TUNGSTEN, TANTALUM AND COLUMBIUM

TUNGSTEN

W., at.wt. 184.0; sp.gr. 18.77; m.p. 3000° C.; oxides, WO₃ (brown); WO₃ (yellow); acids, H₂WO₄, ortho tungstic; H₂W₂O₇, meta tungstic

DETECTION

Minerals. The finely powdered material is decomposed by treating with mixed acids according to the procedure given on page 560. Tungsten is precipitated with cinchinone, the precipitate filtered off and dissolved in ammonium hydroxide, then acidified with hydrochloric acid and reprecipitated with cinchinone as described.

Tungsten oxide may be confirmed as follows:
1. The residue is suspended in dilute hydrochloric acid and a piece of zinc, aluminum, or tin placed in the solution. In the presence of tungsten a blue-colored solution or precipitate is seen, the color disappearing upon dilution with water.
2. A portion of the precipitate is warmed with ammonium hydroxide and the extracts absorbed with strips of filter paper.
   (a) A strip of this treated paper is moistened with dilute hydrochloric acid and warmed. In the presence of tungstic acid a yellow coloration is produced.
   (b) A second strip of paper is moistened with a solution of stannous chloride. A blue color is produced in the presence of tungsten.
   (c) A third strip dipped into cold ammonium sulphide remains unchanged until warmed, when the paper turns green or blue if tungsten is present.

Iron, Steel and Alloys. These decomposed with strong hydrochloric acid followed by nitric acid as directed under Solution of the Sample leave a yellow residue in the presence of tungsten. If this residue is digested with warm ammonium hydroxide and the extract evaporated to dryness a yellow compound, WO₃, will remain if tungsten is present. This oxide may be reduced in the reducing flame to the blue-colored oxide.

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1 Columbium is also known as Niobium.

Chapter by Wilfred W. Scott, A. M. Smoot and J. A. Holladay.

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ESTIMATION

Tungsten occurs principally as wolfram, a tungstate of iron and manganese (FeWO₄, MnO₃), as scheelite, a tungstate of calcium (CaWO₄), as ferberite, Fe₂O₅W₂O₇ and hubnerite, Mn₂O₅WO₃. The best concentrate of hand-picked material contains 70 to 74% tungsten in terms of its oxide, WO₃.

The element is met with in alloys—ferro-tungsten, silico-tungsten, tungsten steels containing as much as 10 to 20% of the metal, used for making high-speed, self-hardening cutting tools; tungsten powder; alkali tungstates for mordanting purposes; tungstic oxide, WO₃; tungsten electric light filaments, etc.

Solution of the Sample

For solution of the sample the following facts should be kept in mind regarding solubilities.

The metal is practically insoluble in HCl and in H₂SO₄. It is slowly attacked by HNO₃, aqua regia and by alkalis. It is readily soluble in a mixture of HNO₃ and HF (=WF₄ or WOF₄).

Oxides. WO₃ is soluble in hot HCl and in hot H₂SO₄ (=red sol.), also in KOH (red sol.). The oxide WO₃ is scarcely soluble in acids, but is readily soluble in KOH, K₂CO₃, NH₄OH, (NH₄)₂CO₃, (NH₄)₂S₂. Both the acid and the alkali solutions deposit the blue oxide on standing.

Acids. Ortho tungstates. A few are soluble in water and in acids. The alkali salts only slightly soluble. The meta tungstates are easily soluble in water. Tungstates are precipitated from alkali salts by dilute H₂SO₄, HCl, HNO₃, H₂PO₃ (aqua) as yellow WO₃·H₂O or white WO₃·2H₂O. Meta tungstates are not precipitated by cold acids, but are precipitated by boiling and by long standing.

Solution of Minerals. The material is best decomposed by acid treatment as described on page 560. Use of a fusion as a means of decomposition of tungsten ores preliminary to either the qualitative detection or the quantitative determination of tungsten cannot be recommended. The precipitation of tungsten by boiling with acids in presence of considerable amounts of alkali salts (such as result from acidification of a fusion) is absolutely worthless inasmuch as large amounts of tungsten always remain in solution. Repeated evaporations do not improve matters. In fact, when the amount of tungsten present is small, and especially if the ore contains much phosphorus, there is small likelihood that any of the tungsten will be precipitated. The use of cinchonine is necessary in order completely to precipitate tungsten under these conditions.

1 TYPICAL ANALYSES

<table>
<thead>
<tr>
<th>Tungsten Powder</th>
<th>Ferro Tungsten</th>
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<tbody>
<tr>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>W, 97 to 98.7</td>
<td>71 to 85.5</td>
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<tr>
<td>Fe, .5 to .6+</td>
<td>14 to 24.5</td>
</tr>
<tr>
<td>C, .1 to .3+</td>
<td>.4 to 2.6</td>
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<tr>
<td>Si, .3 to .7+</td>
<td>.1 to .4</td>
</tr>
<tr>
<td>Mn, 0 to .2</td>
<td>.008 to .02</td>
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<tr>
<td>P, ——</td>
<td>.08 to .04</td>
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<td>S, ——</td>
<td>.01 to .02</td>
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<tr>
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<tr>
<td>Cu, ——</td>
<td>0 to .008</td>
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<tr>
<td>Mg, 0 to .3+</td>
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SEPARTIONS

Separation of Tungsten from Silica. The oxide of tungsten, as ordinarily obtained, is frequently contaminated with silica. The removal of silica is accomplished by heating the mixture in a platinum dish with sulphuric and hydrofluoric acids and volatilizing the silica. After taking to dryness and igniting gently, the last traces of sulphuric acid are expelled by adding ammonium carbonate and again igniting.

In presence of small amounts of silica (0.1 to 0.2%) and large amounts of tungsten (75 to 85%) J. A. Holladay recommends evaporation with sulphuric and phosphoric acids, filtration to remove the bulk of the tungsten, and subsequent ignition and volatilization with sulphuric and hydrofluoric acids.

Separation from Tin. The weighed residue is mixed with six to eight times its weight of ammonium chloride (free from non-volatile residue) in a platinum crucible, placed in a larger crucible, both vessels being covered. Heat is applied until no more vapors of ammonium chloride are evolved. Additional ammonium chloride is added and the treatment is repeated three times. The fourth treatment is followed by weighing of the residue and the treatment repeated once more. If no further loss of weight takes place it is assumed that all the stannic oxide has been driven off. The inner crucible is now placed directly over the flame and heated to dull redness for a few minutes and the oxide, WO₃, weighed.

Separation of Tungsten from Tin and Antimony. Talbot's Process. The mixed oxides are fused with twelve times their weight of potassium cyanide in a porcelain crucible. Tin and antimony are thrown out as metals and the soluble alkali tungstate formed. This is leached out with water and the aqueous extract boiled (hood) with an excess of nitric acid to drive off the cyanogen compounds. The tungstate is then precipitated by the usual methods. If phosphorus is present in the sample it will be found in the solution with tungsten and its removal will be necessary.

Separation of Tungsten from Arsenic and Phosphorus. Both arsenic and phosphorus may be precipitated by cold magnesia mixture in an ammonical solution, tungsten remaining in solution. The separation of arsenic is difficult, as it is tenaciously retained by tungsten as a complex salt. The following process is outlined by Kehrmann.

One to 2 grams of the sample are fused with twice as much sodium hydroxide as is required to combine with the arsenic oxide, the resulting cake is dissolved in a little water and boiled in an Erlenmeyer flask for half an hour. After cooling, three times as much ammonium chloride as is needed to form chlorides with the alkalies present is added, and then ammonium hydroxide equal to one-fourth the volume of the solution under investigation, followed by sufficient magnesia mixture, added cold, drop by drop with constant stirring. After settling several hours, the solution is filtered and the residue washed with a weak solution of ammonia and ammonium nitrate. It is advisable to dissolve the residue in dilute acid and repeat the precipitation several times. The filtrates containing the tungsten are combined and concentrated by evaporation if necessary.

1 J. A. Talbot, J. Sci. (2), 50, 244, 1870.
2 F. Kehrmann, Ber., 20, 1813, 1887.
Separation of Tungsten from Molybdenum, Hommel's Process. The moist oxides of tungsten and molybdenum are digested with concentrated sulphuric acid and a few drops of dilute nitric acid, in a porcelain dish over a free flame for about half an hour. About three times its volume of water is added to the cooled solution, the residue, $WO_3$, filtered off and washed with dilute sulphuric acid (1 : 20) followed by three washings with alcohol. The residue is ignited separately from the paper and weighed with the ash of paper as $WO_3$.

Molybdenum is in the filtrate and may be precipitated in a pressure flask with $H_2S$.

Volatilization of Molybdenum with Dry Hydrochloric Acid Gas. Péchard's Process. The procedure depends upon the fact that molybdenum oxide heated in a current of dry hydrochloric acid gas at 250 to 270°C is sublimed, whereas tungsten is not affected.

The oxides of the two elements, or their sodium salts, are placed in a porcelain boat and heated in a hard glass tube, one end of which is bent vertically downward and connected with a Péligot tube containing a little water. A current of dry hydrochloric acid gas is conducted over the material, heated to 250 to 270°C. From time to time the sublimate of molybdenum ($MoO_3 \cdot 2HCl$) is driven towards the Péligot tube by careful heating with a free flame. This enables the analyst to observe whether any more sublimate is driven out of the sample and to ascertain when the tungsten is freed of molybdenum. From one and a half to two hours are generally sufficient to accomplish the separation. If sodium salt is present it is leached out of the residue, and this is then ignited to $WO_3$. Molybdenum may be determined in the sublimate.

Separation from Vanadium. Tungstic and vanadic acids are precipitated with $HgNO_3$ and $HgO$, the moist precipitate dissolved in $HCl$ and the solution largely diluted; $WO_3$ is precipitated free from vanadium.

Separation from Titanium. The material is heated with $K_2CO_3$ and $KNO_3$, tungsten is dissolved out with water and precipitated as mercuro tungstate.

Separation of Tungsten from Iron. The procedure is given under Solution of the Sample, of Steel and Alloys. The impure oxide $WO_3$ is fused with $Na_2CO_3$ and the melt extracted with water. $Fe(OH)_3$ remains on the filter. The filtrate is evaporated to dryness with $HNO_3$ and the residue extracted with water. The insoluble $WO_3$ is washed with dilute $NH_4NO_3$ solution, then dissolved in $NH_4OH$ and tungsten determined in the solution.

Separation of Tungsten from Uranium. The sample is evaporated with nitric acid to near dryness, 5 cc. $HNO_3$ is added and the uranium is dissolved out by extraction with ether.

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1 E. Péchard, Comp. Rend., 114, 173, 1891.
2 Friedheim, C. N., 61, 220.
3 Defacqz, C. N., 74, 293.
GRAVIMETRIC PROCEDURES FOR DETERMINING TUNGSTEN

Since there is no highly commendable volumetric procedure for determining tungsten, the gravimetric methods are preferred.

The element is determined as tungstic oxide, WO$_3$. It may be isolated preferably by precipitation with cinchonine, or in the form of tungstic acid, ammonium tungstate, or as mercurous tungstic acid, in the usual course of analysis, all of which forms may be readily changed by ignition to the relatively non-volatile oxide, WO$_3$.

Gravimetric Determination of Tungsten in Steel and Alloys

Tungsten alloys may be decomposed by hydrochloric (or sulphuric) and nitric acids. Tungsten precipitates, carrying down chromium and a little iron. The bulk of the iron is filtered off and tungsten determined in the residue, by direct or difference methods.

**Special Reagent. Cinchonine Solution.** 100 grams of the alkaloid dissolved in dilute (1 : 3) HCl and made to 1000 cc. with the dilute acid. **Wash Solution.** 30 cc. of the above solution, with 30 cc. strong HCl diluted to 1000 cc.

Procedure

1. **Decomposition of the Sample.** Two grams of high tungsten alloys or 5 grams of alloys low in tungsten are dissolved in a 350-cc. beaker by addition of 20 cc. strong HCl, the beaker being placed over an asbestos mat on a hot plate or steam bath. (The temperature should be below the boiling point of HCl, since the acid should remain strong to effect decomposition.) Since the reaction is energetic the beaker is covered by a watch glass. Ten cc. of strong nitric acid are added, pouring small portions at a time through the lip of the beaker. The sample is digested until all the black particles have dissolved and only the fine greenish yellow tungstic oxide is evident. Agitation of the liquor to prevent caking assists the reaction.

2. When the sample is decomposed, the beaker is uncovered and the solution evaporated rapidly to about 20 cc. and then cautiously at low heat to about 5–10 cc. 5 cc. of HCl are added to the moist residue and the solution diluted to about 50 cc. and heated to boiling 2–3 cc. of cinchonine reagent are added. Avoid taking to dryness and baking as this will make the tungsten difficult to dissolve in NH$_4$OH. See step 4.

3. The mixture is filtered and the ferric chloride washed out from the tungstic residue with dilute HCl (1 : 10), i.e., until the wash solution passes through the filter colorless. The filtrate is tested for tungsten by addition of more cinchonine. (See step 7.) As small amounts of tungsten come down slowly at least an hour should be given for the test.

4. A clean beaker is placed under the filter and tungsten dissolved out from the impure residue by treating this with warm ammonia water (1 : 5), the filter being half filled with each washing and thoroughly drained. It is advisable to rinse out the beaker in which the decomposition was made, with warm ammonia solution and pour this on the filter. After five washings the filter is cautiously removed and spread out on a watch glass. The residue is washed into a beaker with a stream of ammonia water and digested with about 20–30 cc. of ammonia for about 5 minutes warming to near boiling. The solution is poured through a
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fresh filter into the main extract, the filter is drained and then washed twice more with warm ammonia solution (1:5). All the tungsten should now be in the filtrate. If much residue remains as in case of high silica samples, tungsten is apt to be present. This is recovered by acid sulphate fusion. See Notes.

5. The filtrate is boiled to expel the ammonia. When the odor has become faint, HCl is added until the solution is just acid and about 3 cc. excess is added. The total volume will be 75–100 cc., after boiling. Acidification may cause some tungsten to precipitate, but this does no harm. The ammonia is generally expelled by boiling the filtrate down to half its original volume.

6. 10 cc. of cinchonine reagent are added to the hot solution and the mixture stirred and allowed to settle until cold. If the supernatant solution is cloudy stirring up the precipitate and allowing it to settle will clear the solution. It is well to test the clear liquor with a few drops more of the reagent to ascertain whether all of the tungsten has precipitated.

7. The solution is filtered and the tungsten residue washed three or four times with dilute cinchonine reagent (washing down from the rim of the filter), and once with 5–10 cc. of water.

Note. The filtrate from step 3 may contain some tungsten. If the filtrate treated with cinchonine has become cloudy on standing it must be filtered, the residue washed with cinchonine reagent as in the procedure above and the filter and residue added to that containing the bulk of the tungsten.

8. The filter (or filters) is ignited in a weighed crucible to destroy the carbon, then cooled and weighed as WO₃.

\[
\text{WO}_3 \times 0.7931 = \text{W}
\]

Note. The oxide WO₃ fused with KHSO₄ and the cooled melt extracted with ammonium carbonate reagent should give a clear solution. If the solution is cloudy SiO₂ is indicated. This should be filtered off, ignited and its weight subtracted from the WO₃ obtained above. See optional method below.

The KHSO₄ fusion may be made in a porcelain or platinum crucible.

Optional Method

The impure residue obtained in step 3 of the first procedure is ignited and weighed. The residue is now fused with acid potassium sulphate, KHSO₄ (5–6 grams of salt). The heating is continued until effervescence ceases and the mass changes to a clear solution. The fusion is cooled by rotating the crucible so that the mass is spread in a layer over the sides. It is now dissolved by placing in about 100 cc. of ammonium carbonate solution (10% sol.) and heating to boiling. Iron, chromium and silica will remain insoluble, tungsten will be in solution. The liquor is filtered and washed 4 or 5 times with water containing a little (NH₄)₂CO₃. The residue is ignited, cooled and weighed. The difference of this weight and that of the impure residue is due to the WO₃.

Note. If the carbonate extract is boiled, acidified and cinchonine reagent added tungsten will precipitate as the cinchonine compound. See Notes.

Notes

The use of sulphuric acid in place of hydrochloric acid in the decomposition of the sample offers no advantages as to speed of decomposition. On the
other hand with sulphuric acid treatment tungsten is invariably found in the filtrate (step 3) while with the HCl method it is seldom found in appreciable amounts.

Hydrofluoric acid assists in the decomposition of alloys high in silicon. A large excess must be avoided as this would attack the glass of the beaker with liberation of silicic acid, and fluosilicic acid. With large amount of HF a platinum dish should be used.

WO₃ does not dissolve readily in ammonia after it has been ignited. The moist residue of tungsten precipitated by acids is easily soluble in ammonia. If an appreciable amount of residue remains from the ammonia extraction, it is fused with KH₂SO₄, extracted with a 10% solution of (NH₄)₂CO₃, the CO₂ expelled by boiling and the ammoniacal solution filtered from silica, vanadium, iron, etc., and the tungsten precipitated and determined according to the procedure outlined in steps 5 to 8 inclusive.

SiO₂ is but slightly soluble in dilute ammonia solution. The silica dissolved by 100 cc., 1 : 1 NH₄OH in a 30 hour treatment on a 47% SiO₂ ore amounted to less than 0.005 g. on a gram sample. With a 30 minute treatment the amount was inappreciable. In case of doubt treat the WO₃ with HF in a platinum crucible and again ignite after expelling the acid by evaporation.
THE ANALYSIS OF TUNGSTEN ORES, CONCENTRATES AND METALLIC PRODUCTS\(^1\)

General Considerations

Commercial tungsten minerals are marketed usually in the form of concentrates derived from treatment of lean ores by water concentration, or, sometimes, as specially selected high grade ore which has not been subjected to dressing operations other than hand sorting.

The important commercial minerals are Wolframite—iron-manganese tungstate; Hubnerite—manganese tungstate; Ferberite—iron tungstate; Scheelite—calcium tungstate. The first three grade into each other imperceptibly; commercially, they are all classed as Wolframite although the predominant mineral may, in some cases, be either manganese tungstate or iron tungstate. The determinations usually required are tungstic oxide, manganese, tin, phosphorus, sulphur, copper and arsenic sometimes molybdenum, which occurs more or less frequently in Scheelite, and occasionally bismuth and lead.

The principal minerals associated with tungsten concentrates are pyrite, arsenopyrites, cassiterite, magnetite, columbite, and always more or less quartz and silicates. Scheelite sometimes is associated with baryte.

The following analytical methods have been in practical use for a long time; they have been modified from time to time as experience showed necessary. Many suggestions from Works' chemists and others have been adopted. The descriptions are given in detail where this has been thought to be necessary because much depends upon minor points and upon the experience gained in making many hundreds of determinations.

Methods for the analysis of tungsten powders and ferro-tungsten are also given, since these are the raw materials of manufacturers of special steels.

Gravimetric Determination of Tungsten in Ores and Concentrates

Special Reagents

Cinchonine Solution. Cinchonine solution is made by dissolving 100 grams of the alkaloid in dilute HCl (1 part acid to 3 of water) and diluting to 1000 cc. with HCl of the same strength.

Cinchonine Wash Solution. 30 cc. Cinchonine solution, 30 cc. strong HCl to 1000 cc. of water.

Preparation of the Sample

Ores should be ground in agate to pass a 200-mesh screen; double screening is recommended to insure perfect fineness.

Weigh one gram into a 350 cc. beaker, add 5 cc. of water and shake to spread the ore evenly over the bottom of the beaker. Add 100 cc. of strong HCl, cover the beaker and set it to warm gently for an hour. The temperature should not exceed 60° C.—higher heating expels HCl gas. The ore is slowly decomposed and most of the tungsten is held in solution by the excess of HCl, leaving the undecomposed ore exposed to further attack by the HCl.

Stir the solution with a glass rod once or twice during this digestion to prevent

\(^1\) By A. M. Smoot.
the formation of crusts or cakes on the bottom. The glass rod may be left in the beaker.

After an hour increase the heat and boil until the solution is evaporated one-half or thereabouts. The cover may be removed after boiling begins, or better, it may be supported over the beaker on three glass hooks. After the liquid is reduced in volume to 50 or 55 cc., scrape the bottom of the beaker thoroughly with a glass rod to detach all caked ore and residue—this is very important, otherwise complete decomposition by the acid treatment is difficult if not impossible to accomplish. Add 40 cc. more strong HCl and 15 cc. HNO₃, replace the cover and boil until all danger of spattering (owing to the rapid expulsion of chlorine) is past, remove the cover and evaporate to a volume of 50 cc., then add 5 cc. more HNO₃, replace cover and continue boiling, finally remove cover and evaporate to a volume of 15 cc. or less. All this boiling and evaporation requires about an hour. Occasional stirring to break up crusts, especially when fresh additions of acid are made, is recommended.

Add 200 cc. of hot water to the concentrated solution, stir well and simmer gently just at the boiling point for half an hour. Nearly all the tungstic acid is separated after the addition of nitric acid, and during the subsequent simmering and boiling after dilution, but a little may remain in solution. Add 6 cc. of cinchonine solution, stir well and let stand for half an hour, or longer if convenient, thus precipitating all tungsten.

This method of attack is preferable to that formerly employed wherein less acid was used and HNO₃ was added earlier in the digestion. Most ores are completely decomposed, so far as tungsten minerals are concerned, but it is unsafe to assume that this is the case unless the residue is pure white silicen.

After the tungstic acid residue has settled well and has stood for half an hour, filter the solution through a 9 cm. paper, using a little paper pulp in the filter. Wash the residue well, first by decantation in the beaker and afterward on the paper with a dilute solution of cinchonine and HCl.

It is unnecessary to detach the tungstic acid which adheres to the sides of the beaker, but washing should be thorough to remove all iron, manganese, lime, etc., from the residue and filter paper. Finally wash both beaker and filter once with cold water to displace most of the dilute cinchonine washing solution.

**Procedure for Isolation of Tungsten**

Wash the tungstic acid and residue back from the filter into the original beaker with a fine jet of water from a wash bottle—the residue washes out easily because of the paper pulp which prevents adherence—about 25 cc. of water should be used. Add 6 cc. of strong NH₄OH, cover the beaker and warm it gently for about ten minutes. Tungstic acid dissolves readily, stir well and wash down the sides of the beaker with dilute ammonia, make sure that all the yellow tungstic acid has dissolved, then filter the warm solution through the same filter paper that was used at first, thus dissolving the small amount of tungstic acid that adhered thereto. Collect the filtrate in a 400 cc. beaker, wash the original beaker and the filter paper thoroughly with dilute ammonia (1 part strong NH₄OH—9 parts H₂O). The filtrate should be clear, or at most only slightly cloudy. The addition of about one gram of NH₄Cl to the solution before filtering and the use of a little of the same salt in the wash solution will insure a perfectly clear filtrate; but the use of this salt is not recommended unless the silicious residue tends to pass the filter in large
amount. The residue insoluble in ammonia will usually be free from tungsten; it may consist of tin oxide (cassiterite) silica and undecomposed silicates, titanium minerals or columbite; to make sure, it must be fused as described below.

Cover the 400 cc. beaker and boil it until free ammonia is expelled. The object of boiling off the free ammonia is to minimize ammonium salts since the cinchonine tungsten compound to be precipitated comes down more quickly and completely in solutions free from ammonium salts. Dilute the solution to 200 cc. with hot distilled water, acidulate with 3 cc. HCl and add 6 to 8 cc. of cinchonine solution. Stir very briskly for half a minute, which will cause the flocculent precipitate to agglomerate. It will then settle rapidly, leaving a clear supernatant liquid. Let it stand until cold, filter on an 11 cm. weightless ash filter (B. & L.—A grade) which has been treated to a rather copious dose of paper pulp. If ammonium chloride is used in the prior operation, the solution should be allowed to stand for several hours, best over night, after adding cinchonine. Wash well with dilute cinchonine solution (wash solution described above) holding the beaker with a rubber tipped rod. Follow the cinchonine wash by one washing with cold water, transfer the filter to a small weighed platinum dish or large crucible, dry by heating on the hot plate, then burn the filter slowly over a bunsen burner or in a muffle followed by strong ignition until all carbon is consumed.

The use of paper pulp in the filter promotes ignition, leaving the ignited precipitate as a porous, friable mass, whereas if paper pulp is not used, the ignited precipitate is dense and it is sometimes difficult to burn the carbon completely.

After the carbon is practically all consumed break down the residue with a glass rod flattened at one end, wipe off the end of the rod with a small piece of moistened filter paper, adding it to the dish. Any remaining carbon and the small piece of filter paper are quickly burned, leaving a pure yellow residue.

Moisten the residue with three drops of strong H₂SO₄, add 5 cc. of HF and evaporate slowly on the hot plate until the HF is expelled. It is best to continue heating on the hot plate until the H₂SO₄ is expelled also; there is then no danger of spitting. Ignite the dish cautiously at first, finally at full red heat for ten minutes, cool in a desiccator and weigh as WO₃.

The residue left after the ammonia treatment may in some cases contain WO₃, although with Scheelite and most pure ores and concentrates it does not. It is best in all cases to examine it. In the case of impure ores containing much insoluble residue, the residues from duplicate determinations should be examined separately. When the residue is small and light-colored, it suffices to unite the duplicates for this determination.

Ignite the filter containing the residue in a small porcelain crucible. This is necessary because tin may be present, which would be reduced by the filter paper and ruin platinum. Mix the ignited residue with five or six times its weight (in any case at least one gram) of sodium carbonate plus a very little KNO₃. Transfer the mixture to a platinum crucible and fuse for five or ten minutes. Leach the fusion with 50 cc. of hot water in a small beaker, filter, acidulate slightly with HCl and boil to expel CO₂. Add 5 cc. cinchonine solution. Let the beaker stand for several hours, best over night; long standing is essential because small amounts of tungsten are slowly precipitated by cinchonine in the presence of alkaline chlorides.

If any tungsten precipitate appears, filter it off on a 7 cm. paper and wash it with dilute cinchonine solution, followed by one wash with cold water, dissolve on the filter in warm dilute ammonia, collecting the filtrate in a small beaker, boil out the excess of ammonia, make slightly acid with HCl and reprecipitate the
tungsten with cinchonine. This reprecipitation is done in a very small volume of
clear practically free from salts so the tungsten comes down quickly, let it stand
for an hour, filter on a small weightless ash filter containing a little pulp, wash with
dilute cinchonine solution followed by one wash with water, ignite, cool, treat with a
drop of $H_2SO_4$ and 1 cc. of HF, evaporate, ignite and weigh. Add the percentage
of $WO_3$ thus found to the principal amount.

Factors: $WO_3 \times 0.7931 = W,$
$W \times 2.4739 = PbWO_4.$

**Aqua Regia Method of Watts**

One gram of medium grade, or 0.5 gram of high grade, very finely pulverized
ore, is treated in a 4-oz. flask with 40-50 cc. aqua regia and kept at moderate
heat, below boiling, on a hot plate, until the solution has evaporated to about
15 cc. The solution is shaken frequently to prevent a solid cake forming at
the bottom of the flask, which would prevent complete action of the acid on
the ore.

The solution, removed from the hot plate, is diluted to about 50 cc. with
hot distilled water and set aside to settle for half an hour. The clear liquor
is decanted through a paper filter and the residue washed in the flask twice
by decantation with 25 cc. portions of water slightly acidulated with HCl.

The $WO_3$ in the flask is dissolved with 20 cc. of 1:5 $NH_4OH$ containing
2-3 drops of HCl. The solution is decanted through the filter and any re-
mainung residue washed by decantation twice with the ammonia reagent.

If the residue is white it is transferred to the filter. If any black particles
of undecomposed ore are evident, the residue is again digested with 10-15 cc.
of aqua regia and treated as in the first case, only with relatively smaller por-
tions of solutions. The ammonia extract is added to the filter. And the
filter washed down in the customary way to remove all tungsten solution,
allowing it to flow into the main extract.

The filtrate containing the tungsten is evaporated to dryness in a platinum
dish over a water bath. The ammonia salts expelled by heat. The residue
cooled is treated with 1-2 drops of $H_2SO_4$ and about 2 cc. HF. The silica
is expelled (in Hood), together with the acids by gently heating. The residue
is now heated to dull redness for 5-10 minutes, then cooled in a desiccator and
weighed as $WO_3$. 

Determination of Phosphorus

Treat two grams of ore exactly as in the tungsten determination and evaporate the HCl and HNO₃ solution until only about 10 cc. of liquid remains. Add 5 cc. of strong H₂SO₄ and evaporate to fumes. Cool, take up with 25 cc. H₂O₂ and add about two grams of tartaric acid and heat to boiling. Add 20 cc. of strong NH₄OH thus dissolving the separated WO₃. Filter into a "shaking bottle" (a glass stoppered 250 cc. bottle) and wash the residue with dilute NH₄OH. Reserve the liquid. Ignite the residue and expel SiO₂ with HF and H₂SO₄. In the case of Scheelite this residue may be rather large owing to the insolubility of CaSO₄. Add sufficient Na₂CO₃ to make eight or ten times the weight of the residue and fuse thoroughly. Leach the fusion with hot water and filter, washing the residue with dilute Na₂CO₃ solution. Acidulate the filtrate with HCl and boil to eliminate CO₂—evaporate the solution if necessary to a volume of 75 cc. and make it slightly alkaline with NH₄OH. A precipitate of Al₅(OH)₈ may appear at this point; if it does, make the liquid slightly acid until the precipitate dissolves, and add it to the main ammoniacal solution in the shaking bottle. The presence of tartaric acid in this solution will prevent the separation of alumina. Add 10 cc. magnesia mixture to the bottle (the whole volume of solution should not exceed 160 cc.) and cool to 5°C. or less. Add five or six glass beads to the bottle and shake in a shaking machine for five or ten minutes. The object of the glass beads and the shaking, is to start the formation of magnesium-ammonium phosphate. After shaking, add 25 cc. of strong NH₄OH and let the bottle stand in a refrigerator over night. Filter off the solution and wash the precipitate in the bottle and on the paper with dilute NH₄OH but do not attempt to remove the precipitate adhering to the sides of the bottle. The precipitate consists of magnesium ammonium phosphate and arsenate together with silica and other impurities. Tin, tungsten, molybdenum, vanadium and titanium are eliminated by precipitation with magnesia mixture in the presence of tartaric acid. Dissolve the magnesia precipitate in hot dilute HCl and evaporate to small volume, say 7 or 8 cc. Add 10 cc. of strong HCl and 0.5 gram NaBr and evaporate to dryness. Take up with 5 cc. HNO₃ and evaporate to dryness again. The NaBr serves to reduce As° to As°°. The addition of strong HCl and boiling followed by evaporation to dryness eliminates As and SiO₂. Dissolve residue in 60 cc. HNO₃, S. G. 1.135, add 40 cc. of NH₄OH Sp. Gr. 0.96, cool to 35°C., add 30 cc. molybdate solution (Blair) and finish the determination by the alkalimetric method (Handy) described on page 368.

Determination of Sulphur in Ferberite, Wolframite and Scheelite

Fusion Method. Fuse two grams of pulp mixed intimately with nine grams of Na₂CO₃ and one gram KNO₃. Leach the fusion with water and wash the residue thoroughly with a dilute solution of Na₂CO₃. Acidulate the liquid with HCl and evaporate to dryness. Take up with a little HCl and 150 cc. of water, add 5 cc. of strong cinchonine solution and heat until all soluble salts are dissolved, finally boil for about five minutes. Let the solution stand over night, filter and wash with dilute cinchonine solution, using paper pulp in the filter. Neutralize the filtrate with Na₂CO₃, make slightly acid with HCl (0.5 cc. for each 100 cc. of liquid) heat to boiling and precipitate BaSO₄ by the slow addition of 10% BaCl₂.
solution. Let stand over night; filter, wash and weigh. The cinchonine solutions are the same as those used in the tungsten determinations. Note that the use of cinchonine is essential in this determination because in the presence of a large excess of alkaline chlorides the complete separation of tungsten is only effected by cinchonine. If it is omitted the BaSO₄ precipitate will inevitably contain BaWO₄. Blank determinations on the reagents run parallel with the sample are essential.

Wet Method. In Ferberite and Wolframite only where sulphur is present as associated sulphides. The method is not applicable to Scheelite which may contain BaSO₄.

Treat two grams of the 200-mesh pulp with 20 cc. of a mixture of three parts HNO₃ and one part HCl in a 250 cc. beaker, add 0.5 cc. Br and let stand at room temperature for half an hour. Digest on a steam bath, for half an hour, remove cover and evaporate to dryness on the steam bath. Add 5 cc. strong HCl and again evaporate to dryness. Take up with 3 cc. HCl and 10 cc. H₂O, and digest until all soluble salts are dissolved. Add 250 cc. hot water and 2 cc. cinchonine solution and boil. Let the solution stand until it is cold, filter and wash the residue with water containing a few drops of HCl. Heat the liquid to boiling and precipitate S by adding 10 cc. of a 10% solution of BaCl₂·2H₂O. Let stand over night, filter and wash with hot water. Ignite and weigh as BaSO₄. In this method, the tungsten mineral is only partly decomposed, but all sulphides of iron, copper, etc., are oxidized to sulphates. This method is useful for the analysis of impure concentrates containing much associated sulphides. It is not to be relied upon for the accurate determination of small amounts of sulphur.

Determination of Arsenic in Tungsten Ores and Concentrates

Wet Method. The method is based on the assumption that arsenic in tungsten ores and concentrates is wholly present as associated minerals which may be decomposed by acid treatment and not as complex arsenic-tungsten compounds unaffected by acids, since the treatment used does not wholly decompose the tungsten mineral or associated tin, titanium and niobium minerals.

Treat two grams of the 200-mesh pulp in a round bottom 300 cc. flask with 10 cc. strong HNO₃. Digest for half an hour over a small flame, add 7 cc. of strong H₂SO₄ and evaporate to fumes by shaking the flask over a naked flame and at the same time blowing a mild air current into it to remove HNO₃. Cool the flask, add 10 cc. of water and again evaporate to fumes of H₂SO₄; this is done to expel HNO₃ completely which is important. Cool the flask and add 3 cc. of water, not more, then add two grams of dry FeSO₄ and connect the flask to an Allihn condenser, set up vertically, by means of a rubber stopper carrying a stoppered funnel tube and a wide exit tube. The exit end of the condenser is sealed by allowing it to dip slightly below the surface of 300 cc. of cold water contained in a large beaker.

Add 75 cc. of strong HCl through the funnel tube and boil until the volume in the flask is reduced to 25 or 30 cc., then add 25 cc. more strong HCl and repeat the distillation. Usually two distillations serve to volatilize all arsenic which is collected in the beaker. To make sure, substitute another beaker containing water, add 25 cc. more HCl to the flask and distill again. The second distillate is tested by itself; it seldom shows any arsenic. Pass a rapid current of H₂S into the acid distillate, thus precipitating arsenic as As₂S₃. Let the precipitate settle at a temperature of 60° to 70° for an hour or two, filter through a Gooch crucible fitted with a well washed asbestos pad and wash the precipitate thoroughly with hot water, followed by alcohol, ether and finally CS₂. Dry the precipitate at 105° C.
for an hour and weigh, dissolve the As₂S₃ from the filter by passing warm NH₂OH through it, wash again with water followed by alcohol only, dry at 105° C. for an hour and weigh again. Take the weight of As₂S₃ by difference between first and second weighing. This method is preferable to weighing the Goosh crucible before filtering.

The distillation method depends on the reduction of As⁺ to As⁰⁺ by ferrous sulphate and on volatilization as AsCl₅. This can only be done if the HCl employed is strong. Dilution of the HCl below a gravity of 1.10 will prevent the formation of AsCl₅, since in that case we have a solution of As₂O₃ in HCl rather than AsCl₅.

See also the procedure given on pages 37–39 of this volume.

Preliminary Fusion. In ease the ore or concentrates contains insoluble arsenic compounds not broken up by the simple acid treatment described, it is necessary to fuse two grams of pulp with 15–20 grams of potassium pyrosulphate in a porcelain or fused silica crucible. After the melt is cold, remove it from the crucible which can usually be done easily by inverting and tapping, and break it into small pieces in a porcelain mortar. Transfer the ground melt to the 300 cc. flask, add two grams FeSO₄, and proceed with the distillation as above. The latter modification is unnecessary on most ores, since arsenic is rarely present except as associated arsenical minerals decomposed by acids.

Some trouble may be experienced in distilling owing to the “bumping” caused by separated WO₃ or undecomposed ore. This may be overcome by introducing a few glass beads into the flask.

**Tin in Tungsten Ores and Concentrates**

Fuse two grams of the finely pulverized ore in a spun iron crucible with ten grams of a mixture of equal parts of finely granulated sodium hydrate and sodium peroxide. The ore should be intimately mixed with the flux, fusion should be continued for one or two minutes after the mass is completely liquid, and a rotary motion should be given to the crucible during this period by holding it in the tongs and turning it in the flame; turning should be continued during cooling to spread the fusion.

Dissolve the fusion in 75 to 100 cc. of hot water. This is best done by placing the crucible in water in a large nickel dish since the strongly alkaline solution attacks glass or porcelain. When the mass is thoroughly disintegrated, remove the crucible and wash it; then pour the liquid into a 300 cc. beaker containing 15 grams of tartaric acid dissolved in 50 cc. of water; forthwith add 40 cc. of strong HCl. The solution will, of course, be quite hot. It should become clear on standing a few minutes except for a small amount of iron scale from the crucible, but it may require further heating to dissolve all iron hydrate. There should be no perceptible residue of undecomposed ore but it does not matter if there is a little, because it will be decomposed by the subsequent treatment. Pass a brisk current of H₂S into the warm solution until ferric iron is reduced and tin is precipitated as stannic sulphide. Filter the solution and wash the precipitate thoroughly with warm water containing H₂S. If there is a tendency for the tin sulphide to run through add a little ammonium nitrate to the wash water. It is important to remove chlorides since their presence might entail a loss of tin in the subsequent ignition.

The presence of sufficient tartaric acid prevents the precipitation of tungstic acid when the fusion is acidulated with HCl, but with large amounts of tin or with
the considerable separation of sulphur caused by reduction of ferric iron in the solution some tungsten is likely to be entrained with the precipitate which no reasonable amount of washing will remove; a second fusion is therefore necessary. Ignite the sulphide precipitate in a porcelain crucible and transfer the residue carefully to a small spun iron crucible. The reason for this step is the presence of free sulphur and sulphides which unite with the iron of the crucible, forming iron sulphide when ignition is made in the iron crucible. The film of iron sulphide is vigorously acted upon by peroxide, causing spattering. Mix the ignited residue with about two grams of sodium peroxide and fuse as before. Dissolve the fusion, in the crucible, in 25 cc. of water, transfer to a 250 cc. beaker and boil to decompose peroxide; then add two grams of tartaric acid and 60 cc. of strong HCl. This gives a solution containing 2 vols. of strong HCl to 1 vol. of water. Iron scale from the crucible and iron hydrate dissolve immediately in acid of this strength, leaving a perfectly clear solution, but the object in adding the large excess of HCl is to obtain a solution of such acid strength that arsenic may be precipitated with H₂S while tin sulphide is not formed.

If the foregoing proportions are maintained the separation of arsenic and tin may be accomplished by passing H₂S into the solution, whereby arsenic is separated as sulphide. Pass H₂S into the hot solution for about ten minutes or until practically all ferric iron is reduced. Filter off the arsenic sulphides through a small filter and wash thoroughly with HCl (1.19 sp.gr.) diluted with one half its volume of water. Good quality filter paper will withstand HCl solutions of this strength although an asbestos filter (Gooch) may be used if preferred.

Dilute the acid filtrate with twice its volume of water, add 25 cc. of strong NH₄OH to neutralize part of the free acid, and pass a little more H₂S thus precipitating tin, antimony, copper, etc. as sulphides. Let the sulphides stand until they have settled well, then filter and wash the precipitate with H₂S water slightly acidulated with HCl. Filter the solution through a 9 cm. filter, or better through a Gooch filter, using very moderate suction. Transfer the filter to a small beaker and heat it with 10 cc. of a 10% solution of sodium monosulphide. The tin sulphide and free sulphur dissolve readily leaving, usually, a very small amount of copper sulphide. Filter the solution through a 7 cm. paper and wash the filter several times with a 1% solution of sodium sulphide. Since copper sulphide is usually exceeding small, a single treatment with sodium sulphide suffices to dissolve all the tin sulphide, but if much copper should be present a second treatment is advisable.

The alkaline filtrate and washings contained in a 450 cc. Erlenmeyer flask should measure approximately 60 cc.; add 70 cc. of strong HCl, or a little more than the volume of the liquid. The sulpho-stannate is decomposed, most of the tin sulphide will dissolve, and there will be a separation of free sulphur. If the liquid is fairly cool at the time of adding the acid, there will be no great rise in temperature; if the temperature does not exceed 50-55° C. the liberated sulphur will not agglomerate and subsequent oxidation is easily accomplished by adding about two grams of KClO₃ a little at a time to the cool solution, shaking after each addition. After the solution begins to clear, heat it to boiling to remove chlorine. A perfectly clear solution without agglomerations of sulphur should result. Continue boiling for about ten minutes to insure complete expulsion of chlorine. Add 70 cc. of water to the flask, making the volume approximately 200 cc. containing between one-quarter and one-third of its volume of free HCl; this proportion of free acid is important. Introduce a coil of nickel foil, 1½" x 7", rolled around a
glass rod until it will just slip into the neck of the flask, heat the solution to boiling and boil gently for about 20 minutes; connect the flask by means of a double perforated rubber stopper with a current of CO₂ gas and continue boiling for a few minutes. Remove from heat and while a brisk stream of CO₂ is continued immerse the flask in cold water. When the solution is cooled to room temperature disconnect from the source of CO₂ and immediately titrate the tin with N/20 iodine solution using a few drops of starch solution as indicator. It is unnecessary to remove the nickel before titration. A "blank" should be made on the titration by boiling a solution of hydrochloric acid with a foil of nickel under the same conditions as the determination. The correction may amount to 0.2 cc. The iodine solution should be standardized against pure tin dissolved in HCl and KClO₄ and reduced with nickel under the same conditions as the determination.

Notes. Antimony does not interfere; it is precipitated as metal by the nickel and remains as a black precipitate in the bottom of the flask.
Arsenic in minute proportions does not interfere. Where it is known to be present only in small amounts the steps for its elimination may be omitted. Some tungsten ores, however, contain relatively large proportions of arsenic, usually present as arsenopyrite. When a large amount of arsenic is present it should be eliminated as described, otherwise serious errors may be made.

In place of the cumbersome CO₂ apparatus mentioned for use at the end of the reduction with nickel and during cooling, the "tin reduction" apparatus devised by A. Craig and described in The Engineering and Mining Journal, Vol. 106, p. 26, may be used to great advantage.

Copper in Tungsten Ores and Concentrates

Applicable to All Ores Whether Scheelite, Wolframite or Hubnerite

Treat five grams of the fine pulp with 20 cc. of HCl in a 400 cc. beaker and digest with frequent shaking at a low temperature for an hour. Add 5 cc. of HNO₃ and boil down to a volume of, say, 10 cc., cool and add 10 cc. of H₂SO₄ and evaporate to fumes. Cool, add 150 cc. of water and boil. Filter off the separated tungstic acid. All copper is in the acid filtrate, but it is well to test the residue also to be perfectly sure.

In the case of Scheelite it is necessary to add a few cc. of HCl to the acid solution before filtering off the WO₃, since the large amount of CaSO₄ which separates in sulphuric acid solution alone is troublesome to wash and renders the examination of the insoluble residue difficult unless it is removed.

Neutralize the sulphuric acid solution from the WO₃ with NH₄OH, make it just acid with HCl, avoiding any greater excess than is sufficient to dissolve the iron and manganese hydrates. Add 50 cc. of a solution of sodium bisulphite (150 grams per liter) and let stand in a warm place for half an hour with frequent stirring —iron is reduced to the ferrous condition. Add 5 cc. of sodium sulphocyanate (150 grams per liter) and let stand for another hour stirring from time to time. Copper is precipitated as cuprous sulphocyanate free from molybdenum (which frequently occurs in Scheelite), arsenic or other interfering elements. Filter the cuprous sulphocyanate through a double filter, returning the first part of the filtrate to the filter since the precipitate is very fine and is apt to "run through" at first. To prevent this, add a little paper pulp to the filter.

Wash the precipitate with warm water and transfer the wet filter to a porcelain crucible, dry in an oven heated to 250° to 275°. This will char the paper gradually without danger of loss of precipitate. When the paper is thoroughly charred, heat
the crucible in a muffle or over an open burner until all carbon is consumed. Dissolve the mixture of copper sulphide and oxide remaining in the crucible in a few cc. of strong HNO₃ and finish the determination by the electrolytic or iodide methods. Very small amounts of copper are best estimated colorimetrically by comparing the blue color of the ammoniacal solution with a standard in short color tubes. Since the exact determination of copper is sometimes very important, it is advisable always to take a large initial weight of sample (5 grams) unless copper is present in large amount—say two per cent. This is sometimes the case in scheelites containing cupro-scheelite. In examining the residue left by the acid treatment, dissolve the WO₃ in NH₄OH and wash the filter with dilute NH₄OH. Ignite the filter containing the insoluble matter and undecomposed ore and fuse it with KHSO₄ in a porcelain crucible. Dissolve the fusion in water and make the solution strongly alkaline with NH₄OH. Filter off any iron hydrate and insoluble residue and observe whether or not the filtrate shows a blue color. As little as 0.5 mg. can easily be detected in a volume of 50 cc. If there is no blue color, further examination may be omitted. If the qualitative test indicates copper, dissolve any iron hydrate which may have separated in dilute H₂SO₄. Add this solution to the main liquid and slightly acidulate with HCl. Then add sodium bisulphite and sulpho-cyanate, proceeding as in the main determination.

**Manganese in Tungsten Ores and Concentrates**

Treat one gram of the pulp exactly as in the tungsten determination omitting the use of cinchonine, but letting the solution stand until it is cold after decomposition has been effected. Filter off the insoluble residue and tungstic acid and wash it thoroughly with dilute HCl (25 cc. per liter). It is quite difficult to remove every trace of iron and manganese from the heavy WO₃ residue which invariably retains a little unless the precipitate and residue is washed back from the filter and agitated with the wash liquid. The filtrate contains all Mn.

Neutralize the solution by means of Na₂CO₃ until there is a slight permanent precipitate. Dissolve this by adding dilute H₂SO₄ (1-3) leaving the solution very slightly acid. Add two or three grams of ZnO, ground to a cream with water, heat to boiling and titrate Mn with standard permanganate by Volhard's method. See page 304.
METALLIC TUNGSTEN AND TUNGSTEN ALLOYS

Tungsten in Tungsten Metal and Ferro-Tungsten

Treat one gram of the finely ground sample in a large (60 cc.) platinum crucible fitted with a cover with 5 cc. HF; add HNO₃, drop by drop, until the metal dissolves. Add 3–4 cc. H₂SO₄ and evaporate on a steam bath until HNO₃+HF is expelled. Shake gently over a small Bunsen flame until H₂SO₄ fumes strongly. Cool, transfer to a 250 cc. beaker with water, finally wiping the crucible with a little filter paper. A little WO₃ sticks to the crucible; it cannot be removed by wiping. Reserve the crucible. Dilute the contents of the beaker to about 150 cc. with water, add 3 cc. HCl and boil. Remove from the stove and to the hot solution add 5 cc. cinchonine solution and let stand over night (or at least four or five hours). Filter on “ashless paper” and wash with dilute cinchonine solution. Gently ignite the precipitate in the crucible in which it was originally treated. Heat for five minutes with full Bunsen burner flame, cool and weigh. Add about 5 grams Na₂CO₃ and fuse, running the fusion around the side of the crucible to remove all WO₃. Dissolve the fusion in hot water; filter and wash five or six times with hot water. Place the filter in the crucible and ignite, add a little Na₂CO₃ and fuse again. Dissolve the fusion in water, filter and wash very thoroughly with hot water to remove last traces of Na₂CO₃, ignite in the same dish as at first, cool and weigh. The difference between weight of dish plus residue and weight of dish plus tungstic oxide is WO₃.

Dilute Cinchonine Solution. 30 cc. strong cinchonine solution and 30 cc. HCl to one liter.

Strong Cinchonine Solution. 100 grams cinchonine dissolved in dilute HCl (1 part acid, 3 parts water) and diluted to one liter with acid of the same strength.

Method for Phosphorus in Ferro-Tungsten and Tungsten Metal

Treat one gram of the finely powdered sample in a platinum dish, fitted with a gold cover, with 15 cc. HNO₃ (1.42 sp.gr.), add 3 cc. HF and warm gently. When action subsides, add 3 cc. more HF. After action subsides, boil, remove cover and if decomposition is not complete, add more HF and boil again. When solution is complete, wash off the cover and evaporate at a low heat to a volume of about 10 cc. then add 3–4 drops of concentrated permanganate solution and continue evaporation until crusts of WO₃ begin to form at the edges; that is, to a volume of, say, 6 cc. Add 5 cc. H₂SO₄ and evaporate on the stove at a low heat until HF and HNO₃ are expelled and H₂SO₄ fumes are given off. (Strong heat causes spattering and also cause hard, over-baked crusts to form on the bottom of the dish which resist subsequent treatment.) Cool, add 25 cc. H₂O and boil (by agitating over bunsen flame) until all soluble salts are dissolved. Destroy pink color due to excess of permanganate by adding sulphurous acid drop by drop. The pink color may not be very evident but the SO₃ is added anyway to reduce higher oxides of Mn. Boil for a minute or two after adding the SO₃. Add 1.2 grams of pure tartaric acid and when this is dissolved and the solution is cooled to a temperature of about 50° C., add 20 cc. of NH₄OH (0.90 sp.gr.) diluted with an equal volume of water. The precipitated tungstic acid should dissolve completely, giving a clear solution. The solution is hot from the reaction between H₂SO₄ and NH₄OH. While it is
still hot add 10 cc. magnesia mixture and transfer it from the Pt dish to a six-ounce glass stoppered bottle. Set the bottle in ice water and when it is thoroughly cooled, add four or five glass beads, say 6 mm. diameter. Stopper it tightly and shake in an efficient shaking machine for at least ten minutes. The agitation should be violent. The beads aid in starting the formation of the magnesium precipitate; after agitation add 15 cc. of strong NH₄OH and return the bottle to ice water tank or put it in a refrigerator to stand over night. Phosphorus separates as magnesium ammonium phosphate free from tungsten but containing possibly basic magnesium compounds. After standing over night, filter the solution through a 9 cm. paper containing a little paper pulp and wash the bottle and paper thoroughly by small additions of ammonia wash water (1 part NH₄OH, 3 parts H₂O). Do not attempt to remove all the precipitate from the bottle but remove the beads to the filter. Place the bottle under the filter and pour through the filter 60 cc. of HNO₃ of 1.135 sp.gr. (1 part HNO₃, 1.42; 3 parts H₂O) in five successive portions of 12 cc. each letting the acid fall on the upper edges of the filter paper. This dissolves any ammonium magnesium phosphate and washes it into the bottle where any that remained adhering to the glass is also dissolved. Add 12 cc. of NH₄OH (sp.gr. 0.90) to the liquid, cool to 35°C., add 35 cc. molybdiate mixture and proceed according to either of the methods described on pages 368–370 of this volume.

**Notes.** The usual proportions of HNO₃ and HF are reversed in order to provide a constant excess of HNO₃ to oxidize P. The procedure given takes a little longer than when the sample is treated with HF first and HNO₃ is added a little at a time, but solution is finally complete. It is necessary to keep the platinum dish covered after action begins, as the reaction is somewhat violent.

The platinum dishes recommended are:

- 8 cm. in diameter at top.
- 7.8 cm. in diameter at bottom.
- 4 cm. high.

They have flat bottoms and are wire rimmed at top to give additional stiffness. They weigh 68 to 69 grams each and hold about 175 cc. The covers are made of pure gold (for economy) "dished" like a crucible cover to fit the top of the dishes closely. The dishes have small lips to aid pouring. The "tongue" of the cover overlaps the lip. Ordinary round bottomed dishes may be used but the manipulation is much more difficult; there is greater tendency to spattering and danger of local burning or overheating in evaporating to fumes of H₂SO₄. If the separated WO₃ is overheated locally, it does not dissolve readily in NH₄OH. In a flat bottomed dish, the WO₃ is spread in a thin layer and heat is applied evenly all over the bottom.

A good shaking machine should be used. The magnesia precipitate may be started by shaking the bottles by hand, but it is a tiresome job. The solution must be cold—say 8° or 10° when shaking begins.

Permanganate solution is added to insure complete oxidation of phosphorus, as in steel analysis. The color of the permanganate gradually fades in the hydrofluoric nitric solution, but after evaporating to fumes and adding water, the solution is usually slightly pink.

The amount of tartaric acid is limited to 1.20 grams since ammonium tartrate retards the formation of the magnesia precipitate. Complete precipitation can only be obtained by brisk agitation and by keeping the solution very cold followed by long standing in a cold place. By this method, determinations started at 3 p.m. may be completed by noon the next day.
Determination of Sulphur and Silicon in Ferro-Tungsten and Tungsten Metal

Fuse two grams of the finely powdered metal, intimately mixed with 8 grams of dry Na₂CO₃ and 2 grams of powdered KNO₃, in a large platinum crucible (40 cc.). The fusion is best made in an electric muffle to avoid contamination with sulphur contained in illuminating gas. Leach the fusion with 100 cc. of distilled water in a 250 cc. beaker. Filter into a 12 cm. porcelain casserole and wash the residue several times with hot distilled water. The solution contains practically all of the sulphur and most of the tungsten and silica. The residue contains some of each, but not more than traces of sulphur.

Solution. Render the liquid acid with 20 cc. HCl and evaporate to dryness on a steam bath, thus precipitating tungstic acid. After the residue is dry, heat it to 110°-120° C. in an oven to dehydrate silica, take up with 5 cc. HCl and 50 cc. water, add 3 cc. strong cinchonine solution (see tungsten determination) and boil, or heat just short of the boiling point, for half an hour. Let the solution stand until it is cold. By means of the cinchonine all WO₃ is rendered insoluble. Filter through an 11 cm. filter paper (free from ash) which has been liberally treated with an emulsion of filter paper pulp, and wash the residue with dilute cinchonine solution (see tungsten determination). Reserve the residue. The filtrate contains all the sulphur, heat it to boiling and add 10 cc. of barium chloride solution (100 grams BaCl₂·2H₂O to 1000 cc.) boil for ten minutes, allow it to stand over night, filter on a 9 cm. filter paper (free from ash) wash repeatedly with hot water, ignite in platinum and weigh as BaSO₄. If the work is properly carried out every trace of WO₃ is removed from the solution and there is no danger of including BaWO₃ with the BaSO₄. If one suspects that the BaSO₄ is not quite pure, it should be fused with a little Na₂CO₃, leached with water and filtered, the filtrate should be acidulated with HCl, a few drops of cinchonine solution added and the solution evaporated to dryness on a steam bath. The dry residue should be dissolved in a little water, a few drops of HCl added, and any residue filtered off. In the clear filtrate BaSO₄ should be again precipitated as before. The weight of BaSO₄·0.1373 = S.

A “blank” on all reagents must be made parallel with the determination; this is important since all sodium carbonate obtainable contains sulphur and there is sometimes more or less of it in the cinchonine. All evaporation should be made over steam and the operations conducted in a place free from sulphur gases.

Silicon. The residue of tungstic oxide from which the solution for the determination of sulphur was filtered contains most of the silica. The residue from leaching the original fusion contains the rest.

Wash the residue from the Na₂CO₃ fusion from the filter paper with a fine jet of water into a small casserole, add an excess of HCl and evaporate to dryness on a steam bath, heat the dry residue at 110°-120° C. to dehydrate silica and filter on a small filter paper (free from ash). Wash thoroughly with hot dilute HCl (1-10°) and finally with hot water. Reserve the filter.

Wash the residue of tungstic oxide, silica and filter paper pulp from the filter into a small casserole, add 5 cc. of HCl and heat for a few minutes, then filter again through the same paper and wash it thoroughly with hot water. This second washing is necessary to remove sodium salts completely. (The original washing sufficed to remove all of the small amount of sulphur present.) Transfer the well-washed filter and residue to a platinum crucible, add the small filter containing
the little silica recovered from the Na₂CO₃ fusion residue and ignite both to constant weight in a platinum crucible. On account of the presence of filter paper pulp, the ignited residue is porous and friable; if paper pulp had not been used, the WO₃ would be dense and not easily susceptible to the subsequent treatment. Cool the ignited residue of WO₃ and SiO₂ and weigh it. Add two or three drops of H₂SO₄ and 5 or 6 cc. of pure HF. Digest at a gentle heat for some time, and then slowly evaporate off the HF. When H₂SO₄ fumes are evolved, cool and again add HF, digest as before, evaporate off the HF, ignite gently to expel H₂SO₄, and then strongly for ten or fifteen minutes. Cool and weigh. The loss in weight after expulsion is SiO₂ which multiplied by 0.4693 equals silicon.

**Determination of Manganese in Tungsten and Ferro-Tungsten**

The filtrate from the tungstic acid obtained by digesting the residue after evaporation to fumes of H₂SO₄ and digestion with dilute HCl (see tungsten determination) contains all the manganese. Separate iron from this solution by means of a basic acetate precipitation and wash the precipitate thoroughly with a hot dilute solution of sodium acetate, reject the precipitate, and to the filtrate, which contains all the manganese, add 5 cc. of strong NH₄OH, add about two grams of (NH₄)₂S₂O₈. Digest on a steam bath for 45 to 60 minutes, manganese separates as hydrated peroxide. Filter and wash with hot water. Dissolve the precipitate through the filter with ten or fifteen cubic centimeters of H₂SO₄ containing a few drops of H₂SO₄ and wash the filter paper several times with hot dilute H₂SO₄ (10%). Again filter through the same paper into a 500 cc. flask and wash with hot water. Dilute the liquid to a volume of about 200 cc. and boil it for fifteen or twenty minutes until all SO₂ is expelled. Nearly neutralize the solution with a solution of NaOH but still leave it slightly acid, complete the neutralization by adding 5 grams of zinc oxide emulsified by grinding with water, heat again to boiling and titrate manganese in the hot solution with a N/10 solution of KMnO₄ (Volhard's Method).

Acknowledgement is made to Mr. J. A. Holladay, Electrometallurgical Co., for cooperation in the preparation of these methods.
TANTALUM AND Columbium

Cb, at. wt. 93.5; sp. gr. 7.06; m.p. 1950°; oxides CbO, CbO₂, Cb₂O₅.
Ta, at. wt. 181.5; sp. gr. 14.49; m.p. 2900°; oxides TaO₅, Ta₂O₆, Ta₂O₅.

DETECTION

The finely powdered mineral is digested with strong hydrochloric acid, followed by concentrated nitric acid and the mixture taken to dryness. The residue is treated with hydrochloric acid, diluted with water, boiled and filtered. The residue is digested with warm ammonium hydroxide to remove tungsten and the solution filtered from the insoluble material, in which tantalum and columbium will be found, if present in the sample.

Decomposition of the material may be effected according to the procedure described for the detection of tungsten, page 554.

The residue obtained is digested, in a platinum crucible, with hydrofluoric acid and a saturated solution of potassium fluoride added. The mixture is evaporated to small volume and allowed to cool slowly. Tantalum will separate in acicular rhombic crystals (solubility—a part of the salt in 200 parts of water) as potassium fluorotantalate 2KF·TaF₅; columbium separates in plates as the double fluoride, 2KF·Cbf₅, if HF is in excess, or as a double oxy-fluoride 2KF·CbfO₄, if HF is not in excess; the columbium salt being much more soluble (1 part of the salt in 12 parts of water) crystallizes after the crystals of tantalum have formed.

The crystals may be examined under a lens and then treated as follows: The needle-like crystals are heated in a shallow platinum dish or crucible cover with strong sulphuric acid to fumes, the cooled mixture is transferred to a test-tube with water and boiled to precipitate the tannic acid. An opalescent solution is obtained when this precipitate is treated with an excess of hydrochloric acid. Metallic zinc added to this solution produces no color. A light-brown precipitate is obtained with tannic acid in the presence of tantalum. If the crystals of columbium salt are treated in the same way, metallic zinc added to the acid solution will give a blue coloration, and tannic acid an orange-red coloration. Tantalum acid fused with sodium meta-phosphate gives a colorless bead (distinction from silica). The bead moistened with FeSO₄ and heated in the inner flame is not colored red. Columbic acid fused in the same way gives a blue bead in the reducing flame, and a red bead by addition of FeSO₄, and heating in the flame.

ESTIMATION

Tantalum and columbium occur commonly with tungsten in nature. In the following minerals, however, tantalum and columbium form the more important constituents:

Columbite, (Ta·Cb)x(Fe·Mn)O₄; pyrochlore, R₂Cb₂O₆R(Ti·Th)y; hatchet-tilite, 2R(Cb·Ta)O₆ or R₂(Cb·Ta)O₆; fergusonite, R(Cb·Ta)O₆; yttrotantalite, RR(Cb·Ta)O₄·4H₂O; samarskite, R₃R₄(Cb·Ta)₄O₁₁.

Tantalum is used in electric light filaments; it is also used for hardening steel for drills, files, cutting edges, watch springs, and pen points. It is used in rectifiers for alternating currents.
Solution of the Sample

The statements made for solution of the sample in determinations of tungsten apply here also. It is well to keep the following facts in mind: Tantalum is insoluble in the common mineral acids—hydrochloric, nitric and sulphuric acids, but dissolves in hydrofluoric acid. Columbium is insoluble in hydrochloric, nitric and in nitro-hydrochloric acid, but dissolves in hot concentrated sulphuric acid. The oxides Ta₂O₅ and Nb₂O₅ fused with KOH form soluble salts. Nb₂O₅ (not strongly ignited) is soluble in acids, from which (NH₄)₂S and NH₄OH precipitate columbic acid (containing ammonia). Freshly precipitated tantalic acid is soluble in acids, and reprecipitated by NH₄OH. The acid dissolves readily in HF.

Tantaliferous Minerals. Although decomposition may be effected by fusion with potassium acid sulphate, fusion with potassium hydroxide is recommended as being the best flux for opening the minerals. Simpson's process is as follows:¹

Three grams of pure potassium hydroxide are fused in a nickel or silver crucible and the finely powdered mineral (0.5 gram) added, the contents mixed by gently rotating the crucible and fusion kept at a dull red heat for ten minutes longer. The crucible placed in a hole in an asbestos board, Fig. 65, is heated over a free flame for half an hour, the sample being covered. The lid is removed and allowed to cool reversed, if any material clings to this. The cooled crucible, placed in a beaker, is two-thirds filled with distilled water, and a clock-glass immediately placed over the beaker. After the violent reaction has subsided the contents of the crucible are poured into about 10 cc. of dilute hydrochloric acid (sp.gr. 1.08) in a 300-cc. beaker, and the crucible, basin and the lid washed with water, followed by about 20 cc. of the dilute acid, and again with water, adding the washings to the remaining solution. The total volume of the solution should occupy from 80 to 100 cc. A drop or two of alcohol are added to destroy any potassium manganate formed.

Separations

Isolation of Columbium and Tantalum Oxides. Separation from iron, manganese, copper, cobalt, nickel, calcium, magnesium, titanium, and tin. The solution obtained above is boiled with 5 to 10 cc. of hydrochloric acid (sp.gr. 1.16) (less acid may be used if titanium is absent). Columbium and tantalum hydroxides are precipitated. The solution is now diluted to 200 cc. and boiled for fifteen minutes longer to make sure that the precipitation is complete. After settling, the clear solution is decanted through a close-grained filter and the residue, having been transferred to the filter, is washed with dilute hydrochloric acid (sp.gr. 1.08) until the washings give no indication of iron. The residue may contain tantalum, columbium, tungsten, silica, antimony and tin. The greater part of the tin, titanium, and all of the iron, manganese, cobalt, nickel, copper, calcium and magnesium are removed in the filtrate.

Norza. If the filtrate becomes turbid, it is advisable to dilute the solution and repeat the boiling to recover the columbium and tantalum that may still be in solution.

In the presence of appreciable amounts of titanium a soluble double chloride of columbium and titanium is formed, so that the precipitation of columbium

TUNGSTEN, TANTALUM AND COLUMBIUM

is not complete. (See L. Weiss and Landecker, Chem. News, 101, 2, 13, 26, 1910.) The formation of this compound is hindered by the addition of an oxidizing agent—sodium nitrate—to the alkali.

Removal of Tin, Antimony, Tungsten and Silica. Tungsten is removed by digesting the moist precipitate with ammonium hydroxide or sulphide, tungsten being soluble in these reagents. Antimony and Tin are also removed.

Silica is volatilized by heating the residue with sulphuric and hydrofluoric acids according to the standard procedure.

Tin. The oxide may be reduced with hydrogen passed over the heated residue within a boat placed in a combustion tube. The tin may now be dissolved out with hydrochloric acid.

Determination of Columbium and Tantalum

The insoluble residue obtained, freed from other elements by the procedures outlined, is ignited at a red heat for fifteen or twenty minutes and the residue weighed as $Cb_2O_4 + Ta_2O_4$.

Separation of Columbium and Tantalum, Selenium Oxychloride Method.¹

The method depends on the solubility of columbium oxide and the comparative insolubility of tantalum oxide in a mixture of sulphuric acid and selenium oxychloride as found by Victor Lenher.²

The method worked out by H. B. Merrill is as follows:—

The oxides are separated together with titanium dioxide from the other elements by the usual methods and the total percentage of titanium and columbium pentoxides (with titanium) is determined.

A weighed sample (0.2—0.3 g.) of the ignited oxides is boiled with 50 cc. of a 1:1 mixture of selenium oxychloride and strong sulphuric acid (sp. gr. 1.84) in an Erlenmeyer flask, on a sand bath for half an hour, avoiding heating to voluminous fumes. After cooling the solution is carefully decanted from the residue, with suction, through asbestos in a Gooch crucible that has been weighed. The filtrate is poured into a large volume of water and the solution boiled. A white precipitate indicates the presence of columbium. The residue in the flask is again extracted with 20 cc. of the reagent for fifteen minutes, the extract being poured through the asbestos filter and the filtrate tested as before for columbium. The process is repeated until the filtrate upon hydrolysis gives only a faint precipitate, due to traces of dissolved tantalum pentoxide. Three or four extractions are usually sufficient.

The undissolved tantalum pentoxide is transferred to the crucible with a jet of water from a wash bottle, washing unnecessary. The crucible is ignited and weighed, the gain in weight representing tantalum pentoxide.

Columbium (with titanium) is determined by difference. If titanium is present it is determined colorimetrically in a separate sample and its amount deducted from columbium.

¹Henry Baldwin Merrill, Jour. Am. Chem. Soc. 43, 2378 (Nov. 1921).
URANIUM

\[ U, \text{at.wt. } 238.17; \, \text{sp.gr. } 18.7; \, \text{m.p. } <1850^\circ \text{C}; \]
1 \text{ oxides } \text{UO}_2, \text{ UO}_3,

(oxide \text{U}_3\text{O}_8, \text{formed by ignition } = \text{UO}_2 + 2\text{UO}_3)

DETECTION

The mineral is warmed with a slight excess of nitric acid (1 : 1) until decomposition is complete. The solution is diluted with water and then an excess of sodium carbonate added and the mixture boiled and filtered. Sufficient nitric acid is added to neutralize the carbonate, and after expelling the \text{CO}_2 by boiling, sodium hydroxide is added to the filtrate. A yellow precipitate is formed in presence of uranium. The precipitate is insoluble in an excess of the reagent, but dissolves in ammonium carbonate.

\text{Uranous salts} are green or blue and form green or bluish-green solutions, from which alkalis precipitate uranous hydroxide, reddish brown, insoluble in excess, but readily dissolved by ammonium carbonate. Uranous salts are strong reducing agents.

\text{Uranyl salts} (\text{UO}_2\cdot\text{R}_2) are yellow. Alkali carbonates give a yellow precipitate, soluble in excess. \text{UO}_2 is regarded as a basic radical, known as “uranyl.” The radical migrates to the cathode, upon electrolysis of a uranyl solution. Uranyl salts are more stable than uranous and are better known.

\text{Potassium ferrocyanide}, \text{K}_4\text{Fe(CN)}_6, added to uranous or uranyl solutions gives a reddish brown precipitate (or a red color in dilute solutions). The precipitate dissolves in a large excess of \text{HCl}. If sufficient ferrocyanide is present the color changes to green on boiling. Addition of sodium hydroxide to the ferrocyanide precipitate of uranium changes the color to yellow. (Distinction from cupric ferrocyanide. Ferrocyanide gives a green precipitate with vanadium, the color deepens on addition of nitric acid. A blue color is produced with ferric iron. No color change with chromates. Distinction from vanadium, chromium and iron.)

\text{Barium carbonate} precipitates the uranic ion completely (distinction from the ions of nickel, cobalt, manganese, zinc).

\text{Disodium hydrogen phosphate} added to uranyl solutions, in presence of alkali acetates or free acetic acid gives a yellowish white precipitate, \text{UO}_2\text{HPO}_4\cdot x \text{H}_2\text{O}, soluble in mineral acids. Warming promotes precipitation.

\text{Tartaric acid}, certain organic compounds, hydroxylamine hydrochloride, ammonium carbonate, prevent precipitation of uranium by alkalis and ammonia.

1. \text{Oxides} \text{UO}_2, brown or black; \text{UO}_3, brick red; \text{UO}_2\text{(OH)}_2, yellow. All oxides are converted to \text{U}_3\text{O}_8 on ignition with free access of air.

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URANIUM

ESTIMATION

The element occurs in the following minerals: 1

Pitchblende, or uraninite, containing 40 to 90% UO₂.
Autunite, Ca(UO₃)₂·P₂O₅·8H₂O, contains 55 to 62% UO₂.
Torbernite, Cu₂(UO₃)₂·P₂O₅·8H₂O, contains 57 to 62% UO₂.
Carnotite, a vanadate of potassium and uranium, V₂O₅·U₂O₅·K₂O·3H₂O.
Samarckite, a urano-tantalate of iron and yttrium, etc., 10 to 13% UO₂.
Fergusonite, a columbiate of cerium, uranium, yttrium, calcium and iron.

Nearly all the silicates, phosphates and zirconates of the rare earths contain uranium.

The element is used in the ceramic industry for producing yellow, brown, gray, and velvety-black tints. It produces canary-yellow glass. It is used as a mordant in dyeing of silk and wool. It also finds use in photography. The metal is used in cigarette-lighters and self-lighting burners.

Preparation and Solution of the Sample

The element dissolves in hydrochloric and in sulphuric acids; less readily in nitric acid. It is insoluble in alkaline solutions.

The oxide, UO₂, dissolves in nitric acid and in concentrated sulphuric acid.

U₂O₅ is readily soluble in nitric acid, but dissolves with difficulty in hydrochloric acid. V₂O₅ dissolves with difficulty in nitric acid but easily in hydrochloric (red colored solution); U₂O₅ is readily soluble in a mixture of glacial acetic-nitric acids (100 : 5), V₂O₅ and Fe₂O₃ (ignited) are practically insoluble in this reagent.

The salts, UF₆ and UO₂(HPO₄)₂·4H₂O, are insoluble in water, but dissolve in strong mineral acids.

Solution of Ores. One gram or more of the ore is dissolved with 15 to 20 cc. of aqua regia, by placing the mixture first on the steam bath for ten to fifteen minutes and then gently boiling over a low flame or on the hot plate. The solution is taken to dryness, silica dehydrated as usual, the residue treated with 10 cc. of hot dilute hydrochloric acid and diluted to about 50 cc. with hot water and the silica filtered off. Uranium passes into the filtrate. The solution is now treated as directed under Separations. If much silica or acid-insoluble matter is present, this should be treated in a platinum dish with strong hydrofluoric acid, and evaporated twice on the steam bath with hydrochloric acid to expel HF. The residue, dissolved with hydrochloric acid and water, is added to the first portion of solution obtained.

Carnotite. Solution of the ore is readily effected by boiling with nitric acid to which a little hydrofluoric acid is added. One gram of ore with 20 cc. nitric acid and 5 cc. hydrofluoric acid at boiling temperature will be completely decomposed in five minutes. Some authorities recommend addition of sulphuric acid with ores containing barium to break up the combination of barium and uranium. If the lead acetate separation of vanadium is used, the sulphuric acid should be expelled previously to this separation. Consult the gravimetric procedures following the section on “Separations.”
SEPARATIONS

Separation of Uranium from Copper, Lead, Bismuth, Arsenic, Antimony and the Other Members of the Hydrogen Sulphide Group. The solution containing uranium, etc., having an acidity of about 5 cc. strong HCl per 100 cc. of solution, is saturated with hydrogen sulphide and allowed to settle and again saturated with H₂S. The sulphides are filtered off and washed. The filtrate and washings contain the uranium that was present in the sample.

Separation of Uranium from Iron and from Elements Having Water-insoluble Carbonates. The filtrate from the hydrogen sulphide group is concentrated to about 150 cc., and 15 cc. of hydrogen peroxide added. The solution is now neutralized with sodium carbonate and about 3 grams added in excess. After boiling for about twenty minutes, renewing the water evaporated, the hydroxide of iron, insoluble carbonates, etc., are filtered off, washed with hot water and the filtrate set aside for the determination of uranium. To recover any occluded uranium the precipitate is dissolved in just sufficient nitric acid to effect solution, and iron again precipitated by addition of hydrogen peroxide and sodium carbonate and boiling as directed above. The combined filtrates from this precipitate are concentrated to about 250 cc.

Separation of Uranium from Vanadium. Procedure 1. To be Used in the Gravimetric Determination of Uranium. The solution obtained as directed, under the previous separation, is acidified with nitric acid, adding a slight excess, and CO₂ expelled by boiling. The acid is now neutralized with ammonia in slight excess, then re-acidified with nitric acid in slight excess, finally adding about 4 cc. of the strong acid additional. Vanadium is now precipitated as lead vanadate by adding 10 cc. of a 10% solution of lead acetate, followed by sufficient strong ammonium acetate solution (1 vol. strong NH₄OH + 1 vol. H₂O + sufficient glacial acetic acid to neutralize the NH₄OH) to neutralize the free nitric acid (about 20 cc.). The precipitated lead vanadate is allowed to settle for a couple of hours on the steam bath, and is then filtered off (returning the first portions if not perfectly clear) and washed well with hot water. The uranium passes into the filtrate.

The excess of lead remaining in the filtrate is next removed. A marked excess of ammonia is added to the hot filtrate, which is then boiled for about a minute and filtered. No washing required. The precipitate contains all the uranium as ammonium uranate, perhaps some ferric and aluminum hydroxides and a portion of the lead. Most of the lead passes into the filtrate, which is discarded. The precipitate is now treated on the filter with a strong hot solution of ammonium carbonate containing a little free ammonia until all the uranium is dissolved and then washed with the same solution diluted. Most of the admixed lead and other impurities remain on the filter, the lead as carbonate. Sufficient strong hydrogen sulphide water is now added to the filtrate, or the gas is passed to precipitate all the lead remaining. The mixture is heated to boiling and then allowed to stand until clear. Any iron present is precipitated with the lead. Finally, the uranium solution is filtered off and the precipitate washed with hydrogen sulphide water containing a little ammonium carbonate. The filtrate is boiled to expel the hydrogen sulphide and ammonium carbonate and concentrated to 200–250 cc. Uranium is now precipitated and determined by the gravimetric procedure given on page 581a.
Procedure 2. To be Used in the Volumetric Determination of Uranium.
The separation of vanadium from uranium may be effected by precipitation of
the latter as a phosphate according to the following procedure. The solution is
heated and allowed to run in a small stream through a funnel with constricted
stem, into a boiling solution of 15 grams of ammonium acetate, 5 grams of micro-
scopic salt dissolved in 100 cc. of water containing about 5 cc. of glacial acetic
acid. A rod, with a cup-shaped tip, placed in the solution prevents bumping.
The mixture is allowed to boil for a few minutes, the beaker is then removed from
the heat and the precipitate allowed to settle. This is now transferred to a filter
after first decanting off the clear solution. It is washed once with hot water,
then washed back into the beaker and dissolved in a small amount of hot dilute
nitric acid, the precipitate clinging to the filter being dissolved off by the acid,
which is allowed to run through the filter into the beaker. This nitric acid solu-
tion containing the vanadium is diluted to about 75 cc. and the uranium (together
with aluminum if present) again precipitated as the phosphate according to the
procedure described. The precipitate is again transferred to the filter previously
used, and washed off with hot water four or five times. Vanadium passes into
the filtrate. The phosphate is now dissolved off the filter with 15 cc. of hot dilute
sulphuric acid (1 : 3), and uranium determined by titration with permanganate
according to the directions given under the volumetric method described later.

Glacial Acetic Method for Separating Uranium from Vanadium.* Uranium
nitrate or oxide dissolves readily in a mixture of glacial acetic acid and nitric
acid, 20 parts of the former to 1 part of the latter. The nitrate and oxide of
vanadium are insoluble in the reagent. Addition of water causes vanadium to
dissolve. See method for determining uranium in Carnotite under the "Gravi-
metric" methods.

Separation of Uranium from Molybdenum, Tungsten and Vanadium.*
The residue obtained by evaporating a mixture of uranyl nitrate and nitric
acid with ammonium molybdate, or sodium tungstate, or sodium vanadate
to dryness, is slightly moistened with nitric acid (5 ce. HNO₃—1.42) and ex-
tracted with ether; uranium dissolves completely while molybdenum, tungsten
and vanadium remain insoluble. The evaporation is conveniently conducted
in a glass boat of a size that may be placed in the paper thimble of a Soxhlet
extraction apparatus, commonly used with volatile solvents. The extraction
is generally complete after the ether has siphoned over five or six times.

60 (1920).
URANIUM

GRAVIMETRIC DETERMINATION OF URANIUM AS THE OXIDE, $\text{U}_3\text{O}_8$

Procedure. The filtrate containing the uranium, as obtained according to the method given, under "Separations," is made slightly acid with nitric acid and boiled for a short time to ensure the absence of $\text{CO}_2$, then ammonia is added in marked excess, the mixture boiled for about a minute more and filtered. No washing necessary. Either paper or a weighed Gooch crucible may be used for the filtration. The precipitate is dried and ignited to the oxide $\text{U}_3\text{O}_8$, in which form it is weighed.

$$\text{U}_3\text{O}_8 \times 0.8482 = \text{U}.$$  

Notes. The purity of the oxide may be ascertained by dissolving in $\text{HNO}_3$ and testing for vanadium with $\text{H}_2\text{O}_2$ and for $\text{Al}_2\text{O}_3$ by adding $(\text{NH}_4)_2\text{CO}_3$.

Treadwell recommends that the oxide be reduced by hydrogen passed over the red-hot residue, the brown $\text{UO}_2$ being formed. The oxide is cooled in a current of hydrogen.

GRAVIMETRIC METHOD FOR URANIUM IN ORES*

Take 0.5 gram of the finely ground ore, or more, according to richness. Treat by heating gently in an 8-oz. "copper flask" with nitric or hydrochloric acid, or both, together with about 1–2 cc. of hydrofluoric acid, to effect complete solution of the uranium. Sometimes galena is present, in which case it is best to start with 10 cc. or more of hydrochloric acid and heat until the galena is decomposed. Whenever hydrochloric acid is used, boil almost to dryness to expel most of it before continuing. To this residue, or to the original ore, if hydrochloric acid appeared unnecessary, add 10 cc. of nitric acid and 1–2 cc. of hydrofluoric acid. Boil very gently to effect complete decomposition, and finally to approximate dryness. Allow to cool, add 3 cc. of nitric acid and 50 cc. of hot water, and see that everything soluble is dissolved.

Now make slightly alkaline with ammonia, then just acid with nitric acid, and again alkaline with a little solid ammonium carbonate, followed by about 5 cc. of strong ammonia and 3–4 grams of ammonium carbonate.

Boil for about a minute and then filter, having a wetted wad of absorbent cotton in the apex of the filter. Wash twice with hot water. Boil and concentrate the filtrate in a covered beaker during the next step.

Dissolve the precipitate on the filter with a little hot dilute nitric acid, receiving the filtrate in the original flask. Again neutralize and precipitate as before, washing this second precipitate well with hot water. Add the filtrate to the first one and continue the concentration to 150–200 cc. Now acidify with nitric acid, and then, in case of doubt, add about 1 cc. of hydrogen peroxide. A reddish brown color indicates vanadium.

A. Vanadium Present.—Boil to expel any remaining $\text{CO}_2$ make just alkaline with ammonia, then just acid with nitric acid, finally adding about 4 cc. of the latter in excess. The appearance of the liquid is usually a sufficient indication of the neutralization points. Now add 1 gram of lead acetate crystals and then sufficient ammonium acetate solution (about 20 cc.) to neutralize the nitric acid and precipitate the lead vanadate. Boil for about 10 minutes and then filter through a double filter, returning the first portions if not perfectly

*By Albert H. Low.
clear. Wash with hot water. Receive the filtrate in a large beaker. If bulky, boil down to perhaps 200-250 cc. Now add ammonia in marked excess and boil for a minute to expel any CO₂. Filter hot, paying no attention to a turbid filtrate unless it is yellowish (in which case wash the precipitate once with hot water, re-acidify the filtrate with nitric acid, heat to boiling and again precipitate with ammonia, filtering through the previous precipitate). No washing required. Place the last beaker under the funnel and fill the latter with a strong hot solution of ammonium carbonate, to which some free ammonia has been added. Usually one filling is sufficient to dissolve all the uranium and leave a white residue of lead carbonate, perhaps slightly discolored by a trace of iron. Wash with hot water, using a little more of the ammonium carbonate solution, if apparently necessary. Add to the filtrate sufficient strong hydrogen sulphide water to precipitate all the remaining lead (ordinarily 25 cc. of strong hydrogen sulphide water), or pass the gas for a short time. This also removes traces of iron. Heat to boiling, then allow to stand and settle. Filter, washing with hydrogen sulphide water containing some ammonium carbonate. Boil to expel the sulphide, then acidify with nitric acid and boil off all CO₂. Continue according to C.

B. Vanadium Absent.—Boil the nitric acid solution sufficiently to expel all CO₂, then add ammonia in marked excess and boil a little longer to expel any CO₂ in the ammonia. Filter the hot mixture, returning the first portions if not perfectly clear. No washing required. Dissolve the uranium on the filter with hot ammonium carbonate solution, as described in the last paragraph, and continue from this point as in the same situation above. Do not omit the hydrogen sulphide treatment, for, even in the absence of lead, there will usually be traces of iron to be removed. Continue according to C.

C. Add ammonia in marked excess, boil well for one minute and then filter through an ashless filter, returning the first portions if not clear. No washing required. Ignite filter and precipitate thoroughly in a porcelain crucible and weigh, after cooling, as U₃O₈. Impurities are usually present.

Dissolve the residue in the crucible by warming with a little nitric acid. Dilute and test for vanadium with hydrogen peroxide. A faint brownish tinge may be neglected. Rinse the solution into a small beaker, add solid ammonium carbonate in excess, boil a minute or two and then filter through a small filter, washing with hot water. The residue on the filter may consist of alumina and other insoluble matter. Ignite filter and residue in the original crucible, weigh and deduct the weight from that of the impure U₃O₈ found previously.

Ammonium Acetate Solution.—Eighty cc. of strong ammonia, 160 cc. of water and 70 cc. of 90 per cent. glacial acetic acid.

Note.—A yellow filtrate from the ammonium uranate indicates incomplete precipitation. This may be due to a deficiency in ammonium nitrate, as ammonium uranate is perceptibly soluble in pure water. Add a gram or so of ammonium nitrate to the filtrate, boil and refilter. Or, better, dissolve the precipitate on the filter with dilute nitric acid, so that the mixed filtrates will be markedly acid, and repeat the precipitation with ammonia. The filtrate should be colorless.
URANIUM

GLACIAL ACETIC ACID METHOD FOR DETERMINING URANIUM IN CARNOTITE* 

The following method depends upon the fact that uranium nitrate or oxide is soluble in a mixture of glacial acetic and nitric acids in the proportion of 20 parts by volume of the former to 1 part of the latter, while vanadic nitrate and oxide (V₂O₅) are not.¹

Procedure

Half a gram or more of carnitite ore according to its richness (ground to pass 100-mesh sieve) is taken for analysis and digested at boiling temperature with 25 cc. dilute H₂NO₃ (1 : 1) and 1–2 cc. HF. (An amount that will fill a small crucible lid.) The solution is rapidly evaporated to dryness and baked gently to expel water, but not ignited.

Fifteen to 20 cc. of glacial acetic-nitric reagent (20 : 1) are added, rinsing down the sides of the beaker to remove any adhering material, using a policeman if necessary. (The reagent may be conveniently handled in a small wash bottle, the transferring of precipitates and washing with the reagent being necessary, no water being used at this stage.) The residue transferred to a filter is washed with the reagent five or six times, using small portions of the mixture.

The filtrate and glacial washings are rapidly evaporated to dryness and the residue again extracted with glacial-nitric acids.² This extract, free from vanadium,³ is evaporated to dryness, and gently heated over a free flame until the residue turns dark.⁴ Ten cc. of nitric acid and 40 cc. of water are added and the mixture heated to dissolve the uranium.

The greater part of the free nitric acid is neutralized by addition of ammonia (no permanent precipitate should form). Solid ammonium carbonate is added (covering the beaker during the intervals between additions of the carbonate as loss will occur through effervescence in an uncovered beaker) until a precipitate forms that remains undissolved on stirring. 2–3 grams additional ammonium carbonate and 5 cc. of ammonium hydroxide are now added and the solution warmed to conglutate the hydroxides of iron and aluminum. Uranium passes into solution.

The precipitate is filtered off and washed with hot water. The filtrate and washings (concentrated by boiling to about 150 cc.–200 cc. if the volume is large) is acidified with nitric acid (uranium precipitates and dissolves).⁵ Carbon dioxide is expelled by boiling and a decided excess of ammonium hydroxide added. The boiling is now continued until uranium precipitates completely. If the supernatant solution is yellow, it is again acidified with nitric acid, followed by an excess of ammonium hydroxide and the boiling repeated. This generally effects complete precipitation.⁶

The precipitated uranium is filtered off, washing being unnecessary. The filter and precipitate are placed in a crucible, the greater part of the water expelled by drying and the material then ignited. The greenish black residue is weighed as U₂O₅.

This residue should be soluble when boiled with nitric acid.⁷ If it is not, contamination by iron and aluminum is indicated. Any residue remaining should be filtered off, then washed free of uranium with hot water, and ignited. Its weight is subtracted from the uranium oxide to obtain the true value of U₂O₅.

² Method by Wilfred W. Scott.
2. Uranium dissolves completely in the glacial-acetic mixture. A small amount of the vanadium may dissolve, hence the extract is evaporated and the residue again extracted. A smaller quantity of the reagent may be used in this second extraction. 25 cc. of the reagent will dissolve, at boiling temperature, about 4.5 grams of \( \text{U}_2\text{O}_3 \) in five minutes and about 0.003 gram of \( \text{V}_2\text{O}_5 \). The proportion of glacial acetic acid to nitric acid should not fall below \( \frac{10}{1} \), otherwise vanadium will dissolve in appreciable amount. The author uses a round bottom flask filled with cold water, placing this over the beaker to act as a condenser to prevent loss of acetic acid.

3. The acetic acid extract filters rapidly. The red colored residue contains the vanadium and practically all of the silica, iron and alumina.

4. The residue is ignited to destroy organic matter which would prevent precipitation of uranium by ammonia.

5. Uranium carbonate precipitates and then dissolves in the acid when present in excess. \( \text{CO}_2 \) must, be expelled as this prevents precipitation of uranium by ammonium hydroxide.

6. A colored solution indicates the presence of uranium. The nitrate formed by acidification with \( \text{HNO}_3 \) and making alkaline with ammonia with additional boiling insures complete precipitation of uranium.

7. Nitric acid dissolves uranium oxide very easily. The oxide of iron is practically insoluble. Vanadic oxide difficultly soluble.

8. Hydrogen peroxide added to the nitric extract will produce a reddish brown color if vanadium is present.

Wash water used in transferring the uranium precipitate should contain ammonium nitrate to prevent solution of uranium.

**DETERMINATION OF URANIUM IN CARNOTITE**

The following method, worked out by C. E. Scholl, is adapted for eliminating the difficulties in an accurate determination of uranium, caused by the presence of iron, alumina and vanadium, which commonly occur in carnotite.

**Procedure.** To the sample of material containing about 0.2 gram uranium oxide, are added 25 to 50 cc. 1 : 1 nitric acid and heat applied until all the uranium is in solution. If necessary, allow to stand on the water bath to keep warm overnight. After diluting with warm water to 250 cc. the solution is filtered. Ferric chloride, equivalent to about three times the weight of vanadium present, is added. To the cold or slightly warm solution solid sodium carbonate is now added in small portions until all the acid is neutralized and then an excess of 1 gram added, the beaker being kept covered during the intervals between the additions. The sample is placed on a hot plate and heated to about 90° C., but not to boiling. After keeping hot for 15 minutes, the solution is filtered and washed. The residue contains all the iron and vanadium and the greater part of the aluminum. The filtrate is neutralized cautiously with nitric acid until uranium begins to precipitate. The greater part of the \( \text{CO}_2 \) is removed by boiling. Sodium hydroxide is now added in excess and after boiling 15 minutes the solution is filtered. The filtrate contains the remainder of the aluminum and the vanadium not previously precipitated. The precipitate containing the uranium is dissolved in dilute nitric acid and heated to 90° C. and an excess of \( \text{NH}_4\text{OH} \) added and the solution boiled. The precipitate is filtered off, ignited and weighed as uranium oxide, \( \text{U}_2\text{O}_5 \).

The oxide is tested for its purity with nitric acid as in the previous method.

VOLUMETRIC DETERMINATION OF URANIUM BY REDUCTION AND OXIDATION

Introduction. The determination of uranium by oxidation of the lower oxide UO₂ to UO₃ may be accomplished by means of potassium permanganate in precisely the same manner as in the determination of iron, the Jones reductor being used for the reduction of the uranic salt to the uranous form. The metal must be in solution either as a sulphate, a chloride or an acetate, but not as a nitrate. If present as a chloride the usual preventative solution of phosphoric acid and manganous sulphate solution must be present as in case of the titration of a chloride of iron, hence a sulphate solution is to be preferred. Although the degree of reduction varies with conditions, it is found that with brief contact with the oxygen of the air the oxide UO₂ is formed.

Procedure. Solution. The method for preparation of the sample, isolation of the uranium, has been given under Preparation and Solution of the Sample and Separations. The solution from the ammonium carbonate precipitate is acidified with sulphuric acid and boiled to expel the CO₂.

Reduction. The uranium sulphate solution, diluted to a volume of 100 to 150 cc., containing one-sixth of its volume of sulphuric acid, is heated nearly to boiling and the organic matter that may be present oxidized by addition of just sufficient potassium permanganate solution to produce a faint pink color. Fifteen to 20 cc. of dilute sulphuric acid are passed through the 18-in. column of zinc in the Jones reductor, followed by the hot uranium sulphate solution, flowing very slowly, fifteen to twenty-five minutes being required for 0.2 gram uranic oxide, thirty to forty minutes for 0.3 gram of the oxide, care being taken that the liquid in the reductor always covers the zinc. The uranic solution is followed by 10 to 15 cc. of dilute 1:6 solution of sulphuric acid.

Titration. The olive-green solution is poured into a beaker or casserole. The lower oxides are immediately oxidized to UO₂ by the air, as seen by the slight change of color to sea green. The hot solution is now titrated with tenth normal permanganate. The solution during titration gradually becomes more and more yellowish green, as the highest oxidation is approached, until a faint pink color is obtained. With large amounts of uranium the color appears a yellowish pink.

One cc. N/10 KMnO₄ = 0.11925 gram U.

Note. 55.85 grams Fe is equivalent to 119.25 grams U.—Sutton.

C. A. Pierle claims that high results are obtained by this method.


1 Hydrogen dioxide formed by nascent hydrogen in contact with air would vitiate results.—Gooch.
Determination of Uranium in Alloy Steels and Ferro-Uranium

The following method provides for the analysis of steels containing Cr, Mo, V, W, Co, Ni, C, Mn, Si, Al and Ti. A 2 g. sample is dissolved in 75 cc. of 1:1 hydrochloric acid. After solution is complete the solution is oxidized by the dropwise addition of nitric acid. In the case of samples where tungsten is present an easily filterable product is obtained by diluting to 300 cc. and boiling for 15 min. The tungstic oxide is then filtered out and washed, the filtrate and wash waters being returned to the original beaker for evaporation to dryness, followed by baking at a moderate temperature. On dissolving the residue with 50 cc. of 1:1 hydrochloric acid and diluting with hot water, a solution is obtained from which the balance of the silica and the last traces of tungsten can be separated by filtering. The two precipitates after washing are available for the determination of tungsten and silicon by the usual methods. Filtrates and wash waters from these precipitates are combined and evaporated to a syrupy consistency in preparation for the extraction of most of the iron with ether. In the absence of tungsten the original solution is evaporated to dryness and baked with the object of removing silica. After the extraction of the iron, the aqueous layer is evaporated to a small volume to free it from the excess of acid. It is then diluted to a volume of 150 cc. with hot water, and an excess of sodium carbonate in the form of a saturated solution is added. This solution is boiled and, after settling, filtered, the precipitate being washed with hot water. The precipitate consists of the hydroxides of chromium, iron, manganese, cobalt, nickel, copper, and aluminum, if all of these elements are present, together with traces of silica, titanic oxide, phosphorus, and vanadium compounds. The filtrate contains uranium, molybdenum, vanadium, and traces of the elements which occur chiefly in the precipitates.

Bulky precipitates should be dissolved in hydrochloric acid and reprecipitated one or more times with sodium carbonate solution to insure a complete separation of the uranium.

All filtrates from the precipitate are cautiously acidified with sulphuric acid and boiled long enough to insure the complete removal of all carbon dioxide. Ammonia free from carbonate is then added in slight excess. Boiling precipitates the uranium, much of the vanadium, and traces of impurities. The molybdenum is left in the filtrate. Steels contain only small amounts of phosphorus and the contamination of the uranium from this source is usually negligible. If the amount of phosphorus is large, it may be necessary to dissolve the precipitate in nitric acid, and after suitable oxidation, precipitate the phosphoric acid with ammonium molybdate. The phosphorus can then be removed as ammonium phosphomolybdate. The uranium and vanadium may be reprecipitated from this filtrate along with the manganese, if permanganate is used to oxidize the phosphorus, by adding a few drops of sulphuric acid, a small amount of ammonium persulphate, and enough carbonate-free ammonium hydroxide to give an excess. The precipitate obtained by boiling the solution is in the condition corresponding to the first uranium precipitate mentioned above.

The impure uranium precipitate containing phosphorus in negligible

amounts, or free from it, is transferred to a beaker with a little water and solid ammonium carbonate added. On heating this solution under conditions and for a time calculated to result in only a partial decomposition of the ammonium carbonate, the uranium and vanadium go into solution leaving the manganous, iron, and other impurities undissolved. The filtrate is acidified with sulphuric acid and boiled until free from CO₂, when a slight excess of carbonate-free ammonium hydroxide is added. This precipitates only the uranium and vanadium.

The combined precipitates of uranium and vanadium are ignited at dull redness in a platinum crucible, allowing free access of air to reoxidize any reduced material. The ignited residue is weighed as U₃O₈+V₃O₈. In general, only a small part of the vanadium is present in this precipitate, thus making it unavailable for the vanadium determination. It is necessary, however, to determine the vanadium to correct the weight of uranium oxide. This may be done by almost any of the several known methods for determining vanadium. To this end we determine the vanadium after reduction with hydrochloric acid by permanganate titration, and by oxidation with ammonium persulphate and silver nitrate, followed by electrometric titration. The latter method is the more certain and convenient, but the former gives entirely satisfactory results. For the purpose of either method the precipitate is dissolved in 50 cc. of concentrated hydrochloric acid and evaporated with 30 cc. of sulphuric acid (sp. gr. 1.58) until fumes appear. When the titration is to be completed with permanganate, the sulphuric acid solution is diluted to 250 cc. with hot water and titrated at 80° C. to the first pink color. At the same time like quantities of sulphuric and hydrochloric acids are evaporated, diluted, and titrated in similar fashion to obtain a blank correction for the vanadium. When the titration is to be made electrometrically, the sulphuric acid solution is diluted to 250 cc. with hot water, oxidized with silver nitrate and ammonium persulphate and titrated with ferrous sulphate. The weight of vanadium so found is multiplied by 1.784 to convert it into the corresponding weight of the oxide V₃O₈. This weight is subtracted from the weight of the residue U₃O₈+V₃O₈. The corrected weight of the oxide U₃O₈ is converted into the corresponding weight of uranium by multiplying by 0.8483 from which the percentage of uranium can be calculated.
VANADIUM

V, at. wt. 50.96; sp. gr. 6.025; m.p. 1720° C.; oxides \( \text{VO}_3, \text{VO}_2, \text{V}_2\text{O}_5, \text{V}_2\text{O}_3 \);
vanadates—meta \( \text{Na}_2\text{VO}_3 \), ortho \( \text{Na}_2\text{VO}_5 \), pyro \( \text{Na}_2\text{V}_2\text{O}_5 \), tetra \( \text{Na}_4\text{HV}_2\text{O}_7 \), hexa \( \text{Na}_6\text{H}_2\text{V}_3\text{O}_11 \).

DETECTION

Ammonium Sulphide or Hydrogen Sulphide passed into an ammoniacal solution of vanadium precipitates brown \( \text{V}_2\text{S}_5 \), soluble in an excess of alkali sulphide and in alkalies, forming the brownish-red thio-solution, from which the sulphide may be reprecipitated by acids.

Reducing Agents. Metallic zinc, sulphites (\( \text{SO}_3 \)), oxalic acid, tartaric acid, sugar, alcohol, hydrogen sulphide, hydrochloric acid, hydrobromic and hydroiodic acids (\( \text{KI} \)) reduce the acid solutions of vanadates with formation of a blue-colored liquid. (See Volumetric Methods.) Reduction is hastened by heating.

Hydrogen Peroxide added to a cold acid solution of vanadium produces a brown color, changing to blue upon application of heat.

Solid Ammonium Chloride added to a neutral or slightly alkaline solution of a vanadate precipitates the colorless, crystalline salt, \( \text{NH}_4\text{VO}_4 \), insoluble in ammonium chloride. The amonium metavanadate ignited is decomposed, ammonia volatilizing and the red pentoxide of vanadium remaining as a residue.

The colorless ammonium vanadate solution becomes yellow when slightly acidified. Acids produce a red color when added to the solid salt.

The oxide, \( \text{V}_2\text{O}_5 \), is distinguished from \( \text{Fe}_2\text{O}_3 \) by the fact that it fuses very readily with the heat of Bunsen burner, whereas the oxide of iron, \( \text{Fe}_2\text{O}_3 \), is insubflusible in the heat of a blast lamp. M.p. \( \text{V}_2\text{O}_5 = 658° \text{ C.} \); m.p. \( \text{Fe}_2\text{O}_3 = 1548° \text{ C.} \).

Comparison of Vanadium and Chromium Salts. Vanadium, like Chromium, forms a soluble salt upon fusion with sodium carbonate and potassium nitrate or with sodium peroxide. The solution of vanadates and of chromates are yellow or orange; the color of the chromate becomes more intense when strongly acidified, whereas that of the vanadate is reduced. The yellow color of the vanadate solution is destroyed by boiling with an excess of alkali, but may be restored by neutralizing the alkali with acid. The chromate color is not destroyed. (Yellow with alkalies, orange in acid solution.) Silver nitrate produces a dark-maroon precipitate with a soluble chromate and an orange-colored precipitate with a vanadate; mercurous nitrate produces a red-colored precipitate with chromates and a yellow with vanadates. Vanadates are also distinguished from chromates by the reduction test; reducing agents such as a soluble sulphite, or sulphurous acid added to acid solutions, form a blue-colored liquid with vanadates and a green color with chromates. Ammonium hydroxide added in excess to the cold reduced solutions

1 Reduction with zinc is rapid with vanadates, much less vigorous with chromates. \( \text{V}_2\text{O}_5 \) reduced to \( \text{V}_2\text{O}_3 \), color changes to blue, green, lavender and finally violet. \( \text{Fe}_2\text{O}_3 \) or \( \text{H}_2\text{S} \) reduces \( \text{V}_2\text{O}_5 \) to \( \text{V}_2\text{O}_4 \). \( \text{V}_2\text{O}_5 \) forms vanadyl salts.

Chapter by Wilfred W. Scott.
gives a brown color, or a brown to dirty green precipitate with vanadium, and violet or lavender color or a light green-colored precipitate with chromium, depending upon the concentration of the solutions. Hydrogen peroxide added to the reduced cold acid solutions changes the vanadium blue to reddish brown; the chromium green remains unchanged.

Detection of Vanadium in Steel. Five grams of the sample are dissolved in dilute nitric acid, the nitrous fumes boiled off, the solution cooled, and an excess of sodium bisulfate added. After filtering through an asbestos filter an excess of concentrated ferrous sulphate solution is added, and the solution divided into two equal parts in test-tubes. To one portion 10 cc. of hydrogen peroxide are added and to the other 10 cc. of water. If vanadium is present the peroxide solution will show a deeper color than the untreated solution. A deep red color is produced with high vanadium steels and a brownish-red with low. Since titanium also causes this color, it would interfere, if it were not for the fact that the color produced with titanium is destroyed by hydrofluoric acid and fluorides, whereas that of vanadium is not. In presence of titanium, 5 cc. of hydrofluoric acid are added to the treated sample.

The brown color produced by hydrogen peroxide, with vanadium solutions, will remain in the water portion when shaken with ether. The ether layer is colored a transient blue in presence of chromium.

ESTIMATION

The materials in which the estimation of vanadium is desired may be surmised from the following facts: Industrial application. Vanadium is used in special iron and steel alloys. It increases the strength of steel as well as the compression power, without loss of hardness, and increases the resistance to abrasion; hence vanadium steels are used in locomotive and automobile cylinders, pistons, bushings and in all parts of machines subject to jar. It is used in high-speed tools, vanadium bronzes for gears, trolley wheels, etc. It is used in indelible inks, and in the form of alkali vanadates and hypovanadates it serves as a mordant for aniline black on silk, for calico printing and like uses. Vanadium salts are used in ceramics where a golden glaze is desired.

The element occurs widely distributed in minute quantities. It is found in iron ores, hence occurs in blast-furnace slags as the oxide, $V_2O_5$. The principal ores are:

*Patronite*, a sulphide of vanadium containing 28 to 34% $V_2O_5$, associated with pyrites and carbonaceous matter; the principal source of vanadium.

*Vanadinite*, $(PbCl)Pb(VO_3)_3$, containing 8 to 21% $V_2O_5$.

*Carnotite*, $K_2O\cdot 2UO_3\cdot V_2O_5\cdot 3H_2O$, contains 19 to 20% $V_2O_5$.

*Desolozite*, $(PbZn)_2VO_5$, contains 20 to 22% $V_2O_5$.

*Roscoelite*, a vanadium mica with variable composition.

*Euypnychite*, contains 17 to 24% $V_2O_5$.

*Cuprodesolozite*, $(PbZnCu)_3(OH)VO_6$, contains 17 to 22% $V_2O_5$.

*Calciosilberthite*, $(CuCa)_3(OH)VO_6$, contains 37 to 39% $V_2O_5$.

Vanadium occurs in ores of copper and lead, it is present in certain clays and basalts, in soda ash, phosphate soda, and in some hard coals.
Preparation and Solution of the Sample

In decomposition of the material for analysis the following facts regarding the solubility of the metal, its oxides and principal salts, will be helpful:

Element. The metal is not attacked by aqueous alkalies, but is soluble by fusion with potassium or sodium hydroxide, and sodium carbonate containing potassium nitrate. It is insoluble in dilute hydrochloric and sulphuric acids. It dissolves in concentrated sulphuric acid and in dilute and concentrated nitric acid forming blue solutions.

Oxides. \( \text{V}_2\text{O}_5 \) is easily soluble in dilute acids, giving a lavender-colored solution.

\( \text{V}_2\text{O}_5 \) is insoluble in hydrochloric and sulphuric acids, and in alkali solutions. It dissolves in hydrofluoric acid, and in nitric acid.

\( \text{V}_2\text{O}_5 \) is easily soluble in acids, forming blue-colored solutions. It dissolves in alkali solutions.

\( \text{V}_2\text{O}_5 \) is soluble in acids, alkali hydroxide and carbonate solutions. Insoluble in alcohol and acetic acid.

Salts. Ammonium meta vanadate, \( \text{NH}_4\text{VO}_3 \), is slightly soluble in cold water, readily soluble in hot water. The presence of ammonium chloride renders the salt less soluble. The vanadates of lead, mercury and silver are difficultly soluble in water. Those are dissolved, or are transposed by mineral acids, the vanadium going into solution; i.e., lead vanadate treated with sulphuric acid precipitates lead sulphate and vanadic acid passes into solution.

General Procedure for Decomposition of Ores. One gram (or more) of the finely divided material is placed in a large platinum crucible together with five times its weight of a mixture of sodium carbonate and potassium nitrate (\( \text{Na}_2\text{CO}_3:10, \text{KNO}_3:1 \)). The product is heated to fusion over a blast lamp and, when molten, about 0.5 to 1 gram more of the nitrate added in small portions. (Caution—platinum is attacked by \( \text{KNO}_3 \). A large excess of \( \text{Na}_2\text{CO}_3 \) tends to prevent this.) The material should be kept in quiet fusion for ten to fifteen minutes, when most of the ores will be completely decomposed. The cooled fusion is extracted with boiling water, whereby the vanadium goes into solution. Arsenic, antimony, phosphorus, molybdenum, tungsten and chromium pass into solution with the vanadium. These must be removed in the gravimetric determination of this element. (Iron remains insoluble in the water extract.)

Should there be any undecomposed ore, the residue from the water extract will be gritty. If this is the case, a second fusion with the above fusion mixture should be made.

Small amounts of occluded vanadium may be recovered from the water-insoluble residue by dissolving this in nitric acid and pouring the solution into a boiling solution of sodium hydroxide. Vanadium remains in solution.

Vanadium may be determined volumetrically after removal of the hydrogen sulphide group, by titration with potassium permanganate according to the procedure given later. The isolation and determination of vanadium by the gravimetric procedures are given in detail later.

Ores and Material High in Silica. The sample is treated in a platinum dish with about ten times its weight of hydrofluoric acid (10 to 50 cc.) and 2 to 5 cc. of strong sulphuric acid. The silica is expelled as \( \text{SiF}_4 \) and the hydrofluoric acid driven off by taking the solution to \( \text{SO}_3 \) fumes. The residue is extracted with hot water containing a little sulphuric acid. Any undissolved residue may be brought
into solution by fusion with potassium acid sulphate, KHSO₄, and extraction with hot water containing a little sulphuric acid. By this treatment the iron passes into solution with vanadium.

**Products Low in Silica.** Decomposition may be effected by fusion in a nickel crucible with sodium peroxide and extraction with water. The water should be added cautiously, as the reaction is vigorous. One gram of the finely divided ore is intimately mixed with 3 to 4 grams of Na₂O₂ and 1 gram of the peroxide placed on the charge. The material is then fused as stated.¹

**Iron and Steel.** The solution of the sample, isolation of vanadium and its volumetric determination are given at the close of the chapter.

**Alloys.** These may be decomposed with nitric acid, or aqua regia. The isolation of vanadium with mercurous nitrate or lead acetate are given under the gravimetric methods.

**SEPARATIONS**

Fusion with sodium carbonate and potassium nitrate and extraction of the melt with water effect a separation of vanadium from most of the metals, which remain insoluble as carbonates or oxides. Arsenic, molybdenum, tungsten, chromium and phosphorus, however, pass into the filtrate with vanadium.

**Removal of Arsenic.** This element generally occurs in vanadium ores. It may be removed when desired, by acidifying the water extract of the fusion with sulphuric acid, and after reducing arsenic with SO₃, precipitating the sulphide, As₂S₃, with H₂S gas. Vanadium passes into the filtrate.

**Removal of Molybdenum.** The procedure is similar to that used for arsenic, with the exception that the sulphide of molybdenum is best precipitated under pressure. The solution in a pressure flask is treated with H₂S. The flask is stoppered and heated in the steam bath. It is advisable to resaturate the solution with H₂S before filtering off the sulphide.

**Separation from Phosphoric Acid.** In the gravimetric procedure phosphorus and vanadium are precipitated together as mercuric vanadate and phosphate. The mercury is expelled by heat and the oxides V₂O₅ and P₂O₅ weighed. (V₂O₅ in presence of P₂O₅ does not melt as it does in pure form, but only sinters.) The oxides are fused with an equal weight of sodium carbonate, the melt dissolved in water, then acidified with sulphuric acid and vanadium reduced to the vanadyl condition by SO₃ gas. The excess of SO₃ is expelled by boiling and passing in CO₂. Phosphoric acid is now precipitated with ammonium molybdate (50 cc. of a solution containing 75 grams ammonium molybdate dissolved in 500 cc. of water acid poured into 500 cc. nitric acid—sp. gr. 1.2) in presence of a large amount of ammonium nitrate and a little free nitric acid. It is advisable to dissolve the precipitate in ammonia and reprecipitate in presence of additional ammonium molybdate and nitrate by acidifying with nitric acid. The equivalent P₂O₅ is deducted from the weight of the combined oxides, the difference being due to V₂O₅.

**Note.** Vanadium must be completely reduced to the vanadyl form, as vanadic acid will precipitate with phosphoric acid.

¹Direct reduction and titration of vanadium in presence of a large accumulation of salts leads to erroneous results. The vanadium should be separated by precipitation with lead acetate.
Separation of Vanadium and Chromium. A volumetric procedure for determining vanadium and chromium in the presence of one another is given. If a separation is desired the following procedures may be used:

A. The solution is acidified with nitric acid. If hydrochloric acid is present it is expelled by taking to near dryness twice with nitric acid, the residue is taken up with water and SO₂ gas passed in to completely reduce the vanadium. This solution is poured into a boiling solution of 10% sodium hydroxide. After boiling a few minutes, the solution is filtered and the residue washed. The filtrate contains vanadium, the residue chromium. It is advisable to pour the filtrate into additional caustic to remove the small amount of chromium that passes into the solution.

B. One hundred cc. of the neutral solution is made acid with about 15 cc. of glacial acetic acid and hydrogen peroxide added. The solution is boiled for a few minutes. Chromium is thereby reduced to Cr₂O₃, whereas vanadium appears as V₂O₅. Lead acetate will now precipitate lead vanadate, the reduced chromium remaining in solution. The lead vanadate now treated with strong sulphuric acid is decomposed upon heating. Addition of water precipitates PbSO₄, the vanadium remaining in solution.

GRAVIMETRIC METHODS

The following procedures presuppose that vanadium is present in the solution as an alkali vanadate, the form in which it occurs in the water extract from a fusion with sodium carbonate and potassium nitrate, as is described in the method of solution of ores containing vanadium. Chromium, arsenic, phosphorus, molybdenum and tungsten, if present in the ore will be found in this solution.

Mercurous Nitrate Method for Determination of Vanadium—Gravimetric

Principle. A nearly neutral solution of mercurous nitrate precipitates vanadium completely from its solution. The dried precipitate ignites forms the oxide, V₂O₅, mercury being volatilized.

Procedure. To the alkaline solution or an aliquot portion of the water extract from the sodium carbonate potassium nitrate fusion nearly neutralized with nitric acid ² (the solution should remain slightly alkaline) is added drop by drop, a nearly neutral solution of mercurous nitrate in slight excess of that necessary to precipitate completely the vanadium present, as may be determined by allowing the precipitate to settle and adding a few drops more of the reagent. The mixture is heated to boiling and then placed on the water bath or steam plate and the gray-colored precipitate allowed to settle. The precipitate is washed several times

² Should the alkaline solution of the vanadate be made acid, nitrous acid, from the nitrate fusion, will be liberated and cause reduction of the vanadate to the vanadyl salt, in which form it is not precipitated by mercurous nitrate; hence great care should be used in neutralizing the alkaline solution to avoid making it acid. It is a good practice to measure the acid added, having determined on an aliquot portion the amount necessary to add to neutralize the solution. This is readily accomplished when a comparatively large sample has been prepared for analysis and an aliquot portion taken for analysis, several determinations being made on the same fusion.
with water containing a few drops of mercurous nitrate, washing once or twice by decantation and finally on the filter paper. The precipitate is dried, then ignited in a porcelain crucible in a hood over a Bunsen burner to a red heat. The fused red residue is \( V_2O_5 \).

\[ V_2O_5 \times 0.5604 = V. \]

**Gravimetric Method of Determining Vanadium by Precipitation with Lead Acetate**

**Principle.** From a weakly acetic acid solution, vanadium is quantitatively precipitated by lead acetate. The precipitate is dissolved in nitric acid, lead removed as a sulphate, and vanadium determined in the filtrate by taking to dryness and igniting to the oxide, \( V_2O_5 \).

**Procedure.** To the alkaline solution or an aliquot portion obtained by extraction of the carbonate fusion of the ore with water, just sufficient amount of nitric acid is added to nearly neutralize the alkali present, as in the case of the method described for precipitation of vanadium by mercurous nitrate, and then a 10% solution of lead acetate is added in slight excess with continuous stirring. The precipitate is allowed to settle on the steam bath. The vanadate, first appearing orange colored, will fade to white upon standing. The lead vanadate is filtered and washed free of the excess of lead acetate with water containing acetic acid. The precipitate is washed into a porcelain dish with a little dilute nitric acid, and brought into solution by warming the lead salt with nitric acid. To this, the ash of the incinerated filter is added. Sufficient sulphuric acid is added to precipitate completely the lead, and the solution taken to small volume on the water bath and then to \( SO_3 \) fumes, but not to dryness. About 100 cc. of water are added and the mixture filtered; lead sulphate will remain upon the filter and the vanadium will be in solution. The lead sulphate is washed free of vanadium (i.e., until the washings no longer give a brown color with hydrogen peroxide).

The filtrate containing all the vanadium is evaporated to small volume in the porcelain dish, then transferred to a weighed platinum crucible and evaporated to dryness on the water bath and finally the residue (\( V_2O_5 \)) heated to a dull redness over a Bunsen flame.

\[ V_2O_5 \times 0.5604 = V. \]

**Notes.** Lead may be separated from the vanadium by passing \( H_2S \) through the nitric acid solution, the excess of \( H_2S \) volatilized by boiling and the liberated sulphur filtered off. The filtrate is evaporated to dryness and the vanadium ignites with a few drops of nitric acid to the oxide \( V_2O_5 \).

Lead may also be separated as lead chloride in the presence of alcohol, the solution taken to dryness and vanadium oxidized by addition of nitric acid and ignited to \( V_2O_5 \).

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Volumetric Procedures for the Determination of Vanadium

Reduction of the Vanadate, $V_2O_5$, to Vanadyl Condition, $V_2O_4$, and Reoxidation with Potassium Permanganate

**Principle.** Vanadium in solution as a vanadate is reduced to the vanadyl salt by $H_2S$ or $SO_2$, the excess of the reducing agent expelled and the solution titrated with standard $KMnO_4$, vanadium being oxidized to its highest form, $V_2O_4$.

**Reactions.**

- $a. V_2O_5 + SO_2 = V_2O_4 + SO_3$
- $b. V_2O_4 + O = V_2O_5$

$N/10$ sol. = $\frac{At. \text{ wt. } V}{10}$ grams to the liter.

**Procedure.** An aliquot portion of the solution containing vanadium, as obtained by one of the procedures given for the solution of the sample, is taken for analysis; dilute sulphuric acid (1 : 1) is added to acid reaction and 5 cc. of acid per 100 cc. of solution added in excess. The vanadium content should be not over 0.5 gram V when a tenth normal permanganate is used for the titration. *If arsenic or molybdenum is present* these may be removed from the solution by passing in $H_2S$. The insoluble sulphides are filtered off and washed with $H_2S$ water. The filtrate is boiled down to two-thirds of its volume and the sulphur filtered off. In the absence of members of the $H_2S$ group, this portion of the procedure is omitted.

**Oxidation with $KMnO_4$.** The solution containing the vanadium is oxidized by adding, from a burette, tenth normal potassium permanganate to a faint permanent pink. If the solution has been treated with $H_2S$, the vanadium is in the vanadyl condition, and the amount of permanganate required to oxidize the solution completely will give a close approximate value for the vanadium present, each cc. of $N/10$ $KMnO_4$ being equivalent to 0.0051 gram vanadium.

**Reduction.** The vanadate is now reduced to vanadyl salt by passing through the acid solution, containing approximately 5% free sulphuric acid, a steady stream of $SO_2$ gas. Reduction may also be accomplished by adding sodium metabisulphite, or sodium sulphite, to the acid solution. The excess $SO_2$ is now removed by boiling (a current of $CO_2$ passed into the hot solution will assist in the complete expulsion of the $SO_2$).

**Note.** $KMnO_4$ is reduced by $SO_2$.

**Test for Iron.** A drop test with potassium ferricyanide, $K_4Fe(CN)_6$, on a white tile will give a blue color in the presence of ferrous iron. Since ferrous iron will titrate with potassium permanganate, its oxidation is necessary. This is accomplished by adding tenth normal potassium dichromate solution cautiously to the cold liquid until no blue color is produced by the spot test with $K_4Fe(CN)_6$ outside indicator. If the sample is sufficiently dilute, the blue color of the vanadyl solution will not interfere in getting the point where the iron is completely oxidized. Care must be taken not to pass this end-point, otherwise $V_2O_4$ will also be oxidized and the results will be low.

**Note.** The action of the dichromate is selective to the extent that iron is first oxidized and then $V_2O_4$. If the amount of iron present is large a separation must be effected. In case a sodium carbonate potassium nitrate fusion has been made and
vanadium has been extracted by water, iron will not be present. A special procedure for determination of vanadium in steel is given.

**Potassium Permanganate Titration.** N/10 KMnO₄ is now cautiously added until a pink color, persisting for one minute, is obtained. During the titration the solution changes from a blue color to a green, then a yellow and finally a faint pink. The reaction towards the end is apt to be slow if made in a cold solution.

Norrës. In absence of chromium, it is better to make the titration in a hot solution, 60 to 80° C, the end-point being improved by heat. In case an excess of permanganate has been added, the excess may be determined by a back titration with tenth normal thiosulphate. The solution may be rerun, if desired, by repeating the reduction with SO₂ and the titration with K₅C₃O₇ and KMnO₄.

One cc. N/10 KMnO₄ = 0.0051 gram V₅ or = 0.00912 gram V₂O₅.

For solutions containing less than 0.5% vanadium a weaker permanganate reagent should be used. A fiftieth normal permanganate solution will be found to be useful for materials low in vanadium.

The author obtained excellent results by the above procedure on materials containing small amounts of iron and chromium; with amounts equal to that of vanadium present in the solution no interference was experienced. The titration with potassium permanganate is made in cold solutions if chromium is present, as the permanganate will oxidize chromium in hot solutions. Potassium permanganate added to samples containing chrome salts, and the mixture boiled, will oxidize these quantitatively to chromates. This reaction does not take place in cold solutions to any appreciable extent during a titration and only slowly in warm solutions.

**Volumetric Determination of Vanadium by Reduction with Zinc to V₂O₂**

The procedure proposed by Gooch and Edgar is to reduce vanadic acid, in presence of sulphuric acid, by zinc to the oxide, V₂O₂; oxidation of the unstable V₂O₅ by the air is anticipated by means of ferric chloride or sulphate, in the receiver of the Jones reductor, the highest degree of reduction being registered by the ferrous salt formed by the reaction of the reduced vanadate on the ferric salt, i.e., V₂O₅ + 3Fe₂O₃ = 6FeO + V₂O₅. Compounds reduced by zinc and oxidized by KMnO₄ must be absent or allowed for.

**Procedure.** The Jones reductor is set up as directed in the procedure for the determination of iron by zinc reduction. The receiver attached to the tube containing the column of zinc is charged with a solution of ferric alum in considerable excess of that required for the oxidation of the reduced vanadium. (The amalgamated zinc is cleaned by passing through the column, a dilute solution of warm sulphuric acid. The final acid washings should show no further reducing action on permanganate when the reductor is clean.)¹ Gentle suction is applied, and through the column of clean amalgamated zinc are passed in succession—100 cc. of hot water, 100 cc. of 2.5% sulphuric acid, and then the solution of vanadic acid diluted to 25 cc. in a 2.5% sulphuric acid solution, and finally 100 cc. of hot

¹ Corrections should be made for the action of zinc upon the reagents without the vanadic acids, as it is almost impossible to get a condition where no blank is obtained with permanganate. The reductor is cleaned first by passing about 500 cc. of dilute 2.5% sulphuric acid through the column of zinc. A blank is now obtained with the same quantity of reagents as is used in the regular determination, only omitting the vanadium, and this is deducted from the titration obtained for each sample reduced.
water. To the receiver is added a volume of 4 cc. of syrupy phosphoric acid to
decolorize the solution. The reduced iron salt is now titrated with N/10 KMnO₄.

One cc. N/10 KMnO₄ = 0.0017 gram V, or = 0.00304 gram V₂O₅.

Determination of Vanadium in Steel

The following method is used in analyzing the Bureau's vanadium and chrome-
vanadium steels. The procedure was worked out by J. R. Cain and L. F. Witmer
of the U. S. Bureau of Standards.

Five to 10 grams of drillings are dissolved in hydrochloric acid (1 : 1), a few
drops of hydrofluoric acid 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 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% sodium hydroxide solution, stirring vigorously.
The solution is filtered, and the series of operations are 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 N/50 permanganate after complete expulsion of
the excess of reducing agent.

Volumetric Determination of Molybdenum and Vanadium in
Presence of One Another

Sulphur dioxide reduces V₂O₅ to V₆O₁₄, but does not reduce molybdic acid
provided the sample contains 1 cc. of free sulphuric acid per 50 cc. of solution and
not more than 0.2 gram of molybdic acid. By means of amalgamated zinc V₂O₅
is reduced to V₆O₁₄ and MoO₃ to MoO₂. Upon these two reactions the deter-
mination is based according to the procedure worked out by Edgar.¹ Details
of the method are given in the chapter on Molybdenum, page 321.

Volumetric Determination of Vanadium, Arsenic or Antimony in Presence of One Another. Edgar’s Method

Tartaric or oxalic acid reduces $V_2O_5$ to $V_2O_4$, but does not act upon arsenic or antimony. On the other hand SO$_3$ causes the reduction of all three. Therefore if aliquot portions of the solution are taken, one portion being treated with tartaric acid and vanadium determined by titration with iodine, and another portion reduced with SO$_2$ and again titrated with iodine, the difference between the two titrations is due to the cc. of reagent required for the oxidation of the reduced arsenic or antimony.

Reactions. $\text{V}_2\text{O}_4 + \text{I}_2 + \text{H}_2\text{O} = \text{V}_2\text{O}_5 + 2\text{HI}$.
$\text{As}_2\text{O}_3 + \text{V}_2\text{O}_4 + 3\text{I}_2 + 3\text{H}_2\text{O} = \text{As}_2\text{O}_5 + \text{V}_2\text{O}_4 + 6\text{HI}$.
$\text{Sb}_2\text{O}_3 + \text{V}_2\text{O}_4 + 3\text{I}_2 + 3\text{H}_2\text{O} = \text{Sb}_2\text{O}_5 + \text{V}_2\text{O}_4 + 6\text{HI}$.

Vanadium. One portion is boiled with about 2 grams of tartaric or oxalic acid, until the solution turns the characteristic blue of vanadium tetraoxide. After cooling, the solution is nearly neutralized with potassium bicarbonate, and an excess of standard iodine solution added. Neutralization is now completed, an excess of bicarbonate added, and after fifteen to thirty minutes the excess iodine titrated with standard arsenious acid, starch being used as an indicator. This titration measures the vanadium present.

Arsenic or Antimony. A second portion of the solution is placed in a pressure flask and acidified with sulphuric acid. A strong solution of sulphurous acid is added, the flask closed and heated for an hour on the steam bath. After cooling, the flask is opened and the solution transferred to an Erlenmeyer flask and the excess of SO$_3$ removed by boiling, a current of CO$_2$ being passed through the liquid. The cooled solution is treated with bicarbonate, iodine added and the titration conducted exactly as described for determination of vanadium in the first portion. The difference between the first titration and the second is a measure of the cc. required for oxidation of arsenic or antimony.

Determination of Vanadium and Iron in Presence of Each Other

The solution slightly acidified with sulphuric acid is treated with sulphurous acid, the excess expelled and the reduced vanadium and iron titrated with standard potassium permanganate.

$$10\text{FeO} + 5\text{V}_2\text{O}_4 + 6\text{H}_2\text{SO}_4 + 4\text{KMnO}_4 = 5\text{Fe}_2\text{O}_3 + 5\text{V}_2\text{O}_5 + 2\text{K}_2\text{SO}_4 + 4\text{MnSO}_4 + 6\text{H}_2\text{O}.$$  

The solution is now reduced with zinc in the Jones reductor and again titrated with permanganate. $V_2O_5$ is reduced by zinc to $V_2O_4$, the sample being caught

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2 Gooch, "Methods of Chemical Analysis."
4 When the color has changed from a bluish-green to greenish-yellow the solution is heated to 70 to 80° C., and the permanganate titration completed in a hot solution.
in ferric alum solution (details for determining of vanadium by reduction with zinc are given under the volumetric methods for this element).

\[ 10\text{FeO} + 5\text{V}_2\text{O}_5 + 12\text{H}_2\text{SO}_4 + 8\text{KMnO}_4 = 5\text{Fe}_2\text{O}_3 + 5\text{V}_2\text{O}_5 + 4\text{K}_2\text{SO}_4 + 8\text{MnSO}_4 + 12\text{H}_2\text{O}. \]

The difference between the two titrations multiplied by 0.00456 = vanadic acid (V\(_2\)O\(_5\)) originally present.

**Iodometric Method for Estimation of Chromic and Vanadic Acids in Presence of One Another**

The following procedure developed by Edgar,\(^1\) is given by Gooch ("Methods of Chemical Analysis ").

In carrying out the operation, the alkali salts of the chromic and vanadic acid are put into the Voit flask of the distillation apparatus shown in the cut, Fig. 71.

One or 2 grams of potassium bromide are added, the flask is connected with the absorption apparatus containing a solution of potassium iodide made alkaline with sodium carbonate or sodium hydroxide, and the whole apparatus is filled with hydrogen gas. Fifteen to 20 cc. of concentrated hydrochloric acid are added through the separatory funnel and the solution is boiled for ten minutes, an interval of time found to be enough for the completion of the reduction. A slow current of hydrogen is maintained to avoid back suction of the liquid from the Drexel bottle. The apparatus is disconnected, the Voit flask placed in a beaker containing cold water, and the alkaline solution in the absorption apparatus cooled by running water. The contents of the trap are washed into the Drexel bottle and the solution therein is made slightly acid with hydrochloric acid. The liberated iodine is titrated with approximately N/10 sodium thiosulphate and the color is brought back by a drop or two of N/10 iodine solution, after the addition of starch.

Alkaline potassium iodide is again placed in the absorption apparatus and the latter connected with the Voit flask. The current of hydrogen is turned on and, after the air has been expelled, the apparatus is disconnected momentarily, 1 or 2 grams of potassium iodide are added to the solution in the Voit flask, and connections made again. Through the separatory funnel 10 cc. to 15 cc. of concentrated hydrochloric acid and 3 cc. of syrupy phosphoric acid are added and the solution in the reduction flask is boiled to a volume of 10 cc. to 12 cc. The absorption apparatus is removed and cooled, hydrochloric acid is added and the liberated iodine titrated with approximately N/10 sodium thiosulphate.

The iodine determined in the first titration corresponds to a reduction of the chromic and vanadic acids according to the equation

\[ V_2O_5 + 2CrO_3 + 8HBr = V_4O_7 + Cr_2O_3 + 4Br_2 + 4H_2O \]

while in the second case the iodine corresponds to a reduction of the vanadium tetroxide to trioxide as indicated in the equation

\[ V_2O_5 + 2HI = V_4O_7 + I_2 + H_2O \]

The second titration, therefore, determines the vanadic acid present, and the difference between the first and second furnishes the necessary data for the calculation of the chromium.

**DETERMINATION OF VANADIUM IN FERRO-VANADIUM**

**Standard Methods of the American Vanadium Company**

Dissolve 0.510 gram of the alloy (100 mesh) in a 250-cc. beaker with 50 cc. dilute sulphuric acid (1:2) and 10 cc. (concentrated) nitric acid. If the alloy does not decompose, when heated, add a few cc. of hydrofluoric acid. Take down to copious white fumes. Cool, add 50 cc. dilute sulphuric acid (1:2) and water. Heat until all salts are in solution and transfer to a white casserole containing 100 cc. dilute sulphuric acid (1:2). Dilute the solution to 400 cc. with H$_2$O and heat to 60º C. The solution is ready to titrate.

Add potassium permanganate until a deep red is obtained. Just discharge the red color with ferrous ammonium sulphate.

Get the neutral point by alternating the permanganate and ferrous ammonium sulphate until one drop of the ferrous sulphate just discharges the pink color.

Now add N/10 ferrous ammonium sulphate from a burette until the vanadium is reduced and then 3 cc. in excess.

Titrature the excess of ferrous ammonium sulphate with N/10 potassium bichromate, using potassium ferricyanide as an indicator.

From the cc. of ferrous ammonium sulphate used, subtract the cc. of bichromate used. The number of cc. used gives the per cent of vanadium in the alloy.

The relation between ferrous ammonium sulphate and bichromate is established by adding 150 cc. sulphuric acid (1:2) to a casserole, diluting to 400 cc.

Find the neutral point and then add 25 cc. ferrous ammonium sulphate and titrate with bichromate until the blue spot is just discharged.

**EXAMPLE**

**Blank:**

Ferrous ammonium sulphate used........................................ 25 cc.
Potassium bichromate used.................................................. 24.6 "

25.00
24.60

.40 + 25 = -0.016 factor.

**Alloy:**

Ferrous ammonium sulphate used........................................ 40.00
Potassium bichromate used.................................................. 2.40
40 cc. X -0.016......................................................... = .64 cc.
40.00 - 0.64......................................................... = 39.36 "

Correction on ferrous ammonium sulphate:

39.36 - 2.4......................................................... = 36.96% V.

Solutions used:

N/10 potassium bichromate.
N/10 ferrous ammonium sulphate.
Potassium ferricyanide, a crystal the size of a pea in 50 cc. of water.
Potassium permanganate, 5 grams per liter.

1 Methods developed in the Bridgeville Laboratory. By courtesy of the American Vanadium Company.
Determination of Vanadium in Vanadium Ores

Weigh 0.51 gram of the finely powdered ore in a 1½-in. diameter iron crucible filled three-fourths full of sodium peroxide. Fuse. Dissolve the fusion in water and add 100 cc. H₂SO₄ (1 : 2) in excess and evaporate until white fumes come off. Cool and dilute and filter. Gase the filtrate, which should be about 400 cc., until all H₂S metals are precipitated. Boil and filter. Boil the filtrate until all H₂S is off. Transfer to a 500-cc. casserole and add 50 cc. H₂SO₄ (1 : 2) and heat to above 60° C. Titrate as in the determination of vanadium in ferro-vanadium.

Determination of Vanadium by Precipitation with Phosphomolybdate

The alloy or steel is dissolved in nitric acid and treated, dropwise, with strong potassium permanganate until a precipitate of MnO₂ is obtained on boiling. Ammonium bispalphte solution is now added drop by drop until the manganese dissolves. The solution is boiled until the nitrogen oxides are expelled. 10 cc. of a 5 per cent ammonium phosphate solution and 10 grams of ammonium nitrate are added, the solution heated to boiling, and 50 cc. of ammonium molybdate solution added. The solution is shaken for 3-5 minutes to precipitate all of the vanadium and phosphorus. The precipitate is separated by decanting onto an asbestos filter. The precipitate is dissolved in conc. H₂SO₄, the iron oxidized by HNO₃, the nitric expelled by fuming off and the vanadium now reduced by adding hydrogen peroxide and heating. The addition of peroxide and heating is repeated. The green or blue solution is heated to 80° and titrated with 0.1N KMnO₄ as usual.

Vanadium in Steel—A. S. T. M. Method

**Solutions Required**

"Dilute Hydrochloric Acid (2 : 1).—Mix two parts of HCl (sp.gr. 1.19) with one part of water.

"Dilute Nitric Acid (sp.gr. 1.20).—Mix 380 cc. of HNO₃ (sp.gr. 1.42) and 620 cc. of distilled water.

"Dilute Hydrochloric Acid (1 : 9).—Mix 100 cc. of HCl (sp.gr. 1.19) and 900 cc. of distilled water.

**Method**

"(a) (When Cobalt does not exceed 1 per cent.)

"Treat 2 g. of the steel in a porcelain dish with 70 cc. of dilute HCl (2 : 1) and heat until all action ceases. Cautiously add 10 cc. of dilute HNO₃ (sp.gr. 1.20) and evaporate the solution to dryness or to low bulk. Treat the residue with 45 cc. of dilute HCl (2 : 1) and heat until the soluble portion dissolves. Add an equal volume of water, boil for three minutes, filter and wash the residue thoroughly with dilute HCl (1 : 9) until free from iron. Evaporate the solution to small volume and destroy hydrochloric acid by small additions of nitric acid (sp.gr. 1.42) followed by boiling. If a residue appears, filter the solution. From this point proceed for chromium as in the Determination of Chromium in Chrome-Nickel Steel by the Persulphate Oxidation Method and for Vanadium as in the Determination of Vanadium in Chrome-Vanadium Steel by Reduction with Ferrous Sulphate and Titration with Permanganate.

"(b) (When Cobalt exceeds 1 per cent.)

"See the Determination of Vanadium in Chrome-Vanadium Steel by the Electrolytic Separation Method.

"Proceed as described in this method until the bichromate precipitate has been washed with hot water. Return the paper and precipitate to the flask and add 60 cc. of dilute HCl (2 : 1). Heat the solution, add 10 cc. of HNO₃ (sp.gr. 1.20) and evaporate the solution to dryness or to a small volume. Treat the residue with 45 cc. of dilute HCl (2 : 1) and proceed as described above.

**Notes**

"Tungsten interferes with the determination of vanadium by the above method and must be removed. While chromium can be determined in the presence of tungsten, it is conveniently determined in the same sample as is vanadium and the end point is easier to get when tungsten has been removed.
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"In case hydrochloric acid is present when silver nitrate is added, enough of the latter must be added to take care of this before the regular addition is made.

"The pink color of cobalt interferes with the end point readings. If under 1 per cent, the color does not seriously affect the results, if over this, it should be removed."

Determination of Vanadium in Steel (When Chromium is present)

Dissolve 5.1 grams of steel in a covered 400-cc. beaker with 60 cc. of HCl (concentrated). After total solution, add concentrated HNO₃ sufficient for complete oxidation. Evaporate to a syrupy consistency, add 40 cc. HCl (concentrated) and evaporate to about 20 cc. Cool and transfer contents to a separatory funnel, washing with dilute HCl (2 HCl : 1 H₂O). Add 100 cc. ether, cork and shake for some time, cooling funnel under tap water while shaking. Remove cork, place funnel in stand and allow it to stand for at least five minutes. Run out the lower layer of the separation into the original 400-cc. beaker.

Evaporate the ether off. Add 5 cc. HNO₃ (concentrated) and just bring to a boil, Stir out all nitrous fumes, make alkaline with NaOH (saturated solution). Make just acid with HNO₃ (concentrated) cool solution.

Add above solution to a solution containing 300 cc. cold water and 5 cc. of NaOH (saturated solution). Boil and filter, washing with hot water thoroughly. Make filtrate just acid with HNO₃ (concentrated). Add 40 cc. of a saturated solution of lead acetate. (If lead precipitate forms just clear solution by adding HNO₃ drop by drop and bring to a boil.) Add 60 cc. of ammonium acetate. Boil for twenty minutes. The vanadium is precipitated as lead vanadate.

Filter the lead vanadate onto a Munktell paper, washing with hot water. Put filter containing lead vanadate in a small porcelain dish and burn off paper at a low heat. Add a little HNO₃ and evaporate on the hot plate, then put the dish in the cold end of a muffle to drive off the remaining HNO₃. Avoid baking. Dissolve in HCl (concentrated) and transfer the solution to a 400-cc. beaker. Add 60 cc. dilute H₂SO₄ (1 : 2). Oxidize thoroughly with KMnO₄ (5 grams to a liter.) Add 40 cc. HCl (concentrated) and evaporate to dense white fumes. Cool, add 40 cc. of water and again take to white fumes. Cool, add 150 cc. of water, cool, and titrate with N/50 KMnO₄. Each cc. of permanganate used is equal to 0.00102 gram of vanadium, or in this case, having used a ten-factor weight, each cc. represents 0.02% vanadium.

Notes.

Vanadium is used chiefly in steel for purposes requiring great toughness and torsional strength, common applications being in automobile parts, gears, piston rods, tubes, boiler plates, transmission shafts, gun barrels, and forgings that have to withstand great stresses and wear. The vanadium content in steel usually ranges from 0.1 to 0.4%. Vanadium is also used occasionally in certain tungsten alloy steels for making high-speed steel. Introduced in small proportions, it reduces considerably the amount of tungsten required in steel for a given hardness and toughness. Vanadium differs from tungsten in that it has a good effect not only on tool steel, but on structural steel as well.

Chrome-vanadium steels and chrome-vanadium-molybdenum steels are the latest developments in structural alloy steels that have gained an extensive market. Almost all these steels are made in the open-hearth furnace, chromium and vanadium alloys being added shortly before casting. In their physical properties these steels are much like chrome-nickel steels, but they have a greater contraction of area. Most of the chromium-vanadium steels made go into automobiles. Some manufacturers prefer them because of their greater freedom from the surface imperfections— notably seams—which the steels containing nickel are likely to have.

1 Machinery, June, 1924.
Determination of Vanadium in Ores, Mine and Crude Mill Samples

Reagents Indicator. \( K_2\text{Fe(CN)}_6 \). Make up just before using in a drop bottle which has been washed out with \( \text{NaOH} \) and then with water. Place a small crystal of the salt in the bottle and wash several times to remove the oxidized coat, pouring out the washings, then add about 30 cc. of distilled water and dissolve for use.

Ferrous ammonium sulphate, \( \text{FeSO}_4(\text{NH}_4)_2\text{SO}_4\text{.H}_2\text{O} \). 135 grams of the salt are dissolved in a mixture of 335 sulphuric acid and 3000 cc. of water.

Standardize the solution as follows: Take 25 cc. of the solution and add 25 cc. \( \text{H}_2\text{SO}_4 \). Dilute to 400 cc. and titrate with standard \( K_2\text{Cr}_2\text{O}_7 \) reagent using \( K_2\text{Fe(CN)}_6 \) indicator according to the procedure used in the determination of iron.

Potassium permanganate, \( \text{KMnO}_4 \). 3.162 grams per liter.

Potassium dichromate, \( K_2\text{Cr}_2\text{O}_7 \). 4.903 grams per liter.

Standardize with 1/2 gram of iron wire. (1 cc. = .056 g. Fe.)

PROCEDURE. Solution of the Sample.

Take 2.04 grams of the ore, ground to pass through a 60-mesh screen. Fuse with (about 20 times its volume), sodium peroxide in a 25 cc. iron crucible. (If the mixture can be thoroughly centered, it is better than a complete fusion.) Take up the mass with water in a 600 cc. beaker. Add a solution of 50 cc. strong sulphuric acid diluted with 100 cc. of water. Then dilute to 400 cc. with water.

Titration. Heat to above 80° F. and add just sufficient of the permanganate reagent to make the solution pink. Titrate back with a few drops of ferrous ammonium sulphate reagent until the color of the permanganate just disappears. The solution will now appear green or blue color. Now add the "ferrous" solution until the ferric cyanide spot test shows a faint blue color. Then 2 cc. excess of the "ferrous" solution. Titrate back the excess with the standard potassium dichromate reagent until a drop of the indicator shows no color on the spot plate, with a drop of the solution.

Calculate the ratio of the ferrous solution and the dichromate to a common basis. Deduct the cc. dichromate from the cc. "ferrous" added to the bluish green solution above, and divide the result by 4. With an exactly N/10 solution the result will be the percent vanadium in the sample.

Lead Acetate Method. The solution obtained from the fusion of the ore (see Solution of the sample) is acidified with acetic acid. Then sufficient lead acetate is added to completely precipitate the vanadium (usually 2 or 3 grams, according to the amount of vanadium in the sample), the solution is stirred, allowed to settle and the lead vanadate filtered off and treated as follows.

Take the residue on the filter (this at first appears yellow) and dissolve in a very dilute solution of nitric acid. The acid should be hot. Transfer to an 800 cc. beaker.

Add about 10 cc. of concentrated sulphuric acid and evaporate to fumes of \( \text{SO}_3 \). All traces of nitrous oxide must be expelled. Dilute to 600 cc. with distilled water, add 25 cc. of concentrated sulphuric acid, heat and titrate with standard permanganate according to the first of the volumetric procedures.

Determination of Vanadium in Cupro-vanadium, Brasses and Bronzes

Dissolve 1.020 grams of cupro-vanadium in aqua regia. Evaporate to small bulk and add excess of peroxide of hydrogen. Dilute to 600 cc. and add ammonium until all copper goes into solution. Heat to boiling and add sufficient barium chloride solution to precipitate all the vanadium. Boil and filter. Wash all copper out of filter with hot ammonia water. Transfer the filter to a beaker, add 100 cc. 1 : 2 sulphuric acid, boil and filter on close filter paper. Titrate the filtrate with N/10 ferrous ammonium sulphate and N/10 potassium dichromate the same as in the case of the ferrous alloy, except that this being a two-factor weight, the result must be divided by 2.

Vanadium copper, brasses and bronzes are treated in the same manner except that a ten-factor weight is used and the titration carried out with N/50 solution instead of N/10.

1 Communicated to the author by Theodore Marvin, Dupont Powder Company.
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VOLUMETRIC-PHOSPHOMOLYBDATE METHOD FOR DETERMINATION OF VANADIUM

Reagents

Ammonium Molybdate. See page 1363 for phosphorus in steel.
Ammonium Phosphate. 50 g. salt per liter of water.
Acid Ammonium Sulphate. 50 cc. strong H₂SO₄, 950 cc. water and 15 cc. strong ammonium hydroxide. Use hot, 80° C.
Nitric Acid. 100 cc. strong HNO₃ and 1200 cc. water.
Nitric Acid for Washing. 20 cc. strong HNO₃ per liter.
Potassium Permanganate, Standard. 0.35 g. salt per liter of solution. Standardized against sodium oxalate. Adjust so that 1 cc. will equal 0.0005 g. vanadium, or 0.02 per cent on a 2.5-g. sample. 1 g. Na₂C₂O₄ = 0.7612 g. V.
Potassium Permanganate, for oxidation. 25 g. salt per liter of solution.
Sodium Bisulphite, for reduction. 30 g. salt per liter of solution.

Procedure for Steel

A sample of 2.5 g. of steel in a 300-cc. beaker or Erlenmeyer flask are dissolved in 50 cc. of the nitric acid, and to the boiling solution are added 6 cc. of the permanganate oxidation solution, the boiling being continued until MnO₂ precipitates. The precipitate is now dissolved by cautious additions of sodium bisulphite solution and the boiling continued until no brown fumes are evident. Now 5 cc. of ammonium phosphate solution are added and 10 g. ammonium nitrate. The solution is removed from the heat and 50 cc. of ammonium molybdate reagent immediately added. After standing for 1 minute, the solution is agitated for 3 minutes, then allowed to settle and the clear solution decanted through an asbestos filter, the residue is washed three times with hot acid ammonium sulphate reagent, decanting each time through the filter. The flask containing the bulk of the residue is placed under the filter. (The washings are best conducted with suction, using a bell jar filter.) The precipitate on the filter is dissolved by successive portions of hot strong H₂SO₄, catching the solution in the vessel containing the bulk of the precipitate. The precipitate is now dissolved by heating and to the solution a few drops of the nitric acid are added and the heating continued to strong fumes.

The solution is cooled and hydrogen peroxide added in small quantities with vigorous shaking after each addition, until the solution takes on a deep brown color. The solution is again heated for 4 or 5 minutes, then cooled and 100 cc. of water added, the solution again heated to about 80° C. and titrated to a permanent pink color with standard potassium permanganate.

Note. If the peroxide treatment followed by heating does not result in a clear green or blue color, the solution should be evaporated to strong sulphuric acid fumes and the peroxide treatment repeated. The presence of nitric acid interferes with the reduction of vanadium.
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VANADIUM IN STEEL—ETHER EXTRACTION—HYDROCHLORIC ACID REDUCTION METHOD

Reagents

Hydrochloric Acid. 600 cc. strong HCl and 400 cc. water.

Sulphuric Acid. Equal volumes of strong H₂SO₄ and water.

Other Reagents. See Phosphomolybdic Precipitation Method for Vanadium.

Procedure

A sample of 2.5 g. of steel in a 250-cc. beaker is dissolved in 50 cc. of the HCl, and then small portions of HNO₃ added to oxidize the iron. After expelling the brown fumes by heating, the solution is cooled and transferred to an 8-oz. separatory funnel, together with the rinsings (small portions of HCl) of the beaker. Now 50 cc. of ether are added and the mixture shaken for 5 minutes. After settling for 1 minute the clear lower layer is drawn into another separatory funnel. The first funnel is treated with 10 cc. of strong HCl, again shaken vigorously and the settling repeated, the lower layer being added to the solution in the second separatory funnel. The combined solutions in the second separatory funnel are treated with 50 cc. of ether and shaken for 5 minutes, allowed to settle 1 minute and the clear lower layer drawn into a 150-cc. beaker. This aqueous solution is warmed gently to expel the ether, 25 cc. of the H₂SO₄ (1:1) added and the mixture concentrated to strong fumes. After cooling, 25 cc. of water are added followed by a slight excess of potassium permanganate solution and the sample heated to boiling. 15 cc. of strong HCl are added and heat applied until the solution again fumes. The heating is continued for 10 minutes. After cooling, 100 cc. of water are added, the solution heated to 80° C. and titrated with standard potassium permanganate reagent to a permanent pink color.

Notes. In heating the solution to expel the brown fumes of oxides of nitrogen, the solution should not be boiled.

In presence of chromium, the pink color will fade on standing owing to the oxidation of chromium. The oxidation of chromium is reduced by titrating the solution cold, but only ten seconds are allowed for the pink color to remain. A blank must be run with the same amount of chromium and allowance made for its oxidation. The blank is conveniently made by putting a suitable amount of chrome steel or chrome-nickel steel through the recommended procedure. By varying the amounts of steel and hence the amount of chromium in solution, data for a charted curve may be obtained that will be convenient for a blank deduction.
Preparation of a Gooch Crucible

Asbestos Fibre.—The asbestos for use in Gooch crucibles should be carefully selected. The fibres should be moderately stiff, not the “cottony” type. Cut the fibre into pieces about \( \frac{1}{2} \) inch long. Ignite the asbestos in a platinum dish at low red heat. Cool and transfer to a clean porcelain mortar and masecerate to a pulp with strong hydrochloric acid. Dilute with water and transfer to a large beaker containing 600–800 cc. of water. Stir thoroughly, allow to settle and pour off the milky water. Repeat the washing with water until the milkiness, due to powdered fibres, is scarcely evident. Now filter off the asbestos onto a Buechner funnel. Again wash with water until free of acid. Transfer to a wide mouth bottle, add water in sufficient amount to form with the stirred up fibre a thin suspension of asbestos. This is now ready for use. If preferred the asbestos may be dried and kept in this form until desired.

Preparation of the Filter. The crucible, either of platinum or porcelain, having a perforated bottom, is placed in a funnel tube and the apparatus set up as is shown in Fig. 71a. The suction bottle holding the Gooch is attached to a second bottle, if a water filter pump is used to obtain the vacuum, as there is danger of water being sucked into the apparatus from the tap. Suction is now applied and a small amount of the finely suspended asbestos is poured into the crucible, in amount sufficient to form a thin pad of the material about \( \frac{1}{4} \) inch thick over the bottom of the Gooch. The felt is washed with distilled water, the asbestos drawn down hard. It is possible to see light through the bottom of a properly made filter. The crucible is placed in an oven and the filter dried to constant weight at 110° C. For BaSO\(_4\) and AgCl determinations it is advisable to make the filter about twice the above thickness to prevent the precipitate from passing through. Whenever the Gooch crucible is used, suction should be applied before pouring material into the crucible and the suction continued during the washing of the precipitate.
ZINC

\[ \text{Zn, at.wt. 65.38; sp.gr. 6.48 to 7.19; m.p. 419^\circ; b.p. 920^\circ; ZnO oxide.} \]

DETECTION

The finely powdered material, when heated on charcoal in the reducing flame of a blowpipe, gives an incrustation, yellow when hot—white when cold. On moistening with cobalt nitrate solution and re-igniting, the mass is greenish-yellow. Materials containing above 5% Zn will give positive tests. With experience, less can be detected, but for smaller amounts the regular procedure as given under Titration in Acid Solution, Separating Zn as ZnS, should be followed, using samples as follows: For material containing 0.01–0.05%, 10 to 20 grams; 0.05–0.10%, 5 to 10 grams; 0.10–0.5%, 5 grams; 0.5% on up, 2 grams to 0.5 gram, depending on per cent of zinc present.

In case the material is of interest, only if it carries higher than several per cent of zinc, a shorter and easier wet test is to bring the material into solution by means of hydrochloric or nitric acid, add bromine water and then precipitate iron, aluminum and manganese with ammonia, as given under heading of Determination of Zinc in Acid Solution, Separating Iron, Aluminum and Manganese with Ammonia and Bromine, filter, wash and make the filtrate acid with hydrochloric acid, 10 cc. excess added for each 100 cc. of solution, and potassium ferrocyanide added. Zinc, if present, gives the characteristic precipitate. Copper interferes and if present must be separated with hydrogen sulphide, as given under heading Procedure for Copper-bearing Ores.

In case manganese and copper are known to be absent, a still shorter test may be used: To the solution of the zinciferous material add 2 or 3 grams of citric acid per 200 cc. solution, then make ammoniacal, add ferrocyanide—a white precipitate indicates zinc.

ESTIMATION

The determination of zinc is called for in the buying and selling of ores for smelters, refuse material, e.g., from galvanizing plants, foundries, brass mills, and blast furnaces, in manufacture of brass, white metals, and alloys in general, paints and pigments, zinc chloride for preservation purposes, and in the control work in smelting of zinc and lead ores.

Preliminary. The method to be followed in the estimation of zinc will depend largely on the nature of the material in which it occurs, the quantity present, and the experience of the analyst. Each of the methods outlined will give correct results only on the materials for which they are indicated, there being but one method recommended which is applicable to all zinciferous mate-

ZINC

rial. It cannot be emphasized too strongly that each step has a definite pur-
pose (which may not be at once apparent to the analyst making only an oc-
casional zinc determination), and no part of the procedure should be varied or
omitted, excepting after abundant experience.

Preparation of Sample

The representative sample should be ground to pass a 100-mesh screen or
finer. If the material contains shot metal, it should be screened out and the
percentage present calculated. It is then treated as given under heading Material
Containing Metallies, page 602.

Moisture Determination in the Pulp

One of the commonest causes of differences in zinc ore analysis is the failure
to take moisture determinations on the pulp sample.

In order that analyses made on the same pulp at different times and in different
laboratories may be compared it is absolutely necessary that all determinations be
corrected to a dry basis. It is not sufficient that the sample be dried before or
after having been pulped, but a sample for moisture must be weighed out at the
same time as the sample for analysis, and the analytical result corrected for the
per cent of moisture found at the time of weighing. This is especially true on
roasted zinc ores which contain sulphates of zinc, iron and lime and which take up
moisture quite rapidly under ordinary atmospheric conditions.

The usual temperature for drying should be 110° C., but on special ores, e.g.,
those containing sulphates, it is necessary to dry at 250° C. unless it is first shown
that there is no loss of water above 110° C.

The determination is best made by weighing approximately two grams in a
small glass-stoppered weighing tube and drying to constant weight, the weighing
tube being closed with the glass stopper as soon as the tube is taken from the
drying oven.

SEPARATIONS

Silica. Evaporate with hydrochloric acid or take to fumes of sulphuric
acid. The dehydration with sulphuric acid is complete and gives silica that is
easily filtered and washed.

Cadmium, Lead, Arsenic, Antimony, Bismuth and Copper. Aluminum
may be used to separate all the metals, except cadmium, the latter being only
partially separated. The procedure is as given in the standard method.

The separation may also be made as follows: Evaporate the solution of the
zinciferous material to fumes with 7 cc. of 1 : 2 sulphuric acid. Cool, take up in
about 50 cc. of water and warm, add 10 cc. of 10% sodium thiosulphate, boil
until evolution of sulphur dioxide ceases, then filter. Cadmium if present is not
precipitated. It should be separated by the procedure given under Titration in
Acid Solution Separating Zinc as Sulphide.

Iron, Aluminum and Manganese. This separation may be effected by
precipitation with ammonia and bromine, providing the quantities present are
small. When large amounts are present the basic acetate procedure is followed,
or, better, the zinc separated as sulphide in dilute sulphuric acid solution, page 605.
ZINC

Nickel and Cobalt. When nickel or cobalt are present, the only safe procedure is to separate the zinc as zinc sulphide in dilute sulphuric acid solution, as described under the standard method. Weiss has shown conclusively that zinc can be precipitated free from either cobalt or nickel under the conditions there outlined.

METHODS OF ANALYSIS

I. Gravimetric methods.
II. Electrolytic methods.
III. Titration with standard solution of $K_2Fe(CN)_6$.
   (a) In acid solution.
   (b) In alkaline solution.
   (c) In acid solution, separating Zn as ZnS. (Standard method.)

GRAVIMETRIC METHODS

Weighing as Zinc Oxide

In this case the procedure is the same as in the volumetric method, in which zinc is separated as zinc sulphide up to point where the zinc sulphide is filtered off and washed. It is now ignited in a weighed crucible and heated to 800 to 900° C. in a muffle for one hour and weighed as ZnO. Factor ZnO×0.8034=Zn.

The precipitate of zinc sulphide may also be filtered on a Gooch crucible, and ignited as above.

Weighing as Sulphate

The zinc sulphide is dissolved in hydrochloric acid. Sulphuric acid is added and the solution evaporated in a weighed crucible, all excess acid fumed off and the resulting zinc sulphate finally ignited at a dull red heat and weighed. ZnSO₄×0.405=Zn.

Electrolytic Methods

The determination is best made from an alkaline electrolyte or one slightly acid with acetic acid and containing a considerable amount of sodium acetate. The alkaline electrolyte tends to give high results, due to the presence of zinc oxide or hydroxide in the deposit. The best results are obtained with a solution weakly acid with one of the weaker organic acids. The procedure for the acetate electrolyte is as follows:

The zinc is separated from other elements by precipitating with hydrogen sulphide in dilute sulphuric acid solution, as given under the standard method. The precipitate is filtered and washed, dissolved in hot hydrochloric acid—5 cc. 1:1 sulphuric acid added and the whole evaporated to fumes to expel hydrochloric acid. Cool and dilute, neutralize with sodium hydrate solution, make slightly alkaline, then acidify with acetic acid, and add about 5 grams of sodium acetate. The volume of solution should now be about 100 to 125 cc. Electrolyze with a platinum gauze electrode with 0.5 ampere at 5 volts.

The electrolytic methods, on account of the special apparatus needed, the experience and care necessary to get reliable results, and the unavoidable errors involved in their use, are less desirable than the gravimetric oxide method and still less desirable than the ferrocyanide method.
VOLUMETRIC METHODS

Titration in Acid Solution, Separating Iron, Aluminum, and Manganese with Ammonia and Bromine

General. This method is especially adapted to material low in silica, alumina, iron, and manganese. When the operator gains experience in manipulation, it is possible to obtain good results on samples higher in these elements, but its haphazard use with materials high in these impurities is one of the chief causes of the common inaccuracy of zinc work. If copper or cadmium are present in quantities, the titration in acid solution, separating Zn as ZnS, is to be preferred for accurate work.

Procedure for Ores. One-half or 1 gram (depending on the per cent of zinc present) is weighed in a 250-cc. beaker. Fifteen cc. of hydrochloric acid (sp.gr. 1.2) are added, a cover-glass put on, and the ore agitated to prevent caking. Boil down to a volume of about 5 cc. cool, wash down cover-glass and sides of beaker with a jet of water. Add 10 cc. of saturated bromine water, 5 grams of ammonium chloride and 15 cc. of ammonia water (sp.gr. 0.90) and boil vigorously for a minute or two. Filter off the precipitated hydroxides, and wash four times with hot water, containing 50 grams ammonium chloride and 25 cc. ammonia per liter. The precipitate is now washed from the filter into the beaker in which the original precipitation was made, and the precipitate dissolved in strong hydrochloric acid. Ten cc. of ammonia (sp.gr. 0.9) are added, the solution boiled, filtered and washed as before, the filtrate being combined with the first filtrate. The solution is then diluted to 250 cc., heated to boiling, and 4 drops of ammonium sulphide solution added to destroy oxidizing agents and precipitate small amounts of copper and cadmium. The solution is neutralized with hydrochloric acid, the resolution of the precipitated zinc sulphide serving in lieu of an indicator. Ten cc. excess of concentrated hydrochloric acid are added and the solution titrated, not below 75° C., with standard ferrocyanide, using uranium nitrate (10% solution) as an external indicator.

Standardization of the Ferrocyanide Solution

The potassium ferrocyanide is standardized by weighing out portions of C.P. zinc that will give a titration of approximately the same number of cc. as the sample. Dissolve in 15 to 20 cc. of hydrochloric acid and dilute to about 225 cc.

1 Nitric acid should be added in case of sulphide ores.

2 In case of siliceous ore, it is advisable to evaporate to dryness, and on unknown material to evaporate slowly, in order to make sure of complete solution of the zinc. Certain siliceous and oxide ores are difficultly soluble in hydrochloric acid, and frequently cause low results, where rapid decomposition is the routine.

3 In case of high silica, alumina, iron, and manganese materials, three precipitations are necessary.

4 It is necessary to destroy all oxidizing agents, as they will react with the ferrocyanide.

5 The excess of hydrochloric acid should be carefully measured. A burette is very useful in neutralizing the solution.

6 The strength of the uranium nitrate is a matter of personal preference, some using a saturated solution. On the other hand some prefer ammonium molybdate. The strength of solution given above, however, is recommended as the first choice of a large number of experienced zinc chemists.

7 In presence of manganese 10 cc. of saturated bromine water are added.
Then add 37 cc. strong ammonia, taking care to avoid spattering, heat to boiling, add 4 drops of ammonium sulphide, neutralize and add 10 cc. excess hydrochloric acid and titrate.

**General Notes**

The precipitate with ammonia carries down zinc. This is especially true with siliceous material or material high in iron and alumina. By working with hot ammoniacal ammonium chloride solution and making two or three precipitations, the amount held can usually be made negligible.

The precautions in regard to adding ferrocyanide and keeping conditions of standardization and titration the same, hold here as in all ferrocyanide titrations.

**Titration in Alkaline Solution**

**General.** This procedure is designed for rapid routine work on roasted or oxidized ores, especially those high in silica, alumina, iron, and manganese. It should only be used on unroasted sulphides, copper, or high cadmium-bearing ores, when the operator has had long experience. It is designed to give the zinc content of materials soluble in hydrochloric or nitric acid. For materials containing insoluble zinc, the titration in acid solution, in which zinc is separated as sulphide, is preferred.

**Procedure for Common Ores.** The following method is recommended: The weight of ore to be taken will depend on the approximate amount of zinc present. For material above 50%, take 1 gram; from 10 to 50%, 2 grams; 5 to 10%, 4 grams; and below 5%, 5 to 10 grams. Weigh the sample into a tall 400-cc. beaker, cover with water and add 25 cc. concentrated hydrochloric acid, rotating the beaker to prevent caking. In case sulphides are present, nitric acid also should be added. Place on a hot plate or steam bath and evaporate to dryness. Now add 40 cc. concentrated nitric acid, cover with a watch crystal and boil off all nitrous fumes. When these have disappeared, add about 3 to 4 grams KClO₃ and boil until chlorine fumes do not show. Cool, wash off the watch crystal and sides of the beaker, and dilute to about 100 cc. Wash into 500 cc. graduated flask, make up to the mark and shake well. Filter through a close 24-cm. qualitative paper and without waiting for the whole to run through, measure out 250 cc. of the clear filtrate into a 600-cc. beaker. Add ferrie nitrate solution, if necessary, so as to bring the iron content up to about 300 to 400 milligrams, i.e., if only a small amount is present, add 10 cc.; if 10 to 15% is present, add 5 cc., and proceed exactly as under Standardization.

**Procedure for Copper-Bearing Ores.** Either method is recommended:

*Separation of Copper by Aluminium.* The sample is treated as usual up to

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1 The amounts of acid and ammonia used throughout should be carefully measured, so as to keep the amount of ammonium salts approximately the same. This is very important in order to avoid errors, due to varying blanks.

2 The temperature of the hot plate should not be over 120° C., as ZnCl₂ is appreciably volatile at higher temperatures.

3 Any oxidizing agent such as chlorine or chlorine oxides acts on the ferrocyanide.

4 The graduated flasks should be standardized against one another, i.e., the 500 cc. should be twice the volume of the 250 cc.
the point where manganese has been separated and 250 cc. of the clear filtrate measured out. Add 25 cc. 1:1 sulphuric acid and evaporate to strong fumes, cool, dilute to 100 cc., add a gram or two of 20-mesh zinc-free aluminum. Heat until all the copper separates, filter, wash and proceed with the filtrate as in the regular method, after oxidizing iron with a few drops of nitric acid.

Separation of Copper by Hydrogen Sulphide. After separation of the manganese with chlorate, sulphuric acid is added and the solution taken to fumes, as in above. Cool, dilute to 100 cc., and add sulphuric acid so that 12% is present. Warm slightly and pass hydrogen sulphide through the solution. Filter off the copper sulphide, wash, boil H₂S out of the filtrate, and titrate as usual, after adding ferric nitrate and citric acid.

Material Containing Cadmium. If the material contains cadmium in quantities sufficient to warrant separation (0.15% or more), it is best to use the titration in acid solution, separating zinc as sulphide.

Material Containing Carbonaceous Matter. If the material under examination contains carbonaceous matter, coal, etc., it must be separated by taking to dryness with hydrochloric acid. Take up in acid and water, filter and wash, and evaporate the filtrate to dryness. Take up in nitric acid and proceed as in the regular method.

If the carbonaceous material is not removed, the manganese does not separate cleanly, due to the reducing action of carbonaceous compounds.

Procedure for Material Containing Metallics. On account of the lack of uniformity in the case of metallic zinciferous material containing lead and iron, it is well to work on large samples. Five or 10 grams of the metallics reduced to as fine a size as possible are weighed out and dissolved in nitric acid. The nitrous fumes are boiled off and the whole made up to 500 cc. or 1000 cc. Fifty or 100 cc. are now pipetted off into a 600-cc. beaker and the zinc titrated as usual. In case the metallic portion contains manganese, which is unusual, it can be separated by the regular procedure. Copper is separated as given under Copper-bearing Ores. Material containing cadmium should be analyzed by other methods, as given under Standard Procedure.

Solutions

Potassium Ferrocyanide. 34.8 grams pure salt in 1000 cc. water. One cc. = approximately .0075 g. Zn. This solution should be allowed to stand about four weeks before using.

Ferric Nitrate. One part salt in 6 parts water. It is well to add a little nitric acid to prevent hydrolysis.

Citric Acid. One part acid in 3 parts water. One hundred cc. of nitric acid should be added to each liter to prevent mould growth.

Standardization. The factor for the standard solution varies slightly, as would be expected, with the amount of ferrocyanide used, so that it is best to have at least three sets of factors, one at 40 cc., one at 20 cc., and one at 10 cc.

Weigh into 600-cc. beakers at least three portions of C.P. zinc. Dissolve the metal in about 10 cc. nitric acid, first covering with water. Boil off the nitrous
fumes and dilute to 250 cc. with distilled water. Add 10 cc. of ferric nitrate solution, and 15 cc. citric acid solution, make faintly ammonical, using a piece of litmus paper as indicator. Then add a measured excess of ammonia, as follows: 40 cc. factor, 20 cc. excess; 20 cc. factor, 10 to 12 cc. excess; and for low titrations make only faintly ammonical. Heat the solution to a full boil, and titrate immediately with the standard ferrocyanide, stirring the solution thoroughly and adding ferrocyanide not too rapidly. The titration is completed when a drop of solution gives a bluish-green coloration with a drop of 50% acetic acid on a spot plate. To prevent passing the end-point, or until the operator is experienced, a portion (50 cc.) of the solution may be held back in a small beaker, the end-point passed, and the titration completed after adding the part in the small beaker.

General Notes

A standard zinc solution may be used in case the end-point is passed. However, this is not to be recommended as a usual practice. In any case it should be very dilute, so that 1 cc. = 0.001 gram zinc.

The ferrocyanide should be added gradually and the solution stirred constantly, to prevent occlusion of ferrocyanide or zinc solution by the heavy precipitate.

A moisture sample should be weighed at the same time as the sample for analysis.

The variation of factor with amount of zinc titrated is more marked in this method than in the titration in acid solution. Hence, it is necessary that standards be run covering the whole range of zinces to be titrated. It will be found that the factors from 30 to 50 cc. are almost the same and from 15 to 30 cc. slightly lower, from 5 to 15 cc. still lower.

The zinc used as a standard should be carefully examined for foreign particles and oxidized zinc. In case stick zinc is used, the surface should be scraped clean before cutting. Merek's and Kahlbaum's stick zinc, as well as Baker & Adamson's, Liner & Amend's, or J. T. Baker's powdered zinc answer the purpose as regards metallic impurities. It is desirable to check the factor by means of a standard ore.

The standard of the ferrocyanide solution should be frequently checked, at least once every ten days. A solution of such a strength that 1 cc. equals 10 milligrams of zinc in glass a temperature coefficient sufficient to decrease the factor 0.2% per 5° C. rise in temperature, so care should be taken that no sharp change of temperature occurs between standardization and titration.

The factors in alkaline and acid solution are not identical. In alkaline solution the precipitate closely approaches the normal ferrocyanide, while in acid solution there is formed a double ferrocyanide of zinc and potassium.

Standard Method

Titration in Acid Solution—Separating of Zinc as Sulphide

General. The method of separating zinc as sulphide in a solution slightly acid with sulphuric acid is of almost universal application, and can be used on any class of zinciferous material that has come under the author's observation. The steps fit together, so that copper and cadmium are easily separated and any zinc in the insoluble state, e.g., spinels, etc., can readily be looked for. The method of decomposing (taking to fumes of sulphuric acid) tends to take into solution material that would be overlooked in the rapid decompositions effected in the preceding methods. Moreover, the use of the internal indicator gives a very sharp end-point, so that this method is fully as accurate as any gravimetric method. The method is more time consuming than the ones already given, but
it is not designed for rapid routine work, but rather as a standard procedure that will give absolutely reliable results on all classes of material. This method is also recommended for routine work in case the analyst is called on to make only occasional zinc analyses.

**Standardization of the Ferrocyanide Solution**

**Note.** The standardization of the solution is given first, on account of the method of titration.

Weigh into tall 400-cc. beakers several portions of C.P. zinc, using about 0.35 gram. Cover with water and dissolve in 10 cc. hydrochloric acid (sp.gr. 1.2). Now add 13 cc. ammonia (sp.gr. 0.9), make acid with hydrochloric acid, and add 3 cc. excess. Add 0.03 or 0.04 milligram of ferrous iron in the form of a ferrous sulphate solution and dilute to about 200 cc. with distilled water. Heat to boiling and titrate as follows: About one-quarter of the solution is reserved in a small beaker and the ferrocyanide added to the main solution with vigorous stirring. The solution takes on a blue color, which changes to a creamy white when an excess of ferrocyanide is added. Now add a few cc. more and pour in the reserved portion of zinc solution, excepting about 5 or 10 cc. Add ferrocyanide until the end-point is reached and add about 1/4 cc. more. The last of the reserved zinc solution is then poured into the main beaker, washing out the small beaker with a portion of the main solution, and the ferrocyanide added drop by drop until the blue color fades sharply to a pea green with one drop of ferrocyanide. This is the end-point. Repeat until satisfactory standards are obtained.

**Procedure.** Weigh into a tall 150-cc. beaker an amount of sample so that it gives a titration of about 40 cc., i.e., 5 grams for a 10% ore to 1/2 gram for 60% ore and over. Moisten with water and add 10 cc. of hydrochloric acid (sp.gr. 1.20), cover with a watch-glass. In case of sulphides it is necessary to add nitric acid. Boil moderately on a hot plate for half hour or so. Remove and wash down cover-glass and sides of beaker, add 10 cc. of 1:1 H₂SO₄ and evaporate to strong fumes of sulphuric acid. In case of very siliceous material, it is well to break up the silica with a glass rod before adding the sulphuric acid. After fuming, the solution is cooled and diluted to 40 to 50 cc. and about a gram of 20-mesh aluminum added. Cover with a watch crystal and boil until water white (about ten to fifteen minutes). This will reduce the iron and precipitate all the hydrogen sulphide metals, except cadmium. The silica and precipitated metals are filtered off and washed with hot water.

Add 5 cc. of 1:1 sulphuric to the filtrate and dilute to 100 cc. Pass a rapid stream of hydrogen sulphide through the solution for fifteen minutes. Add dilute ammonia, a drop at a time until yellow cadmium sulphide precipitates. Then heat the solution to 70 to 90° C. and continue to pass hydrogen sulphide for a few minutes. Filter at once through a close paper previously packed by washing with a polysulphide, an acid and water. The precipitate is washed with cold 8 to 10% sulphuric acid and finally with hot water. The filtrate is boiled to remove hydrogen sulphide, cooled, neutralized with potassium hydroxide

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1. It is only by adding an excess of ferrocyanide that one is assured of a precipitate of normal composition.

2. Cadmium is partially precipitated, but goes back in solution.

3. All the cadmium is separated, except about 0.05%, which does not interfere with the titration at the given acidity.
solution, and finally potassium carbonate solution, to within an acidity of a couple of drops of 20% sulphuric acid. Methyl orange is used as an indicator. Add from 2 to 4 cc. of 5% ¹ sulphuric acid per 100 cc. of solution according to the amount of zinc present. Cool thoroughly.³ A rapid stream of hydrogen sulphide is now passed through the solution for forty minutes.² Allow the precipitate to settle ten or fifteen minutes, filter and wash with cold water. A hole is punched in the filter paper and the sulphide washed back into the beaker in which it was precipitated. The filter paper and glass tube are then washed with 10 cc. of hydrochloric acid in hot water, catching the washings in the same beaker. Boil off the hydrogen sulphide, add 13 cc. of ammonia (sp.gr. 0.9), neutralize with hydrochloric acid, add 3 cc. excess and dilute to 200 cc. Heat to boiling and titrate as under Standardization. When cadmium is absent or present in quantities less than 0.05, the procedure is of course shortened considerably.

To Separate Cadmium Electrolytically. After filtering off the silica and precipitated hydrogen sulphide metals, add 1 cc. of 1:1 sulphuric acid, dilute to 125 cc. and electrolyze with 0.8 to 1.0 ampere per 100 sq.cm. of electrode surface for 14 hours at 2.95 to 3.05 volts. Proceed with the residual solution as above. As in all electrolytic separations the current must be carefully watched.

Procedure with Material Containing Insoluble Zinc

Proceed as usual up to point where the solution is to be reduced. Filter off the silica and insoluble material, wash with hot water and proceed with the filtrate as usual. Burn the insoluble residue in a platinum crucible, taking the usual precautions in case lead is present. Fume off the silica with hydrofluoric and sulphuric acids and fuse with acid potassium sulphate. Dissolve in water and sulphuric acid and proceed as in the regular method. The solution may be added to the main portion or titrated separately.

Discussion on Separating Zinc as Zinc Sulphide and Titrating in Acid Solution

Precipitation. The method of precipitating zinc as sulphide in sulphuric acid solution was investigated by G. Weiss (Inaugural Dissertation, München, 1906), and the work confirmed by F. G. Breyer. The main points of Weiss' paper are as follows:

1. "Sulphate solutions are preferable to chlorides." A N/10 chloride solution is not completely precipitated by H₂S. Furthermore, the precipitate of sulphide from HCl solution when quantitative is not crystalline and easy to filter like that obtained from sulphate solution.

2. "The concentration of a sulphate solution is without influence on the completeness of precipitation from N/10 down. That is for solutions containing at most 400 milligrams ZnO per 100 cc."

3. "Sulphate solutions of 400 milligrams ZnO per 100 cc. may be N/100 acid with H₂SO₄ before beginning the precipitation." Even at acidity N/20 before

¹ Bear in mind at this point the acid liberated by the action of H₂S in the zinc sulphate. See Discussion below.
² In cold solution the precipitate is more granular and easier to filter.
³ The hydrogen sulphide should pass through at a rate of at least eight bubbles per second.
precipitation less than a milligram of zinc remains unprecipitated. According to Weiss, if the solution were diluted to 300 cc. 1.3 grams of H₂SO₄ could be added or 64 cc. of 20% H₂SO₄, and still have the precipitation complete. Even if as much as 10 cc. of 20% acid were added the loss would still be only a little more than 1 milligram. Precipitating 300 milligrams from 100 cc., however, only 100 milligrams or 4 cc. of 20% acid could be added. This means that when the solution becomes more acid than 550 milligrams of H₂SO₄ per 100 cc. the precipitation of ZnS ceases. Knowing approximately the zinc content of a solution one can easily calculate the H₂SO₄ freed when the ZnSO₄ is converted into ZnS, and the difference between 550 milligrams and this calculated H₂SO₄ is the amount of acid that may be added when precipitating from 100 cc. of solution. For two hundred cc. of course more acid can be added, being the difference between 1.100 grams and the calculated H₂SO₄ freed from the ZnSO₄. One and one-half times the amount of Zn judged to be present is close enough for the H₂SO₄ freed.

4. "The precipitation, under the above given conditions, is incomplete when a slow current of hydrogen sulphide is used (about four bubbles per second). One must work with as fast a stream as possible without causing mechanical losses (at least eight bubbles per second)." Weiss is the first one to discuss this all-important question in the precipitation of ZnS. His explanation of the efficacy of the rapid stream of H₂S is as follows:

The precipitation takes place according to the following equation:

\[ \text{ZnSO}_4 + \text{H}_2\text{S} \Leftrightarrow \text{ZnS} + \text{H}_2\text{SO}_4. \]

Equilibrium is reached, i.e., the velocity becomes equal in both directions, and precipitation ceases when the amount of H₂SO₄ per 100 cc. reaches a certain point, under a given set of conditions. Let these conditions remain exactly the same with the exception of the H₂S and have the active mass of that increased. The equilibrium will be displaced from left to right and as a consequence ZnS will come down in the presence of more acid than before. H₂S is not very soluble in water at room temperature, but if one increases the surface of contact between the two the H₂S is dissolved much more rapidly and consequently the mass of H₂S active at any time greatly increased. This is exactly what is accomplished when the zinc solution is constantly kept full of bubbles of H₂S. One can easily see how greatly increased the mass of H₂S would be in the extreme case, when the solution is all foam.

5. "A strong current of gas, like that called for above, will precipitate the usual amounts of zinc used in analytical operations in forty minutes."

6. "At temperatures above 50° the precipitation is incomplete; furthermore, at room temperature the ZnS comes down in a form suitable for filtration."

7. "Water only is required for washing the precipitates."

**End-point.** The change of color from blue to pea green is very sharp. It should be observed by looking down through the solution and not from the side. The change in color may be explained as follows: The ferrocyanide, having stood for three or four weeks, has oxidized slightly to ferricyanide, due to dissolved oxygen in the water. The few tenths of a milligram of ferrous iron added acts with this ferricyanide giving the ferro-ferricyanide blue as long as the ferrocyanide is not in excess. When it is in excess the blue is decomposed and gives the colorless ferro-ferricyanide.
Rapid Ferrocyanide Method for Determining Zinc in Ores

Outside Indicator

Removal of Interfering Elements

1. 0.5 gram of ore. 8-oz. Erlenmeyer flask. 5 cc. of HCl, 10 cc. HNO₃. Boil gently almost to dryness. Remove from heat. Add 12 cc. HNO₃ and 5 grams (measured) of KClO₃. Boil gently just to dryness, finishing by manipulating flask (in holder) over free flame.

2. Add 35 cc. of Extraction Solution and heat to boiling, boiling very gently until disintegration is complete. Now add 10–25 cc. of saturated bromine water, according as manganese contents appear low or high, as indicated by brown color of residue.

3. Boil a minute or two longer and then filter through an 11 cm. filter containing a small moistened wad of absorbent cotton in the apex. Receive filtrate in a 400 cc. beaker. Wash out the flask with hot water. Remove adhering residue with rubber-tipped glass rod, or dissolve it with a few drops of HCl, then add 5 cc., or an excess, of NH₄OH and rinse into filter, finally washing out flask several times with hot water. Now wash filter and residue 10 times with hot Wash Solution.

Precipitation of H₂S Group

4. Add a little litmus solution to filtrate as indicator, stir and cautiously add HCl just to acidity, then 3 cc. in excess. Dilute, if necessary, to 200–250 cc. with hot water and heat nearly to boiling. Now add 50 cc. of saturated H₂S water and then the hot liquid is ready for titration.

Titration of Zinc

5. Pour off about half the liquid as a reserve and titrate the balance until the end-point is passed. Use a spot-plate in which about 2 drops of a 15% solution of uranium nitrate have previously been placed in each depression. Transfer the zinc solution to the spot-plate with a glass tube instead of a rod, taking only a drop or two for each test, except for the final tests of the titration, when about 1/4 of a cc. should be taken. After the first end-point is passed add a portion of the reserve and again pass the end-point. Repeat this, each time with more caution, until the reserve is reduced to about 5 cc. Now titrate, 6 drops at a time, until the end is again observed, then pour the entire liquid, or most of it, over the 5 cc. of the remaining reserve and then back into the same beaker again and finish the titration 2 drops at a time until the end-point, or brown tinge, is plainly apparent. Read the burette. Allow a couple of minutes for the tests to fully develop and then deduct from the burette reading for as many tests as show and for 1 drop additional. Multiply the number of cc. of ferrocyanide solution used by the percentage value of 1 cc.
Reagents

6. Extraction Solution. 200 grams of commercial ammonium chloride dissolved in a mixture of 500 cc. of strong ammonia and 750 cc. of water.

Wash Solution. 100 grams of commercial ammonium chloride, 50 cc. of strong ammonia. Dissolve and dilute to 1 liter.

7. Standard Ferrocyanide. \( K_4Fe(CN)_6\cdot3H_2O \) 21.6 grams to the liter. 1 cc. = about 0.005 gram Zn, or 1%. Standardize on about 0.2 gram of pure zinc. Dissolve in 10 cc. of HCl. Dilute somewhat, neutralize as above, complete the dilution, heat and titrate precisely as described above. No filtration or \( H_2S \) water necessary.

Notes

Potassium chlorate is added to precipitate the manganese and to dilute the mass with salts facilitating the subsequent zinc extraction. The presence of HCl is undesirable, hence an excess of \( HNO_3 \) should be present to expel HCl during evaporation. Bromine water is added to insure complete precipitation of manganese.

The degree of acidity is important as it has a direct influence on the end point. Two drops (i.e. one drop excess) are necessary to produce a color at the end point, hence the deduction of one drop is made.

The zinc compound formed has approximately the following composition—\( K_2ZnFe(CN)_6\cdotZnFe(CN)_6\cdot5H_2O \), the precipitating reagent is \( K_4Fe(CN)_6\cdot3H_2O \), two molecules of this reagent (422.37 g. \( \times 2 \)) precipitate three atoms of zinc (65.38 \( \times 3 \)) hence a reagent containing 21.54 grams is equivalent to 5 grams of zinc or to 0.005 g. Zn per cc.

In presence of Fe and M.O. indicator the color is lavender changing to pink at the end point. If phenolphthalein is the indicator, the end point is a pea green (from robin's egg blue) becoming white or gray with an excess of ferrocyanide reagent (\( H_2S \) present in large amount interferes).

Determination of Zinc in Alloys. See chapter in volume 2.

False Endpoint. During the titration with potassium ferrocyanide with too rapid addition of the reagent a false endpoint is obtained. This is recognized by the fact that an additional amount of reagent causes no deepening of the brown color with the uranium indicator. With additional reagent, heating and stirring no further brown color is produced. When the true endpoint is reached an addition of more ferrocyanide results in a deeper color of the spot test. The solution stirred and boiled still gives the test.

If considerable copper and lead are present in the ore, it is advisable to remove these from the solution. The addition of paper pulp assists in the settling of the sulphides, enabling a test to be made with the clear supernatant solution. With the dark suspended sulphides a sharp endpoint can not be obtained, so that it is advisable to allow the solution to settle and test using the clear liquor.
DETERMINATION OF SMALL AMOUNTS OF ZINC

The following method is applicable to samples containing 0.05% Zn or less.

Procedure. A large sample, 10 or 20 grams, is brought into solution by the standard procedure, taken to fumes of sulphuric acid and the zinc precipitated as sulphide after separating groups 5 and 6 by the procedures given under Standard Method, filtered and dissolved in hydrochloric acid. The sample is now washed into a 100-cc. Nessler tube, 5 cc. of ferrocyanide added and the whole made up to the mark, mixed by pouring into a beaker and then back into the tube. A standard containing the same amount of acid is made up and a standard zinc chloride solution added until the turbidity of standard and unknown are the same. From the amount of zinc added to the standard the percentage can be calculated. The standard zinc solution is made up by dissolving C.P. zinc in hydrochloric acid and diluting so that 1 cc. is equal to 1 milligram of zinc.

SPECIAL METHODS

Determination of Metallic Zinc in Zinc Dust

Discussion. There have been various methods proposed for determining the metallic zinc content of zinc dust. Most of these are based upon its reducing power. The latter may be determined by any one of many ways, although the results from different methods will not be concordant, due to the inaccuracies inherent with most of the methods. Potassium bichromate, iodate, ferric sulphate, and iodine have been used for measuring the reducing power of zinc dust. Fresenius also proposed dissolving the zinc dust in dilute sulphuric acid and after drying passing the hydrogen over heated copper oxide in a combustion tube, absorbing the water formed in a calcium chloride tube and weighing.

There have also been methods devised based on the volume of hydrogen evolved when a sample of zinc dust is dissolved in dilute acid. Several investigators have concluded from comparative investigations that the gasometric determination of the hydrogen evolved gives the most consistently accurate results. The best arrangement of apparatus for carrying out this hydrogen evolution method is shown in Fig. 72. The time required for a determination is about 1½ hours.

Procedure. One gram of zinc dust is weighed and transferred as rapidly as possible to a small Erlenmeyer flask A, of 100 or 200 cc. capacity, in which is placed a piece of sheet platinum about 1.5 cm. square. About 5 g. of clean un-oxidized ferrous sulphate crystals are added on top of the zinc dust and the flask nearly filled with distilled water saturated at room temperature with hydrogen gas.

The object of adding the sheet platinum and ferrous sulphate is to increase the rate of hydrogen evolution by catalytic action. A further reason for adding the ferrous sulphate on top of the zinc dust sample is to coagulate the latter as much as possible when it becomes wetted, and thus prevent the floating of more than an unappreciable amount of the sample.
The rubber stopper containing separatory funnel B and connecting tube C is tightly inserted into the neck of the flask. A little distilled water is poured into B and the three-way stop-cock in C turned to connect the flask with the downward outlet. Enough water is now run in from the separatory funnel to displace all the air in the flask and the connecting tube through the bore in its stop-cock. The stop-cock in C is now turned so that the downward outlet is in connection with the measuring tube D. By raising the leveling bottle E, containing 10 per cent. sulphuric acid also saturated with hydrogen at room temperature, all the gas in D is displaced. The stop-cock in C is now turned through 90 deg. so as to connect the decomposing flask A with the measuring tube D. The system is hence completely filled with liquid and ready for the generation of hydrogen. The measuring tube D has a total capacity of 400 cc. and is graduated from 250 to 400 cc. by 0.25 cc.

Thirty cubic centimeters of 1:1 sulphuric acid are now poured into the separatory funnel. A small portion of this acid is allowed to run into the decomposing flask until a brisk but not too rapid evolution of hydrogen takes place. The acid, being much heavier than water, settles to the bottom of the flask and the action commences immediately. The gas evolved, together with some solution and a very small amount of zinc dust passes over into the measuring tube, displacing the acid there. When the action in the decomposing flask has slowed down, more strong acid is introduced until all has been added. During this time the acid in the measuring tube and flask is shaken so as to wash down the particles of zinc dust from the upper parts of the flask and tube now filled with gas. The particles in the measuring tube on coming in contact with the 10 per cent. sulphuric acid are readily dissolved and generate their portion of hydrogen.

When all the zinc dust has been dissolved, water is run in from the separatory funnel to force the hydrogen over into the measuring tube and to fill the flask and connecting tube with water through to the stop-cock which is then closed. After leveling with the leveling bottle the volume of hydrogen generated from the 1-g. sample at the prevailing atmospheric conditions is read from the measuring tube. The percentage of metallic zinc in the sample is then calculated from the following expression:

\[
\text{Per cent. of Metallic Zinc} = \frac{V \times (P - p) \times 0.29196}{(1 + 0.003670)760},
\]

in which \(V\) = volume of gas in measuring tube at atmospheric conditions, \(P = \) barometric pressure, \(p\) = vapor tension of water above 10 per cent. sulphuric acid at room temperature, and \(t\) = room temperature.

**Necessary Precautions.** To obtain results of the highest accuracy, it is necessary when weighing out samples of zinc dust which are very finely divided, to keep the time of exposure as small as possible in order to minimize the oxidation
that takes place with the oxygen of the air. It is also highly important when samples are to be held, that they be kept in ground glass stoppered bottles, completely filled, and sealed with paraffin or wax.

The two variables most likely to affect the results are temperature and barometric pressure. A change in the barometric pressure is practically always extended over a reasonable length of time. A careful reading of the barometer when the volume of gas in the measuring tube is read will eliminate any error from this source. A temperature change, on the other hand, affects not only the volume of gas, according to Charles' law, but also affects the vapor tension of water and hence the actual pressure of the hydrogen when measured.

The rubber connection between the connecting and measuring tubes must be of heavy rubber and should be shellacked.

The vapor tension of water is slightly lower above 10 per cent. sulphuric acid than above pure water, as shown in Fig. 73 and for accurate work should be used in place of the ordinary vapor tension tables.

The result obtained should be corrected for any metallic impurities, as Fe, Al, etc., which evolve hydrogen when dissolved in sulphuric acid.
DETERMINATION OF IMPURITIES IN SPELTHER

LEAD

Electrolytic Method

The sample is thoroughly mixed on a sheet of paper and a magnet passed over to remove iron particles. Any pieces showing discolorations are discarded. The pieces of spelter for the weighed sample are removed from the paper by lifting and not pouring. The amount of sample taken is determined by the amount of lead in the spelter.

For No. 1 or High Grade Spelter a sample of 17.286 grams is weighed into a 600 cc. beaker, 200 cc. of distilled water added, and 60 cc. of concentrated nitric acid added gradually until solution is complete. The solution is boiled down to 200 cc., expelling all nitrous fumes, and then transferred to a 250 cc. beaker, washing out original beaker without unnecessarily increasing volume. Four or five drops of 5% silver nitrate solution are added, to precipitate any traces of chlorine present, and the solution electrolyzed for one and one-half to two hours, with initial temperature of 60–70° C. and current of 1.8 amperes.

For No. 2 or Intermediate grade, a sample of 8.643 grams is weighed into a 250 cc. beaker, 100 cc. of distilled water added, and 40 cc. of concentrated nitric acid added. The solution is boiled until all nitrous fumes have been expelled and diluted to 200 cc. with distilled water, 4 or 5 drops of 5% silver nitrate added and the solution electrolyzed as given under High Grade Spelter.

For the three lower grades of spelter, Brass Special, Selected and Prime western, a sample of 17.286 grams is weighed into a 600 cc. beaker, covered with 200 cc. of water and 60 cc. of concentrated nitric acid added. This solution is boiled down to 200 cc. transferred to a 500 cc. graduated flask and the flask filled to the graduation. After thorough mixing, an aliquot portion of 125 cc. (equivalent to 4.3215 grams) is poured into a 250 cc. beaker, 10 cc. of concentrated nitric acid added, boiled for ten minutes, diluted to 200 cc., with distilled water, silver nitrate added and electrolyzed as given for high grade spelter.

The anode is made of sheet platinum with wire stem and is sand blasted. No gold solder should be used on these cylinders. The surface area is 135 sq. cm. A spiral of platinum wire is used as a cathode. A spiral of aluminum wire may also be used, although its life is much shorter.

When electrolysis is complete, the anode is removed from the solution as rapidly as possible, washed three times with distilled water, once with alcohol, dried in an air bath at 210° C. for thirty minutes, cooled and weighed.

The weight of PbO₂ can be calculated directly to percentage of lead as factor weights of sample were taken.

Lead Acid Method

Weigh 10 grams of the sample into a 400 cc. beaker and add 120 cc. of “lead acid.” When all but about 10% of the zinc is dissolved, filter and wash with lead acid. Retain the filtrate. Wash the metallics back into the beaker and dissolve in nitric acid. Add 40 cc. of “lead acid” and evaporate to strong fumes. Cool and add 35 cc. of water, which is the amount evaporated from the “lead acid,” and heat to boiling. Add the filtrate containing most of the zinc and a little lead sulphate, stir and allow to settle over night. Filter on a Gooch crucible, wash with lead acid, a mixture of alcohol and water (1:1), finally with alcohol and ignite inside a porcelain crucible and weigh as lead sulphate.
ZINC

Lead Acid. Add 1 gram of lead acetate in 300 cc. of water to dilute sulphuric acid (300 cc. acid to 1800 cc. of water). Shake well, allow to cool and settle. Filter off the precipitated lead sulphate. By the use of this sulphuric acid saturated with lead, the solubility of lead sulphate need not be considered, the solution being brought back to the same concentration each time.

Note. The rejection limits for spelter of the American Society for Testing Materials consider five grades as follows:

<table>
<thead>
<tr>
<th>Grade</th>
<th>Pb Not Over</th>
<th>Fe Not Over</th>
<th>Cd Not Over</th>
<th>Pb + Fe + Cd Not Over</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1. High Grade</td>
<td>.07%</td>
<td>.03%</td>
<td>.07%</td>
<td>.10%</td>
</tr>
<tr>
<td>No. 2. Intermediate</td>
<td>.02</td>
<td>.03</td>
<td>.07</td>
<td>.50</td>
</tr>
<tr>
<td>No. 3. Brass Special</td>
<td>.00</td>
<td>.03</td>
<td>.07</td>
<td>1.0</td>
</tr>
<tr>
<td>No. 4. Selected</td>
<td>.00</td>
<td>.04</td>
<td>.07</td>
<td>1.25</td>
</tr>
<tr>
<td>No. 5. Prime Western</td>
<td>.08</td>
<td>.08</td>
<td>.07</td>
<td></td>
</tr>
</tbody>
</table>

IRON

Hydrogen Sulphide Method

Ten grams or more of the sample of spelter, which has been passed under a magnet to remove any metallic iron particles, is weighed out into a 250 cc. beaker and dissolved with 50 cc. of concentrated hydrochloric acid. After standing several minutes until violent action has ceased, about 1 cc. of potassium chlorate solution (50 grams per liter) is added and boiled until all chlorine fumes have been driven off. It is then cooled, 50 cc. of water added, neutralized with ammonia, adding a large excess of the latter, boiled for two or three minutes and then allowed to settle. The solution is filtered, the precipitate on the filter washed with dilute ammonia water and finally with hot water. The precipitate is dissolved into a 500 cc. Erlenmeyer flask, using 10 cc. 1:4 sulphuric acid. The paper is washed thoroughly with hot water. After diluting to a volume of about 300 cc. hydrogen sulphide is passed through for 5 minutes to reduce the iron. The excess of hydrogen sulphide is boiled off, being careful to exclude the entrance of any air. When no trace of hydrogen sulphide is present, as indicated by no test with lead acetate paper, the solution is cooled rapidly, and titrated with a standard solution of potassium permanganate, 1 cc. of which is equivalent to about 0.00034 grams of iron. A blank determination is also run in order to determine the amount of potassium permanganate required to show the pink color on titration. The permanganate solution is standardized against Bureau of Standards Sodium Oxalate.

Colorimetric Method

Solutions. Ammonium Sulphocyanate. One part salt to 2 parts of water.
Potassium Chlorate. One part salt to 20 parts of water.

Standard Iron Solution 1. 500 grams of low iron granulated zinc is dissolved in 800 to 1000 cc. of concentrated hydrochloric acid, sufficient amount of potassium chlorate solution added to oxidize the iron present, boiled several minutes to expel chlorine, cooled and made up to 2500 cc. This solution is standardized by measuring off 50 cc. portions, corresponding to 10 grams of zinc, and determining the iron content by the Hydrogen Sulphide Method.
Standard Iron Solution II. 0.7 grams of ferrous ammonium sulphate is dissolved in water, 10 cc. dilute sulphuric acid added, and the iron oxidized with permanganate. The solution is diluted to 1000 cc. each cc. being equivalent to .0001 gram iron.

Procedure. Ten grams of sample are dissolved and oxidized as given under the Hydrogen Sulphide Method. The solution is cooled and diluted to about 25 cc. and transferred to a comparison tube, 1 2 cc. of the sulphocyanate solution are added, and the volume brought up to 100 cc. and mixed by pouring into the beaker and back into the tube. The red color is compared with the color produced on adding 2 cc. of sulphaonate to 50 cc. of standard iron solution 1, 2 and diluting to 100 cc. Standard Iron Solution II is added until the colors are the same, and the iron present in the unknown calculated. In case the iron is over 0.030, it should be determined by the Hydrogen Sulphide Method.

CADMIUM

Sulphide Method

The determination of cadmium in spelter is best carried out by either of the two following methods, according as the amount to be determined is low or high.

Cadmium in Spelter (Cd — .001% to .02%)

A sample of 500 grams is taken and placed in a 2000 cc. flask with 500 cc. of water and 100 cc. of 1:1 sulphuric acid. Sulphuric acid (1:1) is added in small quantities from time to time, to maintain solution of the zinc (but never any violent action), until about 90% of the sample has been dissolved. This requires about 750 cc. of 1:1 sulphuric acid. When the evolution of hydrogen has become slow, after the last addition of acid, the solution is filtered off, retaining as much of the undissolved metallics as possible in the flask. The metallics are washed twice with water, decanting and pouring the small amount of metallics on the filter. The metallics on the filter are then washed from the paper into the original flask and all dissolved in nitric acid. The solution is washed into a 600 cc. beaker and sufficient sulphuric acid (1:1) added to convert all the metals present to sulphates, leaving an excess of free acid of 10–15 cc. This requires about 95 to 100 cc. of acid. The solution is evaporated until all nitric acid has been expelled.

After cooling, water is carefully added and the beaker heated until all the soluble salts have been dissolved. The lead sulphate is allowed to settle, filtered off and washed. Enough water must be added to keep all zinc sulphate in solution after cooling. Hydrogen sulphide is passed through the filtrate for 15–20 minutes. No precipitate will appear at first, so that a drop or two of ammonia is added and repeated at intervals until a considerable amount of zinc sulphide has been precipitated. The sulphides are then filtered off and washed with cold water. The film of sulphides on the side of the original beaker and the sulphides on the paper are dissolved in 1:2 hydrochloric acid, washing with water, and catching the solution in a tall 400 cc. beaker. 15 cc. of 1:1 sulphuric acid are added and evaporation carried down to fumes. After cooling, 200 cc. of water is added, hydrogen sulphide passed through and ammonia added as above to produce a pre-

1 Clear glass test-tubes ½ in. in diameter, and holding 110 cc. make good comparison tubes.

2 The zinc content of the standard and unknown must be approximately the same. (See references, Bureau of Standards Bulletin, No. 1, Vol. 3.)
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precipitate of cadmium sulphide. The precipitate is treated as before and a third precipitation made. In the case of very low cadmium, a fourth precipitation is advisable. The last precipitate is filtered at once on a weighed Gooch crucible, washed with cold water, dried at 110° C. and weighed as CdS or the cadmium may be weighed as metallic cadmium, by dissolving the last precipitate and electrolyzing as given by the following method:

The last precipitation of cadmium as CdS is filtered off, washed with cold water, and dissolved in dilute hydrochloric acid as in previous precipitations, catching solution and washings in original beaker. Twenty-five cc. of 1 : 1 sulphuric acid are added and evaporation carried to dense fumes. After cooling, a small amount of water is added, the solution neutralized with ammonia (using methyl orange as indicator), then made just acid with sulphuric acid (sp.gr. 1.00) and 3 cc. added in excess. The solution is then transferred to a 250 cc. beaker, (washing out the original beaker), diluted to cover the cylinder (beaker ⅔ full), and electrolyzed over night using a current of one amperc. The cylinder with cadmium deposit is removed, washed with water and alcohol, dried at 110° C., removed from oven as soon as dry, cooled and weighed.

Cadmium in Spelter (Cd —0.2% to 1.0%)

A sample of 10 (or 25) grams is taken and entirely dissolved in a tall 400 cc. beaker with nitric acid, the solution then treated with 25 (or 50) cc. of 1 : 1 sulphuric acid and evaporated to expel all nitric acid. After cooling, water is carefully added and the beaker heated until all the soluble salts have been dissolved. The lead sulphate is allowed to settle, filtered off and washed. The filtrate is diluted to 200 cc. and hydrogen sulphide gas passed through for 15-20 minutes. No precipitate will appear at first, so that a drop or two of ammonia is added and repeated at intervals until a considerable amount of zinc sulphide has been precipitated. The sulphides are filtered off and washed with cold water. They are then dissolved with 1 : 2 hydrochloric acid, catching in the original beaker, 15 cc. of 1 : 1 sulphuric acid added and taken to fumes. This is again diluted to 200 cc. hydrogen sulphide gas passed through, and ammonia added as before to produce a precipitate of cadmium sulphide. This is treated as above and a third precipitation made. The cadmium sulphide from this is filtered at once on a weighed gooch, washed with cold water, dried at 110° C., and weighed as CdS, or the cadmium may be weighed as metallic cadmium, by dissolving the last precipitate and electrolyzing as given under Method for Low Cadmium.

General Remarks

A very retentive filter paper must be used for the cadmium sulphide precipitates.

In dissolving the cadmium sulphide precipitates from the filter paper, the funnel should be covered to guard against loss by spraying. The number of treatments with hydrochloric acid depends upon the amount of sulphides on the paper. The paper may be finally washed with water after all sulphides have dissolved, if desired.

It is not absolutely necessary to wash the final precipitate of cadmium sulphide on the gooch, as this has been accomplished in the transfer of the precipitate from the beaker. This has been included in the methods to safeguard against free acid remaining on the Gooch.
ANALYSIS OF ZINC CHLORIDE SOLUTION

The methods to be used for the analysis of zinc chloride solution or fused zinc chloride are essentially those given under the various chapters for the various elements. It seems advisable, however, to include a set of methods of analysis suitable for the commercial evaluation of zinc chloride.

I. Specific Gravity at 15° C.

The specific gravity is determined by means of a pycnometer. The volume is brought to the graduation after the solution in the pycnometer has been brought to 15° C., using a water bath. The weight of this volume of boiled distilled water is determined at 15° C., and the specific gravity of the zinc chloride solution calculated, compared to water at 15° C.

II. Zinc (Manganese and Copper Absent)

About 25 grams of the well shaken solution is weighed out in a weighing bottle and transferred to a 500 cc. graduated flask. Sufficient nitric acid is added to clarify the solution upon dilution. The flask is filled to the mark with distilled water and thoroughly mixed.

A portion, approximately equivalent to one gram of ZnCl₂ is accurately measured from a pipette or a burette and the zinc determined by titration with a standard potassium ferrocyanide solution as given under procedure for zinc in ores.

Zinc (Manganese or Copper Present)

If manganese or copper is present an aliquot portion is measured out and the manganese or copper separated according to the methods given under procedures for ores, before titration with potassium ferrocyanide.

III. Chlorine

Another portion of this solution, approximately equivalent to .5 grams ZnCl₂ is measured off into a 500 cc. Erlenmeyer flask, 15 cc. of distilled water, 100 cc. of standard N/10 silver nitrate solution and 40 cc. of nitric acid are added to the flask and boiled until all nitrous fumes are driven off. After cooling, the excess silver nitrate is titrated with standard N/10 ammonium thiocyanate solution using 5 cc. (1-6) ferric nitrate solution as an indicator. A blank is run at the same time and the amount of chlorine determined from the difference in volumes of ammonium thiocyanate required. The factor for the standard ammonium thiocyanate solution is best determined with C.P. sodium chloride.

IV. Sulphuric Anhydride (SO₃)

Twenty-five cc. of the original well shaken solution of zinc chloride are measured off with a pipette into a 400 cc. beaker, diluted to 300 cc. with hot water and a few drops of hydrochloric acid added. Any insoluble matter is filtered off, five cc. of bromine water are added to the filtrate and the solution boiled until excess bromine is all driven off. The SO₃ in the filtrate is precipitated with 25 cc. hot 10% barium chloride solution. After standing on the steam plate for 3 hours, the barium sulphate is filtered off, ignited and weighed. The weight of the sample is determined from the specific gravity.
V. Iron (Fe)

A portion of the well shaken solution, equivalent to 10 grams of zinc is evaporated to a syrupy consistency and the iron determined by the colorimetric method as under spelter.

In case the iron is too high to estimate colorimetrically, it is separated with ammonia, filtered off, washed with hot water and dissolved in hot dilute sulphuric acid. This solution is cooled, run through a Jones reductor and titrated with standard potassium permanganate solution, or the iron may be determined by the hydrogen sulphide method as given under analysis of spelter.

VI. Iron and Aluminum (Fe₂O₃ + Al₂O₃)

Either 10 or 20 cc. of the original well shaken solution are transferred to a 400 cc. beaker, diluted with 150 cc. of water and hydrochloric acid added to a very faint excess. (2 drops concentrated acid.) A rapid stream of hydrogen sulphide is passed through the solution for 30 to 40 minutes. The precipitate of zinc sulphide is filtered off and washed thoroughly. The filtrate is boiled for about 15 minutes to remove hydrogen sulphide, cooled, sufficient bromine water added to more than oxidize all the iron, and then boiled to remove the excess bromine. Ammonium hydroxide is now added in slight excess, the precipitate of iron and alumina filtered off and washed with hot water. The precipitate is dissolved from the paper with hot hydrochloric acid (1:4) re-precipitated, filtered off, washed free from chlorides, ignited and weighed.

VII. Manganese (Mn)

Either 10 or 20 cc. of the original well shaken solution are transferred to a 400 cc. beaker, 25 cc. of sulphuric acid (1:1) added and evaporated to practically complete expulsion of all excess sulphuric acid. Nitric acid (1:3) is now added and the manganese determined according to the bismuthiate method.

VIII. Lime (CaO)

Twenty-five cc. of the well shaken solution are measured off with a pipette, a few drops of hydrochloric acid added, and the solution diluted to 150 cc. Twenty grams of ammonium chloride and a few drops of bromine water are added. The iron and manganese are precipitated by ammonia and filtered off after bringing to boiling. The filtrate is evaporated to 150 cc., the lime precipitated with 25 cc. ammonium oxalate solution (saturated solution) and allowed to stand for 3 hours. The calcium oxalate is filtered off and washed four times with hot water. A hole is then punched in the filter paper, the precipitate washed into a 400 cc. beaker, with boiling water, 10 cc. of sulphuric acid (1:1) poured over the paper and the paper washed with boiling water. The solution is diluted to 150 cc. with hot water and titrated with standard potassium permanganate solution.

IX. Magnesia (MgO)

The filtrate and washings from the lime determination is made slightly acid with hydrochloric acid and 15 cc. of a saturated solution of microcosmic salts added. The solution is cooled and the magnesia precipitated by the slow addition of ammonia. Sufficient ammonia must be added to hold all zinc in solution, an excess
of about 50 cc. being required. The precipitate after standing 12 hours is filtered off, and redissolved in hot 1-4 hydrochloric acid. Twenty grams of ammonium chloride are added to this solution, then a few drops of microcosmic solution, and precipitation affected with ammonia as before, the excess of ammonia being only 10 cc. in this case. After standing 12 hours, the precipitate is filtered off, washed six times with 1:10 ammonia water, or until free from chlorides, ignited and weighed as Mg₃P₂O₇.

X. Alkalies (NaCl+KCl)

A sample of about 10 grams is taken and made up to a volume of 500 cc. From this a portion equivalent to approximately 2 grams is measured off, slightly acidified with hydrochloric acid and the zinc precipitated with hydrogen sulphide. After filtering, the filtrate is tested with ammonium sulphide, and any zinc, iron and manganese precipitated is filtered off. The filtrate is boiled for about thirty minutes to drive off the hydrogen sulphide, and cooled. After cooling, the solution is made slightly acid with hydrochloric acid, a few drops of bromine water added and the excess of bromine boiled off. The solution is diluted to about 200 cc. with hot water, and 10 cc. of hot 10% BaCl₂ solution added, to precipitate SO₃. Without filtering off the barium sulphate, the solution is made ammoniacal, one gram of ammonium carbonate and 5 cc. of ammonium oxalate solution added and the precipitates allowed to settle in a warm place. The precipitate is filtered off, washed with hot water, and the combined filtrate and washings evaporated to dryness in a porcelain dish. The ammonium salts are completely driven off by ignition over a low flame. The residue remaining is dissolved in a small amount of water with two drops of hydrochloric acid, transferred to a weighed platinum dish, the porcelain dish being washed with a minimum amount of water, evaporated to dryness on a hot plate, and after cooling weighed.

Any magnesia which may be present with the alkali chlorides is determined, calculated to MgCl₂ and deducted from the weight of salts in the dish. This difference is expressed as combined alkali chlorides KCl+NaCl.

XI. Copper

Twenty cc. of solution are taken, 5 grams of ammonium chloride and 20 cc. of ammonium hydroxide added, diluted to 100 cc. in a color comparison tube and compared with a zinc chloride solution of equal strength, to which a measured amount of standard copper solution is added to give the same depth of color. If iron interferes with the color comparison, it should be filtered off before diluting to volume. When the amount of copper present is over 0.05%, the determination should be carried out by some other method. See chapter on copper.

XII. Barium (Ba)

If sulphuric anhydride (SO₃) is found to be present, it is not worth while to make a determination for barium. If no sulphuric anhydride is present, barium should be looked for and determined by diluting 10-20 cc. to 300 cc. with water, adding a slight excess of hydrochloric acid heating to boiling and precipitating the barium with ammonium sulphate solution (10 per cent.).
ANALYSIS OF FUSED ZINC CHLORIDE

The analysis of fused zinc chloride for zinc, etc., is carried out by the same methods as given under Zinc Chloride Solution, working on a solution of the fused salt in water. This solution is made up by rapidly transferring approximately 20 grams of fused salt to a weighing bottle, weighing, dissolving in water in a 2000 cc. graduated flask to which a few drops of nitric acid has been added to prevent precipitation of basic zinc chloride, and filling to the mark. Aliquot portions are taken from this solution for the various determinations.

Special determinations are sometimes called for with fused zinc chloride which is to be used for some special purpose. It is very essential that such analyses be carried out carefully according to the method prescribed in order that the results, which are largely empirical, may be comparable. One analysis of this sort which is commonly called for is Basicity expressed in some empirical way to give a measure of the relative quantities of the basic zinc chloride, which will settle out upon dissolving fused zinc chloride in water. It may be expressed as the volume of standard hydrochloric acid (usually N/2) required to neutralize 10 cc. of a 40° Baume solution of the fused zinc chloride, diluted with 300 cc. of water, when using Methyl orange as indicator, or the weight of basic chloride obtained by treating 10 grams of the sample, weighed in a weighing bottle, with 400 cc. of water, agitating to complete all possible solution, filtering off insoluble on a gooch crucible and washing with water until combined filtrate and washings total just 1000 cc.

Ammonia (NH₃)

It is often of value to know if ammonium chloride is present. A sample of 5-10 grams is weighed and transferred to a 500 cc. distilling flask, 100 cc. of water, 50 cc. of sodium hydroxide (20 per cent.) and a small quantity of granulated zinc added. The ammonia and water are distilled over into an absorption bottle containing a measured quantity of standard acid. The excess of acid is titrated with standard alkali solution, using methyl orange.

See chapter on nitrogen, page 343, also analysis of paint pigments, volume 2.

1 The addition of granulated zinc aids in the expulsion of the ammonia by hydrogen formed with the sodium hydroxide.
Determination of Zinc in Pig Lead ¹

Solutions Required

Nitric Acid (1 : 4).—Mix 200 cc. of HNO₃ (sp. gr. 1.42) with 800 cc. of distilled water.

Sulphuric Acid (1 : 1).—Carefully pour, with stirring, 500 cc. of H₂SO₄ (sp. gr. 1.84) into 500 cc. of distilled water.

Acidulated Hydrogen Sulphide Water.—Add 20 cc. of HCl (sp. gr. 1.19) to 1000 cc. of distilled water and saturate with hydrogen sulphide.

Ammonium Thiocyanate Solution (2 per cent).—Dissolve 20 g. of NH₄CNS in 1000 cc. of distilled water.

Hydrochloric Acid (1 : 3).—Mix 100 cc. of HCl (sp. gr. 1.19) and 300 cc. of distilled water.

Standard Zinc Solution (0.1 mg. of zinc per cc.).—Dissolve exactly 0.1 g. of U. S. Bureau of Standards pure zinc in 5 cc. of HCl (sp. gr. 1.19) and dilute to exactly 1000 cc. with distilled water.

Potassium Ferrocyanide Solution.—Dissolve 34.8 g. of K₄Fe(Cn)₆.3H₂O in 1000 cc. of distilled water.

Method

Dissolve 222.23 g. of the sample in 1100 cc. of HNO₃ (1 : 4), using a 1300-cc. beaker. When the lead is dissolved, transfer the solution to a 2000-cc. graduated flask and add slowly 150 cc. of H₂SO₄ (1 : 1). Cool, fill the flask to the mark and then pour the solution into a clean 3000-cc. flask provided with a rubber stopper. Rinse the measuring flask with exactly 50 cc. of water, which is equivalent to the volume of lead sulphate which is present. Mix the solution thoroughly by shaking, allow the precipitate to settle and filter through a dry filter until 1800 cc. of filtrate has been obtained.

Place exactly 1800 cc. of filtrate (equivalent to a 200-g. charge) in a No. 9 porcelain evaporating dish and evaporate the solution to approximately 100 cc. Transfer the solution to a 600-cc. beaker, neutralize with ammonia, and then add 5 cc. of HCl (sp. gr. 1.19) for every 100 cc. of solution. Warm the solution and pass in a rapid current of hydrogen sulphide until it is saturated. Digest for 30 minutes on the steam bath, add an equal volume of water and again saturate with hydrogen sulphide. Filter and wash with acidulated H₂S water.

Discard the precipitate and evaporate the filtrate in glassware containing no zinc (such as Pyrex) until the volume of the solution is approximately 100 cc.

Neutralize the solution with ammonium hydroxide, add 5 g. of citric acid, and warm until the acid is dissolved. Add small portions of calcium carbonate to the hot citric acid solution until about 1 g. of calcium citrate has separated and then pass in a rapid current of H₂S as the solution is allowed to cool. Allow the solution to stand for from 2 to 4 hours, part of the time on a water bath, until the supernatant liquid is clear.

Collect the precipitate on a filter, wash with a 2 per cent solution of ammonium thiocyanate and then dissolve the precipitate in hot dilute hydrochloric acid (1 : 3). If the solution has a reddish color (due to iron), the zinc must

¹ Standard Method of the A. S. T. M.
be reprecipitated as above. If the solution is clear, evaporate it to dryness on the steam bath, take up the residue in 3 cc. of HCl (sp. gr. 1.19), add 20 cc. of water and filter if not perfectly clear.

Transfer the solution (Note 2) to a 50-cc. Nessler jar and dilute to 45 cc. Prepare other Nessler jars containing 3 cc. of HCl (sp. gr. 1.19), definite volumes of standard zinc solution, and diluted to 45 cc. Add 5 cc. of potassium ferrocyanide solution to each jar, mix quickly, and compare the turbidities by viewing longitudinally as the jars are held over a sheet of fine print. Add more of the standard zinc solution from a burette to the jar which approximates the turbidity of the unknown most closely, until the turbidities match each other, and calculate the percentage of zinc on the basis of a 200-g. sample or the aliquot portion taken.

Notes. 1. All glassware that contains zinc must be avoided and in umpire work a blank test should be carried along with the test.
2. The whole solution can be used if the lead contains no more than 0.002 per cent of zinc. If more zinc is present, it is best to take such an aliquot portion of the solution as will give approximately 4 mg. of zinc and then to add enough HCl to provide 3 cc.
3. For further details concerning the turbidometric test, consult the "Determination of Small Quantities of Zinc" by Mr. Bodansky, in the Journal of Industrial and Engineering Chemistry, Vol. 13, pp. 696-697 (1921).
4. The addition of calcium carbonate with the formation of a precipitate of calcium citrate serves the purpose of giving a clear filtrate, and prevents the loss of colloidal sulphide.
ZIRCONIUM

Zr, at. wt. 91.2; sp.gr. 4.1 (amorphous) to 6.2 (coherent); m.p. about 1700; \(^3\) oxides, \(\text{ZrO}_2\) (\(\text{Zr}_2\text{O}_5\) and \(\text{ZrO}_3\) in hydrated form).

DETECTION

The material to be tested is brought into solution by one of the methods given in the section on the Preparation of the Sample. In the regular course of qualitative analysis the zirconium will be found in the main precipitate formed either by ammonium hydroxide alone or by the combined action of ammonium hydroxide and ammonium sulphide. This precipitate can be dissolved in sulphuric acid, the acidity then adjusted so that 10% of the solution, by volume, is conc. sulphuric acid, 10 cc. of 3% hydrogen peroxide and 1 cc. more of conc. sulphuric acid added, and then a large excess of \(\text{Na}_2\text{HPO}_4\) or \((\text{NH}_4)_2\text{HPO}_4\) solution, to which has also been added 1/10 its volume of conc. sulphuric acid. A white precipitate proves the presence of zirconium, since no other elements (titanium having been peroxidized) have phosphates which are insoluble in such an acid concentration. \(^5\) This is the simplest and surest method of detecting zirconium. In the regular course of analysis thorium and the rare earths would probably have been precipitated from the acid solution of the ammonium hydroxide precipitate by an excess of oxalic acid (see "Detection" in chapter on thorium). The filtrate would contain almost all of the zirconium, \(^4\) along with titanium, beryllium and the more common elements of the group. The oxalic acid in this filtrate can be destroyed by evaporation with sulphuric acid, and then zirconium, titanium and aluminum precipitated by boiling the weakly acid solution (containing 8 or 10 drops more sulphuric acid than is needed to redissolve the first faint precipitate formed by gradually adding dilute ammonia) with sodium thioulsulphate. This precipitate may be brought into solution by fusing with potassium pyrosulphate, and taking up with sulphuric acid. The phosphate test as just outlined may then be applied.

Turmeric paper on drying after having been moistened with a slightly acid (HCl or \(\text{H}_2\text{SO}_4\)) solution containing zirconium shows a reddish-brown color, similar to that due to boric acid. Titanium gives a like reaction in the tetravalent condition, but if the acidified solution is reduced by adding a piece of zinc, and then promptly tested (before titanium is reoxidized), the test is specific for zirconium.

\(^1\) Paul H. M.-P. Brinton, Professor of Analytical Chemistry, University of Minnesota.

\(^2\) Considerable doubt exists as to the reliability of the physical constants of zirconium.

\(^3\) If the contentions of Cowper and Hevesy that practically all zirconium contains varying amounts of hafnium (more justly called celtium) is true, it is not surprising that such discordant results have been recorded by different investigators.


\(^5\) Oxalic acid produces a precipitation of zirconium oxalate in dilute mineral acid solution, but the precipitate is soluble in excess of oxalic acid. (It is also soluble in ammonium oxalate; and is not reprecipitated by addition of hydrochloric acid, thus differing from thorium.)
From aluminum zirconium may be differentiated by the solubility of zirconium base carbonate in excess of a strong, cold solution of ammonium carbonate (on boiling the hydroxide separates out again); and by the insolubility of zirconium oxyiodate, produced by an alkali iodate in a slightly acid solution. (Thorium and tetravalent cerium also give the iodate test.)

ESTIMATION

The main ores of zirconium are baddeleyite, essentially zirconium dioxide; and zircon, essentially zirconium orthosilicate. While zircon is the most widely distributed ore of zirconium, the most important commercially is now the Brazilian baddeleyite, which, mixed with a little zircon, comes under the trade name of zircite, and contains around 75% of ZrO₂. The determination of zirconium in furnace-lining material, high-temperature laboratory ware, enamels, and steel is at times called for.

Preparation and Solution of the Sample

Acid treatment will not decompose ordinary zirconium ores. The following fluxes are most commonly used.

Sodium peroxide is used in a nickel crucible which has been lined by fusing some sodium carbonate,¹ and causing it to cool in an even layer on the sides and bottom. This prevents in large measure the attack of the crucible by the peroxide, and avoids the subsequent introduction of large amounts of nickel into the solution. Several grams of sodium peroxide are melted in the crucible, after lining with sodium carbonate, and allowed to solidify on the bottom. This prevents particles of the ore from being caught in the carbonate lining and remaining unfused. The sample of finely ground ore (0.5 g.) is mixed with 8–10 g. of sodium peroxide in the crucible thus prepared, and fused at low red heat over a small flame, by gently swirling the crucible, held in tongs. 5–10 minutes should suffice. When cool the crucible is placed in a large platinum dish, or porcelain casserole, and covered with warm water, keeping the vessel covered with a watch glass until danger of loss from effervescence is over, the solution is boiled until the carbonate lining has dissolved, and the crucible is then removed. The solution is next made decidedly acid with hydrochloric acid, and boiled until carbon dioxide is expelled. This should give a clear solution containing the zirconium and all the other constituents of the ore. If a very small amount of undecomposed ore is found here, it should be filtered off, ignited, fused with a little potassium pyrosulphate, dissolved in 5% sulphuric acid, filtered if necessary, and added to the main solution.

Potassium hydrogen fluoride is applied by Smith and James² in the following manner: The finely ground ore is fused with 12 to 15 times its weight of potassium hydrogen fluoride. The latter may be prepared from potassium carbonate or fluoride by treating with a slight excess of hydrofluoric acid, and evaporating over a small flame until a clear fused mass is obtained. When cool the melt may be broken up and preserved for use. The mixture

¹ Private communication from J. A. Holladay, Electro Metallurgical Co., Niagara Falls, N. Y.
² Smith and James, J. Am. Chem. Soc., 42, 1764 (1920).
of ore and fluoride, in a platinum dish, is carefully heated over a small flame. When the mixture has softened it is stirred with a platinum rod, and the size of the flame is gradually increased, finally heating over a Meeker burner until the mass just fuses to a clear liquid. The cooled melt is treated with 50 cc. of 1:1 sulphuric acid, gently heated until nearly all water is expelled, and then more strongly until abundant fumes are evolved. The cold residue is boiled with water. This solution contains all the zirconium. If it is to be used for the selenite method of Smith and James, the zirconium is precipitated (along with many other bases) by ammonium hydroxide, filtered, washed free from sulphates—since sulphates are undesirable for the selenious acid precipitation—and dissolved in hydrochloric acid.

Borax is strongly recommended by Lundell and Knowles for the decomposition of all ores of zirconium. This flux is particularly suited to the decomposition of samples in which zirconium only is to be determined, and by precipitation with cupferron, since boric acid does not interfere with this reagent. If other elements of the sample are to be determined, the boric acid must be removed by volatilization as methyl borate, so in such cases it is better to employ the sodium peroxide fusion. In using the borax method Lundell and Knowles recommend the following procedure: 4 g. of the flux are melted in a platinum crucible and allowed to cool. About 0.3 g. of the finely ground ore is placed on top of the fused borax, the crucible is covered, and heated over a Meeker burner until thorough fusion has taken place, which does not ordinarily require more than half an hour. During the operation it is well to stir the melt occasionally with a short platinum rod or stiff wire, which is allowed to remain in the crucible, and which may be conveniently handled with the crucible tongs. When the decomposition of the ore is complete, the platinum rod is removed, and it is put into the beaker to be used for the solution of the melt. As the melt cools, the crucible is gently twirled in order to run the fusion up on the sides in a thin layer. The cooled melt is dissolved in 150 cc. of 1:5 hydrochloric acid in a 250-cc. beaker, by filling the crucible with acid, inverting in such a manner that one edge of the crucible rests on the crucible cover, which has been placed on the bottom of the beaker—thus allowing free circulation of the solvent—and then gently warming on the steam bath. The solution is transferred to a platinum dish or porcelain casserole, 20 cc. of 1:1 sulphuric acid are added, and the mixture is evaporated until heavy fumes escape. The cooled solution is next diluted to about 100 cc., the impure silica is filtered off and washed with hot water. This solution is allowed to stand warm over night. If the ore contained interfering amounts of phosphorus, it will be thrown down as zirconium phosphate by this digestion. If a precipitate appears, it is filtered and washed with 5% ammonium nitrate solution. This precipitate will contain zirconium,

1 Experiments in the writer’s (Brinton’s) laboratory by Mr. Tohru Kameda indicate that there is no loss of zirconium by volatilization if the process is carried out as here described. Continuing the heating for 5 minutes after clear fusion has been attained may cause a loss of as much as 2 mg. of ZrO₂.


3 During the evaporation boric acid will separate and form a crystal skin over the surface, thus retarding evaporation. Occasional stirring during this period will hasten the evaporation. As the sulphuric acid becomes more concentrated by evaporation, the boric acid eventually dissolves again.
and there is still apt to be a little zirconium in the impure silica first filtered off. Also there may be some phosphoric acid in the filtrate; so to this filtrate 5 g. of ammonium chloride, and then ammonium hydroxide in slight excess are added, and after boiling for several minutes, the precipitated hydroxides are filtered and washed with 2% ammonium nitrate solution. This filtrate is discarded. The precipitate and paper are digested in 100 cc. of hot 5% sulphuric acid solution, and the filter shreds and any insoluble residue are filtered and well washed with hot water. This solution, containing most of the zirconium of the sample, is temporarily set aside. The last residue filtered, the impure silica, and any zirconium phosphate obtained by the over-night digestion are all ignited in the original platinum crucible. The ignition residue is moistened with water, 1 cc. of 1:1 sulphuric acid, and 5 cc. of hydrofluoric acid are added, and the mixture is heated until all sulphuric acid has been expelled. The residue in the crucible is fused with a little sodium carbonate, digested in water, and filtered, washing with hot water. The filtrate is discarded. The insoluble residue is again ignited in the platinum crucible, fused with potassium pyrosulphate; and, after cooling, the melt is dissolved in hot 5% sulphuric acid. This solution is added to the main solution, thus giving one solution in which is contained all the zirconium originally present in the sample.

SEPARATIONS

From Members of the Copper and Tin Groups. The members of these groups are precipitated free from zirconium by hydrogen sulphide in slightly acid solution.

From Iron, Nickel, Cobalt, Manganese, and Zinc. The iron, in acid solution, is reduced by hydrogen sulphide gas, tartaric acid equal to 5 times the approximate weight of the oxides present is added, the solution is made ammoniacal, and then hydrogen sulphide is passed into the solution until the sulphide precipitate has congealed. The precipitate is filtered on close-grained paper, care being taken to keep the funnel well filled, so that oxidation of the sulphides and consequent "running through" is avoided. The sulphides are promptly washed, using the same precaution, with water containing a little ammonium chloride and ammonium sulphide. If the cupferron precipitation of zirconium is to be used, the tartrate need not be destroyed, and it is sufficient to acidify to a total acidity of 10% of conc. sulphuric acid (by volume), and to boil out the hydrogen sulphide. If for further work it should be necessary to remove the tartrate, the solution is acidified with 10 cc. of conc. sulphuric acid, evaporated to a volume of about 50 cc., 10 cc. of conc. nitric acid added, and the solution evaporated to fumes of sulphur trioxide. After cooling, 10 cc. of conc. nitric acid are again added, and the mixture once more evaporated to fumes. At times a third addition of nitric acid and evaporation may be necessary to completely destroy the tartaric acid.

From Titanium. Zirconium may be separated from titanium by precipitating the zirconium with Na₃H₂PO₄ or (NH₄)₂HPO₄ in a 10% (by volume) sulphuric acid solution, in presence of hydrogen peroxide. See Gravimetric Determination as phosphate.
From Thorium and Rare Earth Elements. These elements may be precipitated with an excess of oxalic acid, leaving the zirconium in the filtrate. (See "Detection" in chapter on thorium.) For complete separation the rare earth oxalates should be boiled with conc. sulphuric acid until decomposed, diluted, nearly neutralized with ammonia, and again precipitated with an excess of oxalic acid. The combined filtrates contain all the zirconium. (A method adapted to the determination of small amounts of rare earth oxides in the cupferron precipitate is given later.)

From Aluminum, Chromium, and Uranium. Zirconium is quantitatively separated from these three elements by precipitation with cupferron in 10% (by volume) sulphuric acid solution. The uranium must be in the hexavalent condition or it will contaminate the zirconium precipitate. (Nitric acid should not be used to oxidize uranium, as it decomposes cupferron. Uranium will practically always be in the hexavalent condition without special oxidation. If in doubt, the 10% sulphuric acid solution may be boiled with a little hydrogen peroxide.)

From Molybdenum. By precipitation of molybdenum sulphide in acid solution. (See chapter on molybdenum.)

From Tungsten. By precipitation of tungsten in acid solution by cinchonine hydrochloride. (See chapter on tungsten.)

From Vanadium. By fusion of the mixed oxides with sodium peroxide or sodium carbonate, and leaching out the soluble sodium vanadate with water.

GRAVIMETRIC DETERMINATION OF ZIRCONIUM

By Precipitation with Cupferron. The solution, which has a volume of 300–400 cc., and contains 10% (by volume) of conc. sulphuric acid (any tartaric acid present does not interfere), is cooled to about 10° C., and then an excess of cupferron solution (6 g. dissolved in 100 cc. of cold water and filtered) is added. The formation of a fine white precipitate (nitrosophenylhydroxylamine) which redissolves shows that an excess of the reagent has been added. The zirconium precipitate is white and curdy, but any titanium present is also quantitatively precipitated, and it will impart a yellow color to the precipitate. A brownish color indicates that the previous separation from iron has been faulty. The precipitate is filtered and washed with cold 1 : 10 hydrochloric acid solution. The precipitate and paper are carefully ignited in a weighed platinum crucible, very slowly until the rush of gases from decomposition of the organic matter has ceased; and then to constant weight over a blast or over a large Meeker burner. The weight thus found represents all the zirconium and titanium dioxide, and some rare earth oxides, if these elements have not previously been completely removed.

To correct for titanium and rare earths the ignited oxides are fused with potassium pyrosulphate, dissolved in 1 : 10 sulphuric acid, and diluted to exactly 100 cc. in a graduated flask. By means of a dry 50-cc. pipette exactly one-half of the solution is taken for the determination of titanium, and the pipette and the 100-cc. flask are completely rinsed into another vessel, thus giving the other half for the determination of rare earths.

Small amounts of titanium are determined by the colorimetric method; while for larger amounts the zinc reductor—permanganate titration method —is used. For details of these see chapter on titanium.
Rare earths may be determined according to Hillebrand's method as follows: "Precipitate the hydroxides with an excess of potassium hydroxide, decaent the liquid, wash by decantation with water once or twice and then slightly on the filter. Wash the precipitate from the paper into a small platinum dish, treat with hydrofluoric acid, and evaporate nearly to dryness. Take up in 5 cc. of 5% (by volume) hydrofluoric acid. If no precipitate is visible, rare earths are absent. If a precipitate is present, collect it on a small filter held by a perforated platinum or rubber cone and wash it with from 5 to 10 cc. of the same acid. Wash the crude rare earth fluorides into a small platinum dish, burn the paper in platinum, add the ash to the fluorides and evaporate to dryness with a little sulphuric acid. Dissolve the sulphates in dil. hydrochloric acid, precipitate the rare earths by ammonia, filter, redissolve in hydrochloric acid, evaporate the solution to dryness, and treat the residue with 5 cc. of boiling hot 5% oxalic acid. Filter after fifteen minutes, collect the oxalates on a small filter, wash with not more than 20 cc. of cold 5% oxalic acid, ignite and weigh as rare earth oxides which are to be deducted from the weight of the cupferron precipitate."

While the recovery of the rare earths by this method is not absolutely complete, the error is negligible for the amounts ordinarily found.
The sum of the weights of rare earth oxides and titanium dioxide found are subtracted from the weight of the ignited cupferron precipitate to obtain the true weight of ZrO₂.

By Precipitation with Selenious Acid. The zirconium and other bases should be in about 5% (by volume) hydrochloric acid solution, free from sulphuric and nitric acids, and should be in a volume of about 750 cc. The solution is heated to boiling, and an excess of 12½% selenious acid solution (usually 20–40 cc.) is added. After the precipitate of zirconium selenite has settled it is filtered, washed with 3% hydrochloric acid solution (Smith and James directions; the writer prefers a wash liquid containing 40 cc. of 12½% selenious acid reagent in 750 cc. of 3% hydrochloric acid), ignited to constant weight over a strong Meker burner or blast, and weighed as ZrO₂. For a discussion of the possible interference of large amounts of iron, of titanium, and of phosphoric acid, the original paper of Smith and James should be consulted.

By Precipitation with Ammonium Phosphate. This method is suitable for separations, and for the determination of small amounts of zirconium such as are encountered in rock analysis. In view of the probability that almost all minerals of zirconium contain appreciable amounts of hafnium ("hafnium"), which gives practically all the reactions of zirconium, but which has a very much higher atomic weight, an uncertainty as to the factor ZrO₂/ZrP₂O₇ exists, so the pyrophosphate can hardly be recommended as a weighing form for large amounts of zirconium. The following details are recommended for observance in using this method.

A. Volume of Solution. From 25 cc. for small amounts (i.e., 0.0005 g. ZrO₂) to 200 cc. for amounts ranging around 0.1 g. ZrO₂.

2 Smith and James, loc. cit.
B. Acidity. Twenty per cent sulphuric acid by weight.

C. Hydrogen Peroxide. Sufficient to keep titanium peroxidized; 10 cc. will do no harm.

D. Precipitant. Secondary ammonium phosphate in excess. From 10 to 100 times the theoretical requirement, as expressed by the ratio Zr : \( \text{P}_2\text{O}_5 \), should be used here. The large excess is desirable when small amounts of zirconium are determined.

E. Precipitation Conditions. (1) Temperature: Cold or tepid, preferably 40–50° C. (2) Time: Two hours for amounts of \( \text{ZrO}_2 \) in excess of 0.005 g. Six hours, or longer, for smaller amounts.

F. Filtration. Warm solution, decant as far as possible to avoid clogging the filter.

G. Washing. This should be done with cold 5% ammonium nitrate, since the phosphate is appreciably soluble in pure water.

H. Ignition. Ignite very carefully in a partially covered platinum crucible over a low flame until carbon is destroyed, then blast or heat over a Meeker burner for 15 minutes.

RECOMMENDED METHOD FOR THE DETERMINATION OF ZIRCONIUM IN COMMERCIAL ZIRCONIUM ORES

The following combination gives a method essentially as recommended by the U. S. Bureau of Standards. Details will be found in the respective sections of this chapter.

Decomposition by fusion of 0.3 g. sample with borax, following the procedure under "Preparation and Solution of the Sample" until the sulphuric acid solution containing all the zirconium originally present in the sample is obtained.

Separation from members of the copper and tin groups by precipitation with hydrogen sulphide in an approximately 1% sulphuric acid solution; and then, without intervening filtration, separation from iron, manganese, etc., by treatment with tartaric acid, ammonia, and hydrogen sulphide, as detailed under "Separations," finally obtaining the zirconium in 10% (by volume) sulphuric acid solution. (Removal of tartaric acid is not necessary.)

Precipitation with cupferron, with subsequent corrections for any titanium and rare earths present, just as outlined in the "Gravimetric Determination."

Determination of Zirconium in Steel. See chapter on iron.

Determination as Zirconium Oxide

With pure salts the zirconium may be precipitated completely as the hydroxide by the addition of ammonia, settling and finally igniting and weighing as the oxide, \( \text{ZrO}_2 \).