SULPHUR

S, at.wt. 32.065; sp.gr. 2.035; m.p. 111°; b.p. 444.53°; oxides S₂O₃, SO₃
SO₃, S₂O₃; principal acids H₂S₂O₃, H₂SO₃, H₂SO₄, H₂S₂O₅, and H₂S₂O₇.

DETECTION

The following tests include the detection of free sulphur and its more important combined forms.

Element. Sulphur is a polymorphous, yellow, brittle, odorless and tasteless solid; existing in the rhombic, monoclinic and triclinic crystalline forms, and also in an amorphous state. At 111° it melts to a pale yellow liquid; at 180° it thickens to a dark gum-like material, containing a large percentage of amorphous sulphur; at 200° it becomes a liquid again, and at 444.53° it boils, giving off a brownish-red vapor.

The important commercial forms of elemental sulphur are: Flowers of Sulphur, consisting of rhombic sulphur and not less than 30% of amorphous sulphur with a small amount of occluded free acid; Powdered Sublimed Sulphur (often called Flour Sulphur, a confusing term that should be abolished), consisting essentially of finely ground sublimed sulphur all in the rhombic form though at times a small percentage of amorphous sulphur is present; Refined Brimstone and Roll Sulphur (in some sections termed Virgin Lump Sulphur), consisting entirely of sublimed sulphur in the rhombic form; Powdered Brimstone (often termed Commercial Flour, Superfine Flour and the like); and Brimstone or Crude Lump Sulphur. In these commercial sulphurs the physical form and the presence of certain small amounts of impurity are the characteristics of most importance as all the varieties named, even the Brimstones, usually contain in excess of 99.5% available sulphur.

Heated in the air sulphur burns with a blue flame, and is oxidized to SO₃, a gas with a characteristic pungent odor. This gas passed into a solution of potassium permanganate will decolorize it, if SO₃ is in excess of the amount that will react with the KMnO₄ in the solution.

If sulphur is dissolved in a hot alkali solution and a drop of this then placed on a silver coin, a stain of black Ag₂S will be evident, due to the action of the sulphur.

Sulphides. Hydrogen sulphide, H₂S, is liberated when a sulphide is treated with a mineral acid. This gas blackens moist lead acetate paper. H₂S has a very disagreeable odor, which is characteristic.

Sulphates. A white compound, BaSO₄, is precipitated in presence of free hydrochloric acid when a solution of barium chloride is added to a solution of a sulphate.

Insoluble sulphates are decomposed by boiling or fusion with alkali carbonates, forming water-soluble alkali sulphates.

Chapter contributed by Wilfred W. Scott with additions by Charles A. Newhall.
SULPHUR

Sulphites. Sulphur dioxide, SO₂, is evolved when a sulphite is treated with hydrochloric acid. The odor of the gas is characteristic.

Sulphur dioxide decolorizes a solution of potassium permanganate. (Use very dilute solution.)

Sulphites are distinguished from sulphates by their failure to form a white precipitate, when barium chloride is added to the solution acidified with hydrochloric acid; also by the fact that H₂S is formed when zinc is added to a solution of a sulphite, acidified by hydrochloric acid.

Thiosulphates. Sulphur dioxide is evolved and free sulphur precipitated when a thiosulphate is acidified with dilute mineral acids. In presence of oxidizing agents sulphides will also liberate free sulphur.

Thiosulphates are strong reducing agents.

ESTIMATION

The determination of sulphur may be required in a great variety of substances, minerals, rocks, sulphur ores, acids, salts, water, gas, coal and other organic matter, insecticides, fungicides, stock medicants, fertilizer and other agricultural materials.

The substance occurs in nature principally in the following forms:

Element. Found free, generally mixed with earthy matter. The commercial product is exceedingly pure and may contain over 99.5% S.

Sulphur Dioxide. The gas, together with free sulphur, is found in volcanic regions.

Hydrogen Sulphide. Occurs in mineral waters and in the air, from decaying organic matter.

Sulphide Ores. Iron pyrite, FeS₂ (30 to 50% S); ferro ferric sulphide, Fe₃O₄·5FeS; pyrrhotite, Fe₇S₈; copper pyrites, CuFeS₃; realgar, As₄S₄; orpiment, As₂S₃; galena, PbS; cinnabar, HgS; zinc blende, ZnS.

Sulphate Ores. Gypsum, CaSO₄·2H₂O, very abundant; barytes, or heavy spar, BaSO₄; celestite, SrSO₄; kieserite, MgSO₄·H₂O; bitter spar or Epsom salts, MgSO₄·7H₂O; Glauber salt, Na₂SO₄·10H₂O; sulphates of alkalies in animal and plant fluids.

The gravimetric determination of sulphur, by procedures of technical importance, depends upon its precipitation as barium sulphate, BaSO₄, after converting it into sulphuric acid, or a soluble sulphate, if not already in this form. Oxidation of free sulphur, sulphides, sulphones, metabisulphites, thiosulphates may be accomplished by either dry or by wet methods, details of which are given under subsequent procedures.

The volumetric methods of determining sulphur depend upon titration with oxidizing agents, or by acids, or by alkalies, according to the form of the sulphur compound, or by means of a substance forming an insoluble compound with sulphuric acid. For example sulphides are treated with a strong mineral acid (HCl), the evolved H₂S absorbed in a suitable reagent, and the sulphide formed is titrated with standard iodine. Sulphites may be determined either by oxidation with iodine or by titration with an acid in presence of methyl orange. Acid sulphones or metabisulphites may be determined by the iodine titration or by titration with an alkali in presence of phenolphthalein. Thiosulphates are titrated with iodine.
Preparation and Solution of the Sample

Sulphide. Sulphides of Na, K, Ca, Rb, Cs, Sr, Ba, Mg, Mn, Fe are soluble in dilute mineral acids. The sulphides of Ag, Hg, Pb, Cu, Bi, Cd, Co, Ni require strong acids for decomposition. These are also insoluble in sodium hydroxide and potassium hydroxide solutions. As, Sb and Sn sulphides are insoluble in dilute acids, but soluble in alkalies.

Sulphate. With exception of BaSO₄, CaSO₄, SrSO₄ and PbSO₄, sulphates are soluble in water.

Thiosulphate. Nearly all are soluble in water.

Sulphite. With exception of the sulphites of the alkalies, sulphites of the metals are difficultly soluble in water, but readily decomposed by acids.

Decomposition of Sulphur Ores

The wet procedure for oxidation and decomposition of sulphur ores is given in detail under the Gravimetric Methods, page 498. This process is used for the valuation of the ore, and is applicable to a wide range of substances.

Fusion Method. One gram of the finely ground ore (80 mesh) is intimately mixed with 6 grams of zinc oxide-sodium carbonate mixture (1 part ZnO + 1 part Na₂CO₃), placing 2 grams more of the mixture over the charge. The material is fused and sulphur extracted according to the procedure described for coal—Eschka's method.

Sulphur in Coal, Eschka's Method

One gram of coal is intimately mixed with 3 grams of Eschka's compound, consisting of 2 parts of porous, calcined magnesia and 1 part of anhydrous sodium carbonate. The mixture, placed in a platinum crucible, is covered with about 2 grams more of Eschka's compound. The charge is placed in an open platinum crucible, which is protected from the flame by a shield, as shown in Fig. 65. If possible, a sulphur-free flame should be used to avoid contaminating the material. With proper precautions, the shield will prevent this. Heating in a crucible electric furnace completely avoids sulphur contamination. The mixture is heated very gradually, to drive off the volatile matter, the charge being stirred frequently with a platinum wire to allow free access of air. The heat is increased, after half an hour, to a dull redness. When the carbon has burned out, the gray color having changed to a yellow or light brown, the heat is removed and the crucible cooled.

The powdered fusion is digested with 100 cc. of hot water for half an hour, and the clear liquor decanted through a filter into a beaker. The residue is washed twice more with hot water, by decantation, and finally on the filter, until the volume of the total filtrate amounts to about 200 cc. About 5 cc. of bromine and a little hydrochloric acid are added, and the solution boiled. Sulphuric acid is now precipitated as BaSO₄ by addition of barium chloride to the hot solution, and sulphur determined by the first of the gravimetric procedures.

Sulphur in Rocks, Silicates, and Insoluble Sulphates

The material in finely powdered form is fused in a large platinum crucible with about six times its weight of sodium carbonate (sulphur free) mixed with about 0.5 gram of potassium nitrate. The charge is protected from the flame
by an asbestos board or silica plate with an opening to accommodate the crucible snugly, as shown in Fig. 65. The fusion is extracted with water, the filtrate evaporated to dryness and silica dehydrated. The residue is moistened with strong hydrochloric acid, then taken up with a little water, boiled free of CO₂, and silica filtered off. The filtrate contains the sulphate, which is now precipitated as barium sulphate according to one of the standard procedures.

Barium Sulphate. This is transposed by fusion with sodium carbonate, as stated above. Barium carbonate remains in the water-insoluble residue. It is advisable to wash the residue in this case with hot sodium carbonate solution, to insure complete removal of the sodium sulphate. The filtrate is acidified with HCl, boiled free of CO₂ and BaSO₄, then precipitated.

Lead Sulphate. This may be transposed by digesting the compound with a strong solution of sodium carbonate saturated with CO₂, keeping the solution at boiling temperature for half an hour or more. The sulphate will be in solution and the lead is precipitated as the water-insoluble carbonate.

Strontium or calcium sulphates may be transposed by the procedure described for lead.

SEPARATIONS

Substances Containing Iron

In precipitating barium sulphate, in presence of ferric salts, from hot solutions by the gravimetric procedure commonly followed, considerable iron is carried down by the precipitate. Since Fe₅(SO₄)₂ loses SO₃ upon ignition, and since Fe₅O₇ weighs much less than BaSO₄, low results will be obtained. Hence the removal of iron is necessary, or a method should be followed in which iron does not interfere. It is found that barium sulphate precipitated from a large volume of cold solution, in which the iron has been reduced to ferrous condition, is free from iron. Details of this procedure are given in the second of the gravimetric methods, page 498.

If sulphur is to be precipitated from hot solution of comparatively small volume (200 to 400 cc.), it is necessary to remove iron. This is accomplished by precipitating this as Fe(OH)₃ by addition of ammonium hydroxide in decided excess (5 to 10 cc. excess of strong NH₄OH, sp.gr. 0.90). If the solution is barely neutralized with ammonia, the iron hydroxide carries down considerable of the sulphate. Even with the precaution recommended some of the combined sulphuric acid is occluded by the precipitate, so that it is necessary to recover this by dissolving the precipitate with hydrochloric acid and reprecipitating the ferric hydroxide with an excess of ammonia. The combined filtrates are now treated with barium chloride, upon acidification with hydrochloric acid, according to the procedure first given, page 497, and the sulphate determined.

Separation of Sulphur from Metals Forming an Insoluble Sulphate

This is accomplished by fusion of the compound with sodium carbonate and extraction of the mass with water. The metal remains with the residue and the sulphate of the alkali passes into solution. For details see subject under Preparation and Solution of the Sample, page 494.
SULPHUR

Nitrates and Chlorates. These are carried down with the precipitate as barium salts if they are present in appreciable amount. They may be removed from the solution by evaporation to dryness with hydrochloric acid.

Silica. Silica will be carried down with the barium sulphate precipitate if present in appreciable amounts. It is removed by evaporation of the solution with hydrochloric acid, dehydrating the silicic acid, taking up with HCl and water and filtering.

Ammonium and Alkali Salts. These have a negligible effect on the precipitate of BaSO₄ if this is precipitated from a large volume, according to the second gravimetric procedure.

GRAVIMETRIC DETERMINATION OF SULPHUR

Precipitation as Barium Sulphate

Preliminary Remarks. The procedure depends upon the insolubility of barium sulphate, BaSO₄, in neutral or slightly acid solutions. It was formerly the general practice to precipitate the sulphur by adding a 10% barium chloride solution to the hot sulphate solution, which had been diluted from 200 to 400 cc., according to the amount of sulphur that was present (not over 0.2 gram sulphur per 100 cc.), containing 1 to 3 cc. of free concentrated hydrochloric acid per 100 cc. of solution. Special precautions were given to have the solution boiling hot, and to avoid having a volume of over 400 cc., a smaller sample being taken in high sulphur ores, rather than increase the volume. Extended experiments have shown that it is preferable to precipitate the sulphate from a large volume of cold solution. The product obtained is less apt to occlude impurities, the crystals are larger than those obtained in hot concentrated solutions, and do not pass through the filter. Precipitation may be made in presence of large amounts of iron, copper and other impurities. The procedure requires large beakers of 2- to 2½-liter capacity, special precipitating cups, and a suction apparatus, as shown in Figs. 60, 61, 62 and 63. This apparatus may not always be available, and occasionally it is advantageous to precipitate the sulphur in a small volume, specially when the sulphur content of the material is low, hence, although the second procedure is generally recommended, the older method is also included.

I. Precipitation of Barium Sulphate from Hot Solutions

Procedure. The sulphur should be present in solution either as free sulphuric acid or as a sulphate salt. The solution is made acid by addition of hydrochloric acid (phenolphthalein indicator), and then 4 cc. added in excess (HCl, sp.gr. 1.2). After diluting to a volume of 400 cc. with hot water, the mixture is heated to boiling, and a 10% solution of barium chloride added in a fine stream through a funnel with a capillary stem, or from a burette, at the rate of 10 cc. in two to ten minutes. The reagent is added in slight excess of that required to react with the sulphuric acid or sulphate. (Ten cc. of 10% BaCl₂.2H₂O solution will precipitate about 0.13 g. of sulphur.) The beaker is placed on a steam bath and the pre-

1 E. Hintz and H. Weber recommend adding 100 cc. of N/10 BaCl₂ solution, boiling hot, to the hot sulphate solution all at once in place of slowly, as recommended in general practice. (See Treadwell and Hall, “Analytical Chemistry,” 2, 3d Edition, p. 460.)
cteritate allowed to settle for about two hours. The solution is filtered through
a fine grade of filter paper (B. & A. grade A, or S. & S. grade No. 90), or
through a tared Goeeh crucible. Since the precipitate frequently passes through
the filter it is advisable always to pass the solution through the same filter a
second time. The precipitate is washed ten times with hot water, then dried,
and ignited gently over a Bunsen burner, or in a muffle, for half an hour.
(Blasting is not necessary, nor desirable.) The white BaSO₄ is cooled in a
desiccator, and then weighed. If a filter paper has been used in place of a
Goeeh crucible, the ignition is best made in a porcelain crucible, with free access
of air, the ignited sulphate, upon cooling, is brushed out of the crucible and so
weighed.

Factors. BaSO₄×0.1373 = S, or ×0.4202 = H₂SO₄, or ×0.3766 = FeS,
or ×0.2744 = SO₃, or 0.3430 = SO₄, or ×0.4115 = SO₆.

Note. If much iron or alumina is present it is advisable to precipitate the sul-
phate from a large volume, by the second method, rather than attempt to remove
these substances. If BaSO₄ is present in the original material its weight should be
included with that of the precipitate.

II. Precipitation of Barium Sulphate from Cold Solutions—
Large Volume

Introduction. The method worked out by Allen and Bishop, General Chemical
Company,¹ is especially adapted to the determination of sulphur in iron
pyrites and materials high in sulphur, 30 to 50% sulphur, but by varying the
amount of material used the range may be extended from smaller to greater
amounts. The finely ground sample is oxidized by means of a mixture of bro-
mine and potassium bromide, followed by nitric acid. The nitric acid is expelled
by evaporation to dryness, followed by a second evaporation with hydrochloric
acid, which dehydrates the silica. Iron is now reduced to the terreous condition
and the silica and residue, undissolved by addition of hot water and HCl, is filtered
off. The sulphur is precipitated in a large volume of cold solution, by barium
chloride solution, as BaSO₄ and so weighed.

Reagents. Bromine—Potassium Bromide Solution. 320 grams of potas-
sium bromide are dissolved in just sufficient water to cause solution and mixed
with 200 cc. of bromine, the bromine being poured into the saturated bromide
solution. After mixing well the solution is diluted to 2000 cc.

Bromine—Carbon Tetrachloride Solution. Carbon tetrachloride saturated
with bromine.

Barium Chloride. anhydrous, 5% solution; or crystals, 6% solution.

Procedure. Preparation of Sample. The sample ground to pass 80-mesh
sieve is carefully mixed and quartered down to 10 grams. This is dried for one
hour at 100° C. and then placed in a weighing tube.

A factor weight, 1.373 grams of the sample, is placed in a deep beaker, 300 cc.
capacity, 2½ by 4½ ins.

Oxidation of Sulphur. Ten cc. of the bromine-potassium bromide mixture
for pyrrhotite ore, or bromine—carbon tetrachloride reagent for pyrites ores,
are added and the beaker covered with a dry watch-glass cover. After standing

¹ Paper before Eighth International Congress of Applied Chemistry: "An Exact
Bishop.
fifteen minutes in the cold bath (a casserole of water will do), with occasional shaking of the beaker, 15 cc. of strong nitric acid are added and the mixture allowed to stand fifteen minutes longer, at room temperature, and then warmed on an asbestos board on the steam bath until the reaction has apparently ceased and the bromine has been volatilized. The beaker is now placed within the ring of the steam bath so that the lower portion is exposed to steam heat. The solution is evaporated to dryness, the cover of the beaker being raised above the rim by means of riders (U-shaped glass rods). Fig. 60, 10 cc. of strong hydrochloric acid are now added and the solution again evaporated to dryness to expel the nitric acid. The silica is dehydrated by heating in the air oven at 100° C. for one hour, or overnight if preferred.

Reduction of Iron. Four cc. of hydrochloric acid (sp.gr. 1.20), followed five minutes later by 100 cc. of hot water, are added, the sides of the beaker and the cover being rinsed into the solution. The riders being removed, the sample is gently boiled for five minutes to insure the solution of the sulphate. After cooling for about five minutes, approximately 0.2 gram powdered aluminum is stirred into the solution, keeping covered during the intervals between stirring. When the iron has been reduced, the solution becoming colorless, the sample is filtered into a 2500-cc. beaker, through a 12½ cm. filter paper (S. & S. No. 590 or B. & A. No. A). The beaker should be capped out and the residue on the filter washed nine times with hot water, filling the filter funnel and draining each time.

Precipitation of the Sulphur. The solution in the large beaker is diluted to 1600 cc. with cold water and 6 cc. HCl (sp.gr. 1.20) added, and mixed by stirring. The barium chloride solution is now added by means of a special delivering cup (Figs. 61 and 62), which should drain at the rate of 5 cc. per minute. 125 cc. of barium chloride solution are added for ores containing 30 to 50% sulphur, the factor weight being taken. The solution is not stirred while the barium chloride is being added, but when the cup has drained, the solution is mixed by stirring. The BaSO₄ is allowed to settle, two or three hours being advisable, overnight being preferred.

Filtration. The clear solution is filtered through a weighed Gooch crucible (35 cc.), using suction. This is best done by the automatic arrangement shown in Fig. 63. The beaker containing the solution is placed on a shelf; a siphon dipping to within half an inch of the precipitate at the bottom of the beaker is connected to the Gooch crucible by means of a tightly fitting stopper. The Gooch and thistle tube are best connected by heavy rubber tubing. The
suction flask, or bottle, should have a capacity of about 3 liters. A Geissler stop-cock passes through the rubber stopper in the suction flask to relieve the pressure when the Gooch is to be removed. The precipitate is washed onto the asbestos mat in the crucible and washed with cold water six times, the beaker being copped out as usual.

**Ignition.** The precipitate is dried by placing the crucible on an asbestos board over a flame for twenty-five minutes and then heated over a direct flame for thirty minutes.

**Calculation.** \( \text{BaSO}_4 \times 10 = \text{per cent } S. \) (If factor weight is taken.)

Factor. \( \text{BaSO}_4 \times 0.1373 = \text{gram } S. \)

**Notes and Precautions**

Although barium sulphate is only slightly soluble in water, it is appreciably soluble in the salts of the alkalies (Na, K and NH₄), and in a large excess of hydrochloric acid.

Barium sulphate occludes salts, especially nitrates and chlorides. Ferric chloride is carried down with this precipitate, though ferrous chloride is not; hence the reduction of iron is necessary. Oclusion of iron causes low results, as will be seen from the fact that with heating of Fe₃(SO₄)₃, SO₃ is volatilized, the salt decomposing to Fe₂O₃ + SO₃. With the iron reduced the precipitate burns perfectly white, whereas with ferrie iron present the precipitate is invariably red or yellow. Aluminium powder used by W. H. Seaman, for reduction of iron in determination of sulphur, suggested its value in the method above given.

Potassium bromide is added to the bromine mix as a diluent to prevent too vigorous a reaction. Cooling the solution is for the same purpose as a loss of sulphur will result if the reaction is violent. This is especially the case in pyrrhotite ore.

Otto Folin shows that precipitation of BaSO₄ in a large volume of cold solution produces large crystals.

Mechanical loss and reduction of BaSO₄ is avoided by the Gooch crucible.

The method has been thoroughly tested in the laboratories of the Gen. Chem. Co. and has become a standard method for sulphur.

**Evolution Method for Determining Sulphur in Iron, Steel, Ores, Cinders, Sulphides and Metallurgical Products**

**Introduction.** The method depends upon the fact that hydrogen sulphide is evolved when a sulphide is acted upon by a strong acid such as hydrochloric acid. This gas, absorbed by a suitable reagent, may be determined gravimetrically by weighing directly the precipitated sulphide, or by oxidation of either the hydrogen sulphide evolved or the sulphide formed in the absorbing reagent.

---

1. Chemical Engineer, September, 1908.
3. Gravimetrically. (a) Evolution of \( \text{H}_2\text{S} \) into solutions of \( \text{ZnCl}_2, \text{KOH, KMnO}_4, \text{AgNO}_3, \text{Hg(CN)}_2 \), \( \text{H}_2\text{O}, \text{Br}^- + \text{HCl} \) and subsequent oxidation to sulphate when necessary, and precipitation as \( \text{BaSO}_4 \). (b) Absorption of \( \text{H}_2\text{S} \) by neutral or alkaline solutions of lead, oxidation of \( \text{PbS} \) to \( \text{PbSO}_4 \) and weighing as such. (c) Absorption of \( \text{H}_2\text{S} \) in solutions of \( \text{AgNO}_3, \text{CdCl}_2 \), and weighing the precipitated sulphide.
and precipitating sulphur as BaSO₄. It may be determined volumetrically by titrating the precipitated sulphide with iodine or by titrating the acid, formed by the reaction, with standard caustic. The iodine and caustic titrations may be made on the same run, or the sulphide may be weighed and the filtrate containing the free acid titrated, thus double checking results. The following reaction takes place when the gas is evolved and absorbed by neutral cadmium sulphate:

\[ \text{H}_2\text{S} + \text{CdSO}_4 = \text{CdS precipitate} + \text{H}_2\text{SO}_4 \text{ free acid.} \]

The method is especially adapted to the determination of sulphur in iron and steel or in metallurgical products containing small amounts of sulphide. It may be applied to products containing larger amounts of sulphur as sulphides or sulphates, the latter condition requiring a special preliminary treatment.

The method is not applicable for determining free sulphur or sulphur in iron pyrites.

**Reagents. Iodine Solution.** Two strengths of this reagent should be at hand for general work:

For iron and steel and low sulphur briquettes, etc. = .01 to 0.5% S ...... N/30 I

For sulphur products containing over 0.5% S ...... N/10 I

**Starch Solution.** Made from a good grade of soluble starch, 1 gram per 200 cc. of water. Fresh solutions are desirable, as the deteriorated material produces a greenish-brown color in place of the delicate blue desired. Flocks of insoluble starch will cause the same difficulty.

**Cadmium Chloride or Cadmium Sulphate Solutions. Ammoniacal Solution.** Fifty-five grams of CdCl₂·2H₂O or 70 grams of the sulphate are dissolved in 500 cc. of distilled water. To this are added 1200 cc. NH₄OH (sp.gr. 0.90) and the solution diluted to 2500 cc. The solution is of such strength that 50 cc. will precipitate approximately 0.175 gram sulphur evolved as H₂S. This is equivalent to about 3.5% sulphur on a 5-gram sample.

---

[1] Volumetrically. (a) Absorption in a solution of KOH, CdCl₂ or CdSO₄, ZnCl₂ or ZnSO₄, Na₂H₂AsO₄, and titration with iodine solution. (b) Absorption in iodized KI and titration of the excess of iodine with Na₂S₂O₃ solution. (c) Absorption in a neutral solution of a metallic salt and titration of the liberated acid. (d) Absorption in caustic alkali and addition to an acid solution of a reducible salt, e.g., Fe₃O₄ and titration of the lower oxide, FeO.

Neutral Solution. To be used where titration with caustic is desired. Seventy grams of CdSO₄ are dissolved in water and made up to 2500 cc. The solution should be neutral to methyl orange, otherwise add the requisite amount of H₂SO₄ or NaOH necessary, determined by titration of an aliquot portion.

Hydrochloric Acid. One part concentrated acid to an equal volume of distilled water.

Sulphuric Acid. One volume of concentrated acid to four volumes of distilled water.

Reducing Mixture for Reduction of Sulphates. Five parts of NaHCO₃, 2 parts of C.P. aluminum powder and 1 part of pure carbon, best made by charring starch. A blank should be determined on this material and allowance made accordingly.

Stannous Chloride. Ten-per cent solution.

Fine Granular Aluminum or Zinc Metal. Sulphur free, 20 mesh.

Apparatus. The apparatus shown in the illustration, Fig. 64, is the author's modification of the form used at Baldwin Locomotive Works. This consists of an Erlenmeyer flask A of about 500-cc. capacity with large base. With material in which violent foaming occurs, during the evolution of hydrogen sulphide, it is advisable to use a wash bottle with large base, in preference to an Erlenmeyer flask. Through a rubber stopper is inserted a thistle tube with glass stopcock D, by which the acid is introduced into the flask. The hydrogen sulphide passes through a potash connecting bulb with trap as shown. A hole blown in the side of the tube prevents liquid being swept through. Connected to the potash bulb is the absorption bulb C, which is suspended by a wire attached to the thistle tube. The apparatus is compact, so that on a large hot plate, 30 by 20 ins., a dozen outfits may readily be accommodated. With the use of this apparatus the writer has been able to make over seventy-five determinations of sulphur in steel in an ordinary day's run.

Preparation and Amount of Sample

The amount of material to be taken for the determination depends upon the sulphur content as shown by the following table:

<table>
<thead>
<tr>
<th>Approximate % of Sulphur Present</th>
<th>Amount to take for Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 to 1</td>
<td>5 grams</td>
</tr>
<tr>
<td>1.0 to 10</td>
<td>1</td>
</tr>
<tr>
<td>10.00 to 30</td>
<td>0.5</td>
</tr>
<tr>
<td>Above 30</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The class of material will govern the method of procedure.

Iron and Steel. A 5-gram sample of drillings or finely divided material is treated directly in the evolution flask with hydrochloric acid, 1:1, and the hydrogen sulphide absorbed in ammoniacal cadmium chloride. The sulphide formed is titrated with iodine.

Iron Ore Briquettes and Materials Containing Sulphates. Low Sulphur. Preliminary Reduction. A 5-gram sample is intimately mixed with an equal weight of reducing mixture (NaHCO₃+Al+C) and wrapped in a 9-cm. ashless filter. The charge is placed in a 50-cc. nickel crucible with cover. The crucible

W. W. Scott.
is inserted half way into an asbestos board or perforated silica plate (see Fig. 65) and after covering, placed over a low flame of a Méker blast burner. The flame of the blast is gradually increased during the first five minutes and the charge blasted for about twenty minutes. The crucible will appear a bright red and carbon monoxide gas escaping from under the crucible lid will burn. The loss of sulphur, however, is not appreciable. The crucible is cooled without removing the cover. When cold the fused mass is quickly pulverized and placed in the dry evolution flask containing a mat of aluminum granules or C.P. zinc dust or granulated tin. Hydrogen sulphide is best evolved with hydrochloric acid to which 4 or 5 cc. of 10% stannous chloride has been added to reduce ferric iron. The gas is absorbed in ammonical cadmium chloride and the cadmium sulphide formed titrated with iodine.

**Iron Sulphide for Available H₂S.** Since this product runs over 20% available hydrogen sulphide not over 0.5 gram sample should be taken. The H₂S is evolved by addition of dilute sulphuric acid, 1:4, in place of hydrochloric acid, and is absorbed by neutral cadmium sulphate. The acid formed by the reaction is titrated by standard N/10 NaOH.

**Sodium Sulphide or Water-soluble Sulphides for Available H₂S.** Ten grams dissolved in water and diluted to 1000 cc.; 50 cc. = (0.5 gram) taken for analysis.

**Details of Procedure**

**Evolution of Hydrogen Sulphide.** One-half to 1 gram of aluminum or zinc granules, 20 mesh, is placed over the bottom of the evolution flask and the sample placed above this mat of metal. The stopper with the thistle tube and condenser is inserted snugly into the neck of the flask. An absorption bulb containing about 20 cc. of distilled water is attached to the condenser. This bulb serves as a trap for the HCl that is driven out of the flask during the boiling. To this bulb is attached a second bulb containing 50 cc. of ammoniacal cadmium chloride. A third bulb may be attached if the sulphur content of the material examined is high; this, however, is seldom necessary when ammoniacal cadmium chloride is used. The rubber stopper and all rubber connections being air tight, 100 cc. of warm HCl, 1:1, is poured into the flask through the thistle tube, the stem of which should now dip well below the acid. The stopcock is closed during the violent action of the acid on the sample and opened when this has subsided. The acid trap prevents loss of H₂S through the thistle tube. The apparatus is now placed on the hot plate and the sample boiled vigorously for about twenty minutes. The flask is taken off the hot plate and the contents allowed to cool. At this stage it may be advisable to draw a current of air through the apparatus to sweep out any residual H₂S that may remain in the flask. Hydrogen gas is preferable to air.

**Titration.** (a) The contents of the bulbs are poured into a 600-cc. beaker containing about 400 cc. of distilled water. The bulbs are washed out first
with water and then with dilute acid. The excess of ammonia is neutralized with concentrated HCl, 5 cc. of starch solution added and the sulphide immediately titrated with standard iodine, additional hydrochloric acid being added from time to time during the titration to insure complete decomposition of the sulphide. The liquid appears yellowish red, orange, purplish red and finally a deep blue. Since the sulphide, when present in appreciable quantity, decomposes slowly, the solution should be strongly acid at the completion of the titration, and five minutes should be allowed for a permanent end-point.

Knowing the amount of iodine necessary, a check run may be made by adding to the neutral solution an excess of iodine followed by 5 cc. of starch solution and a large excess of concentrated hydrochloric acid. The excess of iodine is titrated with N/10 thiosulphate, Na$_2$S$_2$O$_3$, solution. (Arsenous acid will not do.) This procedure will prevent the loss of H$_2$S, which is apt to occur in samples high in sulphide.

(b) An alternate method is frequently advisable in high sulphurs. The precipitate is separated from the solution containing ammonia by filtration. The cadmium sulphide is now placed in the 600-cc. beaker with water and an excess of iodine run in. Starch is added, followed by hydrochloric acid. The excess of iodine is titrated with sodium thiosulphate, Na$_2$S$_2$O$_3$. By this method the heat action during the neutralization of ammonia is avoided and only the precipitate is titrated.

When the iodine titration exceeds 50 cc. of N/10 iodine, a smaller amount of the sample should be taken for analysis; the iodine titration for amounts of sulphur exceeding 0.1 gram is not satisfactory, owing to a fading end-point. The method for determining available hydrogen sulphide in high sulphide products, dealing with the titration of the free acid formed during the reaction, permits of larger samples being taken. Details of this method are given on page 509.

One cc. N/10 iodine = 0.001604 gram S.

**Tenth Normal Equivalents**

<table>
<thead>
<tr>
<th>One cc. of N/10 iodine</th>
<th>0.001704 gram H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;&quot;</td>
<td>= 0.004396 gram FeS</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.003904 gram Na$_2$S</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.003907 gram CaS</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.008471 gram BaS</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.00561 gram Sb$_2$S$_3$</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.011959 gram PbS</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.011634 gram HgS</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.004782 gram CuS</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.007224 gram CdS</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.004872 gram ZnS</td>
</tr>
<tr>
<td>&quot;&quot; &quot;&quot;</td>
<td>= 0.003269 gram Zn</td>
</tr>
</tbody>
</table>

**Combustion Method for Evaluation of Sulphide Ores.** When a sulphide ore (pyrrhotite) is heated to redness in presence of oxygen both sulphur dioxide and trioxide are evolved. The first may be absorbed in suitable reagents and estimated volumetrically or gravimetrically. The trioxide mist is best retained by asbestos and weighed. The combustion furnace with silica tube used for determinations of carbon is adapted for sulphide ores. The finely powdered
dry sample, spread in a thin layer in a 3-inch porcelain boat, is placed in the red hot tube and burned in a current of oxygen, which has been purified by passing through sodium hydrosulphite, strong sulphuric acid and phosphorus pentoxide. The trioxide mist is removed by passing the evolved gases through an asbestos filter (P₂O₅ bulb with asbestos in one arm adjacent to the combustion tube and P₂O₅ in the other). The SO₃ is absorbed in a mixture of bromine and nitric acid, and the sulphuric acid formed is titrated after removing the reagent by evaporation; or it is absorbed in an excess of standard iodine, the excess titrated with sodium arsenite or thiosulphate, and sulphur calculated. The iodine method is preferable to the bromine, as it is more rapid and the reagent less disagreeable to handle. The gravimetric method is the most reliable. The dioxide is absorbed in chromic acid (caustic will not give correct results owing to its affinity for carbon dioxide, a product of combustion of the free and combined carbon, that are generally present in sulphide ores. Pyrrhotite frequently contains as much as 1% carbon) and weighed. The combustion method cannot be recommended for extreme accuracy. The procedure may be used for the estimation of available sulphur, but does not give the total sulphur of the ore, since .2 to .5% remains in the cinder. Error may result from the following causes: (1) Incomplete combustion of the sulphur—due to sublimation of the sulphur to cooler zones of the combustion tube, and to a fine mist of sulphur passing unburned into the asbestos, where it is retained with SO₃ and weighed as such. (2) Error due to combined water of the ore. The results are apt to be .05 to 0.5% lower than those obtained by the barium sulphate procedures, the sulphur of the cinder being included with the available sulphur.

VOLUMETRIC METHODS FOR DETERMINING SOLUBLE SULPHATES

Combined sulphuric acid in soluble sulphates is best determined gravimetrically; occasionally, however, a volumetric procedure is of technical value. A number of volumetric methods are based on the insolubility of barium sulphate. Two general procedures deserve mention: addition of barium chloride in known amount in slight excess of that required by the sulphate, and titrating the excess either with a soluble carbonate or a chromate; or addition of barium chromate and titrating the alkali chromate formed by the reaction. The sulphate is also determined by precipitation with a weak organic base benzidine, added in form of the hydrochloride salt; the benzidine sulphate, filtered off, is titrated with caustic. The typical procedures given below will meet general requirements for the volumetric determination of sulphates.

Determination of Sulphur by Titration with Barium Chloride and Potassium Chromate—Wildenstein's Method Modified

Reaction.

\[ \text{Na}_2\text{SO}_4 + \text{BaCl}_2 = \text{BaSO}_4 + 2\text{NaCl} \text{ and excess } \text{BaCl}_2 + \text{K}_2\text{CrO}_4 = \text{BaCrO}_4 + 2\text{KCl}. \]

Procedure. The substance containing the sulphate in solution is diluted to 50 cc. in a small flask, acidified with hydrochloric acid, if necessary, heated to

boiling, and precipitated with a slight excess of N/4 barium chloride added from a burette (1 cc. BaCl$_2$ = 0.01 gram SO$_4$). The precipitate settles rapidly, so that a large excess of the reagent may readily be avoided. The mixture is cautiously neutralized with ammonia, free from carbonate (CO$_2$ may be precipitated with CaCl$_2$ solution), the solution heated to boiling, and N/4 potassium chromate added from a burette in .5 cc. portions, each time removing the flask from the heat, allowing the precipitate to settle and examining the clear solution. A faint yellow color will appear as soon as the excess of barium has been precipitated and a few drops of the chromate in excess are present in the solution. The value of the chromate being equivalent to the barium chloride cc. per cc., the difference between the two titrations is due to the barium chloride required by the sulphate.

One cc. N/4 BaCl$_2$ = 0.01 gram SO$_4$.

Notes. Salts of the alkalies, alkaline earths (Sr and Ca) and zinc and cadmium do not interfere. Nickel, cobalt and copper, however, give colored solutions which prevent the yellow chromate being seen. Should the latter be present, the end-point may be recognized by using ammoniacal lead acetate as an outside indicator (1 vol. NH$_4$OH + 4 vols. Pb(C$_2$H$_3$O$_2$)$_2$, 5% sol.), the indicator and titrated solution being mixed drop per drop on a white tile. A yellowish red color indicates the presence of chromate.

Precipitation of the Sulphate with Barium Chromate and Titration of Equivalent, Liberated Chromate with Iodine and Thiosulphate, Hinman's Method.\(^1\)

The sulphate, precipitated by barium chromate, liberates an equivalent amount of chromic acid, which is determined by treating with potassium iodide and titrating the liberated iodine with thiosulphate.

\[ \text{Reactions.} \quad \text{Na}_2\text{SO}_4 + \text{BaCrO}_4 = \text{BaSO}_4 + \text{Na}_2\text{CrO}_4, \]

\[ \text{Na}_2\text{CrO}_4 + 3\text{KCl} + 8\text{HCl} = 2\text{NaCl} + 3\text{KCl} + \text{CrCl}_3 + 4\text{H}_2\text{O} + 3\text{I}, \]

\[ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6. \]

Procedure.\(^2\) The solution of the sulphate, containing not over 2 per cent of SO$_4$ if acid, is almost neutralized with potassium hydroxide, then heated to boiling, and an excess of barium chromate solution added.\(^3\) After boiling for one to five minutes, the hot solution is neutralized by adding calcium carbonate\(^4\) until no further effervescence occurs. The precipitate is filtered off and washed with hot water. The combined filtrates containing the chromate liberated by the sulphate through double decomposition, is acidified with 5 cc. strong


\(^2\) See p. 716.

\(^3\) The barium chromate used should be free from soluble chromate, barium carbonate or soluble barium salt. The compound may be prepared by precipitating with potassium chromate added to a boiling solution of barium chloride. The precipitate is washed with boiling water containing a little acetic acid, and finally with pure water, and then dried. Four grains of the dry salt are dissolved in a liter of normal hydrochloric acid.

\(^4\) In presence of iron, zinc and nickel, the solution is neutralized with ammonium hydroxide and an excess added; after boiling, the solution is filtered. By using calcium carbonate insoluble basic chromates of these elements would be formed, and low results for SO$_4$ would follow. This is avoided by the use of ammonia.
hydrochloric acid per each 100 cc. of filtrate and an excess of potassium iodide added. Iodine equivalent to the chromic acid is liberated. This is titrated with N/10 sodium thiosulphate.

One cc. of N/10 thiosulphate = 0.003269 gram H₂SO₄.¹

**Benzidine Hydrochloride Method—Raschig**

Benzidine sulphate, C₁₅H₈(NH₃)₂·H₂SO₄, is scarcely soluble in water containing hydrochloric acid. The weak base benzidine is neutral to phenolphthalein and the acid in its sulphate may be titrated with an alkali.² The method gives reliable results in the analysis of all sulphates, provided no substances are present which attack benzidine, and provided the amount of other acids and salts present is not too great.³

**Reaction.**

\[ \text{Na}_2\text{SO}_4 + \text{C}_15\text{H}_8(\text{NH}_3)_2 \cdot 2\text{HCl} = 2\text{NaCl} + \text{C}_15\text{H}_8(\text{NH}_3)_2 \cdot \text{H}_2\text{SO}_4 \]

and

\[ \text{C}_15\text{H}_8(\text{NH}_3)_2 \cdot \text{H}_2\text{SO}_4 + 2\text{NaOH} = \text{C}_15\text{H}_8(\text{NH}_3)_2 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4. \]

**Reagent.** Benzidine hydrochloride is prepared by taking 6.7 grams of the free base, or the corresponding amount of the hydrochloride and mixing into a paste with 20 cc. of water in a mortar. Twenty cc. of hydrochloric acid (sp.gr. 1.12) are added and the mixture diluted to exactly 1000 cc. One cc. of this solution corresponds to 0.00357 gram H₂SO₄. The solution has a brown color. Brown flakes are likely to separate out on standing, but these do no harm.

**Procedure.** The sulphate solution is diluted with water so that there is at least a 50-cc. volume for each 0.1 gram sulphuric acid present. An equal volume of the reagent is vigorously stirred in, and the precipitate allowed to settle for ten minutes. The solution is filtered onto a double filter, placed on a porcelain, perforated plate in a funnel (a Büchner is O.K.), gentle suction being applied. The last portions of the precipitate are transferred to the filter by means of small portions of the clear filtrate, and the compound then washed with 20 cc. of cold water added in small portions and sucked dry with each addition. The precipitate and filter are placed in an Erlenmeyer flask, 50 cc. of water added, and the mixture shaken until homogeneous. Phenolphthalein indicator is now added, the mixture heated to about 50° C. and titrated with N/10 sodium hydroxide. When the end-point is nearly reached, the liquid is boiled for five minutes, and the titration then completed.

One cc. N/10 = 0.004904 gram H₂SO₄.

**Determination of Free Sulphuric Acid**

Other free acids being absent, sulphuric acid may be accurately determined by titration with standard alkali. The method for determining sulphuric acid in presence of commonly occurring acids, and in mixed acids are given in Volume II, in the chapter on Acids, Vol. II.

1 cc. N/1 NaOH = 0.04904 g. H₂SO₄.

¹ N/10 Na₂S₂O₃ = \( \frac{\text{H}_2\text{SO}_4}{30} = 98.08 + 30 = 3.269. \)


³ Friedheim and Nydegger (Z. a. Chem., 9, 1907) have found that there should not be more than 10 mol. HCl, 15 mol. HNO₃, 20 mol. H₂Cr₂O₇, 5 mol. alkali salt, or 2 mol. ferric iron present to 1 mol. H₂SO₄. See Treadwell and Hall, "Analytical Chemistry," pp. 714–716.
DETERMINATION OF PERSULPHATES

Ferrous Sulphate Method

Ferrous salts in cold solutions are oxidized to ferric form by persulphates. Advantage is taken of this action in the quantitative determination of persulphates. Reaction. \(2\text{FeSO}_4 + \text{H}_2\text{S}_2\text{O}_8 = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4\).

Reaction. \(2\text{FeSO}_4 + \text{H}_2\text{S}_2\text{O}_8 = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4\).

Procedure. About 2.5 grams of the persulphate are dissolved in water and diluted to 100 cc. Ten cc. of this solution, equivalent to one-tenth of the sample, weighed out, are placed in a flask and a considerable excess of standard ferrous sulphate solution added, say 100 cc. measured out from a burette. The solution is diluted with an equal volume of hot, distilled water (70 to 80° C.), and the excess ferrous sulphate titrated with N/10 potassium permanganate. This titration is deducted from the permanganate equivalent of 100 cc. of the ferrous solution taken (if this amount was used). The difference is due to persulphate oxidation.

One cc. N/10 KMnO₄ = 0.0009708 gram H₂S₂O₈; or = 0.0114 gram (NH₄)₂S₂O₈; or = 0.01352 gram K₂S₂O₈.

Oxalic Acid Method

Oxalic acid, in presence of silver sulphate, reduces persulphates in accordance with the reaction, \(\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{S}_2\text{O}_8 = 2\text{H}_2\text{SO}_4 + 2\text{CO}_2\).

\(\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{S}_2\text{O}_8 = 2\text{H}_2\text{SO}_4 + 2\text{CO}_2\).

Procedure. About 0.5 gram of the persulphate is placed in an Erlenmeyer flask, 50 cc. of N/10 oxalic acid added, together with 0.2 gram silver sulphate in 20 cc. of 10% sulphuric acid solution. The mixture is heated on the water bath for about half an hour to expel carbon dioxide. When the evolution ceases the liquid is diluted to 100 cc. with warm water and titrated warm (about 40° C.) with N/10 potassium permanganate. The excess of oxalic acid is titrated, the difference is due to oxidation by the persulphate.

For calculation see factors in previous method.

Alkali Titration of the Boiled Solution

The aqueous solutions of potassium, sodium, and barium persulphates are decomposed by boiling as follows (\(M = \text{metal Na, K, or Ba}\)):

\(2\text{M}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} = 2\text{M}_2\text{SO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4\).

Procedure. About 0.2 g. of the persulphate salt is dissolved in 200 cc. of water and the solution boiled about 15 minutes, then cooled and titrated with N/10 NaOH, using methyl orange indicator.

1 cc. N/10 NaOH = 0.02008 g. BaS₂O₄H₂O, or 0.01191 g. Na₂S₂O₈ or

Ammonium persulphate cannot be determined by the above method but may be determined by the ferrous sulphate method—which see above.

1 Method suggested by Le Blanc and Eckardt, C. N., 81, 38.
2 About 30 grams of ferrous sulphate or ferrous ammonium sulphate crystals are dissolved in 900 cc. of water and the volume made to 1000 cc. with concentrated sulphuric acid. The reagent is standardized against N/10 potassium permanganate and the value per cc. in terms of the standard permanganate noted, the cc. permanganate solution required divided by the cc. of ferrous sulphate solution taken for titration, gives value of the reagent in terms of the permanganate.

The solutions are best verified upon a persulphate of known purity.
DETERMINATION OF SULPHUR IN COMBINATION AS SULPHIDES, SULPHITES, BISULPHITES, METABISULPHITES, THIOSULPHATES, SULPHATES, AND HYDROSULPHITES

Available Hydrogen Sulphide in Materials High in Sulphide Sulphur. Iron Sulphide, Sodium Sulphide, etc.

Evolution Method. Since it is desired to obtain the \( \text{H}_2\text{S} \) that ordinarily would be obtained when the sulphide is treated with a strong acid, the mat of metallic aluminum or zinc and the addition of stannous chloride solution used in the procedure given on page 503 is omitted here.

Procedure. 0.5 to 1 gram of the sulphide is placed in the dry evolution flask. All connections are now made as directed in the general procedure. Three absorption bulbs containing neutral solution of cadmium sulphate are connected to the condenser, and supported by wires attached to the thistle tube and the arm of the condenser. All connections being tight, 100 cc. of dilute sulphuric acid, 1:4 are added through the thistle tube and \( \text{H}_2\text{S} \) evolved. The procedure is now the same as described on page 503.

Titration. When the evolution of the \( \text{H}_2\text{S} \) is complete, the bulbs containing the precipitate are emptied into a beaker and carefully washed out. The precipitate is now filtered and washed five or six times until free of acid. Methyl orange is added to the filtrate and the free acid titrated with N/10 NaOH.

The precipitate may be titrated with iodine according to (b) under general method of procedure, using an excess of iodine, followed by starch and acid and then titrating back with sodium thiosulphate solution. A double check may thus be obtained. See page 504.

If it is desired to weigh the CdS precipitate, it is best to evolve the \( \text{H}_2\text{S} \) into a neutral solution of cadmium salt. The precipitate formed in a neutral or slightly acid solution is crystalline and easily filtered, whereas that formed in an ammoniacal solution is gelatinous.

When a neutral \( \text{CdSO}_4 \) or \( \text{CdCl}_2 \) solution is used, \( \text{H}_2\text{S} \) should be evolved by sulphuric acid and not by hydrochloric acid, as the latter is volatile, and will pass through the condensing bulb recommended in the general procedure.

\[
\text{One cc. N/10 NaOH} = 0.001704 \text{ gram H}_2\text{S} \\
\text{“ “} = 0.004396 \text{ gram FeS} \\
\text{“ “} = 0.003904 \text{ gram Na}_2\text{S}.
\]

Hydrogen Sulphide and Soluble Sulphides

Direct titration of hydrogen sulphide water, and soluble sulphides in solution may be made in absence of other substances acted upon by iodine. The solution containing the sulphide is added to an excess of N/10 iodine solution, made acid with hydrochloric acid, and the excess iodine titrated with N/10 sodium thiosulphate. The following reaction takes place:

\[
\text{H}_2\text{S} + \text{I}_2 \rightarrow 2\text{HI} + \text{S}. 
\]

The cc. \( \text{Na}_2\text{S}_3\text{O}_3 \) are subtracted from cc. \( \text{I}_2 \) reacting with \( \text{H}_2\text{S} \). One cc. N/10 iodine = 0.00174 gram \( \text{H}_2\text{S} \).

Note. The soluble sulphide may be determined gravimetrically by oxidizing with bromine, the reagent being added until the solution is colored brownish red, the excess of the halogen removed by boiling and the sulphate precipitated as \( \text{BaSO}_4 \).
**Determination of a Sulphide and a Sulphhydrate in Presence of Each Other**

When a mixture of sulphide and sulphhydrate is treated with iodine the following reactions take place:

\[ \text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S} \quad \text{and} \quad \text{NaHS} + 2\text{I}_2 = \text{NaI} + \text{HI} + \text{S}. \]

It will be noticed that the acidity produced by the first reaction is twice that caused by the iodine action on the sulphhydrate, and that the acidity in the latter titration remains unaffected. The reactions with the alkali salts is effected by addition of a standard iodine solution containing a known amount of hydrochloric acid. The reactions in this case are as follows:

\[ \text{Na}_2\text{S} + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{S} \quad \text{and} \quad \text{NaSH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{S}. \]  

The iodine reacts with the \( \text{H}_2\text{S} \) as follows: \( \text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S} \).

From the second set of reactions it is evident that the quantity of hydriodic acid formed by the action of iodine on the sulphide is equivalent to the hydrochloric acid required to decompose the sulphide, so that the acidity remains unchanged. On the other hand with sulphhydrate, NaSH, the hydriodic acid formed by the iodine oxidation, is twice the equivalent of hydrochloric acid required to decompose the acid salt. Hence it is evident that the acidity is a measure of the quantity of sulphhydrate present in the mixture. From the second set of reactions the following procedure is devised.

**Procedure.** To a measured amount of \( \text{N}/10 \) iodine solution containing a measured amount of \( \text{N}/10 \) hydrochloric acid (the mixture diluted to 400 cc.) is added the solution containing the sulphide and sulphhydrate from a burette, until the stirred solution becomes a pale yellow color. (The cc. of solution added is noted and its equivalent of the sample calculated.) Starch is now added and the excess of the iodine titrated with \( \text{N}/10 \) sodium thiosulphate. The cc. of thiosulphate in terms of \( \text{N}/10 \) solution subtracted from the cc. \( \text{N}/10 \) iodine solution taken give cc. iodine required by the sample added. The acidity of the solution is now determined by titration with \( \text{N}/10 \) sodium hydroxide. The cc. NaOH required by the HI give total NaOH minus cc. \( \text{N}/10 \) HC1 present in the iodine solution.

**Calculation.**

A. Cc. \( \text{N}/10 \) iodine required by the sample minus twice the cc. of \( \text{N}/10 \) NaOH required by III formed by the reaction multiplied by 0.003903 give weight of Na\( \text{S} \), (i.e., cc. I - 2 cc. NaOH) \( \times \) 0.003903 = gram Na\( \text{S} \).

B. Cc. \( \text{N}/10 \) NaOH required by the III multiplied by 0.00560 gives gram weight of NaHS. Or in brief: cc. NaOH \( \times \) 0.005608 = gram NaHS.

The above weights multiplied by 100 and divided by the weight of sample used in the iodine titration give per cent of constituents in the sample.

The method is of value in the analysis of alkali sulphides in absence of other compounds, which are decomposed by hydrochloric acid and which react with iodine.

**Determination of Thiosulphate in Presence of Sulphide and Sulphhydrate**

The sulphide and sulphhydrate sulphur is removed from the solution by adding an excess of freshly precipitated cadmium carbonate. The solution is filtered and diluted to a definite volume and the thiosulphate determined on an aliquot
portion by running it into an excess of N/10 iodine solution and titrating the excess of iodine with N/10 thiosulphate solution.

One cc. N/10 iodine = 0.024822 gram Na₂S₂O₃·5H₂O.

**Determination of Sulphates and Sulphides in Presence of One Another**

In one portion of the sample the sulphide is decomposed and the hydrogen sulphide expelled by boiling the solution (in presence of CO₂ replacing air in the flask) after acidifying with hydrochloric acid. The sulphate sulphur may now be precipitated as BaSO₄ by the usual methods.

In a second portion total sulphur is determined after oxidizing the sulphide with an excess of bromine and boiling out the excess of halogen. Total sulphur minus sulphate sulphur = sulphide sulphur.

The sulphide may be oxidized with fuming nitric acid by boiling the solution in a flask with reflux condenser. The nitric acid is expelled by evaporating the solution down to a moist residue. The sulphate is now precipitated by taking up the residue with water, adding HCl and then sufficient BaCl₂ to cause complete precipitation.

**Determining the Sulphur in Thiocyanic (Sulphocyanic) Acid and its Salts**

Oxidation of the sulphur may be accomplished as described for sulphides in the preceding method either by means of bromine or by fuming nitric acid. The sulphur is then precipitated as BaSO₄ as usual.

**Determination of Sulphurous Acid (SO₂ in Solution) Free, or Combined in Sulphites, Acid Sulphites, Metabisulphites and Thiosulphates**

**Gravimetric Method, Oxidation to Sulphate and Precipitation as BaSO₄.**

Sulphur dioxide, free or combined in a soluble salt, may be oxidized to SO₃ or sulphate by means of an oxidizing agent such as chlorine, or bromine, or hydrogen peroxide (alkaline solution). The sulphuric acid or sulphate may be then precipitated and determined as BaSO₄ in the usual way.

**Procedure.** The halogen (bromine preferred) is added (in a water-saturated solution) in large excess to the sample, the free halogen then boiled out, and sulphuric acid precipitated, from a solution made slightly acid with hydrochloric acid, by addition of a solution of barium chloride, according to the standard procedure.

If hydrogen peroxide is used, the solution should be made alkaline with ammonia and the peroxide added, the excess boiled out, and the solution then made acid as directed above.

BaSO₄×0.3517 = H₂SO₄, or ×0.5401 = Na₂SO₃, or ×0.4458 = NaH₂SO₃, or ×0.3387 = Na₂S₂O₃, or ×0.2745 = SO₃.

**Note.** If hydrogen peroxide is used, it should be tested for H₂SO₄ and allowance made accordingly.
Volumetric Methods

Titration with Iodine. Sulphurous Acid, Sulphites, Metabisulphites, Thiosulphates. Sulphurous acid, combined or free, may be titrated with iodine solution, the following reaction taking place:

$$\text{SO}_2 + 2\text{I} + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HI}.$$ 

The titration is accomplished by adding the solution of sulphurous acid, sulphite, or thiosulphate to the iodine, not in the reverse order, since in the latter order low results are obtained, unless the solution is very dilute (less than 0.04% SO₂).\(^1\)

Procedure. Five grams of the sample (sulphurous acid solution titrated directly) are dissolved in a little water and transferred to a 500-cc. graduated flask, then made to volume. Each cc. of this solution contains 0.01 gram of the sample; 100 cc. of N/10 iodine, or their equivalent if the solution is stronger or weaker, are placed in a beaker together with a few drops of hydrochloric acid. A portion of the sample in a 100-cc. burette is now run into the iodine, with constant stirring, until the color of the free iodine has almost faded out; a little starch solution is now added and the titration continued to the complete fading of the blue color.

Since each cc. of the sample contains 0.01 gram of the material, it follows that the 100-cc. iodine equivalent in terms of the material titrated expressed to the fourth decimal place as a whole number, if divided by the cc. of the sample required, will give the per cent of the substance sought, provided other titratable substances are absent.

Example. Suppose sodium sulphite is being titrated, then since 100 cc. of N/10 iodine are equivalent to 0.6304 gram Na₂SO₃, 6304 divided by the cc. Na₂SO₃ solution required gives per cent Na₂SO₃. If 63 cc. were required the salt would be 100% pure.

Note. When the iodine equivalent is over unity, it is necessary to take a larger sample per 500-cc. volume to avoid having a titration of over 100 cc. For example in the analysis of sodium thiosulphate, a 20-gram sample is diluted to 500 cc. and a portion of this added to 100 cc. of N/10 iodine solution. In this case it must be kept in mind that each cc. of the sample contains 0.04 gram of thiosulphate and the percentage calculated accordingly upon completing the titration.

If the titration of the iodine is made in a casserole, the end-point may readily be recognised without the addition of starch.

Equivalents. 100 cc. N/10 iodine solution will oxidize:

- Sodium sulphite (anhydrous), Na₂SO₃ = 0.6304 gram, or 0.3203 gram SO₂.
- Sodium sulphite, Na₂SO₃·7H₂O = 1.2606 grams.
- Acid sodium sulphite, NaHSO₃ = 0.5204 gram.
- Sodium metabisulphite, Na₂S₂O₅ (anhydride of NaHSO₃) = 0.47535 gram.
- Sodium thiosulphate, Na₂S₄O₆·5H₂O = 2.4822 grams.

Note. Hydrogen sulphide or sodium sulphide are also titrated with iodine. Equivalents for 100 cc. N/10 iodine = 0.1704 gram H₂S, or 0.3904 gram Na₂S.

Determination of Sodium Thiosulphate. The iodine titration is described on page 512. See also the chapter on iodine.

Acidimetric and Alkalimetric Methods

Titration of Sulphites, Acid Sulphites (Metabisulphite) or Sulphurous Acid. The choice of indicator is important as the titration with one may be different from that obtained in presence of another. For example the titration of sulphurous acid by an alkali in presence of phenolphthalein is twice the titration necessary to obtain an alkaline reaction with methyl orange. The reason for this is evident by the fact that Na₂SO₃ is neutral to phenolphthalein and alkaline to methyl orange, whereas NaHSO₃ is neutral to methyl orange but is acid to phenolphthalein. Advantage is taken of this in the analysis of salts containing a mixture of the normal and acid salts.

Reaction. With phenolphthalein \( \text{H}_2\text{SO}_3 + 2\text{NaOH} = \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O} \).

With methyl orange \( \text{H}_2\text{SO}_3 + \text{NaOH} = \text{NaHSO}_3 + \text{H}_2\text{O} \).

On the other hand if a salt is being titrated, methyl orange cannot be used for the titration of metabisulphite or acid sulphite, since these salts are neutral to this indicator, hence phenolphthalein is required and an alkali titration made.

Reaction. \( \text{NaHSO}_3 + \text{NaOH} = \text{Na}_2\text{SO}_3 \) \( (\text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = 2\text{NaHSO}_3) \). Again if sodium sulphite, \( \text{Na}_2\text{SO}_3 \), is to be titrated, phenolphthalein would not do as an indicator, since \( \text{Na}_2\text{SO}_3 \) is neutral to this indicator. Here an acid titration is required with methyl orange indicator present:

\[ 2\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_3 = 2\text{NaHSO}_3 + \text{Na}_2\text{SO}_4 \]

A. Sulphurous Acid

For the alkali titration of this acid it is advisable to use methyl orange as indicator, since this is not affected by carbon dioxide, which is very frequently present.

Reaction. \( \text{H}_2\text{SO}_3 + \text{NaOH} = \text{NaHSO}_3 \).

One cc. N/1 NaOH = 0.06407 gram SO₂, or 0.08209 gram H₂SO₃.

B. Sodium Metabisulphite

Sodium acid sulphite does not exist in dry form, since the salt loses water and the anhydride \( \text{Na}_3\text{S}_2\text{O}_7 \) results. This is analogous to sulphurous acid, which exists only in water solution. It has been found that the acid sulphite solution evaporated to crystallization yields a product, which though dried with extreme care, forms the anhydride salt, \( \text{Na}_3\text{S}_2\text{O}_7 \). For correct report, therefore, the solid should be reported as metabisulphite, and the solution of the salt as acid sulphite.

Since metabisulphite in solution, or acid sulphite, is neutral to methyl orange, phenolphthalein indicator must be used and an alkali titration made. Carbon dioxide-free water and reagents should be used.

Reaction. \( \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = 2\text{NaHSO}_3 \) and \( \text{NaHSO}_3 + \text{NaOH} = \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \).

Procedure. 9.507 grams of the finely ground powder are dissolved in about 50 cc. of cold saturated salt solution, to which has been added from a burette 50 cc. of normal sodium hydroxide. The salt solution should be made neutral to
phenolphthalein. One cc. of 0.1% solution of the indicator is added and the excess acid sodium sulphite titrated with normal sodium hydroxide until a permanent faint pink color is obtained.

Since the normal equivalent of the salt has been taken for analysis the cc. alkali titration, including the 50 cc. originally present, will give the percentage directly in terms of Na$_2$SO$_3$.

Note. The NaCl serves to give a sharp and more permanent end-point. It may be necessary to add more of the indicator towards the end of the titration.

C. Sodium Sulphite, Na$_2$SO$_3$

Sodium sulphite, Na$_2$SO$_3$, is neutral to phenolphthalein and alkaline to methyl orange. The titration of this salt is accomplished by addition of standard acid in presence of methyl orange.

Reaction. 2Na$_2$SO$_3$ + H$_2$SO$_4$ = Na$_2$SO$_4$ + 2NaHSO$_3$.

Procedure. The normal factor weight (12.6 grams) of the salt is dissolved in about 250 cc. of distilled water, 1 cc. of methyl orange added, followed by normal sulphuric acid, added from a burette until a faint orange end-point is obtained. As in the case of the metabisulphite, each cc. of normal sulphuric acid equals 1% Na$_2$SO$_3$. Hence the percentage is obtained directly from the burette reading.

Notes. Organic coloring matter may be removed from the solution by filtering through charcoal.

If sodium carbonate is present, it will also be titrated. A correction must be applied for this. In the presence of sodium carbonate the solution will be alkaline to phenolphthalein. An approximate estimation of this may be obtained by titration with normal acid in presence of this indicator, remembering that sodium bicarbonate, NaHCO$_3$, is neutral to phenolphthalein, hence twice this titration must be deducted from the total methyl orange titration, i.e., Na$_2$CO$_3$ + H$_2$SO$_4$ (M.O.) = Na$_2$SO$_4$ + H$_2$CO$_3$ and 2Na$_2$SO$_3$ + H$_2$SO$_4$ (P.) = 2NaHSO$_4$ + 2NaHCO$_3$. (Alkaline hydroxides will also be titrated.) CO$_2$ may also be obtained by the standard procedure under carbon, the SO$_2$ being oxidized by addition of chronic acid. Na$_2$CO$_3$ x 1.5 = equivalent Na$_2$SO$_3$.

Sodium carbonate may be detected in a sulphite or metabisulphite by adding cold, dilute acetic acid (25%) to the dry powdered salt. An effervescence is due to the presence of carbonate, since a sulphite or metabisulphite does not effervesce under similar conditions.

Determination of Sulphites, Metabisulphites, Thiosulphates, Sulphates, Chlorides and Carbonates in Presence of One Another

1. Sodium Sulphite, Na$_2$SO$_3$

This is determined by titration with standard acid in the presence of methyl orange indicator according to the standard procedure previously described. If a carbonate is present, allowance must be made for this as stated.

One cc. N/1 H$_2$SO$_4$ = 0.126 gram Na$_2$SO$_3$. Calculate to per cent.
Na$_2$CO$_3$ x 1.5 = equivalent Na$_2$SO$_3$. 

514 SULPHUR
2. Sodium Metabisulphite, Na₂S₂O₅

This is determined by titration with a standard alkali in the presence of phenolphthalein indicator according to the procedure previously described.

One cc. N/1 NaOH = 0.09507 gram Na₂S₂O₅. *Calculate to per cent.*

3. Sodium Thiosulphate, Na₂S₂O₃

One gram of the mixed salts is placed in 100 cc. of N/10 iodine solution, **and** the excess of iodine titrated with N/10 sodium thiosulphate according to the standard procedure.

**Calculation.** \[
\left\{(\text{cc. } N/10 \text{ I} - \text{cc. } N/10 \text{ Na}_2\text{S}_2\text{O}_3) - \left(\% \text{ Na}_2\text{S}_2\text{O}_3 \times 2.104\right) + \left(\% \text{ Na}_2\text{SO}_3 \times 1.5864\right)\right\} \times 1.5814 = \% \text{ Na}_2\text{S}_2\text{O}_3.
\]

4. Sodium Sulphate

The sample is dissolved in a little water, hydrochloric acid added, and the solution boiled to expel all of the SO₂. Barium sulphate is now precipitated and determined according to the standard procedure.

\[\text{BaSO}_4 \times 0.6086 = \text{Na}_2\text{SO}_4.\]

**Note.** The amount of the sample required is governed by the per cent Na₂SO₄ present.

5. Sodium Chloride

The sample is dissolved in water, nitric acid added and the solution boiled until all the SO₃ has either been volatilized or oxidized. The chlorine of the chloride is now precipitated with silver nitrate from a hot solution by the usual procedure.

\[\text{AgCl} \times 0.4078 = \text{NaCl}.\]

**Note.** The amount of the sample taken is governed by the per cent of NaCl present.

6. Sodium Carbonate, Na₂CO₃

Carbon dioxide is evolved from the mixture by means of chromic and sulphuric acids, the former being used to oxidize the SO₂ of the sample. The evolved gas is bubbled through a mixture of strong sulphuric and chromic acids to remove any SO₂ that may have escaped oxidation. Fig. 20. The CO₂ is absorbed either in caustic and weighed or is passed into a standard solution of barium hydroxide and titrated according to the standard procedures given under carbon.

**Note.** The amount of the sample taken is governed by the per cent of Na₂CO₃ present.
ESTIMATION OF SODIUM HYDROSULPHITE

Standard Indigo Solution. To about 150 cc. concentrated sulphuric acid in a casserole, are added 4.2 grams of indigo, slowly with stirring. The solution is kept at 80° C. for an hour in an oven, stirring once or twice during this time. After cooling the solution it is made up to four liters with distilled water. This reagent is now standardized against N/50 KMnO₄ solution. To do this 25 cc. of the indigo solution is diluted in a casserole with 300 cc. of water and titrated with N/50 KMnO₄ reagent.

1 cc. N/50 KMnO₄ is equivalent to 0.0015 g. indigotin.

1.505: 1 = gram indigotine : z, where z = gram Na₂S₂O₄ in 25 cc. Indigo solution.

\[ 2 \times 10,000 \times \text{cc. titration} = \% \text{Na}_2\text{S}_2\text{O}_4 (2.5 \text{ grams of solid}) \text{ or grams per liter (25 cc. sample made up to 500 cc.).} \]

Procedure

Titration of Sodium Hydrosulphite Against Standard Indigo Solution. Fifty cc. of standard indigo solution are pipetted into a 300 cc. Erlenmeyer flask. The titrating apparatus as well as the 500 cc. volumetric flask are filled with CO₂ gas (C₂H₂ may be used in place of CO₂). Two and a half grams of the solid are now taken, or 25 cc. of the solution (if the material is already dissolved as a 10% solution) and placed in the 500 cc. flask and made to mark with distilled water. The flask is stoppered and connections made with the burette, etc., as shown in Fig. 65a. The burette is filled with the sample and the flask containing the indigo solution is placed under the burette as shown in the figure. The air is displaced from the apparatus by CO₂, the flow of this gas being continued during the titration. The hydrosulphite solution is now added to the indigo solution until it changes from the blue to a yellow or brown color.

Factor for Indigo: \( \frac{\% \text{Na}_2\text{S}_2\text{O}_4 \text{ in solids, or grams per liter in liquids}}{\text{cc. titration}} \)

Notes. The hydrosulphite solution should be made alkaline with NaOH, then made up rapidly to volume and titrated in an atmosphere of CO₂ to prevent oxidation.

The size of the sample may be varied, but the titration should be over 10 cc.

The tip of the burette should dip below the surface of the indigo until near the endpoint, then withdrawn and the titration completed with the tip above the surface.

The above method was outlined by J. H. Brackett.
SULPHUR

DETERMINATION OF FREE SULPHUR IN A MIXTURE

Free sulphur is an essential constituent in many types of mixtures and the method of estimation will vary with the nature of the other ingredients. Hydrated lime, chalk, gypsum, dry lime sulphur, calcium arsenate, nicotine sulphate in infusorial earth carrier, sodium polysulphide, sodium chloride, epsom salts, and the usual fertilizer materials are the substances most commonly found in the mixtures now on the market. All commercial forms of sulphur are found in these mixtures and the value of the mixture usually depends largely on which form of sulphur was used. For example, an insecticide dust containing coarse crude or refined sulphur, instead of flowers or superfine, would be valueless even though the chemical analysis showed that the mixture contained the specified percentage of total sulphur. Therefore, the microscope and a little ingenuity will indicate the proper combination of methods to follow.

From 1 to 10 grams of the material, depending upon the amount of sulphur present, is extracted in a Soxhlet extractor (see modified form, Fig. 66) with carbon bisulphide (freshly distilled) for twelve hours. The extract is evaporated to dryness, adding 10 cc. of bromine-carbon tetrachloride mixture together with 15 cc. of nitric acid. The residue is taken up with 10 cc. of hydrochloric acid, diluted with 150 cc. of distilled water, heated to boiling and the sulphuric acid precipitated with 10% barium chloride solution, washed, dried, ignited and weighed according to the procedure for sulphur.

\[
\text{BaSO}_4 \times 100 \times \frac{0.1373}{\text{Weight of sample}} = \% \text{ free rhombic sulphur.}
\]

After extraction carefully dry the thimble and contents. Examine under a microscope a small portion of the dried material. Remaining sulphur if present will be in the amorphous form and have the characteristic "droplet" structure seen in flowers of sulphur. Presence of much sulphur at this stage indicates that flowers of sulphur were used in the mixture, and the proper procedure to follow will depend on the nature of the other constituents. If a soluble sulphate such as nicotine sulphate or epsom salts is indicated, then an aliquot of the residue in the extraction thimble can be leached with hot water and the sulphur determined by one of the usual methods after wet oxidation. If an insoluble material such as gypsum is indicated, then the free sulphur may be burned off in the air and the combined sulphur determined in the residue after solution by one of the standard methods; the total sulphur having first been determined in another aliquot after wet oxidation with bromine and nitric acid. What-
ever procedure is followed, the content of amorphous sulphur is calculated by
difference and thus the percentage of flowers established by adding the amount
thus found to the CS₂ soluble sulphur.

Sanders' extraction apparatus¹ has several advantages that make this
apparatus desirable for laboratory use, where a number of daily extractions
are required. As may be seen from Fig. 66, by simply removing the glass
stopper D the cylinder may be charged without disconnecting the apparatus,
as is necessary with the Soxhlet type of apparatus. The extraction is carried
on with the traps A and B closed, the siphon t-t' acting automatically as in
case of the Soxhlet. With A closed and B open the apparatus may be used
as a reflux condenser. The solvent liquid may be drawn off by opening A.
With B closed and A open the apparatus may be used as a condenser and the
ether, chloroform, carbon disulphide, etc., distilled from C. The globe-shaped
Soxhlet condenser may be replaced by Allihn's or Liebig's condenser, if desired.
The ball form, however, is more compact.

EVALUATION OF SPENT OXIDE FOR AVAILABLE SULPHUR

Spent oxide is the by-product of gas works, and refers to the spent Fe₅O₄, used
in the scrubber for the removal of hydrogen sulhide from the gas. The FeS,
as in case of pyrites, is used in the manufacture of sulphuric acid, and is evaluated
by its available sulphur content.

Total Sulphur. The oxide is sampled, brought into solution and the sulphur
determined exactly as is given under the standard method for determination of
sulphur in pyrites ore.

Residual Sulphur. Two grams of the material are ignited to expel volatile
sulphur, a porcelain crucible being used. The residue is treated with strong
hydrochloric acid and after digestion on the steam or water bath is diluted with
water and filtered. (If SiO₂ is present evaporation to dryness is necessary.)
Sulphur is determined in the filtrate as usual.

Available Sulphur. The per cent of residual sulphur is subtracted from the
per cent total sulphur, the difference being available sulphur.

Iron. This may be determined on an ignited sample according to a standard
procedure for iron. See chapter on Iron.

1910.
SULPHUR

ANALYSIS OF REFINED SULPHURS AND BRIMSTONE

The impurities in commercial sulphurs and brimstones are seldom more than a few tenths per cent. Arsenic, acidity, chlorine, and the amount of amorphous sulphur present (CS₂ insoluble) are required. Also the fineness and specific volume (degrees Chancel) are often required for sulphurs used in agriculture.

Moisture. The powdered sample, weighing 50 grams, is spread out on a watch-glass and dried for an hour at 100° C., then cooled in a desiccator and weighed.

Loss of weight in grams multiplied by 2 = per cent moisture.

Arsenic. Ten grams of the material are treated with 30 cc. of carbon tetrachloride mixture (3 parts CCl₄ + 2 parts Br) and after standing for ten minutes 25 cc. strong nitric acid are added in small portions (a watch-glass covering the beaker during the intervals of addition). HNO₃ and Br are expelled by evaporation on the steam bath. Water is added and the evaporation repeated. Arsenic is now determined on the residue by the Gutzeit Method for arsenic.

Note. Arsenic-free reagents should be employed.

Chlorine. One hundred grams of the brimstone are extracted with hot water, the filtered extracts oxidized with 10 to 15 cc. of nitric acid and a few crystals of ammonium persulphate by boiling and treated with 5 cc. of 10% solution of silver nitrate. The solution, brought to boiling, is placed in a dark place and the silver chloride allowed to settle. This is now filtered off in a weighed Gooch crucible and chlorine calculated from the AgCl.

\[ \text{AgCl} \times 0.2474 = \text{Cl} \text{ or } 0.4078 = \text{NaCl} \]

Mineral and Organic Impurity. Ash 100 gms. of the sample by igniting a little at a time in a tared porcelain or silica ware dish. Carry on the combustion in plenty of air and without the aid of any external heat except toward the last. In igniting the sample use a small pin flame gas jet such as the petroleum chemist uses in making flash and fire tests. Do not use match or taper or alcohol to ignite the sulphur as a small amount of organic matter is certain to get into the sample from these sources and cause trouble in the combustion. The sulphur once ignited will burn evenly and clean unless organic matter is present. All refined sulphurs should burn completely without the aid of any external heat. With American Gulf Coast brimstone and with oil or asphalt contaminated sulphur the organic matter present in even minute amount will cause trouble in burning unless special precautions are taken. A film of melted asphalt or oily matter forms over the surface of the molten sulphur and shuts off the air so that the flame from the burning sulphur is put out. When this film of dark oily matter is first noticed, touch it lightly with the pin flame and it will usually break or char, allowing the sulphur to burn evenly. Toward the last apply very gentle heat to the dish and thus char the organic matter but keep the temperature well below the red so that this organic material is not ignited. When all the sulphur is burnt off as indicated by no more odor of SO₂, cool the dish and weigh; this weight giving the combined organic and mineral matter. Then ignite the residue at low red heat to burn off all organic material; again cool and weigh; this weight
giving the mineral impurity or ash. The difference between the two weights represents the organic impurity.

**Acidity.** Boil 100 gms. of the pulverized sample with about 500 cc. water. The addition of a little neutral alcohol at the start will aid in wetting the sulphur which sometimes floats and causes trouble. Cool and make up to a standard volume. Pipette or filter off an aliquot and titrate with N/10 alkali, using phenolphthalein. Calculate acidity as H₂SO₄ and express as per cent acidity.

**Available Sulphur.** Add together moisture, organic matter, ash, arsenic, acidity, chlorine and report available sulphur as the difference.

**Amorphous Sulphur (CS₂ insoluble).** Weigh five to twenty grams of the finely pulverized sample into a tared Extraction Thimble and extract with carbon bisulphide. The rate of extraction is regulated so that one filling of the chamber takes about five minutes. The extraction should be complete in thirty minutes. It is important that the extraction be stopped as soon as the loss in weight of the thimble and contents becomes constant as long-continued extraction will carry some of the amorphous sulphur into solution. Note: A Soxhlet type extraction apparatus is best as other types where the thimble is not immersed in the liquid give erratic results at times on account of the tendency of the CS₂ solution of sulphur to "crawl" to the top of the thimble and there deposit out a hard scale of rhombic sulphur. When the extraction is completed, the thimble and contents are freed from CS₂ by exposure to a rapid current of dry air and then dried for thirty minutes in a water oven through which air circulates. (Finely divided sulphur, CS₂, and air is a mixture liable to spontaneous combustion, so get rid of the bulk of the CS₂ in the cold dry air current before exposing to the heat of the oven.) The weight of the contents of the thimble less ash and arsenic and organic matter is taken as the amorphous sulphur. Flowers of sulphur must contain in excess of 30% amorphous sulphur. (Flowers are often sophisticated by the addition of ground sulphur when the content of amorphous sulphur is lowered in proportion—this should not be reported as flowers but flowers with so much adulteration.) Refined lump sulphur, roll sulphur and rubber makers sulphur should contain no amorphous sulphur. Powdered sublimed sulphur usually contains some small percentage of amorphous sulphur. Note: Direct sunlight, heat and some chemical fumes cause the amorphous sulphur in flowers to revert to the soluble rhombic modification. Therefore be careful in the preparation and treatment of samples of flowers of sulphur.

**Fineness and Specific Volume of Degree Chancel.** Examine the sample under the microscope. Use a recessed slide and wet the specimen with alcohol or preferably with concentrated sulphuric acid. Flowers of sulphur appear as loose agglomerations of opaque yellow spherical droplets. Ground refined sulphur and ground brimstone appear as clear angular fragments almost colorless. High quality flowers consists entirely of minute droplets all of uniform size and barely touching each other. In low quality flowers the droplets are of large and irregular size and are more or less fused together. The smaller and the more uniform the size of the sulphur particles—whether the droplets of the flowers or the grains of a pulverized sulphur—the greater will be the specific volume and the Degree Chancel. This is determined by the
Chancel Sulphurimeter.\textsuperscript{1} a tall glass tube, glass-stoppered, graduated into 100 degrees of \( \frac{1}{2} \) cc. each. Five grams of the sulphur sample are accurately weighed out and dusted into the tube which is half filled with ether or alcohol. The sulphur and alcohol is strongly shaken and the tube and contents allowed to stand in a vertical position. The reading of the sulphur level is taken as soon as the subsidence ceases or at the end of an hour and this is reported as the degree Chancel. (If a Chancel Sulphurimeter is not obtainable, a tall glass-stoppered graduate of 25 cc. capacity will serve, remembering that each quarter cc. represents a degree in the Chancel scale. Of course this reading will not be as accurate as on the Sulphurimeter where the scale is larger on account of the smaller diameter of the Chancel tube.)

The cylindrical glass tube should have the following dimensions: The cylinder should be 23 cm. long and 15 mm. in diameter, with a scale starting from below, graduated upwards into 100 degrees, each degree being \( \frac{1}{4} \) cc.; the 100 degrees (25 cc.) occupy a length of 100 mm. The cylinder is closed at the lower end, and glass stoppered, as shown in Fig. 66a. The sulphur is first passed through a sieve 1 mm. mesh, in order to break down the lumps formed with storage. As stated, a 5 gram sample is placed in the tube and this half filled with anhydrous ether, having a temperature of 17.5\(^\circ\) C. The sieved sample is shaken and additional ether added until the level stands 1 cc. over the 100\(^\circ\) mark and the whole again shaken in an upright position, the sulphur allowed to settle and the degrees Chancel read off.

The procedure for analysis of refined sulphurs was contributed by Chas. A. Newhall.


QUANTITATIVE ESTIMATION OF SMALL QUANTITIES OF SULPHIDE SULPHUR; METHOD OF W. A. DRUSHEL AND C. M. ELSTON

The method is a colorimetric method and consists essentially of the comparison of the depth of color of lead sulphide stains obtained from the sulphide sulphur of a given weight of a sample to be analyzed with a standard series of stains prepared from sulphide solutions of known sulphur content. A set of stains varying in depth of color from a faint yellowish brown to black representing from 0.0002% to 0.004% of sulphide sulphur may be prepared and used indefinitely for comparison. With a set of standard stains at hand the method has the advantage that within the range given the sulphide sulphur of a sample may be determined with a fair degree of accuracy in less than ten minutes.

Preparation of Standard Set of Sulphide Stains. The apparatus used for preparing standard stains and for making analyses is very simple. The inner tube of a Liebig condenser with its larger end about 18 mm. in internal diameter is cut off 15 cm. in length. The smaller end is drawn down somewhat, rounded and fitted to a sound cork stopper which in turn is fitted to a 100 cc. round-bottom flask. The condenser tube then serves as a sort of reflux condenser. To the upper and larger end of this tube a filter paper moistened with a dilute solution of lead acetate is smoothly fitted and tied, so that the steam passing up through the tube and carrying hydrogen sulphide is required to pass out through the lead acetate paper. A similar tube with the internal diameter of its larger end about 30 mm. is also prepared and used for sulphide sulphur samples containing 0.001% or more of sulphur.

A solution of sodium sulphide is made up with pure distilled water and carefully standardized. The solution is then diluted to contain exactly 0.01% of sulphide sulphur. This solution is used for making up standard solutions containing 0.0002, 0.0004, 0.0006, 0.0008, 0.001, 0.002, 0.003 and 0.004% of sulphide sulphur respectively, taking care to use distilled water free from traces of nitrites in making the dilutions. It is found that the more dilute sulphide solutions when made up with ordinary distilled water lose their sulphide content either wholly or in part on standing for several hours in stoppered bottles. This difficulty is obviated by using nitrite free distilled water in making up the solutions.

Carefully measured portions of 1 cc. to 5 cc. of the standard solutions are pipetted into the 100 cc. flask and 25 cc. of hydrochloric acid of about 0.5% strength is added. The flask is immediately attached to the condenser tube fitted with moistened lead acetate paper as previously described. The mixture is then gently boiled for a few minutes at such a rate that the steam issued not too rapidly from the upper end of the condenser tube. In this way the sulphide sulphur is quantitatively liberated as hydrogen sulphide and evenly deposited as lead sulphide on the moistened lead acetate paper. The undecomposed lead acetate is then washed out, the paper dried and labeled with the amount of sulphide sulphur present as one of the set of standard stains. In the same way complete sets in duplicate are prepared ranging in sulphide sulphur from 0.0002% to 0.004%.

SULPHUR

In making these estimations the larger condenser tube is used where a preliminary trial indicates that the amount of sulphide sulphur is equal to or greater than 0.001%. In all other cases the smaller tube is used. The maximum error, depending upon the amount of sulphur present, with the larger tube was 0.001% and with the smaller tube 0.0003%. These errors may be reduced by repeating the determination and taking the mean of several values found. In this way in the practical applications of the method the errors may be kept within reasonable limits.

Practical Applications. (1) In gas analysis. Twenty-five liters of air are slowly drawn through a Geissler bulb of the most modern type containing dilute potassium hydroxide solution. This solution is then washed into a measuring flask and made up to the mark with nitrite free distilled water and aliquot portions of this solution are used for determining the sulphide sulphur as previously described.

(2) In coke analysis. The simplest method of estimating sulphur in coke given by Fresenius is to boil 5 grams to 10 grams of powdered coke in dilute hydrochloric acid, and to absorb the hydrogen sulphide evolved in dilute potassium hydroxide solution. The sulphur is then oxidized to the sulphate condition by chlorine water or bromine water and weighed as barium sulphate. This method is used as a control to check up the results obtained by the colorimetric method. In this method the hydrogen sulphide is liberated and absorbed as suggested by Fresenius and aliquot portions of the sulphide containing potassium hydroxide solution are transferred to the distillation flask and the previously described procedure is followed.

(3) In paper analysis. In order that tissue paper may be used for wrapping polished metal without producing a tarnish the paper must be relatively free from sulphide sulphur. A weighed amount of paper, 1 gram to 2 grams, is cut into small pieces and transferred to the distilling flask and digested with gently boiling 0.5% hydrochloric acid, collecting the hydrogen sulphide as lead sulphide on lead acetate paper as previously described.
THORIUM

Th, at.wt. 232.15; sp.gr. 11.0–12.2; m.p. 1450°; oxides, ThO₂ (ThO₃ and Th₂O₃ known only in hydrate form)

DETECTION

In the regular analytical procedure thorium is found in the precipitate of the tri- and tetra-valent hydroxides produced by ammonium hydroxide, provided a sufficiently thorough decomposition of the sample has been obtained (see section on preparation and solution of sample). Along with rare earth elements, and a little zirconium, thorium may be obtained as oxalate by dissolving the hydroxide precipitate in hydrochloric acid and adding a slight excess of oxalic acid to the hot, weakly acid (not over 0.5 normal) solution. The precipitate should be allowed to stand six or eight hours before filtration. After having been washed with water containing 2 cc. of 6 normal hydrochloric acid per 100 cc., the precipitate is rinsed into a beaker with pure water, using about 50 cc. To this mixture 5 g. of solid ammonium oxalate are added, and the mixture is heated for half an hour nearly to boiling, and well stirred. Two volumes of water are added, the mixture is allowed to stand half an hour and then filtered. To the filtrate 20 cc. of 6 normal hydrochloric acid are added. A white precipitate indicates the presence of thorium. This precipitate can be put into solution by strong heating with conc. sulphuric acid, and taking up with ice-cold water. One of the following characteristic tests may be used as confirmation of thorium.

A sensitive test for thorium consists in the precipitation of thorium iodate in nitric acid solution. Two reagent solutions are necessary: (I) 15 g. of potassium iodate, 50 cc. of conc. nitric acid, and 100 cc. of water. (II) 4 g. of potassium iodate, 50 cc. of conc. nitric acid, and 450 cc. of water. The solution to be tested for thorium, which must contain no hydrochloric acid, is boiled with a little sulphuric acid to reduce any cerium present. To this solution is added twice its volume of reagent (I), which causes precipitation

1 It is shorter to add oxalic acid directly to the filtrate from the hydrogen sulphide group, after boiling out the excess of hydrogen sulphide. This, however, causes complications in the analysis of subsequent groups, and may also contaminate the oxalate precipitate with calcium; so it is better to first precipitate the hydroxides with (carbonate-free) ammonium hydroxide as described.

2 Thorium oxalate is soluble in ammonium oxalate. Zirconium oxalate, and traces of the oxalates of the yttrium earths also dissolve, but the yttrium earth oxalates are reprecipitated on dilution. The addition of an excess of mineral acid to the ammonium oxalate solution of thorium and zirconium precipitates thorium oxalate, but not zirconium oxalate.


Chapter by Paul H. M.-P. Brinton.

522
of thorium iodate, and more or less rare earth iodates according to their concentration in the solution. By now adding reagent (II) in volume equal to four times the original volume, and boiling, any rare earth iodate is dissolved, while thorium iodate (also any zirconium iodate) remains undissolved. If the absence of zirconium is not known with certainty, the iodate precipitate may be boiled with 50 cc. of 10% oxalic acid solution ¹ until iodine vapors are no longer given off. Any precipitate remaining is thorium oxalate.

Sodium pyrophosphate produces in solutions of an acid normality of 0.2-0.3 a white precipitate of thorium pyrophosphate. To make certain that this precipitate is entirely free from rare earths it should be redissolved, any tetravalent cerium reduced with sulphurous acid, and then the thorium reprecipitated as pyrophosphate as described later under Gravimetric Determination. Zirconium and titanium would also be precipitated under these conditions, but they would be separated from thorium on the basis of their non-precipitation by excess of oxalic acid.

Spectrum analysis, and the determination of radioactivity ² are also useful in the detection of thorium.

ESTIMATION

The estimation of thorium is required chiefly in connection with the incandescent gas mantle industry. The main source of thorium is monazite sand, of which the greater part comes from Brazil and India. The South Carolina monazite is of poor quality and of very little commercial importance. Monazite is essentially an orthophosphate of the cerium earths, and carries from about 4% to nearly 10% of ThO₂. The highest grade material comes from Travancore, India. Thorite and thorianite, the silicate and the uranate respectively of thorium, are now of limited importance.

Preparation and Solution of the Sample

Thorite. The very finely pulverized sample is digested with conc. hydrochloric acid at a temperature just below boiling. This usually effects complete decomposition, but for safety any insoluble residue should be filtered, after dilution, ignited, and then fused with potassium pyrosulphate. This fusion is taken up with 6 normal hydrochloric acid and added to the main solution. Silica and the hydrogen sulhide group are removed in the conventional way, leaving thorium, rare earths, etc., in the acid solution.

Monazite, Thorianite, Gas Mantle Residues, etc. While fusion with potassium pyrosulphate effects the decomposition, yet it is more convenient to attack larger samples with conc. sulphuric acid. In the case of monazite sand, large samples are necessary to insure uniform and representative samples. Thorianite and Carolina monazite should be finely ground, but Brazilian and Indian monazite are fully decomposable without grinding, and filtration from the insoluble residue is easier if the sample is taken as it comes. A batch of sand should be very carefully mixed before sampling, to avoid the tendency toward segregation arising from the different sizes and densities of the constituent grains.

² Helmick, J. Am. Chem. Soc., 43, 2003 (1921), gives details for the quantitative, as well as the qualitative, determination of thorium in minerals.
The following method for the decomposition of monazite is recommended by Dr. H. S. Miner,\textsuperscript{1} of the Welsbach Co.: 50 g. of the sand are weighed out and placed in a porcelain casserole of about 50 cc. capacity. 75 cc. of conc. sulphuric acid are added, and the mixture is heated for about four hours with frequent stirring, a gentle evolution of fumes being maintained during the course of the operation. When the mass has become pasty, it is allowed to cool, and the sulphates are extracted by the addition of about 400 cc. of ice-cold water, or enough to cool the solution sufficiently so that the sulphates become soluble. This solution is decanted into a liter-graduated flask, and the remaining sulphates are extracted with small portions of cold water and decanted into the flask. A point is reached toward the end of the extraction when, due to the decreasing acidity, the small wash portions show a slight separation of rare earth phosphate. A few more extractions are made beyond this point, but these portions are not added to the graduated flask. They are temporarily preserved in a separate beaker. To the remaining sand, which has been dried, 10 cc. of conc. sulphuric acid are added, and the digestion is carried out as before, except that a somewhat higher temperature is used, enough to maintain copious evolution of white fumes, and the duration of the digestion need not exceed one and a half hours. After cooling, extraction is started with the last portions of the previous extraction liquor, i.e., those decanting which showed slight precipitates of rare earth phosphates, and which were preserved in the separate beaker. The sand is now thoroughly washed with cold water, and the washings are all decanted into the liter flask. This flask now contains all the thorium and rare earths as soluble sulphates. A little suspended silica is usually visible at this point, but this will not be mistaken for undissolved sulphates.

After cooling, the sulphate solution is made up exactly to the liter mark, thoroughly mixed, and filtered through a dry filter, discarding the first 25 or 30 cc., and receiving the remainder in a dry flask or bottle. The whole need not be filtered, and, of course, no washing is to be done. Each 100 cc. of this solution represents 5 g. of the sample.

\textsuperscript{1} U. S. Bureau of Mines, Bulletin 212, p. 53 (1923).
SEPARATIONS

Thorium is separated from practically all elements excepting the rare earth elements and scandium by precipitation as oxalate in slightly acid solution. Zirconium may be in part precipitated along with thorium and the rare earths, especially in the absence of a sufficient excess of oxalic acid; and if considerable quantities of calcium, and to less extent strontium and barium, are present, there may be contamination unless the mineral acid concentration be kept dangerously high. In the presence of much calcium, it is better to first separate thorium from it by precipitation with freshly distilled ammonium hydroxide, and then to precipitate the thorium as oxalate. The details of the oxalate separation have been given under Detection.

The main problem, then, is the separation of thorium from the rare earth elements. The iodate method has already been given in detail. Two other much used methods will now be described.

The Pyrophosphate Method.\textsuperscript{1} An aliquot portion of the sulphate solution, prepared as already described, and usually representing 2.5 g. of monazite sand, is diluted to about 450 cc., and 5 cc. of conc. hydrochloric acid are added. The solution is heated nearly to boiling and the iron and cerium are reduced by adding sulphurous acid solution until the yellow color is discharged. 15 cc. of sodium pyrophosphate solution (50 g. Na\textsubscript{4}P\textsubscript{2}O\textsubscript{7}.10H\textsubscript{2}O in 1 liter of water) are slowly added, with constant stirring, and the mixture is then heated to gentle boiling for 5 minutes. After standing 5–10 minutes—not more—the precipitate of thorium phosphate is filtered and washed twice with water containing 1 drop of hydrochloric acid per 100 cc. A slight cloud in the first filtrate, due to atmospheric oxidation of iron (and possibly of cerium), with consequent precipitation of pyrophosphate may be neglected.\textsuperscript{2} The filter paper and precipitate are freed from excess liquid by wrapping for a moment in cheap filter paper or blotting paper, and then dropped into a dry 250-cc. Kjeldahl flask. 15 cc. of conc. sulphuric acid and a few crystals of ammonium perchlorate are added, a small funnel is placed in the neck of the flask, and the contents are heated until the filter is disintegrated. When a clear brown solution is obtained more perchlorate\textsuperscript{3} is added, and the heating is continued until the mixture is pure white (or very slightly yellow if much cerium was carried down in the first precipitate). The flask is placed in

\textsuperscript{1}Curney and Campbell, J. Am. Chem. Soc., 36, 1134 (1914).
\textsuperscript{3}The oxidation of the filter paper requires 10 or 15 minutes, and about 1.5 g. of perchlorate. Heating should not be continued far beyond the point at which the organic matter is fully destroyed, as the perchloric acid may break up and cause considerable foaming. Cartledge (J. Am. Chem. Soc., 41, 49 (1919)) shows that fuming nitric acid may be satisfactorily substituted for ammonium perchlorate. In this case the precipitate and paper are shaken with 15 cc. of conc. sulphuric acid in the Kjeldahl flask for about two minutes, cooling, if necessary, until the flask is just a little too hot to be held comfortably in the hand. To the charred mixture 2–4 cc. of fuming nitric acid (sp. gr. 1.33) are added, and after a minute or two the solution is gradually raised to the boiling point. Occasionally as fumes of sulphur trioxide appear a second charring occurs, in which case 0.5 cc. more nitric acid, poured cautiously down the neck of the flask, will complete the oxidation. (If the mixture has once been white or slightly yellow, no harm is done if during cooling oxides of nitrogen redissolve in the acid, thereby restoring a yellow color.)
ice-water and then slowly, with shaking, about 100 cc. of ice-cold water are added. Complete solution may at times require several hours. Occasionally a slight cloud of suspended silica persists. This may be neglected as it will be removed in the next step.

The sulphate solution is rinsed into a solution of 30 g. of sodium hydroxide in 125 cc. of water, contained in the original beaker in which the pyrophosphate was precipitated,\(^1\) boiled for several minutes, and washed several times with hot water. The paper and precipitate are then placed in the beaker just used, 10 cc. of conc. hydrochloric acid are added, and after a few minutes of stirring, 150 cc. of water are added, and the solution is boiled. The paper shreds are filtered off and washed, and the filtrate is diluted to about 400 cc. 3 cc. of saturated sulphuric acid solution are added, the solution is heated to boiling, and the thorium is again precipitated with sodium pyrophosphate. The precipitate is washed and changed to sulphate and hydroxide in the manner just described. This second sulphate should always be perfectly white, and should dissolve entirely clear. The final hydroxide is free from rare earths, and aside from zirconium and titanium, which are precipitated as pyrophosphate, it should contain only a trace of iron as impurity. These three foreign elements will be separated from the thorium by the final precipitation of the latter as oxalate. The last hydroxide precipitate is dissolved in as little conc. hydrochloric acid as possible (never more than 10 cc.) and filtered free from paper. This chloride solution is now ready for the gravimetric determination of thorium by precipitation as oxalate.

The Thiocarbonate Method.\(^2\) 200 cc. of the sulphate solution prepared as described under Preparation of Sample, and representing 10 g. of monazite sand, are diluted to 1 liter, and poured into 150 cc. of a cold saturated solution of oxalic acid. The sulphate solution should be fed in very slowly, preferably from a separatory funnel, and vigorous stirring should be maintained to convert the gummy precipitate to the crystalline form. Only in this way is it possible to get the oxalate precipitate free from considerable amounts of phosphate. After standing not less than fifteen hours the precipitate is filtered, washed free from acid, and dried.

The filtrate and first washings are neutralized with ammonia, and hydrochloric acid is then added in an excess of from 10 to 15 cc. This precipitates the remaining rare earths (and any thorium still in solution) as oxalo-phosphates. This precipitate is also allowed to stand fifteen hours, and then it is filtered and washed with weak oxalic acid solution. This precipitate, after drying, is ignited in a porcelain dish, moistened with a little water, and dissolved by warming with conc. hydrochloric acid. The solution so obtained is filtered, largely diluted, and precipitated by the addition of a large excess of oxalic acid, warming to convert the precipitate to a crystalline form. After standing two or three hours, this oxalate precipitate is filtered, washed, and dried.

The oxalate precipitates are ignited together. If "total rare-earth oxides" are wanted, they may be weighed at this point. The oxides are transferred to a 800-cc. beaker, moistened with a little water, and dissolved by warming

---

\(^1\) Thorium pyrophosphate adheres rather tenaciously to the glass, and this procedure eliminates the necessity for the tedious cleansing of the beaker after the first precipitation.

\(^2\) The details here given are essentially those in use in the laboratories of the Western Co. See H. S. Miner, loc. cit.
with 100 cc. of 6 normal hydrochloric acid. The solution is transferred to a 1500-cc. beaker, diluted to about 700 cc., and ammonia is added until the precipitate formed just ceases to redissolve, leaving the solution neutral or very slightly acid. Conc. hydrochloric acid is now added, a drop at a time, until the precipitate just dissolves, and then 6 to 8 drops more. 100 cc. of a boiling 30 per cent sodium thiosulphate solution are added to the boiling solution, and boiling is continued for 45 minutes. The precipitate is filtered on a 2\(\frac{1}{4}\)-inch Büchner funnel, and washed with hot water. It is well to fold the filter paper so as to cover the whole of the inside of the funnel.

To the filtrate 10 cc. more of the thiosulphate solution are added, and it is boiled for half an hour longer. The small precipitate thus obtained is filtered, set temporarily aside and designated as "Residue No. 1." The filtrate is discarded.

The paper containing the first large precipitate is put into the original 1500-cc. beaker and boiled over a low flame with 75 cc. of 6 normal hydrochloric acid. When the thorium precipitate has dissolved and the paper is pretty well disintegrated, usually about 5 minutes, without filtering off the filter paper and sulphur, the mixture is diluted to 700 cc., and neutralized with ammonia just as before, finally having an excess of 6 to 8 drops of conc. hydrochloric acid. It is then heated to boiling and 60 cc. of boiling 30 per cent sodium thiosulphate solution are added. After boiling 30 minutes the precipitate is filtered on a Büchner funnel as before and washed. This filtrate is reserved.

The paper and precipitate are dropped into the original beaker and all the operations described in the paragraph immediately preceding are repeated, the final filtrate, however, being this time discarded.

The paper containing the thorium precipitate is boiled with 40 cc. of 6 normal hydrochloric acid. When the paper is well disintegrated, it is filtered off, well washed, and this residue is designated as "Residue No. 2." The solution is temporarily set aside.

Residues Nos. 1 and 2 are combined, ignited in a porcelain crucible, and fused with sodium pyrosulphate. The fusion is extracted with dil. hydrochloric acid and this solution is added to the reserved filtrate from the second thiosulphate precipitation. Ammonia is now added in excess, the precipitate is filtered, and dissolved in hydrochloric acid. This solution is diluted to 300 cc. nearly neutralized with ammonia, leaving only a faint acidity, heated to boiling, and precipitated by the addition of 20 cc. of boiling 30 per cent sodium thiosulphate solution. After boiling 20 minutes, the precipitate is filtered on a small Büchner funnel, washed, and dissolved in 50 cc. of 6 normal hydrochloric acid. Without filtering, the solution is diluted to 300 cc., almost neutralized with ammonia, and the thiosulphate precipitation is repeated. The last precipitate is dissolved by boiling in a mixture of 5 cc. of conc. hydrochloric acid and 20 cc. of water, the sulphur is filtered off, and the chloride solution is combined with the solution obtained at the end of the preceding paragraph.

This solution now contains all the thorium from the original sample and it is ready for the Gravimetric Determination of thorium by precipitation as oxalate.
GRAVIMETRIC DETERMINATION OF THORIUM

Thorium is nearly always precipitated as oxalate and ignited to ThO₂, in which form it is weighed. The solubility of thorium oxalate in very dilute mineral acids is slight, especially in the presence of excess oxalic acid. It is well, however, not to have over 2 cc. of cone. mineral acid per 100 cc. of solution. More strongly acid solutions may be partially neutralized with ammonium hydroxide. Thorium oxalate does not filter readily if precipitated rapidly, or from a cold solution. The solution should be boiling hot and dilute (200–500 cc.); and should be precipitated by adding very slowly a boiling-hot solution of oxalic acid, which has been saturated in the cold; or by stirring in the oxalic acid added in solid form. Both methods insure a slow rate of precipitation, but the first method seems to be the better. The precipitate is allowed to stand not less than 10 or 12 hours before filtration, and it is washed with water containing a few drops of hydrochloric acid.

The thorium oxalate is ignited with the filter paper in a porcelain or platinum crucible over the blast to constant weight. If a platinum crucible is used, the full heat of a Meeker burner is sufficient. The ThO₂ finally weighed should be pure white in color. A yellow color shows cerium earths or iron and is an indication of faulty work.
TIN

Sn, at.wt. 118.7; sp.gr. 6.56; m.p. 232°; b.p. 2275°; oxides SnO₂ and SnO.

DETECTION

Tin is separated, together with arsenic, antimony, gold and platinum, from the hydrogen sulphide precipitate of the metals of the second group, by the action of yellow ammonium sulphide. (Normal ammonium sulphide does not readily dissolve the sulphides of tin.) If the ammonium sulphide solution is acidulated with hydrochloric acid and the acid solution reduced with iron, antimony, arsenic, platinum and gold are precipitated in the metallic form. The presence of tin, which is present as stannous chloride, is indicated by the reducing action of the solution on mercuric chloride, a white precipitate of HgCl₂ or a gray precipitate of Hg being thrown down.

Reduce the hydrochloric acid solution of the sample by means of a small piece of iron wire. Treat with an excess of cold potassium hydroxide. Filter if the solution is not clear. Add an ammoniacal solution of silver nitrate. (One part AgNO₃ : 16 parts NH₃OH.) A brown precipitate of metallic silver indicates the presence of tin. Antimony, arsenic, platinum and gold are precipitated by the iron, while all of the heavy metals remaining, except lead, tin, aluminum, chromium, and zinc, are removed by the treatment with potassium hydrate.

Welch and Weber¹ recommend the following method for detection of tin: Add 10 cc. concentrated hydrochloric acid to the superficially dried precipitated sulphides from the ammonium sulphide separation. Filter off arsenic which does not decompose. Dilute filtrate to 70 cc. volume. Saturate with H₂S. Heat to expel excess H₂S. Add 5 cc. of hydrogen peroxide and heat until precipitate is redissolved. Add 5 to 10 grams of oxalic acid and pass H₂S into the hot solution. Antimony separates as a red sulphide. Filter. Filtrate contains the tin. Reduce with test lead and add mercuric chloride. White or grayish precipitate indicates presence of tin.

ESTIMATION

The estimation of tin is required in connection with the analysis of tin ores, dross, ashes, dust, tin plate, alloys such as solder, canned foods, and general analysis.

Opening Up Tin Ores

As the oxides of tin are not readily soluble in acids the tin can be most easily removed by assay. Ores, slags, dross, and ashes are first subjected to the assay process. The button obtained is then analyzed either volumetrically or gravi-

Chapter contributed by Wilfred W. Scott and B. S. Clark.


525
metrically by one of the methods given below. Having the weight of the button and the per cent of tin in it, the per cent of tin in the sample as received can be calculated.

There are two general processes of assaying, namely, the Cyanide Process and the Carbonate of Soda Process.

The Cyanide Process

The theory of this method is that the oxides are reduced to the metal by the action of potassium cyanide, the reaction being represented as follows:

$$\text{SnO}_2 + 2\text{KCN} = \text{Sn} + 2\text{KCNO}.$$  

Potassium cyanide reduces other metals also so that the button obtained is not pure.

Procedure. Take 100 grams of the sample which has been dried and finely powdered. (For complete analysis the moisture should be determined in the usual way.) Mix thoroughly with four times its weight of powdered potassium cyanide. Place about 1 in. of potassium cyanide in the bottom of a number H (height 5½ in., diameter 3½ in.) Battersea clay crucible. Place the mixture of sample and cyanide on top of the cyanide in the crucible and cover with enough more cyanide to fill the crucible to within 1 in. of the top.

Place the crucible in the assay furnace and heat slowly until it has been thoroughly warmed and the cyanide begins to melt. Then increase the heat gradually to a pure white, taking care that the cyanide does not boil over. Grasp the crucible with the tongs and tap it gently on the hearth to assist in settling the metal. Continue the heating until all of the organic matter has disappeared, adding more cyanide from time to time if necessary. Near the end of the process the molten mass becomes clear and transparent and finally pasty and translucent. When this last condition appears, remove the crucible from the furnace and allow it to cool slowly at the temperature of the room.

When cool, break the crucible and slag away from the button. The appearance of the button and the slag immediately surrounding it indicates whether or not the process has been properly manipulated. The button itself should be firm and compact and the slag around it should be white or greenish in color. If the button is spongy or if the slag has a dirty black color, the assay should be discarded and a new determination made, using a fresh sample.

\[\text{Weight of Button } = \text{ per cent Metal in Sample}.\]

\[
\frac{\text{Weight of Metal} \times \text{per cent Sn}}{100} = \text{per cent Sn in the Sample}.\]

Note. This process should be carried on under a hood in a segregated room, and every precaution should be taken to avoid breathing the poisonous fumes of potassium cyanide.

1. Lunge advises that the cyanide should not be allowed to boil. He uses a small sample (10 grams). "Technical Methods of Chemical Analysis" 1, Part 1, p. 256. It is our experience that satisfactory results are not obtained unless the extreme heat of the furnace is used.

The Sodium Carbonate Method

The sample is fused with equal parts of sodium carbonate and sulphur. The fusion is then dissolved in water. The tin goes into solution as a thiostannate of sodium. Iron and copper are then separated by the addition of sodium sulphite, leaving arsenic, antimony and tin in solution.

Other Methods of Opening Tin Ores

Fusion with Sodium Hydrate. The sample of ore is fused with ten times its weight of sodium hydrate. The process is carried out in an iron crucible and then transferred to nickel. The fused mass is dissolved in water and the tin determined in the usual way.

Reduction by Means of Hydrogen. The ore may be reduced by strongly igniting in a porcelain tube in a current of hydrogen. The reduced metal is then dissolved in hydrochloric acid and the tin estimated by a standard method.

Fusion with Sodium Peroxide. J. Darroch and C. Meiklejohn opened ores, slags, etc., by fusing with sodium peroxide in a nickel crucible. They dissolve the fused mass in hot water and acidity with hydrochloric acid. The sample is then ready for the necessary separations.

SEPARATIONS

Tin is separated from iron, aluminum, chromium, etc., by the insolubility of its sulphide in dilute hydrochloric acid. Tin, together with antimony, arsenic, platinum and gold, is separated from lead, mercury, copper, cadmium and bismuth, by the solubility of its sulphide in yellow ammonium sulphide. Antimony, arsenic, platinum and gold are precipitated as metals from a hydrochloric acid solution by the action of metallic iron, leaving tin in solution.

A few special separations are of interest.

Tin and Lead. For the analysis of an alloy of lead and tin, it is usually preferable to make the estimations on different samples. In this case, lead is estimated by Thompson's method and the tin by Baker's modification of the iodine method. Lead can also be separated from tin by the method given below for the separation of tin and copper.

Tin and Copper. This alloy can be dissolved in concentrated hydrochloric acid by the addition of potassium chlorate. A large excess of ammonium tartrate is added and the solution made alkaline with ammonia. Copper is then precipitated as sulphide by the addition of hydrogen sulphide water until no more precipitate is formed.

1 Very finely divided carbon is sometimes preferred. Air must not be allowed to enter the crucible. Else decomposition is not complete. Mellor, "A Treatise on Chemical Analysis," 1913, p 270. If carbon is used instead of sulphur the process becomes one of reduction to the metal and is carried out in the assay furnace. The details of operation are similar to the cyanide process. The metal separates as a button in the bottom of the crucible. The button contains other metals with the tin and must be analysed further for exact percentages.

2 Mellor objects to the method as being tedious and dirty.


4 Engineering and Mining Journal, 81, 1177, 1906.
Tin and Antimony. Antimony is separated, in the metallic form, from the hydrochloric acid solution of the alloy, by the action of metallic iron placed in the solution. The tin may be determined by the iodine method without the removal of the antimony. If the antimony is desired, it may be filtered off and determined in the usual way.

As in the case of lead, it is usually quicker and more accurate to make these determinations on separate samples. The tin can be determined by the iodine method. The antimony can be determined volumetrically by various methods, preferably the bromate. (See chapter on Antimony.)

Tin and Phosphorus. One-half gram of the alloy is dissolved in 15 cc. of concentrated hydrochloric acid containing potassium chloride. This is diluted to 200 cc. with water and warmed. It is then treated for a long time with hydrogen sulphide gas. The tin is all precipitated as sulphide while the phosphorus remains in solution.

Tin and Iron and Aluminum. Tin is separated from iron and aluminum by precipitation, as sulphide, from the hydrochloric acid solution.

Iron may also be separated from tin with copper, and lead by precipitation as sulphide from the alkaline ammonium tartrate solution.

Tin and Tungstic Acid. Donath and Mullner 1 separate tin oxide from tungstic acid by mixing the sample with zinc dust and strongly igniting in a covered crucible for fifteen minutes—boiling with dilute hydrochloric acid; oxidizing with potassium chlorate to change the blue tungstic oxide to tungstic acid and diluting with water. It is then allowed to stand overnight and filtered. The tin is in solution.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF TIN

Determination of Tin or the Oxides of Tin by Hydrolysis

This method depends upon the precipitation of meta-stannic acid in the presence of ammonium nitrate when the stannic chloride is diluted to considerable volume and heated to boiling. It is especially applicable to the determination of tin oxide in tin paste, but may be extended to all chloride solutions of the higher oxides. The reaction involved proceeds as follows:

\[ \text{SnCl}_4 + 4\text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O} \]

\[ = \text{H}_2\text{SnO}_3 + 4\text{NH}_4\text{Cl} + 4\text{HNO}_3. \]

Stannous tin may be determined by oxidizing the chloride solution to the stannic form. The method gives concordant results and is rapid.

Procedure. For the analysis of tin paste take a catch weight of about 10 grams for a sample. Dissolve this sample by heating it in a No. 6 beaker with 300 cc. of concentrated hydrochloric acid. Transfer the acid solution to a 500-cc. volumetric flask and make up to the mark with dilute (1 : 1) hydrochloric acid.

2 Fresenius, "Quantitative Chemical Analysis," 1, 406, 1903. Sodium sulphate may be used instead of ammonium nitrate. In that case the reaction is

\[ \text{SnCl}_4 + 4\text{Na}_2\text{SO}_4 + 3\text{H}_2\text{O} = 2\text{H}_2\text{SnO}_3 + 4\text{NaCl} + 4\text{NaHSO}_4. \]
Take 50 cc. (approximately 1 gram) for a working sample. (If the determination is to be made on tin paste, the sample may be obtained directly by one of the methods described under Opening Tin Ores.) Dilute to 100 cc. with cold water. Nearly neutralize with strong ammonia and finish by adding drop by drop from a burette, dilute ammonia until a slight permanent precipitate is formed. A large amount of ammonia will tend to precipitate iron, if present, as a hydrate and to re-dissolve the meta-stannic acid.\(^1\) Add 50 cc. of a saturated solution of ammonium nitrate. Dilute to 400 cc. with boiling water, stirring constantly. Bring the solution to an incipient boil, remove from the flame and allow the beaker to stand on the steam bath until the precipitate has settled.\(^3\) The solution above the precipitate should be clear. Decant the supernatant liquor through a 12\(\frac{1}{2}\) cm. S. & S. 590 filter paper and wash the precipitate by decantation\(^4\) six times, using 200 cc. of boiling water and allowing the precipitate to settle thoroughly at each washing. Transfer the precipitate to the filter, "cop" out the beaker and wash down with hot water in the usual way. After the precipitate has been allowed to drain, transfer to a porcelain or a silica crucible and dry carefully on an asbestos board over a Bunsen flame.\(^4\) When dry, ignite at a low temperature until the filter paper has been consumed. Increase the heat and finally blast to constant weight.

\[
\frac{\text{Weight SnO}_2 \times 100 \times .7877}{\text{Weight of sample}} = \text{per cent Sn.}
\]

**Determination of Tin as Sulphide**

The determination of tin as a sulphide involves many difficulties and should be avoided if possible. Better results can be obtained by the volumetric methods and in most cases without the necessity of preliminary separations of interfering metals. If tin must be separated as a sulphide, better results would be obtained if the precipitate were dissolved and the tin content determined by the iodine method.

Having the hydrochloric acid solution of tin after the interfering metals have been separated, to precipitate tin sulphide, neutralize with ammonia and then acidify with acetic acid. Pass hydrogen sulphide until the solution is saturated. Allow the precipitate to settle overnight. Pour the supernatant liquor off through a Gooch crucible and wash the precipitate six times by decantation, using a solution of ammonium nitrate\(^6\) for wash water. Finally transfer to the crucible and wash free from chlorides. Dry the crucible in an oven at 100° C. Heat slowly in a Bunsen flame until all the sulphur has been expelled. Care should be taken at this point to avoid forming fumes of stannic sulphide by heating too rapidly.

---

\(^1\) Some practice is required to judge accurately the exact point when the necessary amount of ammonia has been added. The precipitate should appear white.

\(^3\) If the boiling continues more than a few seconds the precipitate will not settle properly. Time will be saved in this case if the sample is discarded and a new determination commenced.

\(^4\) If meta-stannic acid is washed over onto the filter at this point, clogging will result and a great deal of time will be lost.

\(^6\) Spattering is likely to occur here, causing loss.

\(^6\) Sulphide of tin separates as a slimy mass which tenaciously retains alkaline salts, especially in the absence of ammonium salts. Mellor, "Treatise on Chemical Analysis," p. 308, 1913.

\(^6\) Bichloride of tin, Acker process, page 425.
530

TIN

*Remove the lid of the crucible, which should be kept in place during the first portion of the heating, and raise the temperature gradually, finally finishing with the blast.* As sulphuric acid is usually present in some quantity, the crucible should be cooled and a small piece of ammonium carbonate should be placed in it. Repeat the ignition to drive out the acid. Cool and weigh as SnO₂.⁴

**BICHLOORIDE OF TIN**

Bichloride of tin is of great importance in some of the industries, especially the textile. It is necessary to have exact analytical control of the processes in which this compound is used in order to insure uniform results and to certify the efficiency and economy of the process. Several methods have been developed for this purpose. The ones given below have had practical application and have proven to be satisfactory.

**Stannic Acid Method.**—**Hot-water Precipitation.** In the textile industry where bichloride of tin is used, the efficiency of the process depends directly on the neutrality of the tin liquor. If there is more than enough chlorine present in the bichloride solution to exactly oxidize all the tin to the stannic form, the excess is called “free HCl.” If there is not enough chlorine present to do this, the deficiency is spoken of as “basic HCl.” The difficulty of determining the “free” or “basic” HCl is apparent when it is known that SnCl₂ readily decomposes in water, liberating free acid. The following method has been developed especially for this purpose and has given good results.

The important point in this analysis is to determine whether the liquor has “free” HCl present or whether it is “basic” in nature. It has been found that hot water precipitates tin from the SnCl₂ solution as stannic hydroxide and at the same time liberates the chlorine as free HCl.

\[
\text{SnCl}_2 + 4\text{H}_2\text{O} = \text{Sn(OH)}_4 + 4\text{HCl}. \tag{1}
\]

The Sn(OH)₄ separates in a colloidal precipitate which may be filtered off and the tin estimated as SnO₂. The liberated acid may be determined in the filtrate and from this data the “free” or “basic” HCl can be calculated.

**Procedure.** For accurate work about 20 grams of the liquor should be weighed out in a tared weighing bottle, but for works control, where time is an important factor, it is sufficiently accurate to get the specific gravity of the liquor by means of a hydrometer and take a measured quantity for a sample, calculating the weigh from these data.

Transfer the sample to a 100-cc. volumetric flask. Make up to volume with cold distilled water. Draw out of this solution 10 cc. (approximately 2 grams) and place in a 150-cc. tall beaker. Fill the beaker nearly full with boiling hot water, stirring continuously while the water is being poured in.⁵ Place the beaker on top of the steam bath and allow the precipitate to settle. Decant the liquor.

1 This method is generally used only when minute traces of tin are present, and then it is considered best to dissolve the sulphide in hydrochloric acid and make the final determination by the iodine method. (See analysis of Canned Foods for “Salt of Tin,” page 536.)
3 If the solution is not stirred at this point, the precipitate will not settle and trouble will be experienced during the filtering process.
through an 11 cm. 590 S. & S. filter and wash the precipitate six times by decantation, using hot water. Now transfer the precipitate to the filter and continue the washing until 1 drop of the filtrate gives no test for chlorine. After most of the water has drained out of the filter, place the paper and precipitate in a tared silica crucible. If there is plenty of time, dry the contents of the crucible on an asbestos board over a low Bunsen flame. In case the analysis must be made in a hurry, cover the crucible and heat it very carefully over a low flame until all the water has been driven out and the paper has been charred. Then remove the cover and increase the heat to the full Bunsen flame and finally blast to constant weight. Weigh as SnO₂. Titrate the filtrate with N/1 NaOH, using methyl orange as the indicator.

Calculation:

\[
\begin{align*}
SnO_2 \times 0.7877 &= Sn \\
Sn \times 2.1945 &= SnCl_4 \\
SnCl_4 - Sn &= Cl \text{ equiv. to } Sn \\
Cl \times 1.0282 &= HCl \text{ equiv. to } Sn
\end{align*}
\]

\[
\frac{HCl}{\text{Weight of sample}} = \text{per cent } HCl \text{ equiv. to } Sn
\]

\[
\frac{\text{cc. } N/1 \text{ NaOH} \times 0.03646}{\text{Weight of sample}} = \text{per cent } HCl \text{ (actual)}
\]

The difference between these last two figures equals "free" or "basic" HCl.

The Acker Process Method. The theory of this method is practically the same as that of the hot-water method, except that in this case the liberated acid is neutralized with ammonia before the stannic hydroxide has been filtered off, the advantage being that any solution of the stannic hydroxide, by either acid or alkali, is prevented. The method is not applicable for the determination of "free" or "basic" HCl.

Procedure. Weigh out 25 cc. of the bichloride of tin solution. Transfer to a 500-cc. flask (volumetric) and make up to volume with cold water. With a standardized pipette, transfer 25 cc. of this solution to a No. 4 beaker. Dilute with hot water to precipitate most of the tin as stannic hydrate. Add 10 drops of phenolacetonitrile (1 gram of phenolacetonitrile dissolved in 200 cc. of water). Titrate very carefully with dilute ammonia until the appearance of a rose-red color. Boil a few minutes on the hot plate. Allow the tin precipitate to settle. Decant through an 11-cm. filter paper (S. & S. 580, black ribbon brand). Wash rapidly with hot water without allowing the precipitate to cake down in the filter until the washings are free from chlorine. Dry the precipitate in an oven at 100°C. When dry, invert the filter into a tared porcelain crucible and heat on a gauze until the paper has disappeared. Remove the gauze and heat with the full

1 Time may be saved by using a platinum cone with the filter and applying a gentle vacuum. This can be done with very little danger of breaking the paper.
2 This precaution must be taken, else there will be a loss by decrепitation.
3 Kindness of W. F. Dorflinger, chief chemist of Perry-Austin Manufacturing Company.
4 Luteolin may be used as indicator, giving a yellow color at the end-point. It is slightly more delicate but much more expensive.
Bunsen flame for a few minutes. Finally blast to constant weight.\(^1\) Weigh as SnO\(_2\).

Take the filtrate and washings and dilute them to a volume of 1000 cc. Warm 500 cc. of this solution and saturate it with hydrogen sulphide. If any tin separates, filter and ignite in a tared porcelain crucible. Moisten with a little nitric acid and heat very slowly to drive out the acid. Ignite to constant weight. Weigh as SnO\(_2\). Add this result to the SnO\(_2\) obtained above when calculating the final result.

### Determination of Tin in Bichloride of Tin as Sulphide

This method is given as an alternative for the Acker Process Method and may be used as a check on that process. Uniform and concordant results have been obtained by the use of the two methods.\(^2\)

**Procedure.** Weigh out 25 cc. of bichloride and dilute to 500-cc. volume with cold distilled water. Take 25-cc. portions of this solution for analysis. Dilute the sample to 250 cc. Saturate with hydrogen sulphide. Warm the mixture on a hot plate at a temperature of about 65° C. until the precipitate is coagulated. Test the clear supernatant liquor for unprecipitated tin by adding a little hydrogen sulphide water. Filter on an ashless filter and wash free from chlorides. Make the filtrate and washings up to 1000 cc. volume for further determinations. Dry the tin sulphide precipitate on the filter in an oven at 100° C. Remove the precipitate from the paper as completely as possible. Ignite the paper in a weighed porcelain crucible. Cool and add a few drops of nitric acid. Repeat the ignition, heating very carefully at first until the acid has nearly all been driven out. Now place the main tin precipitate in the crucible. Cover, heat gently for a few minutes, moisten with fuming nitric acid, ignite very carefully for one-half hour and then blast for fifteen minutes. Weigh as SnO\(_2\).\(^3\)

### Volumetric Determination of Tin

Volumetric methods for the determination of tin are based upon the reducing power of stannous compounds. They vary according to the oxidizing agent used and the details of manipulation.

**Lenssen’s Iodine Method as Modified by Baker.**\(^4\) This method is a modification of Lenssen’s Iodine Method for the determination of tin in alkaline solutions. It is especially applicable to the determination of “salts of tin” in canned foods and to the estimation of tin coating on tin plate, but is accurate, rapid and very satisfactory for alloys and general analysis.

The method is based on the action of iodine in the presence of stannous chloride in hydrochloric acid solution. The reaction involved is:

\[
\text{SnCl}_2 + I_2 + 2\text{HCl} = \text{SnCl}_4 + 2\text{HI}.
\]

A. Jilek reduces tin by means of iron, filtering off precipitated Sb, Cu and excess of Fe, in an atmosphere of CO\(_2\). The reduced tin solution is now titrated with standard iodine.

\(^1\) If there has been any reduction, a few drops of nitric acid may be added and the ignition repeated, heating slowly at first to prevent loss by decrepitation.
Iron, lead and antimony do not interfere with the reaction. Copper in small quantities does not interfere with the determination, but if it is present in large quantities as a salt, it is likely to produce low results. Determinations made by the writer show that results are accurate when less than 10% of copper, as copper chloride, is present. Larger amounts gave consistently low results. The reason for this fact centers around the difficulty of reducing all the copper to the cuprous form. If any CuCl₂ is left in the solution, it reacts with the potassium iodide of the iodine solution, causing the precipitation of CuI and the liberation of free iodine.

\[ \text{CuCl}_2 + 2\text{KI} = \text{CuI} + 2\text{KCl} + \text{I}_2. \]

Copper present as the metal is not easily soluble or goes into solution in the reduced form and is not likely to disturb the determination.³

**Solutions—Standard Tin Solution.** Dissolve 5.79 grams of Kahlbaum’s C. P. tin in C. P. hydrochloric acid. The solution of the tin is effected by placing about 150 cc. HCl in an Erlenmeyer flask, together with the tin, and boiling. After the tin has all been dissolved, transfer to a volumetric liter flask and make up to the mark with dilute hydrochloric acid.

1 cc. = .00579 gram Sn.

**Standard Iodine Solution.** Dissolve 12.7 grams of C. P. iodine in a water solution of 20 grams of potassium iodide. Make up to one liter and standardize against the standard tin solution. For tin plate analysis, it is convenient to adjust the iodine solution so that 1 cc. equals exactly .00579 gram of tin. Then, if a sample of the plate having a total surface of 8 sq. ins. is taken, 1 cc. of the iodine solution is the equivalent of one-tenth of a pound per box.

**Indicator.** Dissolve 5 grams of pure soluble starch in 1 liter of water. Add 20 cc. HCl and allow the resulting gas to escape. Keep in a stoppered bottle.²

**Procedure.** For practical purposes, take a sample, such that the tin content will be between .2 gram and .5 gram. A larger sample should be taken for extreme accuracy in order to decrease the possible technical error. Place the sample in flask A of the Selars apparatus, Fig. 68, together with 100 cc. of conc. C. P. HCl. Stopper the flask and connect tubes B and D, as shown in the illustration. Boil until the metal is all dissolved. This point is indicated by the cessation of the hydrogen evolution and the appearance of large well-developed bubbles. If a sufficient amount of metallic iron is present in the sample, complete reduction is assured. If no iron was present in the sample, or if there was not enough to reduce all of the tin, make sure that the tin is all converted to the stannous form by adding aluminum foil (about 1 gram). Replace the stopper and connect as originally. Boil until normal bubbles reappear. Open cock C to allow CO₂ gas to enter. Place the flask in cooling bath F without disconnecting the apparatus. After the solution has become thoroughly

¹ Mr. B. S. Clark.
² Sulphates must not be present. They tend to have an oxidizing effect and spoil the results.
³ There should always be an excess of bicarbonate of soda present in order that carbon dioxide will be generated during the washing process, thus preventing air from entering the flask at any time during the analysis.
⁴ Carbon dioxide generated in a Kipp apparatus is likely to contain oxygen. It is much better to use liquid CO₂ such as can be purchased in the open market.
cool, disconnect tubes B and D from the splash bulbs. Wash the bulbs with "air free" water, allowing the washings to drain into the bulk of the sample. Remove the stopper and wash down the sides of the flask. About 50 cc. of water should be used in the washing so that the final sample contains about 25% HCl. Add 5 cc. starch solution and titrate with the standard iodine solution.

\[
\frac{\text{cc. iodine} \times \times 0.00579 \times 100}{\text{Weight of Sample}} = \text{per cent Sn},
\]

or

\[
\frac{\text{cc. iodine}}{10} = \text{pounds per "base box".}^2
\]

**The Sellars Apparatus.** This apparatus is a device designed by Mr. W. S. Sellars of this laboratory for the purpose of facilitating the solution of tin samples out of contact with air. Added to this advantage, it is equipped with a water cooler. It is also constructed so that the tubes and scrubbing bottles can be cleaned by flushing with water. The use of this apparatus practically eliminates the usual sources of error in connection with the iodine method, and at the same time greatly increases the speed of the determination. Fig. 67 shows the apparatus in operation.

A. 300-cc. Erlenmeyer flask.
B. Connection with reduced pressure line from liquid carbon dioxide cylinder.
C. Glass manifold.
D. Exit connection to trap.
E. Water trap to prevent escape of HCl fumes and to prevent air from backing into the flask.
F. Cooling tank.
G. Low-pressure water wash-out manifold.
H. Perforated feed pipe to water cooler.
K. Outlet for cooler.
L. Electric hot plate.
M. Lead drain pipe.

1 See Fig. 68, page 535.
2 "Basebox"—112 sheets of tin, 14×20 ins.
**Ferric Chloride Method.**¹ This method depends upon the reduction of ferric chloride by stannous chloride in hot solution.

\[ \text{SnCl}_2 + 2\text{FeCl}_3 = \text{SnCl}_4 + 2\text{FeCl}_2. \]

---

Antimony, copper, arsenic, bismuth, mercuric chloride, tungsten and titanium must be absent.\footnote{Lunge, \textit{"Technical Methods of Chemical Analysis,"} 2, Part I, p. 267.}

The Standard Solution of Ferric Chloride is made by dissolving pure iron wire in hydrochloric acid. To standardize this solution, dissolve 1 gram of pure tin in 200 cc. of C. P. HCl, preventing air from coming in contact with the solution by means of a trap, or by passing carbon dioxide over it.\footnote{The Sellars apparatus can be used with advantage for this purpose.} Titrate this standard sample with the ferric chloride solution. The end-point is indicated by the yellow color, due to a slight excess of the iron solution.

Procedure. Tin is first separated from the interfering metals in the usual way. If lead, copper, arsenic, antimony or bismuth are present, the sample is first reduced, in the hydrochloric solution, with iron wire. The solution is then filtered. Lead and tin remain in the filtrate. Neutralize by adding strips of zinc until the action ceases. Tin and lead are precipitated. The clear liquid should show no trace of tin with hydrogen sulphide. Allow the precipitate to settle and wash by decantation, keeping the precipitated metals in the flask. Add 150 cc. of concentrated hydrochloric acid, keeping the contents of the flask protected from the air, and bring to a boil. When everything is dissolved, titrate to a yellow color with the ferric chloride solution.\footnote{The end-point can be easily identified by looking at a blue Bunsen flame through the solution. When a small quantity of ferric chloride is present, the flame appears green. Melior, \textit{"A Treatise on Chemical Analysis,"} p. 310, 1913.} This part of the analysis should be done very quickly to prevent oxidation by the oxygen of the air.

\footnote{H. A. Baker, Eighth International Congress of Applied Chemistry.}
VOLUMETRIC METHOD FOR TIN IN ALLOYS

The titration of stannous solutions by iodine may be represented by the following reaction:

\[ \text{SnO} + 2\text{I} + \text{H}_2\text{O} = \text{SnO}_2 + 2\text{HI} \]

Sn is equivalent to O or to 2H, hence a normal solution contains one-half the molecular weight of Sn, or 59.35 grams per liter of solution.

**Apparatus.** This consists of a 300-cc. Erlenmeyer flask, with a one-hole stopper, through which passes a quarter-inch glass tube, connected with a rubber tube 12 to 15 inches in length, the other end of the rubber tubing is connected with 2–3 inches of glass tubing, which dips in the beaker containing a bicarbonate of sodium solution.

**Reagents.** 0.1N iodine solution. Standardize against a sodium arsenite (arsenious acid) solution. 1 cc. 0.1N I = 0.005935 g. of Sn.


**Procedure.** Decomposition of the Sample. Tin alloys generally decompose in hydrochloric acid, but more readily in strong, hot sulphuric acid.

A factor weight 0.5935 gram of the tin alloy is placed in a 300-cc. Erlenmeyer flask and 10 cc. of strong sulphuric acid added. The mixture is heated, preferably over a free flame, until the alloy completely disintegrates. Nearly all of the excess of free acid is expelled, keeping the flask in motion over the flame to lessen the tendency towards bumping, which is apt to occur during the concentration. The moist residue is allowed to cool.

100 cc. of (air-free) water are added followed by 50 cc. of strong hydrochloric acid and the mixture gently warmed until the solution begins to clear. The apparatus is now assembled as shown in the figure, about 15 cc. of 10% (saturated solution) sodium bicarbonate being placed in the test tube (or 50 cc. in the beaker, if this is preferred to a test tube).

About 1 gram of very finely powdered antimony metal is placed in the flask, followed by 10 cc. of saturated sodium bicarbonate solution, the stopper being removed during the addition and then immediately replaced. The air is displaced by the CO₂ generated.
The apparatus is now placed on a hot plate, or on an inverted sand-bath dish over a flame, and the solution is gently boiled for 10 to 15 minutes. The antimony should be of such fineness as to remain suspended during the ebullition of the liquid at this stage.

The test tube is now nearly filled with saturated sodium bicarbonate and the apparatus removed to a desk for a few minutes, and then placed in a cold water-bath of running water or under tap water, until the solution cools down to near room temperature. During this cooling carbonate will be sucked back into the flask “A” to establish pressure equilibrium, CO₂ being generated in the flask. Sufficient solution will remain in the test tube to act as a seal and prevent admission of air, which would spoil results by its oxidation of the tin.

The tube B and the test tube C are disconnected and 5 cc. of starch solution added by means of a pipette passing through the hole in the stopper (which should be loosened in the throat of the flask).

Standard iodine solution is now added, the tip of the burette passing through the hole of the stopper, agitating the solution by a “swirling” motion of the flask. The end-point is a blue color, which does not fade on stirring the solution.

If a factor weight has been taken, each cc. of the iodine of 0.1N strength is equivalent to 1 per cent of tin.

Notes. In the presence of copper a separation must be effected as over 3 per cent copper interferes in this volumetric method especially when the percentage of the tin is low. High copper alloys do not decompose readily in hydrochloric or sulphuric acids, but easily in dilute nitric acid. The solution obtained is evaporated to dryness, the residue is taken up with strong nitric acid, the oxide of tin (and antimony) remains insoluble, hot water is added and the solution filtered (hot) and the oxide washed once or twice with hot water. The tin (and antimony) is now best dissolved by digesting for 3–5 minutes with 50 cc. of water saturated with SO₂ (at 60–70° C.), then 10 cc. of strong HCl are added to the solution heated to boiling and the SO₂ expelled by boiling. The solution is now ready for reduction with antimony by the method outlined above.

Tin may be reduced by iron wire or nails, the precipitated Cu, Sb and the excess of Fe filtered off, under an atmosphere of CO₂, and tin titrated with iodine.

¹ Earnest Stelling, Ind. and Eng. Chem., 16, 346 (April, 1924).
ESTIMATION OF TIN IN CANNED FOOD PRODUCTS

The tin in the canned food products is obtained as a sulphide precipitate from wet combustion, with nitric and sulphuric acids, of 100 grams food product.

The clear sulphuric acid residue is diluted, neutralized with ammonia and then rendered about 2% acid with hydrochloric acid, after which it is thoroughly saturated with hydrogen sulphide gas. This precipitate is then filtered on a Gooch crucible with a false bottom. The precipitate may contain foreign substances, such as lime, phosphorus, and silica, some lead, or even small amounts of iron, but none of these will cause any trouble subsequently in the titration, so that the labor of separating the tin completely from the precipitate is obviated.

After washing the precipitate three or four times in a Gooch crucible, it is transferred to a small porcelain dish by simply forcing out the false bottom of the Gooch crucible and its asbestos pad and rinsing off the crucible.

The precipitate, mixed with asbestos, is now transferred to a 300-cc. Erlenmeyer flask and boiled with strong hydrochloric acid, potassium chlorate being added from time to time to insure the complete breaking up and solution of the tin sulphide, as well as the elimination of the sulphur. This is accomplished in a very few minutes. A few strips of pure aluminum foil, free from tin, are then added to the flask until all of the chlorine is eliminated. The flask is then attached to the Sillars apparatus and the determination completed, according to the details given under the Iodine Method, using N/100 iodine solution.

Gravimetric Method. The sample is first digested to a colorless or pale yellow solution as described under Baker's method.

Add 200 cc. water to the digested solution and pour into a 600-cc. beaker. Rinse out the Kjeldahl flask with three portions of boiling water so that the total volume of the solution is about 400 cc. Allow to cool and add 100 cc. concentrated ammonia. This amount of ammonia should render the solution nearly neutral, unless more than 50 cc. sulphuric acid have been used for digestion. The solution should be tested to see that it is still somewhat acid. In case of a large excess acid, add ammonia until just alkaline and then make about 2% acid with hydrochloric or sulphuric acid. Pass in a slow stream of hydrogen sulphide for an hour, having the covered beakers on an electric hot plate at about 95° temperature. Allow to digest on the hot plate for an hour or two.

Filter the tin sulphide on an 11-cm. filter. Wash with three portions of wash solution alternated with three portions of hot water. The wash solution is made up of 100 cc. saturated ammonium acetate, 50 cc. glacial acetic acid, and 850 cc. water. The filter papers used in this method are C. S. & S. No. 500, white ribbon.

Place the filter and precipitate in a 50-cc. beaker and digest with three successive portions of ammonium polysulphide, bringing to a boil each time and filtering through a 9-cm. filter. Wash with hot water. Acidify with acetic acid, digest on the hot plate for an hour and filter through a double 11-cm. filter. Wash with two portions of wash solution alternated with hot water and dry thoroughly in a weighed porcelain crucible. Thorough drying is essential to the success of the determination. Ignite very gently at first and later at full heat of Bunsen flame. Finally heat strongly with large burner, or Meker burner, having the crucible partly covered. Stannic sulphide must be gently roasting to the oxide, but the oxide may be heated strongly without loss, due to volatilization.

Weigh the stannic acid and convert to metallic tin by the factor .7877.

1 H. A. Baker, Eighth International Congress of Applied Chemistry.
TITANIUM

$\text{Ti, at. wt. } 47.9; \text{ sp. gr. } 4.5^1; \text{ m.p. } 1795^\circ\text{C. (±15°)}^1; \text{ oxides } \text{TiO}_2, \text{ Ti}_2\text{O}_3, \text{ TiO}_3, \text{ TiO}_4.$

DETECTION

The powdered ore is fused with potassium bisulphate, KHSO$_4$, until effervescence ceases. The cooled mass is dissolved in dilute sulphuric acid by boiling. *Hydrogen peroxide*, $\text{H}_2\text{O}_2$, added to this titanium solution, produces a yellow to orange color, according to the amount of titanium present. Hydrofluoric acid, or fluorides, destroys the color. Vanadium also produces this color with hydrogen peroxide, but the color is not destroyed by HF. The yellow color, according to Weller $^4$ is due to TiO$_3$ formed.

*Morphine* produces a crimson color with solutions of titanium in sulphuric acid.

*Zinc* added to hydrochloric acid solutions of titanium produces a blue color,$^5$ tin a fine violet solution.$^6$

If *sulphur dioxide*, $\text{SO}_2$, is passed into the solution of titanium to reduce the iron, and the slightly acid solution then boiled, yellowish white metatitanic acid, $\text{TiO(OH)}_2$, is precipitated.

**Bead Test on Charcoal.** A small portion of the powdered mineral heated on charcoal with microcosmic salt and tin produces a violet-colored bead if titanium is present.

OCCURRENCE

The element is widely distributed in minerals, soils, clays and titaniferous iron, FeTiO$_3$. It is found in granite, gneiss, mica, slate, syenitic rocks, granular limestone, dolomite, quartz, feldspars and a large number of other minerals. The principal commercial minerals are:

- Ilmenite, FeTiO$_3$, containing about 52.7% TiO$_2$.
- Rutile, TiO$_2$, containing 90 to 100% TiO$_2$.
- Titanite, CaTiSiO$_4$, containing 34 to 42% TiO$_2$.
- Perovskite, CaTiO$_3$, containing about 60% TiO$_2$ and 5 to 6% Y$_2$O$_3$.

*Titaniferous ores of variable titanate oxide content.*

APPLICATION

Titanic oxide is now extensively used as a white pigment for paint. For this purpose the titanium oxide is usually precipitated upon or coalesced with

---

$^1$ By Wilfred W. Scott and L. E. Barton.
$^2$ Hunter, Eighth Int. Congress Applied Chem., 2, 125.
$^3$ Burgess and Waltenburg, U. S. Bureau of Standards.
$^5$ Deville, C. N., 4, 241.
$^6$ Cahn and Wootton, *"The Mineralogy of the Rarer Metals."

538
TITANIUM

precipitated barium sulphate, making a product containing about 25% titanic oxide. The white titanium pigments are characterized by their exceptional hiding power, excelling in this respect any other commercial white pigments.

Another important application of titanium is the use of ferrotitanium in the iron and steel industry. The function of the titanium is to deoxidize the steel and consequently to yield a product free from blowholes and segregation of impurities. In a steel thus purified the natural strength and resistant properties of the material are developed in the highest degree.

Titanium has also found application in the textile and leather industries. In the dyeing of leather, titanium potassium oxalate has been found particularly well adapted. The use of titanous chloride and titanous sulphate for bleaching or discharging colors is increasing. Such bleaching agents are particularly applicable for silk and wool, which are injured by the action of those bleaching agents in which chlorine is the active element.

Titanium compounds are also used for electric light filaments, are carbons, ceramics, fine brown glazes, paint for iron and steel, etc.

ESTIMATION

Preparation and Solution of the Sample

A knowledge of the solubility of the element and its oxides is of value in the solution of the sample.

Element. This is feebly soluble in cold dilute hydrochloric or sulphuric acids; more readily so when the acids are heated. It is soluble in cold, concentrated hydrochloric acid; readily soluble in hot, concentrated hydrochloric or sulphuric acids. It is scarcely acted upon by nitric acid, but readily dissolves in hydrofluoric acid. It is soluble by fusion with the alkalies.

Oxides. TiO₂, which has a black or blue color, is soluble in concentrated hydrochloric or sulphuric acids; forming, in the latter case, a violet-colored solution. The oxide is insoluble in water and in ammonium hydroxide.

TiO₂ is difficultly soluble in concentrated sulphuric acid, less soluble if strongly ignited. The metatitanic acid, TiO(OH)₂, requires strong hydrochloric or sulphuric acid to effect solution; the orthotitanic acid, Ti(OH)₄, however, is readily soluble in hot or cold, dilute or concentrated acids. From titanie solutions orthotitanic acid is precipitated by ammonia, the precipitation being assisted by warming. Boiling a slightly acid solution precipitates the metatitanic acid, TiO(OH)₂. TiO₂ is soluble upon fusing with alkalies. TiO₂ is soluble in hydrofluoric acid, forming TiF₄, which is volatile, unless an excess of sulphuric acid is present (distinction from silica). The ignited oxide is best dissolved by fusion with KHSO₄ and heating the fused mass with dilute sulphuric acid solution.

Salts. Many titanic salts are decomposed in the presence of water, precipitating titanic acid, the extent of the decomposition depending on the quantity of water used. Titanic sulphate is readily soluble in water and the solution is remarkably stable unless largely diluted with water. Some of the double salts are readily soluble and their solutions stable, i.e., potassium titanium oxalate.

¹ Ebeln, A. Ch. (3), 20, 392, 1847.
Solution of Steel. The sample may be dissolved in hydrochloric acid (1:2). If a residue remains, it is treated with a mixture of equal parts of hydrofluoric and sulphuric acids and a few drops of nitric acid, in a platinum dish, and the mixture evaporated to sulphuric anhydride fumes and to complete expulsion of hydrofluoric acid. The colorimetric procedure is now used for estimating titanium. For determination of titanium in hydrochloric acid solution see page 545.

Note. Titanium in steel treated with ferro carbon-titanium exists in two conditions: (1) Titanium soluble in hydrochloric acid. (2) Titanium insoluble in hydrochloric acid. Of the very small amount of titanium in treated steel the greater part will usually be found in the second form. When the amount of titanium in the steel is exceedingly small, the soluble titanium frequently exceeds the insoluble, and it is then occasionally desirable to determine also that existing in the second form.

Alloys. These are dissolved in concentrated nitric acid, aqua regia or a mixture of the dilute acids. Should nitric acid be used, the excess is expelled by evaporation to dryness with hydrochloric acid. The metals of the hydrogen sulphide group are removed in an acid solution by precipitation with H₂S, and titanium determined colorimetrically in the filtrate.

Ores. One to 5 grams of the ore are treated with 10 to 50 cc. of a mixture of sulphuric and hydrofluoric acids (1 to 5), a few drops HNO₃ added, and the solution evaporated to fumes to expel HF. If a residue remains upon taking up with water containing a little sulphuric acid, it is filtered off and fused with KHSO₄ as directed under the fusion method.

Fusion Method for Ores. The finely powdered sample is fused with four to five times its weight of potassium bisulphate, KHSO₄, and the cooled fusion dissolved with dilute sulphuric or hydrochloric acid. In the presence of silica potassium fluoride is added to assist in the decomposition of the material.

(See Analysis of Titaniferous Ores, page 551.)

Titaniferous Slags. One-half gram of the finely ground sample is decomposed in a platinum dish by a mixture of 5 cc. water, 5 cc. concentrated sulphuric acid, 2 cc. nitric acid, and 10 cc. of hydrofluoric acid, the reagents being added in the order named. The solution is evaporated rapidly to SO₃ fumes to expel fluorides and the excess sulphuric acid until residue is left nearly dry. After cooling it is taken up with 40 cc. of dilute hydrochloric acid (1:3), which will give a clear solution containing all the constituents of the slag except silica, which has been volatilized as SiF₄. The solution is diluted to 200 cc. with cold water. Iron and titanium are precipitated by ammonia in slight excess and filtered at once without boiling. The precipitate is dissolved in cold dilute hydrochloric acid and reprecipitated with ammonia. Titanium is now separated from iron by reducing iron with SO₂ and precipitating titanium from a boiling acid solution as described on page 542.
SEPARATIONS

Details of the isolation of titanium are given in the methods for its estimation.

Separation of Titanium from the Alkaline Earths, etc. The hydroxide is precipitated when a titanium solution containing ammonium chloride is treated with ammonium sulphide, whereas barium, strontium, calcium and magnesium remain in solution. Titanium hydroxide may be precipitated by making the solution containing titanium slightly ammoniacal with $\text{HNO}_3\cdot\text{OH}$.

Separation from Copper, Zinc, Aluminum Iron, etc. Titanium is precipitated from a slightly acid solution by boiling, passing sulphur dioxide through the solution to keep the iron reduced and prevent its precipitation.

Separation from the Bivalent Metals, Manganese, Nickel, Cobalt, Zinc. Titanium is precipitated along with aluminum and iron by hydrolysis of its acetate in a hot, dilute solution, whereas manganese, nickel, cobalt and zinc remain in solution. Details of the basic acetate method are given on page 298.

Separation of Titanium from Aluminum. Small amounts of titanium from large amounts of aluminum. (One part Ti to 50 parts Al.) Cupferron, $\text{Ca}_2\text{H}_6\text{(NO)}\cdot\text{N} \cdot\text{ONH}_4$, added to a decidedly acid solution containing titanium and aluminum precipitates titanium, but not aluminum. The precipitate is washed by decantation and then on the filter with very dilute hydrochloric acid to remove traces of aluminum. The procedure affords a separation of titanium from chromium, nickel, cobalt, manganese, etc. Copper and iron, however, precipitate with the titanium, if present in the solution. The yellow titanium salt has the composition $(\text{CaH}_6\text{(NO)}\cdot\text{NO})\cdot\text{Ti}$.

Separation of Titanium from Iron. See Gravimetric Method for Determination of Titanium, Modified Gooch Method, below.

\[1\] Acidity exactly 0.5% is best according to Levy, C. N., 56, 209.
\[2\] Analyst, 36, 520, 1912, method of J. Bellucci and L. Grassi.
GRAVIMETRIC METHODS

Gravimetric Determination of Titanium. Modified Gooch Method

This method is applicable to minerals and metallurgical products that are comparatively high in titanium. The method provides for the separation of titanium from iron and from aluminum and phosphoric acid with which it commonly occurs. The procedure as proposed by F. A. Gooch and modified for non-aluminous rocks by Wm. M. Thornton has been found by the author to give reliable results. The details of the method with a few slight changes found to be advantageous are given below. Iron is separated from titanium by precipitation as a sulphide in presence of tartaric acid, the organic acid is destroyed by oxidation and titanium precipitated from a boiling acetic acid solution. In the presence of alumina and phosphoric acid the impure precipitate is fused with Na₂CO₃ and the impurities leached out with boiling water. In presence of zirconium, titanic acid is incompletely precipitated. Hillebrand's modification for the removal of zirconium is given in the notes.

Procedure. Preparation of the Sample. Ores High in Silica. These may be decomposed by taking to SO₂ fumes with a mixture of 10 to 15 cc. of 50% hydrofluoric acid, HF, and 3 to 4 cc. of concentrated sulphuric acid per gram of sample.

Oxides. Decomposed by fusion with sodium or potassium bisulphate. The fusion is dissolved in 10% sulphuric acid, keeping the volume as small as possible. The sample should contain not over 0.2 gram titanium.

Precipitation of Iron. To the solution containing titanium, tartaric acid, equal to three times the weight of the oxides to be held in solution, is added. This should not exceed 1 gram of the organic acid, as the subsequent removal of larger amounts would be troublesome. H₂S is passed into the solution to reduce the iron and NH₄OH added to slight alkalinity followed by a further treatment with H₂S to completely precipitate FeS. The solution should be faintly alkaline (litmus) otherwise more ammonia should be added. After filtration and washing of the ferrous sulphide with very dilute and colorless ammonium sulphide, the titanium is entirely in the iron-free filtrate.

Oxidation of Tartaric Acid. Since titanium cannot be precipitated by any reagent in the presence of tartaric acid, the organic acid is oxidized by addition of 15 to 20 cc. of concentrated sulphuric acid to the sample placed in a 500-cc. Kjeldahl flask. The solution is evaporated to incipient charring of the tartaric acid. After cooling slightly, about 10 cc. of fuming nitric acid are added cautiously, a few drops at a time, and when the violent reaction has subsided the flask is heated gradually (hood), a vigorous reaction taking place accompanied by much effervescence and foaming with evolution of copious brown fumes. The organic matter gradually disappears, the effervescence becomes steady and finally ceases and white fumes of SO₃ are given off. The solution is cooled and the pale yellow syrup poured into 100 cc. of cold water, the flask washed out, adding the rinsing to the main solution. If cloudy, the solution is filtered.

² W. W. Scott.
³ Cupferron precipitates titanium in presence of tartaric acid.
Precipitation. Ammonia is added until the solution is nearly neutral, a point where the solution is slightly turbid, the precipitate dissolving upon vigorous stirring. If a trace of iron is suspected about 1 cc. of 10% ammonium bisulphate is added. Five cc. of glacial acetic acid followed by 15 grams of ammonium acetate or its equivalent in solution is added and the volume of the solution made up to about 350 cc. The solution is brought rapidly to boiling and maintained in ebullition for about three minutes. The titanium will precipitate in white flocculent and readily filterable condition. The precipitate is washed first with water containing acetic acid and finally with pure water. The filter and the precipitate are ignited cautiously over a low flame and finally blasted over a Meker blast for twenty minutes. The residue is weighed as TiO₂.

In the presence of large amounts of alumina and phosphoric acid, the residue above obtained is fused with sodium carbonate in a platinum dish and the fusion leached by boiling with pure water. Alumina and phosphoric acid go into solution as soluble sodium salts and titanium oxide remains insoluble in the residue.

Ignited insoluble residue = TiO₂.

Note. Titanium may be separated from aluminum by fusing the residue with potassium acid sulphate, K₂H₂O₄, and precipitation of titanium in an acid solution by eupferron. Al₂O₃ is in solution.

Determination of Titanium in Ferro Carbon Titanium.
Gravimetric Method

Into a 6-in. porcelain evaporating dish, weigh 0.6 gram (factor weight) of alloy.
Dissolve in a mixture of 15 cc. of dilute sulphuric acid (one acid to one water), 5 cc. of nitric acid, and 10 cc. of hydrochloric acid. Evaporate to fumes of sulphuric anhydride.
Cool and take up by boiling with 50 to 60 cc. of water and 5 to 10 cc. hydrochloric acid. Filter into a 500-cc. beaker and wash the residue with hot water and dilute hydrochloric acid.
In the filtrate precipitate iron and titanium by ammonia in slight excess. Filter without boiling and wash precipitate twice on filter with hot water.
Reject filtrate. Dissolve the precipitate in a very little dilute hydrochloric acid, washing the filter with hot water and collecting the solution and washings in the original beaker.
 Nearly neutralize the solution with ammonia or ammonium carbonate; dilute to 300 cc.; saturate with sulphur dioxide gas, and boil until titanic acid is precipitated and the solution smells faintly of sulphur dioxide.
Filter and wash with hot water and dilute sulphurous acid.
Dry, ignite, and weigh as titanic oxide.
Since the factor weight of sample has been used, one milligram of titanic oxide is equal to 0.1% metallic titanium.

¹ Methods of analysis used in the laboratories of the Titanium Alloy Manufacturing Company.
TITANIUM

VOLUMETRIC METHODS

The Determination of Titanium by Reduction, Addition of Ferric Salt and Titration of Reduced Iron with Potassium Permanganate

Principle. Titanic acid is reduced by means of zinc, an excess of ferric sulphate is added and the ferrous salt, formed by reduction by titanous salt, is titrated with standard permanganate. The method is more accurate than direct titration of the titanous salt with permanganate.

Reaction. \[ \text{Ti}_2(\text{SO}_4)_3 + \text{Fe}_2(\text{SO}_4)_3 = 2\text{Ti}(\text{SO}_4)_2 + 2\text{FeSO}_4 \]

or \[ \text{TiCl}_3 + \text{FeCl}_3 = \text{TiCl}_4 + \text{FeCl}_2 \]

Preparation of the Sample

Procedure. One to 2 grams of the ore is decomposed by hydrofluoric and sulphuric acids or by fusion with potassium bisulphate or a combination of the two according to the methods already described. Members of the \( \text{H}_2\text{S} \) group, if present, may be removed by \( \text{H}_2\text{S} \). If iron is present it may be determined by boiling off the \( \text{H}_2\text{S} \) in the filtrate containing \( \text{Fe} \), \( \text{Ti} \), etc., and allowance made in the titration for titanium. If other interfering elements are present in this filtrate, titanous acid may be precipitated by boiling the slightly acid solution (sulphurous acid) according to directions given in the gravimetric method. The washed oxide is dissolved in strong \( \text{H}_2\text{SO}_4 \) and diluted as directed below.

Reduction. The solution is washed into a 100-cc. flask and diluted with water so that it will contain 10% of sulphuric acid. This acid holds titanous acid in solution and at the same time is insufficient to oxidize the reduced titanium oxide. Sufficient zinc to cause complete reduction is added and a rubber stopper carrying a Bunsen valve tube and a thistle tube with glass stop-cock is inserted in the neck of the flask. The evolved hydrogen expels the air and reduces the titanous oxide to the titanous form. Iron if present is also reduced. Gentle heat is applied until the excess of zinc dissolves. The solution is cooled and an excess of ferric sulphate added through the thistle tube, followed immediately by cold distilled water until the flask is filled to the neck. The contents of the flask is poured into a No. 6 beaker containing 150 to 200 cc. of cold distilled water and the ferrous iron, formed by the reducing action of titanous salt, is titrated with \( \text{N}/10 \text{KMnO}_4 \) solution.

\[ \text{One cc. N}/10 \text{KMnO}_4 = 0.00481 \text{ gram Ti} \quad \text{or} \quad 0.00801 \text{ gram TiO}_2 \]

---


The Determination of Titanium by Reduction with Zinc and Titration with Permanganate

In a contribution from the U. S. Bureau of Standards, the authors have reported a study of this method, the results of which indicate that:

The reduction of titanium in a Jones reductor proceeds rapidly and is quantitative, provided the reduced solution is caught under a 3–5-fold excess of ferric sulphate.

The reduction is conveniently carried on in solutions containing 3–5% by volume of sulphuric acid and may be done at any temperature between 25° and 100°.

The determination is carried out as follows:

Using a Jones reductor of 19 mm. internal diameter, with zinc column 43 cm. in length, there is added in order 25–50 cc. dilute sulphuric acid, 3 to 5% by volume; 150 cc. of the titanium solution containing 3 to 5% by volume of sulphuric acid; 100 cc. more of acid and finally 100 cc. of water.

The reduction is performed at a speed of about 100 cc. per minute.

The reduced solution is delivered through a tube from the reductor under and into a ferric sulphate solution containing about 0.02 g. of iron per cc. in 8% by volume sulphuric acid. The ferric sulphate solution should be from 3 to 5 times that theoretically required by the titanium. The reduced solution is titrated with tenth normal potassium permanganate.

The original article suggests means for separating tin, arsenic, antimony, molybdenum, iron, chromium, vanadium, tungsten and uranium, which would interfere with determination of titanium by the method described.

Volumetric Method by Reduction of Titanium and Titration with a Ferric Salt

The following volumetric method recommended by the Titanium Alloy Mfg. Co., is essentially that described by P. W. & E. B. Shimer, Proceedings of Eighth International Congress of Applied Chemistry, the method hereafter described differing principally in the form of reductor and also in a few details of operation.

Reagents. Standard ferric ammonium sulphate solution.

Dissolve 30 grams of ferric ammonium sulphate in 300 cc. water acidified with 10 cc. of sulphuric acid; add potassium permanganate drop by drop as long as the pink color disappears, to oxidize any ferrous to ferric iron; finally dilute the solution to 1 liter.

Standardize this solution in terms of iron. The iron value multiplied by 1.4329 gives the value in titanic oxide (TiO₂); and the iron value multiplied by 0.86046 gives the value of the solution in terms of metallic titanium.

Indicator. Saturated solution of potassium thiocyanate.

Reducer. As a reductor a 500-cc. dispensing burette is used. The internal dimensions of the burette are 1½ by 22 ins.

The reductor is charged with 1200 grams of 20-mesh amalgamated zinc, making a column about 12 ins. high and having an interstice volume of about 135 cc. This form of reductor is convenient, and when used as hereafter described

TITANIUM

is adapted to maintaining hot solutions, which facilitates complete reduction of the titanium.

The reductor is connected to a liter flask for receiving the reduced titanium solution, through a three-hole rubber stopper which carries also an inlet tube for carbon dioxide supply, and outlet tube for connecting with the suction pump.

Procedure. Determination of Titanium in Ferro-Carbon Titanium. One-half gram of sample is dissolved in a 6-in. porcelain evaporating dish in a mixture of 10 cc. water, 10 cc. sulphuric acid, 5 cc. of hydrochloric acid, 5 cc. of nitric acid.

The solution is evaporated to fumes of sulphuric anhydride; taken up by boiling with 50 cc. water and 10 cc. of hydrochloric acid; filtered and washed with hot water and hydrochloric acid.

The filtrate and washings should be about 100 cc. in volume.

The reductor is prepared for use by first passing through it a little hot dilute sulphuric acid followed by hot water, finally leaving sufficient hot water in the reductor to fill to the upper level of the zine.

The hot titanic solution prepared as described above is now introduced, about 100 cc. of water being drawn from the reductor into the original beaker to bring the solution to about the upper level of the zine. The water thus removed will not contain any titanium if the operation has been conducted as described; but it serves as a safeguard and is also convenient to acidify this water with 10 cc. of sulphuric and reserve it on the hot plate to be used as an acid wash after the reduction of the sample solution.

The titanium solution is allowed to remain in the reductor for ten minutes.

While the solution is being reduced the receiving flask is connected to the reductor and the air completely displaced by carbon dioxide, conveniently drawn from a cylinder of the liquefied gas.

When the reduction is complete the receiving flask is connected with the suction pump, and while still continuing the flow of carbon dioxide the reduced solution is drawn out, followed by the reserved acid wash and then three or four 100-cc. washes with hot water. The displacement of the sample solution and washing of the zine is so regulated by means of the stop-cock that the reductor is always filled with solution or water to the upper level of the zine.

When the washing is complete, gradually release the suction to prevent air being drawn back into the receiving flask.

Disconnect the flask, add 5 cc. of potassium thiocyanate solution as indicator and titrate immediately with standard ferric ammonium sulphate solution, adding the solution rapidly until a brownish color is produced which will remain for at least one minute.

The method is also well adapted for determining titanium in other titanium products, suitable means being employed for bringing the titanium into sulphuric acid solution.

The brown color developed at the end point indicates that an excess of ferric ammonium sulphate has been added and the depth of color is roughly proportional to such excess. Ordinarily the excess ferric ammonium sulphate amounts to about .05 cc. which is deducted from the burette reading before calculating the titanium, thus increasing the accuracy of the result. It is desirable for each operator to establish for himself, by running a few blanks, the proper amount to deduct from the burette reading as a correction.
Colorimetric Determination of Titanium with Hydrogen Peroxide

Preliminary Considerations. Hydrogen peroxide added to acid solutions of titanium produces a yellow to orange color, the depth of the color depending upon the amount of titanium present. Upon this fact the method is based. It is of especial value in determining small amounts of titanium, as it is possible to detect less than one part of the metal per hundred thousand parts of solution. Color comparisons can best be made on samples containing 0.05 to 5 milligrams of the element; larger amounts produce too deep a color for accurate comparison.

The following interferences should be made note of, e.g., molybdenum, vanadium and chromium also produce a color that would lead to error. Iron if present to the extent of 4% or over produces a color that must be allowed for; e.g., 0.1 gram FeO in 100 cc. of solution is equivalent to about 0.2 gm. of TiO₂ oxidized by H₂O₂ in 100 cc. of solution. Fluorides destroy the color, hence must be absent.¹ Phosphoric acid and alkali sulfates have a slight fading action,² hence must be allowed for by adding equivalent amounts to the standard if they are present in the sample. The addition of an excess of sulphuric acid partly counteracts the action of phosphates or alkali sulfates.³ The color intensity is increased by increase of temperature, hence the standard and the sample

DIRECTIONS FOR THE USE OF A DUBOSCO TYPE OF COLORIMETER

The mirror is turned so that the two halves of the field appear to be equally illuminated with the cups clean and empty. The solutions are then poured into the cups. The cup containing the standard solution is then lowered to a definite thickness of the standard solution between the bottom of the cup and the end of the plunger. With this movement the half of the field corresponding to the standard solution is seen to darken, while the other half remains luminous and colorless. If the cup containing the unknown solution is now moved in its turn, the two halves of the field are brought to the same intensity, after which the height at which the two liquid columns display this equal absorptive power is read by means of this scale. The proportion of coloring matter in two solutions is inversely proportional to the heights of the two columns necessary to obtain the same intensity of illumination, thus if the standard tube is set at 10 mm., and the solution under examination is the same intensity of color at 20 mm., the latter is just one-half the concentration of the standard. This is usually expressed by the formula:

\[
\text{Color of test solution} = \text{Color of stand. sol.} \times \frac{\text{Height of stand. sol.}}{\text{Height of sol. to be tested}}.
\]

If, therefore, the scale reading is 20 mm. for the standard, and 15 mm. for the solution to be tested, the formula reads: \( \frac{20}{15} = 1.33 \).

If, for example, the standard solution contains 4 ml. of coloring matter in 100 ml., the solution under test will be found to contain \( 4 \times 1.33 = 5.32 \) ml. in 100 ml.

¹ W. F. Hillebrand, J. A. C. S., 17, 718, 1895. C. N., 72, 158, 1895.
² P. Faber, Zeit. an. Chemie, 46, 277, 1907.
examined should have the same temperature. Since metatitanic acid produces no color with hydrogen peroxide, its formation must be prevented; the presence of 5% of free H₂SO₄ accomplishes this.

The procedure is very satisfactory for magnetic or other iron ores. It is fully as accurate as the best gravimetric method and very much more rapid.

**Solutions Required. Standard Titanium Solution.** This may be prepared by precipitations of TiO₂ from K₂TiF₄ according to the gravimetric procedure and purification by solution and reprecipitation, the fluorine being first removed by taking the compound to fumes with H₂SO₄ and then hydrolyzing titanium with NH₄OH. The washed precipitate is ignited over a Meker flame for fifteen minutes, cooled in a desiccator and placed in tightly stoppered bottle, since TiO₂ is slightly hygroscopic.

0.5 gram of TiO₂ is fused with about twenty times its weight of K₂H₂SO₄ in a platinum dish, keeping at fusion heat until the oxide has dissolved. A high temperature is not advisable. The fusion is dissolved in 5% sulphuric acid by gently heating. The solution washed into a 500-cc. graduated flask is made up to volume with 5% H₂SO₄. One cc. contains 0.001 gram TiO₂, or 0.0006 gram Ti.

**Hydrogen Peroxide.** Thirty per cent solution. If this is not available sodium peroxide dissolved in dilute sulphuric acid will do.

**Apparatus.** Colorimeter—Fig. 69. Also see Fig. 43, page 283.

**Preparation of the Sample.** The solution of the sample having been obtained by one of the procedures given under Preparation and Solution of the Sample, the element may be determined according to the procedure given below. If interfering substances are present, e.g., comparatively large amounts of iron, or if tungsten, vanadium or chromium are present it will be necessary to precipitate titanic acid by adding ammonium hydroxide to the boiling solution as directed under the gravimetric determination of the element. The washed precipitate is dissolved in sulphuric acid.

**Procedure.** The sulphuric acid solution of titanium should contain 5% of free sulphuric acid. It is poured from the beaker in which solution was effected into a 100-cc. Nessler tube, 2 cc. of hydrogen peroxide, 30% solution are added and the volume made up to 100 cc. with 5% sulphuric acid. The standard is prepared by pouring 40 or 50 cc. of 5% sulphuric acid into a second 100-cc. Nessler tube, adding 2 cc. of 30% hydrogen peroxide, H₂O₂, followed by sufficient

---

1 Hillebrand.
2 Dunnington, C. N., 64, 302; J. A. C. S., 12, 210, 1891.
standard titanium solution to exactly match the sample and the solution made
up to 100 cc. with 5% sulphuric acid. The titanium solution is added from a
burette, noting the exact volume required. From this the percentage of titanium
in the sample can readily be calculated. If iron is present in the sample, an equiva-
lent amount should be added to the standard. If a colorimeter is used, a
standard should be prepared which is deeper in color than the sample examined.
The standard is poured into the comparison cylinder and the two tubes compared.
By raising or lowering the plunger (see illustration) the standard solution is
forced in or drawn out of the comparison tube. When the colors match, the
cce. in the comparison tube will indicate the amount of TiO₂ present in the sample.
The solution may be mixed by stirring with a platinum spiral.

Example. One-gram sample required 20 cc. of titanium standard solution,
1 cc. of which contained 0.001 gram TiO₂. Then the sample contains

\[
\frac{0.001 \times 20 \times 100}{1} = 2\% \text{ TiO}_2.
\]

If the colorimeter has been used and 150 cc. of standard made by adding
30 cc. of standard titanium solution and it is found that the column of liquor
in the standard comparison tube stands at 85 cc., the calculation would be as
follows: 150 cc. contains 30 \times 0.001 gram TiO₂, therefore 85 cc. are equivalent
to \[
\frac{85 \times 0.03}{150} = 0.017 \text{ gram TiO}_2 \text{ per gram or } 1.7\%.
\]

For the practical application of the colorimetric method in determining
Titanium in steel the following procedure is given.

Note. Separation of Titanium from Iron. J. H. Walton, Jr.¹ separates titanium
from iron by fusing the finely powdered substance with three or four times as much
sodium peroxide, and extracts the fusion with water. The filtrate contains the sodium
peritanate whereas the iron oxide remains on the filter paper. The filtrate is acidified
with H₂SO₄ until 5% of free acid is obtained and the color of this solution compared
with a standard obtained by fusing a known weight of TiO₂ with Na₂O₂ and extracting
and treating with H₂SO₄ as in case of the sample.

Colorimetric Determination of Titanium in Steel Treated with
Ferro-carbon Titanium²

The titanium in steel treated with ferro-carbon titanium exists in two con-
ditions:

1. Titanium insoluble in hydrochloric acid.
2. Titanium soluble in hydrochloric acid.

Of the very small amount of titanium in treated steel the greater part will
usually be found in the first form, and ordinarily the determination of titanium
in this form answers every purpose of identifying and judging the quality of
titanium-treated steel.

When the amount of titanium in the steel is exceedingly small, the soluble
titanium frequently exceeds the insoluble and it then is sometimes desirable to
determine also that existing in the second form.

² By L. E. Barton. Method of analysis recommended by the Titanium Alloy
Manufacturing Company.
Reagents. Peroxide Solution. Dissolve 4 grams of sodium peroxide in 125 cc. dilute sulphuric acid (1 of acid to 3 of water), and dilute to 500 cc.

Concentrated Standard Titanium Solution. Stock Solution. One-fourth gram of a standard 20% carbonless ferro-titanium is dissolved in 30 cc. dilute sulphuric acid (1 acid to 3 water). When solution is complete it is oxidized by the least possible quantity of concentrated nitric acid, boiled for a few minutes, cooled and diluted to such a volume that 1 cc. will contain 0.0005 gram of titanium.

When using a 5-gram sample 1 cc. is therefore equal to 0.01% titanium.

Dilute Standard Titanium Solution. This solution is made, just before making the determination, by diluting one volume of the concentrated standard titanium solution to ten volumes.

One cc. of this solution contains 0.00005 gram of titanium and is equal to 0.001% of titanium when using a 5-gram sample.

Apparatus. Pipettes and Burettes. The pipettes for measuring the concentrated standard solution and burette for delivering the dilute standard solution should be carefully calibrated.

Nessler Jars. These should be graduated with 50-cc. mark. It is convenient to have a set of four.

Colorimeter. The colorimeter or comparator consists of a rectangular block 2¾ by 4 by 7 ins. high—the height being about ¾ in. less than the height of Nessler jars—through which two chambers 1½ ins. diameter and 1½ ins. between centers are bored lengthwise—the chambers being of such diameter as to just receive the jars.

To one end of the block is fastened the base, which is ¼ in. thick and through which two ½-in. holes are bored concentric with the chambers, thus forming a shoulder which supports the jars and also exclude light from the sides of the tubes. To prevent shadows and give better lighting the holes in the base are beveled outward at an angle of 45°. The construction will be apparent by reference to Fig. 70. The interior of the chamber is painted dead black.

(a) For Determination of Titanium Insoluble in Hydrochloric Acid

Procedure. Dissolve 5 grams of steel in 100 cc. of dilute hydrochloric acid (one of concentrated acid to two of water) by boiling gently. Wash off the cover and wash down the sides of the beaker with water and filter out the slight insoluble residue, washing with hot water and dilute hydrochloric acid until free from iron. For filtration it is advisable to use either a close-grained paper or double rapid-filtering papers such as S. & S. No. 589 white ribbon.

Ignite the residue gently in a platinum crucible to burn off carbonaceous matter. Treat the residue in the crucible with a mixture of 3 cc. dilute sulphuric acid (1 : 1), 2 or 3 cc. hydrofluoric acid, and a few drops of nitric acid.

1 Ferro-titanium suitable for the preparation of standard titanium solutions is made and supplied by the Titanium Alloy Manufacturing Company, Niagara Falls, N. Y.
Heat and evaporate to fumes of sulphuric anhydride to complete expulsion of hydrofluoric acid.

Cool, add a few cc. of water and heat until the solution is perfectly clear. The ignited residue may also be rapidly and completely brought into solution by fusion with about 3 grams of potassium bisulphate and dissolving the fusion in water and sulphuric acid.

In either case wash the contents of the crucible into one of a pair of Nessler jars and dilute with cold water nearly to the 50-cc. mark, and in the other jar place an equal volume of distilled water.

Place the jars in the colorimeter and observe if the sample solution is colorless. If the sample solution is colored slightly yellow by iron, the water in the standard tube should be brought to the same color by addition of a few drops of a ferric solution. For this purpose a solution of ferric ammonium sulphate, 30 grams per liter, is very convenient.

If the work up to this point has been carefully performed, the addition of ferric solution will usually be unnecessary; and if more than a few drops of ferric solution are required the analysis should be rejected and a new sample started. After adjusting the color—if necessary—bring the volume of solution in both jars to the 50-cc. mark.

The volumes now being equal and the solutions practically colorless, add 2 cc. of the peroxide solution to each. If the sample contains titanium even in minute quantity it will be indicated by the immediate development of a yellow color.

Match the colors by running into the standard jar freshly prepared dilute standard titanium solution, keeping the volumes equal by adding an equal quantity of water to the sample, placing the jars in the colorimeter for comparison of colors.

As before stated, each cc. of the dilute standard solution is equal to 0.001% titanium when using a 5-gram sample.

The determination may be made in less than an hour and requires little attention.

(b) For Determination of Titanium Soluble in Hydrochloric Acid

For the determination of soluble titanium the filtrate from the insoluble titanium residue obtained as before described may conveniently be used.

Dilute the solution in which the iron is already in the ferrous state to 180 cc. Add 10 cc. of alum solution made by dissolving 40 grams of crystallized alum in a liter of water.

The aluminum here added is subsequently precipitated as alumina with the titanium and serves to collect quickly the exceedingly small precipitate of titanium hydroxide and facilitate its separation from the solution by filtration.

Heat the solution to about 90° C. and add ammonia or ammonium carbonate solution, stirring constantly until a slight permanent precipitate is produced. Add dilute hydrochloric acid (1 to 1) drop by drop from the wash bottle until the precipitate is just redissolved and the solution perfectly clear; then add 1 cc. more of the dilute hydrochloric acid.

Add 3 cc. of phenylhydrazine dissolved in 10 cc. hot water, which will precipitate the titanium and aluminum. Stir thoroughly and filter immediately
on a 7-cm. filter paper in a Büchner funnel, using suction. Wash thoroughly
with hot water.

Calcine the precipitate gently in a platinum crucible to destroy organic
matter and dissolve the residue exactly as described under (a), except that 6 cc.
of dilute sulphuric acid is used instead of 3 cc.

The solution, which has a very light yellow, or greenish-yellow color, is trans-
ferred to one of a pair of Nessler jars and diluted to the 50-cc. mark. About 40
cc. of water are placed in the other jar and the color of the sample solution exactly
matched by addition of ferric ammonium sulphate and copper sulphate solutions,
which are conveniently delivered from burettes.

For matching the original color of the solution nearly saturated solutions
of ferric ammonium sulphate and copper sulphate are suitable.

Only a few drops of such solutions are required, but it is frequently neces-
sary to use both blue and yellow to match the greenish-yellow tone of the sample
solution.

The standard is finally diluted to the 50-cc. mark. The volumes now being
equal and identical in color, add to each 2 cc. peroxide solution to develop the
titanium color and finish the determination as before described under (a).

(c) For Determination of Total Titanium

The total titanium is given by the sum of the insoluble and soluble titanium
determined as under (a) and (b); but if desired may be determined in one
operation.

To determine total titanium, dissolve as before in hydrochloric acid and
without filtering proceed as directed under (b) for determination of soluble
titanium.

Determination of Titanium when Interfering Elements
are Present

If chromium, vanadium or molybdenum is present in the steel, fuse the
residue insoluble in hydrochloric acid or the calcined phenylhydrazine pre-
cipitate containing the interfering element with a mixture of sodium carbonate
and a little sodium nitrate.

Dissolve the fusion in water and filter. The residue on the filter will contain
the titanium, free from interfering element. Bring the residue into sulphuric
acid solution by methods before described and determine the titanium as usual.

Colorimetric Determination of Titanium with Thymol

Principal and Preliminary Considerations. Titanium dioxide dissolved
in sulphuric acid is colored red by addition of thymol, the depth of color being
directly proportional to the amount of titanium present. The intensity of the
color is claimed by Lenher and Crawford to be twenty-five times that produced
by hydrogen peroxide with the same amount of titanium.

As in case of hydrogen peroxide, fluorides destroy the color, hence must be
absent. Dilution with water has no effect until the concentration of sulphuric
acid falls below 79.4 (e.g., sp.gr. 1.725). The color then fades in direct propor-

tion to dilution. Warm solutions are lighter in color than cold solutions with the same amount of titanium, hence the standard and the sample compared must have the same temperature. The color fades on heating but returns on cooling. The temperature should be kept below 100° C. Chlorides, phosphates and tin seem to have no effect. Tungsten, WO₂, interferes, as it intensifies the color of the solution in direct proportion to the amount present; hence it must be removed or allowance made by adding an equivalent amount to the standard or subtracting the equivalent blank.

Special Reagents. Thymol Solution 1%. The thymol is dissolved in a little glacial acetic acid containing 10% ethyl alcohol, and this solution added to concentrated sulphuric acid. Addition of the thymol directly to the acid would produce a colored solution. The reagent should be kept protected from strong light, otherwise it will become colored.

Apparatus. See Colorimetric Determination of Titanium with Hydrogen Peroxide, Figs. 69, 70, also Fig. 43.

Procedure. About 0.3 gram of the material is fused with potassium acid sulphate, KHSO₄, and the melt dissolved in concentrated sulphuric acid. Enough thymol reagent is added so that there is present at least 0.0006 gram thymol for every 0.0001 gram TiO₂. Concentrated sulphuric acid is added to bring up the volume to 50 or 100 cc, in a Nessler tube exactly as in the case of the colorimetric determination of titanium with H₂O₂. The depth of color is compared with a standard solution of titanium dissolved in a concentrated sulphuric acid added to 5 cc. of thymol solution made up to a convenient volume with concentrated sulphuric acid. The procedure is the same as described in the H₂O₂ method.

THE ANALYSIS OF TITANIFEROUS ORES

Determination of Titanium

Decompose the ore by fusion with potassium bisulphate, dissolving the fusion in water, hydrochloric and sulphuric acids. If an insoluble residue remains, filter it out. Calcine the residue, add a few drops of sulphuric acid and sufficient hydrofluoric acid to dissolve silica, evaporate to fumes of sulphuric anhydride and then heat to redness.

If a residue now remains, bring it into solution directly in acids or fuse with a little potassium bisulphate, etc., finally adding the solution to the main solution obtained as before described.

If desired, the sample of ore can first be partially dissolved in hydrochloric and sulphuric acids, and the insoluble residue then fused with potassium bisulphate or treated with sulphuric and hydrofluoric acids.

Some ores may be completely decomposed by a mixture of nitric, hydrofluoric and sulphuric acids, evaporating to fumes of sulphuric anhydride in a platinum dish to free the solution from nitric and hydrofluoric acids.

The complete decomposition of the sample having been accomplished, the titanium in the solution is determined by either the gravimetric or volumetric methods for Determination of Titanium in Ferro-Carbon Titanium. Pages 542 and 547.

1 Method of Analysis used in the laboratories of The Titanium Alloy Manufacturing Company.
Determination of Iron in Presence of Titanium

The sample is decomposed as directed under the Determination of Titanium. The sulphuric acid solution, which should have a volume of 150 to 200 cc., is saturated with hydrogen sulphide gas to reduce the iron, and filtered to separate any precipitated sulphides and free sulphur. The filtrate is collected in a flask fitted with a rubber stopper through which pass two glass tubes, one reaching nearly to the bottom for conducting gas into the solution, the other a short exit tube. Unless the solution after filtration is still highly charged with hydrogen sulphide, more gas should be passed into the solution to reduce any iron that may have been oxidized by the atmosphere during filtration. The excess hydrogen sulphide is now expelled by boiling the solution while passing a current of carbon dioxide.

When the exit gases cease to darken a piece of filter paper moistened with lead acetate solution, the flask is cooled while still passing the carbon dioxide. When the flask has partially cooled the carbon dioxide is shut off and the flask quickly cooled in running water and immediately titrated with standard permanganate solution.

Determination of Silica

This determination is conveniently combined with the determination of iron the ore being preferably decomposed by fusion with potassium bisulphate. The fusion is dissolved and evaporated with excess sulphuric acid to fumes of sulphuric anhydride and the silica determination finished as usual—weighing, volatilizing with hydrofluoric acid, etc. If the ore contains quartz or a silicate unde-composable by treatment with potassium bisulphate and hydrofluoric acid, the residue filtered from the sulphuric acid solution should be fused with sodium carbonate and the silica then determined as usual.

Determination of Alumina

After making determination or separation of titanium by gravimetric method use the filtrate for determination of alumina.

Phenylhydrazine Method for Determination of Aluminum in Presence of Iron

The iron and aluminum should be in hydrochloric or sulphuric acid solution. Nearly neutralize the solution with ammonium carbonate. Pass sulphurous acid gas to complete reduction of the iron. Boil until the excess sulphurous acid is driven off and if titanic acid separates filter it out.

After filtering out titanic acid again nearly neutralize with ammonium carbonate, pass a little sulphurous acid gas and heat for a few minutes to reduce any iron that might have been oxidized during filtration. If titanium has not been detected the second treatment with sulphurous acid may be omitted. In either case the solution still containing a little free sulphurous acid is nearly neutralized with ammonium carbonate, diluted to 300 cc. and 3 cc. of phenolhydrazine added. Stir thoroughly, let settle and filter out the alumina. If the precipitate is discolored by iron, dissolve in hydrochloric acid, and repeat the reduction, neutralization and precipitation by phenylhydrazine. Ignite and
TITANIUM

weigh $\text{Al}_2\text{O}_3+\text{P}_2\text{O}_5$. Since the alumina precipitate may be contaminated by phosphoric anhydride ($\text{P}_2\text{O}_5$), determine it by analysis and correct the alumina determination accordingly.

**Determination of Phosphorus**

Phosphoric acid may be separated from titanite acid by repeatedly fusing the ore with alkali carbonate and extraction of alkali phosphate with water.

The determinations of other constituents of the ore are conducted by the usual methods of ore analysis.

**ANALYSIS OF MIXED PIGMENTS CONTAINING TITANIC OXIDE**

Weigh one gram sample into a 400-cc. Pyrex glass beaker, add 10 grams sodium sulphate and 40 cc. concentrated sulphuric acid (93%). Heat on hot plate for one-half hour and then increase the heat, as by placing the beaker directly over the coils of an electric hot plate and boiling for about 10 minutes. The solution should acquire a temperature of about 335° C.

Cool, dilute the solution to 300 cc., boil 20 minutes, filter while hot and wash residue and precipitate with 5% sulphuric acid. On the filter will be silica and undecomposed silicates and all the lead and barium as sulphates. This residue and precipitates can be analyzed by well-known methods if desired. The filtrate will contain the titanium, iron, aluminum, zinc and calcium.

To the filtrate while still hot add an excess of ammonia, filter and wash precipitate with hot water. Re-dissolve precipitate in hydrochloric acid (1 to 1) and again precipitate with ammonia. Filter and wash with hot water, combining filtrate with that from first separation. By this procedure the titanium, iron and aluminum will have been separated from the zinc and calcium. The use of an excess of ammonia as described would tend to carry a little aluminum into solution but in the presence of titanium and iron substantially all the aluminum will be found in the precipitate. If desired, the filtrate can be tested for presence of aluminum and then used for determination of calcium and zinc.

The precipitate of titanium, iron and aluminum hydroxide is again re-dissolved in dilute hydrochloric acid and the titanium separated and determined as before described and with all precautions given under the head of "Gravimetric Method for the Determination of Titanic Oxide."

The filtrate after separation of the titanium can be used for determination of iron and aluminum if desired.

In case it is not desired to determine iron and aluminum separately, the hydroxides obtained after second separation by ammonia can be calcined and weighed as total oxides of titanium, iron and aluminum. The titanium can be determined by the volumetric method before given and deducted from total oxides thus giving the iron and aluminum together by difference.