weight running into the milligrams.

If tubes are weighed full of oxygen, care is necessary to secure a uniform atmosphere in them. Even though the attempt is made to keep the apparatus always full of oxygen, air is admitted when the boat is pushed into the combustion tube and a much longer time is required to displace this than is usually allowed. The same is true if the tubes are weighed full of air by displacing the oxygen left in them after the steel is burned. Another source of error may arise from the air admitted when putting the boat into the tube, if this air contains much carbon dioxide, as is the case when a gas furnace is used. The boat is usually pushed at once into the hot furnace, and as combustion begins almost immediately there is no opportunity for aspirating out this air before the steel begins to burn.

2. GRAPHITE IN IRONS

Two grams of iron are dissolved in nitric acid (sp. gr. 1.20), using 35 cc and heating very gently. The residue is collected on an asbestos felt, washed with hot water, then with a hot solution of potassium hydroxide (sp. gr. 1.10), followed by dilute hydrochloric acid and finally by hot water. After drying at 100° C the graphite is burned in the same manner as the total carbon, but without admixture of ferric oxide.

3. COMBINED CARBON IN IRONS

This is obtained by subtracting graphitic carbon from total carbon.

4. SILICON

The insoluble residue obtained in preparing the iron or steel for the gravimetric sulphur determination (p. 7) is filtered off, ignited in platinum, and weighed. Evaporation with a little hydrofluoric acid and one drop of sulphuric acid and subsequent ignition gives by the loss in weight the silica corresponding to the silicon of the sample.

5. TITANIUM IN IRONS

Five grams of the sample are dissolved in 40 cc of hydrochloric acid (sp. gr. 1.10).[1] The insoluble matter is filtered off, washed with water, ignited in a platinum crucible, and treated with hydrofluoric and sulphuric acids to eliminate silica. The residue is fused with sodium carbonate, the fusion dissolved in water and acidified with sulphuric acid. A sufficient

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[1] With this strength of acid all but a negligible quantity of the titanium present remains in the residue. The filtrate, when freed from most of the iron by ether extraction, gives but a faint test for titanium with hydrogen peroxide.

amount of ferric alum is added to the standard titanium solution to give the same tint as the sample when they are at the same dilution (for the residue from the silica always contains a little iron along with the titanium). Hydrogen peroxide is added to the solution and the standard and these are compared in a colorimeter. (Consult Bull. 422, U. S. Geological Survey, for details regarding the determination of titanium.)

6. PHOSPHORUS

(*a*) **Preparation of solution and precipitation of phosphorus.**—Two grams of sample are dissolved in nitric acid (sp. gr. 1.135) and the solution is boiled until brown fumes no longer come off. Ten cc of permanganate solution (15 grams to 1 liter) are added and the boiling is continued. Sodium sulphite solution is added to dissolve the oxide of manganese and the solution is again boiled and then filtered. With irons the insoluble residue should be tested for phosphorus. After cooling the filtrate, 40 cc of ammonia (sp. gr. 0.96) are added, the solution is agitated, and when the temperature is at 40° C, 40 cc of molybdate solution (Blair, Chemical Analysis of Iron, 6th ed., p. 97) are added and the solution is shaken vigorously for five minutes. After settling out, the yellow precipitate is treated according to one of the following methods, *b* or *c:*

(*b*) **Alkalimetric method.**—The precipitate is washed with 1 per cent nitric acid solution followed by 0.1 per cent potassium nitrate solution until the washings are no longer acid. The precipitate is dissolved in a measured excess of standardized sodium hydroxide solution and titrated back with standardized nitric acid using phenolphthalein. The solutions are standardized against a steel with a known amount of phosphorus.

(*c*) **Molybdate reduction method.**—The precipitate is washed with acid ammonium sulphate (prepared according to Blair) until the washings no longer react for iron or molybdenum. It is dissolved in 25 cc of ammonia (5 cc ammonia of 0.90 sp. gr. to 20 cc water). The filter is washed well with water and 10 cc of strong sulphuric acid added to the filtrate, which is run through the reductor at once and titrated against a $\frac{N}{20}$ permanganate solution.

7. SULPHUR BY OXIDATION

Five grams of iron or steel are dissolved in a 400-cc Erlenmeyer flask, using 50 cc of strong nitric acid. A little sodium carbonate is added, the solution is evaporated to dryness and the residue baked for an hour on the hot plate. To the flask 30 cc of strong hydrochloric acid are added and the evaporation and baking are repeated. After solution of the iron in another 30 cc of strong hydrochloric acid and evaporation to a sirupy consistency, 2 to 4 cc of the same acid are added, followed by 30 to 40 cc of hot water as soon as all the iron is dissolved. The solution is then filtered and the residue washed with hot water. (See paragraph below for the treatment of this residue for its sulphur content.) The sulphur is precipitated

in the cold filtrate with 10 cc of a 10 per cent solution of barium chloride. After 24 to 48 hours the precipitate is collected on a paper filter, washed first with hot water (containing 10 cc of concentrated hydrochloric acid and 1 gram of barium chloride to the liter) until free from iron and then with hot water till free from chloride. The washings are kept separate from the main filtrate and are evaporated to recover dissolved barium sulphate.

With irons the paper containing the insoluble residue above mentioned is put into a platinum crucible, covered with sodium carbonate free from sulphur, and charred without allowing the carbonate to melt. The crucible should be covered during this operation. Sodium nitrate is then mixed in and the mass fused with the cover off. An aclohol flame is used throughout. The melt is dissolved in water and evaporated with hydrochloric acid in excess to dryness in porcelain. The evaporation with water and hydrochloric acid is repeated to insure removal of nitrates. The residue is extracted with a few drops of hydrochloric acid and water, the insoluble matter is filtered off and barium chloride is added to the filtrate. The barium sulphate obtained is added to the main portion.

Careful blanks are run with all reagents.

8. SULPHUR BY EVOLUTION

Five grams of sample are dissolved in 60 cc of concentrated hydrochloric acid [2] in an evolution apparatus whose connections are all of glass, the air being first displaced by hydrogen. The gases evolved are passed through a solution containing 5 cc of 3 per cent hydrogen peroxide (made from "perhydrol") and 25 cc of ammonia (sp. gr. 0.90). The solution in the evolution flask is boiled vigorously for several minutes after the metal has dissolved. The contents of the absorption tube are transferred to a beaker and, if not already so from acid which has distilled over, are made slightly acid with hydrochloric acid, boiled and precipitated with 10 cc of boiling barium chloride solution (10 per cent). The beaker is then placed on the hot plate for 10 or 15 minutes. The precipitate is filtered off at once on paper, washed several times with hot water, ignited and weighed.

9. MANGANESE

The Ford-Williams and the bismuthate methods as described by Blair (Chemical Analysis of Iron, 6th ed., pp. 118–128) are used at the Bureau of Standards.

(a) **Ford-Williams method.**—Two grams of metal are dissolved in 30 cc of nitric acid (sp. gr. 1.20). With irons the insoluble matter is filtered off; steels usually do not require filtration. The solution is concentrated to 15 cc, 2 grams of potassium chlorate are added and it is boiled for 10 or 15 minutes. Then 10 cc of concentrated nitric acid and 1 gram of potas-

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[2] At first the practice was to use acid of half strength. Certain steels, however, do not yield as much sulphur in volatile form with the weaker acid as with the stronger.

sium chlorate are added and the boiling is continued for 10 minutes. The precipitate is filtered on asbestos and washed two or three times with strong nitric acid, then with water. The pad of asbestos is transferred to a flask and shaken up with a measured excess of ferrous sulphate solution, which is slightly acid with sulphuric acid, until the manganese oxide is dissolved. The excess of ferrous iron is titrated with permanganate. The iron solution is compared with the permanganate on the day it is used.

(b) **Bismuthate method.**—One gram of drillings is dissolved in 50 cc of nitric acid (sp. gr. 1.135) in a 200-cc Erlenmeyer flask. Irons should be filtered. The solution is cooled, about 0.5 gram of sodium bismuthate is added, and it is then heated until the pink color has disappeared. Any manganese dioxide separating is dissolved in a slight excess of a solution of ferrous sulphate or sodium sulphite. The solution is boiled till free from nitrous fumes. After cooling to 15° C an excess of bismuthate is added and the flask is shaken vigorously for a few minutes. Then 50 cc of water containing 30 cc of nitric acid per liter are added and the solution is filtered through asbestos. A measured excess of ferrous sulphate is run in and the excess titrated against permanganate solution which has been compared with the iron solution on the same day.

III. METHODS FOR SPECIAL ALLOY STEELS

1. INTRODUCTION

As yet (in July, 1911) the Bureau has issued but one special alloy steel, and, though several others are in process of analysis, no decision has been reached in some cases as to the best methods for the determination of their constituents. This statement holds for some of the commoner as well as special elements, for the presence of the latter may necessitate modification or abandonment of one or another of the methods applicable to ordinary steels.

It was expected that each of the Bureau's special steels would contain of the more unusual elements only those characteristic of that steel, aside from such traces as might occur in any steel, according to the composition of the ores and fluxes used in its making. Some of them, however, were found to contain unexpected elements in determinable and even considerable amounts. Thus, the vanadium steel contains 0.006 per cent molybdenum, 0.009 per cent chromium, and 0.009 per cent nickel. The nickel steel contains about 0.15 per cent tungsten and the chrome-vanadium steel about the same amount of nickel. As to the sources of these constituents the Bureau has little positive information. They are certainly to be sought in some cases in the ores and in others perhaps in crucibles, hearth linings, etc., which had been used for other special alloys, or in scrap. It seems probable that the condition is one of common occurrence. In any case the need for watchfulness on the part of the analyst is sufficiently indicated.

The methods that differ from those given under Section II of this circular will be found below, so far as occasion has arisen hitherto for their use at the Bureau.

2. COPPER

Ten grams of the sample are dissolved in sulphuric acid of 10 per cent strength and the hot solution is saturated with hydrogen sulphide, then filtered through paper. The filter is washed free from iron with very dilute sulphuric acid containing hydrogen sulphide. The use of this reagent is merely precautionary, to prevent possible solution of copper while filtering, for copper seldom if ever dissolves while the steel is dissolving, if air is wholly excluded. The paper with its contents is incinerated in a porcelain crucible, digested therein with nitric acid, transferred to a platinum crucible, and evaporated with hydrofluoric and sulphuric acids till the former acid has removed silica and itself suffered expulsion. The residue, if not soluble in sulphuric acid, is fused at a low heat and only just long enough to effect the purpose, with sodium or potassium pyrosulphate. The copper is then deposited electrolytically from the acid solution or is determined by colorimetry in an ammoniacal solution.

The method is applicable to irons and common steels.

3. MOLYBDENUM (IN SMALL AMOUNTS) WITH AND WITHOUT COPPER

The treatment is the same as for copper up to the first filtration, when it is advisable to filter through asbestos in glass or porcelain, instead of through paper, and to digest with aqua regia without igniting. The filtrate is evaporated with sulphuric acid, so as to have no other acid present. The residue is diluted, sulphuric acid added if need be, and molybdenum (copper, too, if present) precipitated by hydrogen sulphide from the hot solution, preferably in a closed pressure bottle after saturating the cold solution with the precipitant.

The precipitate is collected on a Gooch crucible, dried, and converted by careful ignition to trioxide of molybdenum if copper and other metals are absent.

If copper is present, the sulphides are dissolved in nitric acid, and the solution is boiled with potassium hydroxide to precipitate cupric oxide. After filtration and re-solution the copper can be determined in any way desired. From the filtrate, acidified with sulphuric acid, the molybdenum may be thrown out as sulphide in the manner described above.

4. NICKEL

The dimethylglyoxime method of Brunck[3] is used without other modification than the adoption of Prettner's[4] recommendation to wait an hour before filtering. As here described the method applies to nickel and chrome-nickel steels, but it is equally serviceable with irons and ordinary steels, provided a larger initial weight of sample is used.

One-half gram of the metal is dissolved in 10 cc of fairly concentrated hydrochloric acid, and then sufficient nitric acid is added to oxidize the iron.

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[3] Stahl u. Eisen, **28** (1), p. 331; 1908.   [4] Chem. Ztg., **33**, p. 396; 1909.

The solution is filtered, if need be, and to it is added 2 to 3 grams of tartaric acid, and then water till the volume is 300 cc. It is then made ammoniacal, and if no iron precipitates is again made acid and heated nearly to boiling. Dimethylglyoxime (20 cc of a 1 per cent alcoholic solution) is added and then ammonia, drop by drop, till in slight excess. After standing an hour the deep-red precipitate is collected on a weighed Munroe or Gooch crucible, washed with hot water, dried for 45 minutes at 110–120° C, and weighed. It contains 20.31 per cent nickel.

5. CHROMIUM

For small amounts of chromium, as in the vanadium steel, the method used was substantially that described by Blair,[5] the final determination being made colorimetrically.[6]

6. PHOSPHORUS

The acetate separation, followed by double precipitation as magnesium phosphate, is used for phosphorus in vanadium steels. There is great difficulty in precipitating all the phosphorus by the molybdate reagent in presence of vanadium, and the latter is apt to contaminate the phospho-molybdate that does form. Hence, the acetate method is considered more reliable.

7. MANGANESE

The Ford-Williams method (see p. 8) is preferred to the bismuthate method for manganese in vanadium steels, since the use of the latter involves an uncertain correction on account of the vanadium.

8. VANADIUM

The first and second of the following methods were used in analyzing the Bureau's vanadium steel (No. 24). They are reproduced here on that account. Method III is that used for the chrome-vanadium steel now in preparation. It was also used to redetermine the vanadium in No. 24, with a result (0.145 per cent) in almost exact agreement with the average obtained by Methods I and II (0.143 per cent). All three methods were devised or adapted by Mr. John R. Cain, of this Bureau. The third will be described in detail in a forthcoming publication of the Bureau and in the Journal of Industrial and Engineering Chemistry.

(*a*) **Method I.**—Five to 10 grams of drillings are dissolved in hydrochloric acid (1:1), a few drops of hydrofluoric are added, and the solution is boiled for a few minutes. The insoluble matter is filtered off, ignited, fused with a little sodium carbonate, the fusion dissolved in water and

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[5] The Chemical Analysis of Iron, 6th ed., p. 209 et seq.
[6] See Hillebrand, Bull. 422, U. S. Geological Survey, p. 147.

added to the main filtrate. This is then oxidized with the minimum amount of nitric acid needed, and boiled till free from fumes. The iron is extracted with ether and the excess of ether removed from the aqueous layer by evaporation on the steam bath. After concentration on the bath strong nitric acid is added to the solution and it is evaporated to dryness. The residue is dissolved in strong nitric acid, the solution is diluted with water and nearly neutralized with strong sodium hydroxide solution. It is then poured slowly into 150 to 200 cc of a 10 per cent sodium hydroxide solution, stirring vigorously. The solution is filtered, and the series of operations is repeated with the precipitate until it is free from vanadium, as shown by dissolving it in nitric acid and testing with hydrogen peroxide. In the latter treatments the amount of sodium hydroxide solution used may be smaller. From the combined filtrates the vanadium is precipitated with mercurous nitrate solution, after making nearly but not quite neutral with dilute nitric acid. After settling, the precipitate is collected on paper and washed with dilute mercurous nitrate solution. The filter is burned off in a platinum crucible and the precipitate ignited till all the mercury is expelled. The impure vanadium pentoxide left is ·fused with a little sodium carbonate, the fusion is dissolved in water and filtered (on asbestos) from insoluble matter. A second precipitation with mercurous nitrate is then made. Sometimes a further fusion and precipitation may be necessary in order to get a product sufficiently pure for the next step, which is a final fusion with sodium carbonate. The fusion is dissolved in dilute sulphuric acid and the vanadium is reduced by sulphur dioxide gas and titrated against $\frac{N}{50}$ permanganate after complete expulsion of the excess of reducing agent.

Option.—Preliminary solution may be in 1.20 nitric acid, followed by evaporation to dryness, baking, resolution in concentrated hydrochloric acid, and filtration to get rid of silica. The first method is shorter and is just as effective.

(*b*) **Method II.**—Five to ten grams of the steel are dissolved in hydrochloric acid (1:1) in a flask fitted with a Bunsen valve or in a current of carbon dioxide or hydrogen. The cooled solution is almost neutralized with sodium carbonate and the neutralization finished with a slight excess of barium carbonate. The barium carbonate should be previously finely ground in a mortar and should be tested for freedom from vanadium by dissolving in nitric acid and adding hydrogen peroxide, which should give no brown color. The flask is stoppered loosely and left thus over night. The precipitate contains all the vanadium with but little iron, and this may be treated from this point (after solution in nitric acid) substantially as described under Method I, omitting the section relating to preliminary solution, extraction, and conversion into nitrate. It is desirable to protect the iron solution at all times as thoroughly as possible against oxidation by the air, as this increases the amount of iron going into the precipitate.

(*c*) **Method III.**—Two to four grams of steel are dissolved in 40 to 60 cc of sulphuric acid (10 per cent by volume), in a covered 300-cc Erlenmeyer flask. The residue is filtered off, washed two or three times with water, ignited and fused for a few minutes with potassium pyrosulphate, adding the aqueous solution of the fusion to the main solution. If the steel will not dissolve readily in sulphuric acid, hydrochloric may be used.[7] The solution is nearly neutralized with sodium carbonate. Finely powdered cadmium carbonate is then added in small portions at intervals of four or five minutes, boiling vigorously between times and keeping the flask well covered. A gram or two of carbonate should remain undissolved finally.

Boiling for 15 or 20 minutes suffices and for a shorter time with vanadium steels containing little or no chromium. The precipitate is allowed to settle and then filtered rapidly so as to prevent oxidation and precipitation of iron on the filter. It is washed twice with hot water, no special care being taken to remove all of it from the flask. It is then dissolved in the minimum amount of nearly boiling sulphuric acid (10 per cent) and the filtrate is caught in the original flask and boiled to insure solution of adhering matter. The solution is cooled and nearly neutralized with ammonia; there should be no more free acid present than is necessary to prevent the iron from precipitating by hydrolysis when the solution is boiled. A rapid current of hydrogen sulphide is then passed for a few minutes while the solution is boiling vigorously. When settled, the precipitate of cadmium sulphide is filtered off and washed two or three times with hot water. The filtrate is concentrated if necessary and electrolyzed at 5 to 6 amperes and 6 to 7 volts in a specially constructed separatory funnel,[8] the volume of solution being 60 to 70 cc. About 200 grams of mercury are used as cathode in the bottom of the funnel, the outlet tube of which projects up into the funnel and so traps the mercury. Electrical connection with the mercury is made by means of a wire let into the lower part of the funnel.

When ferricyanide shows no test for iron all of any chromium that may be present is usually removed. With an unusually large amount of chromium relatively to the iron this might not be so. In that case the test should be made by removing three or four cubic centimeters of the solution, adding a few drops of hydrogen peroxide and boiling for a few minutes after the brown color, due to vanadium peroxide, disappears. If the solution now remains clear and colorless on adding ammonia, the electrolysis is ended. The test portion should be acidified with sulphuric acid before returning it to the electrolyzing apparatus.

When the solution no longer gives a test for iron or chromium it is removed from the apparatus into a flask by opening the stopcock and is followed by 25 to 30 cc of water to wash the mercury, the current still passing.

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[7] In this case the subsequent carbonate precipitate must be dissolved in sulphuric acid and the separation repeated in sulphate solution, for the precipitate first obtained contains enough chloride to give trouble if dissolved in sulphuric acid and directly electrolyzed.

[8] Bull. Bureau of Standards, **7**, p. 389; J. Ind. and Eng. Chem., **3**; July, 1911.

To the reduced solution two or three cubic centimeters of sulphuric acid (1:1 by volume) are added, then it is heated to 70° or 80° C and permanganate is added from a pipette until there is a strong pink color. Into the boiling solution sulphur dioxide gas is passed for a few minutes, then carbon dioxide rapidly until the escaping steam gives no test for sulphur dioxide. If any turbidity shows, the solution is filtered through a Munroe or Gooch crucible (not through paper), and titrated against $\frac{N}{50}$ permanganate at 70° to 80° C. The reduction by sulphur dioxide and the titration may be repeated as often as desired, and such repetition is recommended.