ALUMINUM

Al, at.wt. 26.96; sp.gr. 2.583; m.p. 658.7°; b.p. 2200°; oxide Al₂O₃.

DETECTION

General Procedure. The sample is prepared by one of the procedures outlined under "Preparation and Solution of the Sample." Silica is removed by taking the solution to dryness, boiling the residue with hydrochloric acid and filtering. The members of the hydrogen sulphide group are removed as usual with H₂S, the filtrate boiled to expel the excess of H₂S, iron oxidized with nitric acid, and aluminum, iron and chromium precipitated as hydroxides by addition of ammonium hydroxide in presence of ammonium chloride. On treating the precipitate with sodium peroxide, aluminum and chromium hydroxides dissolve, whereas ferric hydroxide remains insoluble. Aluminum hydroxide is precipitated by acidifying the alkaline solution with hydrochloric or nitric acid, and neutralizing with ammonia; chromium remains in solution.

Cobalt Nitrate Test. The white gelatinous precipitate of aluminum hydroxide may be confirmed by adding a drop of cobalt nitrate solution and burning the filter. The residue will be colored blue by the resulting aluminum cobalt compound.

Sodium Thiosulphate Test. Na₂S₂O₃, added to a neutral or slightly acid solution, containing aluminum, precipitates aluminum hydroxide, upon boiling the solution. Sodium sulphite, or ammonium chloride added in large excess, will also cause this precipitation.

Alizarin S Test. The reagent used is a 0.1% filtered solution of commercial alizarin S, the sodium salt of alizarin monosulphonic acid (yellow with acids, purple with alkalies).

To 5 cc. of the neutral or acid solution under examination is added 1 cc. of the reagent, and then ammonia until the solution is alkaline, as shown by the purple color. The solution is boiled for a few moments, allowed to cool, and then acidified with dilute acetic acid, when red coloration or precipitate remaining is conclusive evidence of the presence of aluminum. The red calcium, strontium, barium, zinc and magnesium salts, and salts of other metals later than Group II are readily soluble in cold dilute acetic acid, and do not interfere with the coloration.

Phosphates or chromium do not interfere and comparatively large amounts of iron may be present (0.003 milligram Al in presence of 1 milligram ferric iron, 10 milligrams chromium salt). In presence of greater quantities of iron citric acid is added to keep this in solution. One part of aluminum may be detected in 10 million parts of water.

1 Also spelled Aluminium.

By W. W. Scott and H. V. Churchill.
ALUMINUM

ESTIMATION

The determination of aluminum, in terms of alumina, Al₂O₃, is required in the estimation of aluminum ores, bauxite, Al₂O₃(OH); diaspore, AlO(OH); alunite, K₂O.3Al₂O₃.4SiO₂.6H₂O, etc. It is determined in the analysis of feldspar, halloysite, clays, granite, gneiss, porphyry, mica schist, slate, obsidian or pumice stone, cryolite, limestone, and in the complete analysis of a large number of mineral substances. The estimation of alumina is required in the analysis of cements, plaster, ceramic materials, aluminum salts, and is especially important in the control of processes in the manufacture of aluminum products. As a metal it is determined in commercial aluminum, and its alloys.

Preparation and Solution of the Sample

In dissolving substances containing aluminum it will be recalled that alumina, although ordinarily soluble in acids, is very difficult to dissolve when it is highly heated. It may be best dissolved, in this case, by fusion with sodium carbonate or with acid potassium sulphate, followed by an acid extraction. The metal is scarcely acted upon by nitric acid, but is readily soluble in the halogen acids and in hot concentrated sulphuric acids.

General Procedure for Ores. One gram of the finely powdered ore, taken from a representative sample, is placed in a platinum dish, 5 cc. of concentrated sulphuric acid are added, followed by about 20 cc. of strong hydrofluoric acid. The mixture is evaporated over a steam bath as far as possible and then taken to SO₂ fumes on the hot plate. Upon cooling, a little dilute hydrochloric acid is added and the mixture warmed. The solution is diluted with distilled water and filtered if any residue remains.

The insoluble residue remaining on the filter may be brought into solution by fusing the ignited residue with sodium carbonate or acid potassium sulphate. If barium is present sodium carbonate fusion is made and the melt extracted with water to remove the sodium sulphate. The residual carbonates may now be dissolved with hydrochloric acid.

Sulphide Ores should be oxidized with nitric acid and bromine according to the general procedure for decomposing pyrites in the determination of sulphur.

The solution of the sample having been effected, aluminum is separated from elements that interfere in its estimation. Directions for the removal of these substances are given under "Separations." The element is now in solution in such form that it may be determined gravimetrically or volumetrically.

Fusion Method. Sodium Carbonate. The air-dried material, ground to a fine powder, is placed in a glass-stoppered bottle. If the determination is to be made on the dry basis, moisture is driven out by placing the material in the hot air or steam oven for an hour (100° to 110° C.). One gram sample, placed in a large platinum crucible, is mixed with 4 to 5 grams of anhydrous sodium carbonate and the material heated to fusion, the heating being continued until the molten mass appears clear. The liquid mass may be poured on a large platinum crucible lid, or if preferred, allowed to cool in the crucible, a platinum prod being held in the fusion until it solidifies. By gently heating the crucible over a flame the fusion loosens from the sides and may be lifted out on the prod. In either case the cooled mass is dissolved by placing it, together with the crucible in which the
fusion was made in a casserole, and treating with hydrochloric acid, the casserole being covered with a clock glass during the reaction.

Silica is removed by evaporating the solution to dryness on the water or steam bath and drying in the oven at 110° C. for an hour or more. The residue is extracted with hot dilute hydrochloric acid and silica filtered off.

If the solution is cloudy upon treatment of the fusion with acid, it indicates either the presence of barium sulphate or incomplete decomposition of the sample. In the latter case the residue is gritty and the fusion of this material should be repeated.

Solution of Metallic Aluminum and its Alloys. The metal may be dissolved in dilute hydrochloric acid, 1:1, or in a solution of sodium hydroxide or potassium hydroxide.

Alloys of aluminum are best brought into solution with a mixture of hydrochloric and nitric acids.

SEPARATIONS

General Considerations. In the usual course of analysis, aluminum is in solution as a sulphate or as a chloride, silica having been removed by dehydration, as described under "Preparation and Solution of the Sample." The following interfering elements may be present in the solution: iron, manganese, arsenic, antimony, titanium, phosphoric acid, and more rarely chromium and zirconium. In alloys of aluminum other elements may be added to this list. The separation more commonly required is from iron, aluminum and iron being precipitated together as the hydroxides. In usual practice the two are weighed together as Fe₂O₃ and Al₂O₃, after ignition to this form, and iron then determined, either on a separate portion of the sample, or by solution of the precipitate by fusion with sodium carbonate or potassium bisulphate and subsequent extraction with hydrochloric acid.

Removal of Silica. This compound has already been considered under "Preparation and Solution of the Sample," SiO₂ being removed by taking the solution to dryness, dehydrating the oxide by additional heating in the oven, followed by extraction of the soluble constituents with dilute hydrochloric acid and filtration. Under the first procedure for solution of the ore by sulphuric and hydrofluoric acids silica is expelled as gaseous SiF₄.

Separation from Iron. 1. Aluminum hydroxide is precipitated by the addition of a salt of a weak acid to the neutral or slightly acid aluminum solution; iron remains in solution. Details of the procedure for precipitation of aluminum hydroxide by means of sodium thiosulphate are given under "Gravimetric Methods for Determination of Aluminum," page 9.

2. Aluminum chloride is precipitated from a concentrated solution of hydrochloric acid and ether saturated with HCl gas. Details of the procedure are given under the gravimetric methods for aluminum, page 10.

Note. The following additional procedures for separation of iron and alumina have been suggested:

(a) Precipitation of iron as FeS in presence of organic acids, citric, tartaric, salicylic, etc., aluminum remaining in solution.

(b) Precipitating iron by adding sodium peroxide to a cold neutral solution of the elements until the precipitate first formed dissolves, then decomposing the sodium ferrate by boiling, Fe(OH)₃ precipitates, Al remaining in solution. (Glaser, J. S. C. I., 1897, 936.)
Phosphoric Acid. In presence of phosphoric acid, the phosphates of iron and alumina together with the phosphates of the other elements of the group and those of the alkaline earths will be precipitated upon making the solution alkaline with ammonia. Should iron and alumina be the only elements of these two groups present in the solution, they may be precipitated together as phosphates, iron determined by titration and calculated to the phosphate salt, and alumina obtained by difference. Occasionally, however, it is necessary to remove phosphoric acid.

Removal of Phosphoric Acid. The material is fused with about six times its weight of a mixture of 4 parts Na₂CO₃ and 1 part SiO₂ (silex), and the melt extracted with water containing ammonium carbonate. Iron and aluminum remain on the filter, upon filtration, while sodium phosphate passes into solution. Both the precipitate and filtrate contain silica. The precipitate of iron and alumina is dissolved in hydrochloric acid and taken to dryness, the residue dehydrated as usual, then treated with dilute hydrochloric acid and silica filtered off. The solution contains iron and alumina in form of chlorides.

Separation of Aluminum from Chromium. The solution is made strongly alkaline with sodium or potassium hydroxides and chromium oxidized by passing in chlorine gas or by adding bromine. The solution is now acidified with nitric acid and aluminum hydroxide precipitated by addition of ammonium hydroxide, chromium remaining in solution as a chromate.

Separation of Aluminum from Manganese, Cobalt, Nickel, Zinc, the Alkaline Earths, and Alkalies. Iron and aluminum are precipitated as basic acetates, the other elements passing into solution. Details of the procedure are given under the basic acetate method on page 298.

In absence of phosphates, these elements do not interfere in the determination of aluminum by precipitation as the hydroxide.

Separation of Aluminum from Titanium. Details of the procedure are given under "Titanium."

Separation of Aluminum from Uranium. Aluminum is precipitated as Al(OH)₃ in presence of a large amount of ammonium salts by addition of a large excess of ammonium carbonate and ammonium sulphide, while uranium remains in solution as the complex compound UO₂(CO₃)₃(NH₄)₄.

Separation from Glucinium. Aluminum is soluble in the fixed alkalies and remains in solution on boiling; glucinium also dissolves, but is precipitated on boiling. Glucinium is soluble in an excess of ammonium carbonate, aluminum is not.

For additional separations see chapter on element in question.
ALUMINUM

GRAVIMETRIC METHODS FOR THE DETERMINATION
OF ALUMINUM

There are two general procedures for the gravimetric determination of aluminum. *A.* Direct determination, when it is possible to precipitate the hydroxide or phosphate of the element, free from impurities. *B.* Indirect determination when the element is precipitated and weighed along with iron, the latter then determined by titration and aluminum estimated by difference.

**Determination by Hydrolysis of an Aluminum Salt with Ammonium Hydroxide**

**Principle.** The method depends upon the hydrolysis of a soluble salt of aluminum by neutralizing the free and combined acid with ammonia. This hydrolysis takes place in presence of ammonium chloride, which prevents the precipitation of magnesium hydroxide by NH₄OH, the common ion, NH₄⁺, repressing the ionization of the base, NH₃·H₂O. (See Notes.) The direct determination of aluminum by this procedure excludes the presence of elements undergoing hydrolysis with similar conditions. Iron, chromium, titanium, zirconium, thallium, cerium interfere. In their presence a separation must be made.

**Reaction.** \[ \text{AlCl}_3 + 3\text{NH}_4\text{OH} = \text{Al(OH)}_3 + 3\text{NH}_4\text{Cl} \]

If phosphoric acid is present in the solution aluminum will be precipitated as the phosphate, \( \text{AlPO}_4 \).

**Procedure.** To the solution, containing aluminum, free from phosphoric acid and the elements precipitated by ammonium hydroxide, are added 10 cc. of ammonium chloride (10%) and 5 cc. of concentrated nitric acid. The solution is diluted to about 150 cc. and heated to boiling. Upon cooling slightly, carbonate-free ammonium hydroxide is added slowly from a burette until a slight permanent precipitate forms, and then drop by drop until the solution reacts alkaline to litmus paper and the odor of ammonia is faintly perceptible. The precipitate is allowed to settle on the water bath for a few minutes, then filtered hot and washed first several times by decantation and finally on the filter with a hot solution of ammonium nitrate. (Twenty cc. strong nitric acid diluted and neutralized with ammonium hydroxide and made to 1000 cc.)

The precipitate is purified, if other members of the ammonium sulphide group and following groups are present, as the gelatinous precipitate is apt to occlude some of these. This is accomplished by dissolving the precipitate in a small amount of hot, dilute hydrochloric acid, 1 : 1, the solution being caught in the beaker in which the first precipitation was made. The precipitation of the hydroxide is repeated exactly as is stated above. The precipitate, washed free of chlorides (AgNO₃ test), is drained of water and placed together with the filter paper in a platinum crucible.

The ignition of the precipitate is conducted slowly at first until the paper is thoroughly charred, the heat is now increased to the full power of the Meker blast, the crucible being covered to prevent mechanical loss. Blasting for thirty minutes is generally sufficient to dehydrate the oxide, \( \text{Al}_2\text{O}_3 \). It is advisable, however, to repeat the heating until the weight becomes constant. The residue is weighed as \( \text{Al}_2\text{O}_3 \).

\[ \text{Al}_2\text{O}_3 \times 0.5303 = \text{Al} \]
ALUMINUM

Notes. Ammonia should be free from carbonates. Upon long standing with frequent exposure to air the ammonia takes up CO₂, forming carbonate of ammonia. Freshly distilled ammonia will be pure, the carbonate being precipitated by addition of lime in the distilling flask. Ammonia is best kept in a ceresine or paraffine bottle. It will then remain free from silica, which it invariably contains when confined in glass bottles.

Long heating of the mixture containing the aluminum precipitate is objectionable. 1. The solution is apt to become acid owing to the decomposition of ammonium salts and the volatilization of ammonia.

2. The precipitate will become slurry and will be difficult to wash and filter. It is preferable to redissolve and again precipitate if this condition occurs.

3. The CO₂ of the air is apt to be absorbed by the solution, causing the precipitation of calcium carbonate, etc., should the solution be exposed for any length of time.

4. Silica from the beaker will contaminate the precipitate. Hence it is advisable to filter as soon as possible after making the precipitation of Al(OH)₃.

S. and S. N0. 589, black hand filter paper filters well and may be used to advantage with precipitates of the nature of aluminum hydroxide. B. and A. No. B. filter is also good.

Washing the precipitate with ammonium nitrate prevents the aluminum from passing through the filter and keeps it from puckering. It favors the formation of the insoluble hydrogel form of the hydrate while preventing the formation of the soluble hydrosol. Ammonium chloride may be used in place of nitrate. 1

Aluminum hydroxide is soluble in acids and alkalies. The ignited oxide, Al₂O₃, is insoluble in acetic acid but is soluble in mineral acids and the fixed alkalies. It is rendered very slightly soluble in acids by strong ignition, generally requiring fusion with sodium carbonate or potassium bisulphate with subsequent acid treatment to effect solution.

Al₂O₃, m. w., 102.2; s. p. gr., 3.73 to 3.99; m. p., 2020° C.

A yellow or reddish precipitate indicates the presence of iron, an element from which the solution is free of aluminum. Should this be the case, iron must be determined, either in a separate portion of the sample, or in the residue obtained by the procedure outlined. The amount of Fe₂O₃ is subtracted from the total residue, and Al₂O₃ obtained by difference.

If phosphoric acid is present, the phosphate of alumina will precipitate together with the phosphates of elements insoluble in alkaline solutions. Should phosphoric acid be present either its removal is essential, or the phosphate method for alumina should be followed.

Fluorides hinder the precipitation of aluminum. 2 Evaporation to dryness and heating the residue to redness will transform fluorides to oxides and overcome this difficulty.

Sulphates tends to hold up aluminum from precipitation and a certain amount of sulphuric acid is occluded by the aluminum hydroxide precipitate. Magnesium is more apt to precipitate with alumina in prescence of sulphates. 3 Ammonium chloride greatly lessens this difficulty.

Traces of alumina may be recovered from the filtrate by evaporation to dryness, ignition and resolution with HCl. The Al(OH)₃ is now precipitated with NH₃OH.

Since alumina absorbs moisture from the air, the crucible containing this compound should be kept covered in a desiccator until weighed.

Ammonium hydroxide, in presence of sufficient NH₄Cl, will not precipitate Mg(OH)₂, since the addition of NH₄Cl increases the ammonium ions in the solution and, by the common ion effect, represses the hydroxyl ions of the base, NH₃OH, so that there are insufficient hydroxyl ions for the solubility product of Mg(OH)₂ to be exceeded; therefore magnesium remains in solution. A discussion of the theory of solubility product and law of mass action may be found in the author's work on Qualitative Chemical Analysis, published by D. van Nostrand Co. Reference is also made to Vol. I of The Elements of Qualitative Chemical Analysis, by Julius Stiegeltz, publ. by the Century Co.

Determination of Aluminum by Hydrolysis, Neutralizing the Mineral Acid by Addition of a Salt of a Weak Acid. 
Sodium Thiosulphate Method

If a salt of a weak acid and strong base is added to a neutral or slightly acid solution of an aluminum salt containing a mineral acid, transposition takes place and aluminum is hydrolyzed.

Reaction. \(2\text{AlCl}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 6\text{NaCl} + 3\text{S}_2\text{O}_3 + 38\).

Procedure. If the solution is acid, dilute ammonia is added until a precipitate forms that dissolves with difficulty, but not enough ammonium hydroxide to cause a permanent precipitation. The solution is diluted so that it contains about 0.1 g. Al per 200 cc., then an excess of sodium thiosulphate is added, and the solution is boiled free of SO₂. Al(OH)₃ precipitates along with free sulphur. If iron is absent it is advisable to add a few drops of ammonium hydroxide until the solution has a slight odor of ammonia. The mixture again boiled is filtered and the residue of Al(OH)₃ and sulphur washed with hot water containing ammonium chloride or nitrate. The precipitate is dried, separated from the filter, the latter ignited and the ash added to the main precipitate. Alumina is now determined by blasting to constant weight, the residue being weighed as Al₂O₃.

Notes. The above method may be employed for separation of aluminum from iron, the addition of ammonia, following the neutralization of the mineral acid by thiosulphate being omitted. The precipitation of Al(OH)₃ by this procedure gives a more dense and better filtering precipitate than does ammonia alone.

Note. G. Wynkopp suggests the use of sodium nitrite as the salt of a weak acid for neutralizing the mineral acid. (J. Am. Ch. Soc., 19, 434 (1897)).

I. Ivanov recommends neutralizing the aluminum solution with sodium thiosulphate then diluting to 100 cc. and adding potassium iodide, followed by a 3% solution of KI₄ and additional KI (10% sol.) until precipitation is complete. The excess of iodine is expelled by boiling. The Al(OH)₃ is filtered and washed with NH₄NO₃ sol. (2% sol.) and then ignited to Al₂O₃.

Precipitation of Aluminum as a Phosphate

Principle. This procedure, developed by Carnot, is of special value in determination of aluminum in iron and steel. It is founded on the reaction that aluminum is precipitated as the neutral phosphate, from a boiling solution faintly acid with acetic acid. Iron, reduced to the ferrous condition by addition of sodium hyposulphite, does not interfere.

Procedure. A sample of 10 grams of iron or steel, in a platinum dish, covered with a piece of platinum foil, is dissolved by addition of hydrochloric acid. The solution is diluted to about 100 cc. and filtered into a flask, the residue of carbon, silica, etc., is washed thoroughly and the filtrate is neutralized by addition of ammonium hydroxide and ammonium carbonate; no permanent precipitate should form. A little sodium hyposulphite is added, and when the liquid, at first violet, becomes colorless, 2 or 3 cc. of a saturated solu-

E. Schum (Chem. Zeit., 1909, XXXIII, 877) recommends neutralizing the solution of aluminum with NH₄OH, just avoiding a precipitation of Al(OH)₃. After diluting to 250 cc. the aluminum is precipitated by adding 20 cc. of a 6% sol. NH₄NO₃. The oxides of nitrogen are expelled by boiling and the Al(OH)₃ settled on hot water bath 20 min. The sol. is decanted and the precipitate washed with neutral (2% sol.) ammonium nitrate and ignited as usual. The method is considered very accurate.
tion of sodium phosphate and 5 or 6 grams of sodium acetate, dissolved in a little water, are added. The solution is boiled until free of sulphurous acid odor (about three-quarters of an hour). The solution is filtered off from the precipitated aluminum phosphate (mixed with a little silica and ferrie phosphate) and washed with boiling water. The precipitate on the filter is treated with hot dilute hydrochloric acid the filtrate caught in a platinum dish, and then evaporated to dryness and heated at 110° C. for an hour to dehydrate silica. The residue is taken up with dilute hydrochloric acid and the solution filtered free of silica. Upon dilution to about 100 cc. with cold water, the solution is neutralized as before, a little hypo sulphite is added to the cold solution and then a mixture of 2 grams of sodium hypo sulphite and 2 grams of sodium acetate. The material is boiled for half an hour or more, filtered and the aluminum phosphate residue washed with hot water, then dried, ignited and weighed as aluminum phosphate. The residue contains 22.19% Al.

\[ \text{AlPO}_4 \times 0.2219 = \text{Al.} \quad \text{AlPO}_4 \times 0.4185 = \text{Al}_2 \text{O}_3. \]

Note. Properties of \( \text{AlPO}_4 \), m.w., 122.14; sp.gr., 2.59; infusible, insoluble, in \( \text{H}_2 \text{O} \) and in \( \text{HC}_2 \text{H}_3 \text{O}_7 \), soluble in mineral acids and in alkalies; white, amorphous salt.

Precipitation of Aluminum as Aluminum Chloride

Principle. Gooch and Havens found that aluminum chloride is practically insoluble in a mixture of concentrated hydrochloric acid and ether saturated with HCl gas, 5 parts of AlCl₃·6H₂O equivalent to 1 part of Al₂O₃ dissolving in 125,000 parts of the mixture. The method serves for a separation of aluminum from iron, berillium, zinc, copper, mercury and bismuth, the chlorides of these elements being soluble under the above conditions. Barium, however, is precipitated as a chloride with aluminum, if it is present in the solution.

Procedure. To the concentrated aqueous solution of aluminum is added a convenient volume of strong hydrochloric acid (15 to 25 cc.) and an equal volume of ether. The mixture is best placed in a large platinum crucible, which is kept cool in running water. HCl gas is passed into the solution to saturation. The precipitated chloride of aluminum is filtered upon asbestos in a weighed Gooch crucible and then washed with a mixture of ether and water 1 : 1, saturated with HCl gas. The precipitate is dried for half an hour at 150° C., then covered with a layer of C.P. mercuric oxide (1 gram) and heated at first, gently over a low flame (hood) and then blasted to constant weight. The residue is weighed as Al₂O₃.

Notes. HCl gas is generated by dropping strong sulphuric acid into concentrated hydrochloric acid according to the procedure described under the determination of arsenic by volatilization as arsenious chloride. The gas may be produced in a Kipp generator by the action of concentrated sulphuric acid on ammonium chloride.

The filtrate from aluminum contains iron, berillium, copper, zinc, etc., if these are present in the original solution. If much iron is present it is necessary to increase the amount of ether to prevent precipitation of the ferric salt.

VOLUMETRIC METHODS FOR THE DETERMINATION OF ALUMINUM

Volumetric Determination of Combined Alumina in Aluminum Sulphate and Aluminum Salts

Introduction. Aluminum salts dissociate in hot solutions and react acid to phenolphthalein indicator; the acid readily combines with fixed alkalies, forming the neutral alkali salt. The end point of the reaction is indicated by the pink color produced upon phenolphthalein by the excess of alkali. From the amount of caustic required the percentage of combined $\text{Al}_2\text{O}_3$ may be calculated. The following reaction takes place:

$$\text{Al}_2(\text{SO}_4)_3 + 6\text{NaOH} = 2\text{Al(OH)}_3 + 3\text{Na}_2\text{SO}_4.$$  

Procedure. The factor weight, 3.4067 grams, is dissolved in a 4-in. casserole with 100 cc. of distilled water, 1 cc. of phenolphthalein indicator added, and the sample titrated boiling hot with $\text{N/2 NaOH}$, added from a chamber burette, graduated from 50 to 100 cc. in tenths of a cc. The solution is kept boiling during the titration and is constantly stirred. Towards the end of the reaction the alkali is added cautiously drop by drop until a permanent pink color is obtained.

Cc. of NaOH required divided by 4 = per cent combined $\text{Al}_2\text{O}_3$.  
Combined $\text{Al}_2\text{O}_3$ + free $\text{Al}_2\text{O}_3$ = total $\text{Al}_2\text{O}_3$.

Notes. If iron is present a correction must be made for it after determining the ferrous and ferric forms as given below.

The amount of phenolphthalein indicator used should be the same in each determination. An excess of indicator causes low results. It has been noted in case of alums where iron does not interfere that best results are obtained with three or four drops of phenolphthalein solution. Iron tends to mask the end point, hence a larger amount of indicator is necessary if this is present.

Correction for Iron if Present. Since iron salts will also dissociate and titrate with aluminum salts, by this method a correction has to be made for iron if present. Total $\text{Al}_2\text{O}_3$ in presence of iron =

combined $\text{Al}_2\text{O}_3$ - (FeO × .47 + Fe₂O₃ × .64) + basic $\text{Al}_2\text{O}_3$ + an additive factor.

The additive factor is obtained by subtracting

(Combined $\text{Al}_2\text{O}_3$ + basic $\text{Al}_2\text{O}_3$) - (FeO × .47 + Fe₂O₃ × .64) volumetric,
from total $\text{Al}_2\text{O}_3$ obtained by gravimetric analysis of an average sample.

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1 Large samples must be taken for salts containing less than 13 per cent $\text{Al}_2\text{O}_3$ if the chamber burette is to be used. E.g., potash alum twice this amount is advisable.
2 Otto Schmatolla, Berichte, xxxviii, No. 4, C. N., 91-2375-238 (1905).
3 If free acid is present (see next method), the equivalent volume in terms of $\frac{1}{4}$ N acid must be deducted from the total titration for combined alumina before dividing by 4.
Ferrous Iron, Ferric Iron, and Total Iron A five-gram sample is dissolved in water and the iron oxidized with a few drops of strong potassium permanganate solution; the solution should be pink; the excess of permanganate is destroyed by a drop or so of normal oxalic acid solution and the total iron determined by stannous chloride solution method for iron. On a separate sample ferrie iron is determined. Ten grams of the sample are dissolved in an Erlenmeyer flask by boiling with hydrochloric acid, 2:1, in an atmosphere of CO₂ to prevent oxidation, and the iron titrated with standard stannous chloride. The difference between total iron as Fe₂O₃ and ferric oxide = ferrous iron in terms of FeO. This multiplied by .9 = FeO.

Combined Sulphuric Acid

Provided no free acid is present, the per cent combined sulphuric acid in aluminum sulphate is obtained by multiplying the cc. caustic titration for total alumina by 0.72.

In case free acid is present, the per cent free acid deducted from total acid found by titration gives combined acid.

Sulphuric acid combined with the fixed alkalies is not titrated.

Determination of Free Alumina or Free Acid by the Potassium Fluoride Method

Introduction. The method suggested by T. J. I. Craig (J. S. C. I., 1911, 30, 185), has been modified by the author, after a personal investigation of the details involved. In this modified form it has been used successfully as a rapid method. Frequent gravimetric checks on a large number of determinations have shown it to be accurate.

The procedure is based upon the fact that an excess of neutral potassium fluoride decomposes aluminum salts, forming two stable compounds, which react neutral to phenolphthalein, while the free acid remains unaltered, the following reaction taking place:

\[ \text{Al}_2(\text{SO}_4)_3 + 12\text{KF} + x\text{H}_2\text{SO}_4 = 2\text{AlF}_3\text{KF} + 3\text{K}_2\text{SO}_4 + x\text{H}_3\text{SO}_4. \]

The precipitate AlF₃KF is insoluble in an excess of the potassium fluoride reagent and is not appreciably attacked by acids or alkalies. Although theoretically about 7 parts by weight of potassium fluoride is sufficient to combine with 1 part of aluminum sulphate, in practice it is advisable to use twice this amount.

Reagents Required. Half Normal solutions of sulphuric acid and potassium hydroxide.

Phenolphthalein indicator, 0.1% alcoholic solution.

Potassium fluoride solution; made by dissolving 1000 grams of potassium fluoride in about 1200 cc. of hot, CO₂-free water, then neutralizing the solution with hydrofluoric acid or potassium hydroxide as the reagent may require, using 5 cc. of phenolphthalein as indicator. Dilute sulphuric acid may be used in place of hydrofluoric acid in the final acid adjustment to get a neutral product. One cc. of the solution in 10 cc. of CO₂-free water should appear a faint pink. The concentrated mix is filtered if necessary and then diluted to 2000 cc. with CO₂-free water. The gravity will now be approximately 1.32 or about 35° Bé. One cc. contains 0.5 g. potassium fluoride.

ALUMINUM

Method of Procedure

Solids. 3.4067 g. of the finely ground sample, or an equivalent amount in solution (100 cc. of sample containing 34.067 g. per liter), are taken for analysis. The powder is dissolved by boiling with 100 cc. of distilled water in a 4-inch casserole with clock glass cover. To the hot solution 10 cc. of N/2 H$_2$SO$_4$ are added and after cooling to room temperature, 20° C., 18 to 20 cc. of the potassium fluoride reagent are added and 0.5 cc. of phenolphthalein. The solution is now titrated with N/2 KOH, added drop by drop until a delicate pink color, persisting for one minute, is obtained. This titration shows whether the product is basic or acid.

Basic Alumina. This is indicated when the alkali back-titration is less than the amount of acid added. Free Al$_2$O$_3$ = (cc. H$_2$SO$_4$ - cc. KOH) ÷ 4.

Free Acid. In case the back-titration of the alkali is greater than the cc. of acid added, free acid is present. Free acid = (cc. KOH - cc. H$_2$SO$_4$) × 0.72.

Liquors. In works control it is necessary to test the concentrated liquors to ascertain whether these are basic or acidic. The Bé. or sp.gr. of the solution has been taken, 5 cc. is diluted to 100 cc. with distilled, CO$_2$-free water. If H$_2$S is present, it is expelled by boiling the solution, which should be acid, 10 cc. of N/2 H$_2$SO$_4$ is added, the solution cooled, and KF and phenolphthalein added and the titration made as in case of solids.

If basic (cc. H$_2$SO$_4$ - cc. KOH) × (0.245 × 3.473 × 100) ÷ (5 × sp.gr.) = Al$_2$O$_3$.

If acid (cc. KOH - cc. H$_2$SO$_4$ × 2.43) ÷ wt. of sample = per cent free acid (H$_2$SO$_4$).

If neutral, the back titration of the alkali is the same as the cc. acid added.

Notes. CO$_2$-free water must always be used when phenolphthalein indicator is necessary. This may be obtained by boiling distilled water for several minutes to expel CO$_2$. This reagent is very sensitive to carboxic acid.

If the sample does not dissolve clear, a prolonged digestion with previous addition of the required amount of standard acid, 10 cc., is advisable. This is best accomplished in an Erlenmeyer flask with a return condenser.

Darkening of the solution during the back titration with the alkali, indicates that an insufficient amount of fluoride has been added. If this is the case it will be necessary to make a fresh determination.

The fluoride method has the following advantages. Determinations may be made by gas or electric light. The end point is easily detected. No neutral standard is necessary as in case of the tinn method.

Ammonium salts, if present, must be expelled by boiling the sample with an excess of standard KOH and this excess determined.

3.4067 × 2.45225 × 3.473 × 4 (i.e. gms H$_2$SO$_4$ per 100 cc. N/2 acid multiplied by 4 times factor to equivalent Al$_2$O$_3$). Derived directly from mol. wt. of Al$_2$O$_3$ = (1022 × 100 × 4) ÷ (6 × 2). 0.72 = 2.8792 ÷ 4 (i.e. factor Al$_2$O$_3$ to H$_2$SO$_4$ ÷ 4).

The main details of the above volumetric procedures were worked out at the Laurel Hill Laboratory, General Chemical Company, and are published by courtesy of this company.
Colorimetric Estimation of Minute Amounts of Aluminum with Alizarin S.—Attack’s Method

Reagent. See page 3.

Procedure. The original solution (5 to 20 cc.) is acidified with hydrochloric or sulphuric acid. Ten cc. of glycerin and 5 cc. of a 0.1% solution of alizarin S are added, the solution made up to about 40 cc. with water (in presence of much iron or chromium citric acid is added to form the double citrates) and then rendered slightly ammoniacal. After standing for five minutes, the cold solution is acidified with dilute acetic acid, the alizarin S acting as indicator (red coloration) until no further change in the coloration occurs. The liquid is then made up to 50 cc. and compared with a standard. Suitable amounts of aluminum for estimation are 0.005 to 0.05 milligrams, the solution under examination being suitably diluted if necessary.

BAUXITE ANALYSIS

<table>
<thead>
<tr>
<th>Characteristic bauxites</th>
<th>H₂O</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arkansas</td>
<td>6.4%</td>
<td>1.43%</td>
<td>87.3%</td>
<td>3.99%</td>
<td></td>
</tr>
<tr>
<td>Georgia</td>
<td>36%</td>
<td>9-15</td>
<td>1-14</td>
<td>42-62</td>
<td>1.8-2.3</td>
</tr>
<tr>
<td>Tennessee</td>
<td>27.6</td>
<td>18.4</td>
<td>4.1</td>
<td>49.9</td>
<td></td>
</tr>
</tbody>
</table>

Sampling. The bauxite received in cars is sampled during the unloading according to the standard procedure for ores. If the sample is a composite aliquot parts of the total weights are taken and mixed, e.g., suppose three cars contained respectively 23,000, 32,500, and 26,340 pounds, then the aliquots would be 23, 32.5 and 26.34 pounds, which mixed, would make a representative sample of the shipment. The ore is broken down, quartered, ground down and again quartered. The moisture is determined on 1000 grams, dried in the oven at 100°C for one hour, the sample being spread out on a sheet of manilla paper. The dried sample is placed in a large bottle for analysis.

Extraction of Ores of Aluminum for Their Commercial Valuation. Twenty-five grams of bauxite, alumite or clay, placed in an 600 cc. Kjeldahl flask with reflux condenser are digested for one hour with 60 cc. 10 N (48%) sulphuric acid. Time being taken when the mix begins to boil. The flame is so regulated that the water drips back into the flask from the condenser at the rate of 12 to 15 drops per minute. When the digestion is completed 150 cc. of hot water are introduced through the condenser. The mixture is now filtered using a Buchner funnel and suction. The residue is washed with six 100 cc. portions of water and the filtrate made up to 1000 cc. A 200 cc. aliquot is made up to 1000 cc. and 100 cc. of this taken for determination of alumina as stated on next page.

2 Bauxite and kaolin are two sources of alumina of commercial importance. The alumina of certain grades of clay is made available for acid extraction by roasting at a definite temperature. 550°-700° C.
ALUMINUM

Insoluble Residue. The residue on the filter paper is ignited in a platinum dish over a low flame until the paper chars, and then over a good Meker blast for 15 to 20 minutes.

Weight of the residue × 4 = per cent insoluble residue.

Soluble Alumina. 100 cc. of the above solution (0.5 g.) is diluted with an equal volume of water, 10 cc. of hydrochloric and 2 cc. of nitric acids added and the solution boiled. Iron and alumina are now precipitated and determined in the usual way.

Soluble Iron. 200 cc. of the solution (1.0 g.), is oxidized by adding a few crystals of potassium chlorate and the solution taken to dryness. The residue is taken up with 10 to 15 cc. of concentrated hydrochloric acid and again evaporated to dryness to expel chlorine. Then taken up with 25 cc. hydrochloric acid and the iron determined by titration. The stannous chloride method is used for samples containing less than 5% iron and the dichromate method for ores containing over 5%.

Determination of Total Silica, Titanium Oxide, Ferric Oxide and Alumina

The method by the Aluminum Company of America is to digest 1 gram of the dried bauxite in 90 cc. of an acid mixture containing 12 parts of dilute sulphuric acid, 1 : 3, together with 6 parts of strong hydrochloric acid and 2 parts of nitric by volume, to this are added 10 cc. of concentrated sulphuric acid. The mixture is heated until sulphuric acid fumes are evolved, then diluted with water and filtered.

Silica. The residue is ignited and the ash fused with potassium bisulphate. The cooled fusion is taken up with 5 cc. sulphuric acid and 20 cc. of water and digested until only a white residue remains. This filtered off, washed and ignited = SiO₂.

Titanium Oxide. This is best determined colorimetrically on a 0.1 gram sample according to the procedure outlined in the chapter on Titanium.

Iron and Alumina. These are determined by the usual procedure;—oxidation with potassium chlorate, precipitation with ammonium hydroxide and ignition. Iron may be determined in a separate sample (100 cc. = 0.5 g.) by titration. Al₂O₃ = difference between weighed oxides and Fe₂O₃, after subtracting TiO₂ if present.
VOLUMETRIC DETERMINATION OF THE AVAILABLE ALUMINA IN BAUXITE AND CLAYS

This method is based on the solution of the sample in a known amount of sulphuric acid, and the titration of the excess acid with standard sodium hydroxide solution, and the alumina estimated from the amount of acid used to combine with it. It has been proven with long practice that this method is accurate within 0.5%, and is very satisfactory as a works control method. It is much more rapid than the regular gravimetric procedure.

Take a five gram sample that has been ground to pass through a 60-mesh sieve and put it into a 300 cc. Kjeldahl flask with about 28 to 30 grams of 40° Bé sulphuric acid, which is weighed from a weighing burette. (This acid may be measured with a burette and the weight calculated if so desired with a reasonable chance of error introduced.) Digest this at a gentle boil for one hour, giving the flask an occasional shaking. Care must be taken that good condensation is effected, otherwise a loss in acid will give high results. After the digestion wash down the condenser and filter the insoluble residue off on a Buchner funnel with suction, washing the residue acid free. Make the filtrate up to 2000 cc. in a volumetric flask. To a 200-cc aliquot add 20 cc. KF reagent, and 1 cc. phenolphthalein indicator and titrate to a permanent pink with standard N/10 NaOH.

Reagents: The 40° acid must be made up very accurately and standardized against standard caustic.

4000 grams of potassium fluoride are dissolved in 1200 cc. of hot CO₂ free water, and then neutralized with HF or KOH as may be necessary, using phenolphthalein indicator. Filter this solution and dilute to 2000 cc. This solution should be kept in a wax-lined bottle.

Take 20 cc. of KF reagent and add 5 cc. of N/2 NaOH and one cc. of phenolphthalein indicator, and titrate with N/2 H₂SO₄. Apply this correction to the titration of the sample.

Calculations:

\[(\text{cc. N}/10 \text{ H}_2\text{SO}_4 - \text{cc. N}/10 \text{ NaOH}) \times \frac{3473}{100} = \% \text{ Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3\]

weight of sample

\[% \text{ Fe}_2\text{O}_3 \times .64 = \text{Fe}_2\text{O}_3 \text{ equivalent to } \text{Al}_2\text{O}_3\text{ which can be subtracted from the total oxides above, the result being the available alumina.}\]

Determination of Aluminum in Bronze. A sample weighing 0.5 to 1.0 g. is dissolved in 10 cc. of HNO₃ (2:1) and heated to expel nitrogen oxides. 50 cc. of water are added and the precipitate allowed to settle (oxide of Sn, PbO₂, and some Cu) and then filtered. The filtrate is treated with 5 cc. H₂SO₄ and evaporated to fumes, then taken up with about 50 cc. of water and saturated with H₂S, and the precipitate filtered off. The filtrate containing the iron, aluminum, zinc, etc. is boiled to expel H₂S and oxidized by boiling with 5 cc. HNO₃. Iron and aluminum are now precipitated as hydroxides by addition of NH₄OH and filtered off and washed as usual. Iron and aluminum are separated by dissolving the hydroxides in a little HCl and neutralizing the free acid with Na₂CO₃ solution. Any permanent precipitate is dissolved by a few drops of HCl. For each 0.1-0.2 g. of the metals present the solution is diluted to about 250 cc. and an excess of Na₂S₂O₃ is added. Aluminum hydroxide is precipitated, iron remains in solution in the ferrous form. 2Al₂O₃ + 3Na₂S₂O₃ + 3H₂O = 2Al(OH)₃ + 3SO₂

+3S + 6NaCl. The Al(OH)₃ is filtered off and washed with hot water, then dried and the hydroxide and filter ignited separately, the ash of the paper added to the alumina and the ignition continued until a constant weight is obtained. An electric furnace of a Moker burner may be used to expel the combined water. Weigh as Al₂O₃.

\[\text{Al}_2\text{O}_3 \times 0.5303 = \text{Al}\]

1 By Harold E. Martin.
DETERMINATION OF ALUMINUM IN IRON AND STEEL

The method is especially adapted for determination of aluminum in iron and steel, but may be extended to iron ores and materials high in iron.

Procedure. Solution. Ten grams of iron or steel are dissolved by adding about 50 cc. of hot hydrochloric acid, 1 : 1, preferably in a platinum dish, covered with a platinum foil.

Precipitation. When the solution of iron is complete, it is diluted to about 100 cc. and filtered free of carbon, silica, etc. Two grams of sodium phosphate are added and the solution neutralized with ammonium hydroxide or carbonate, then cleared by hydrochloric acid with about 1 cc. excess. Twenty cc. of acetic acid are now added and the solution diluted to 300 to 400 cc. with hot water and, on boiling, 10 grams of sodium thiosulphate added. The solution is boiled free of sulphurous acid, (no odor of SO₂) about 20 to 30 minutes being necessary. The phosphate is filtered off and washed with hot water. It is again dissolved in a little hydrochloric acid and aluminum precipitated by neutralizing with ammonium hydroxide and adding about 1 gram of sodium phosphate together with 10 grams of sodium thiosulphate, following the above procedure. The precipitate will now be free of iron.

Ignition and Calculation. The precipitate and filter are ignited wet, first over a low flame, then gradually increasing the heat to full blast of a Meker burner. The residue contains 22.19% Al or 41.85% of Al₂O₃.

Factor Al₂O₃ to Al = .0219.
Factor Al₂O₃ to Al₂O₃ = .4185.

Notes. Interfering substances. Copper may be removed by H₂S. Other members of this group will also be eliminated.

Manganese and nickel are eliminated together with small amounts of iron at the second precipitation.

Titanium may be estimation colorimetrically or separated from alumina.

Vanadium, if present, may be separated according to directions given in the chapter on Vanadium.

Chromium is eliminated by fusion of the mixed phosphates with Na₃C₄O₄, extraction with water, and precipitation of aluminum phosphate by adding ammonium acetate and sodium phosphate. Chromium remains in solution.

Other Methods. L. Belasio adds crystalline tartaric acid to hold up the precipitation of other metals that commonly interfere. I. Ivanov neutralizes the slightly acid solution of aluminum with Na₃S₂O₃, then dilutes to 100 cc. adds KI in excess, then a 5% sol. of KI₂O₃ with additional KI until precipitation is complete. The excess of iodine is expelled by boiling and the Al(OH)₃ washed with neutral 3% NH₄NO₃ sol. and ignited as usual, to Al₂O₃. E. Schum (Chem. Zeit., 32, 877, 1900) neutralizes the solution with NH₄OH just avoiding precipitation of Al(OH)₃. After dilution to 250 cc. 20 cc. 6% ammonium nitrite sol. are added, the solution boiled to expel NO₂, the Al(OH)₃ settled 20 min. and filtered and washed with ammonium nitrite solution and the precipitate ignited as usual to Al₂O₃.

ALUMINUM

ANALYSIS OF ALUMINUM AND ALUMINUM ALLOYS. METHODS OF THE ALUMINUM COMPANY OF AMERICA

_Determination of Silicon_ 

_Fusion Method_

In some cases a portion of the silicon in aluminum and its alloys is not oxidized when the metal is dissolved in acids. This is more frequently observed when the silicon is higher than regularly found as an impurity. It is made evident by a brown or dark gray film coating the liquid and container after dissolving the metal in acid mixture, and has been referred to as graphitic silicon. In such a case a fusion of the residue is needed to give a complete oxidation. A fusion is useful also for cleaning up residues contaminated with insoluble material other than SiO₂.

Dissolve 1 gram of well-mixed drillings in 35 cc. of acid mixture No. 1 (450 cc. water, 150 cc. conc. H₂SO₄, 300 cc. conc. HCl, 100 cc. conc. HNO₃), using a 250-cc. flat bottom casserole or Pyrex beaker and cover glass. When the drillings are completely dissolved, place on a moderately heated plate and boil the solution to dryness, then increase the heat till the H₂SO₄ distills as shown by flowing down the cover. Continue till a few drops have fallen from the center of the glass. This insures the complete removal of HCl and HNO₃ and the dehydration of SiO₂. These effects can also be secured by heating at the moderate temperature for an hour after boiling dry. Cool, add 10 cc. 1 : 3 H₂SO₄ and about 100 cc. water, boil to complete solution of the sulphate, filter, wash well and ignite in a platinum crucible.

Fuse the residue with 8 to 10 times its weight of Na₂CO₃ and treat the fused mass in a casserole or beaker with 20 cc. 1 : 3 H₂SO₄, washing out the crucible. Evaporate the solution until it fumes strongly to separate the SiO₂. Cool, dilute to about 100 cc., boil till the salts are dissolved, filter, wash well, ignite in a platinum crucible and weigh. Treat the ash with HF and a few drops of H₂SO₄ evaporate till dry, ignite and weigh.

From the difference between the two weights deduct a blank obtained from the reagents and filter. The rest of the loss in weight represents SiO₂ corresponding to the Si in the metal.

\[ \text{SiO}_2 \times 4676 = \text{Si} \]

_Solution Method_

When only a small amount of silicon is present such as the few tenths per cent commonly found in commercial aluminum, it is practically all oxidized by the acid treatment, and a direct weight of the ignited insoluble residue considered as SiO₂ gives a measure of the original Si sufficiently accurate for general use.

Proceed as in the fusion method until the first insoluble residue has been filtered and washed. Ignite it in a crucible, allow to cool, brush the residue on the balance pan and weigh directly. Deduct a determined blank. Consider the remainder SiO₂ and calculate to Si as above.

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1 By courtesy of the Aluminum Company of America, E. Blough, Technical Director. H. V. Churchill. Chief Chemist.
Determination of Iron

Permanganate Method

Cool the filtrate from the insoluble residue obtained in the determination of silicon. It should contain 3 to 5% H₂SO₄. Add KMnO₄ solution till a pink color persists. Reduce the iron present by passing the solution through a Jones reductor. See chapter on Iron. Titrate immediately with a solution of KMnO₄ of such strength that 1 cc. = .001 gram Fe. A blank, determined by carrying out the procedure without a sample, is deducted from each titration.

Cautions. (1) The KMnO₄ solution should not be permitted to come in contact with organic substances. It should be kept in a glass-stoppered bottle in a dark closet. Glass-stoppered burettes should be used.

(2) Always have the iron solution cool before reduction.

(3) There should be a solid column of solution or water passing during use. The zinc should be kept covered with water when not in use.

(4) When the sample contains copper, the reductor will be kept cleaner if the copper is precipitated with a little granulated zinc, and the solution decanted from the precipitated copper before passing through the reductor.

Determination of Copper

Iodide Phosphate Method: Cu up to 1%

Dissolve 2 grams of well-mixed drillings in a tall 300-cc. beaker with 40 cc. of 25% caustic soda solution. When the aluminum is completely dissolved, dilute to 200 cc. with hot water that has been boiled. Allow the residue to settle, filter and wash thoroughly with hot water.

Using as small amount as possible of hot 1:1 nitric acid, completely dissolve the residue from filter paper into a 250-cc. wide mouth Erlenmeyer flask containing 0.1 cc. of concentrated sulphuric acid. If much manganese or iron is present, more concentrated sulphuric acid (about 0.5 cc.) should be used to prevent the formation of MnO₂ or Fe₂O₃, which will obscure the end point. Place the flask on a hot plate and evaporate to complete dryness. Cool. Add 25 cc. water and 3 cc. 99.5% acetic acid. Heat to complete solution.

Remove flask from hot plate, at the same time adding 5 cc. of a saturated solution of Na₂HPO₄, shake thoroughly and cool in any convenient manner.

The ferric sulphate which later would react with potassium iodide thus:

\[ \text{Fe}_2(\text{SO}_4)_3 + 2\text{KI} = 2\text{FeSO}_4 + \text{K}_2\text{SO}_4 + \text{I}_2 \]

will be precipitated and rendered inactive by the reaction,

\[ \text{Fe}_2(\text{SO}_4)_3 + 2\text{Na}_2\text{HPO}_4 = 2\text{FePO}_4 + 2\text{NaHSO}_4 + \text{Na}_2\text{SO}_4 \]

To the cooled solution add 5 cc. potassium iodide solution (30 grams of potassium iodide to 100 cc. water) and shake thoroughly to mix solutions.

\[ 2\text{Cu(C}_2\text{H}_3\text{O}_2)_2 + 4\text{KI} = \text{Cu}_2\text{I}_4 + 4\text{KC}_2\text{H}_3\text{O}_2 + \text{I}_2 \]

Titrate the free iodine with a solution of sodium thiosulphate of 0.001 copper value which has been standardized by the copper sulphate method. A few drops of fresh starch solution, which is used as an indicator, are added near the end of the titration. This solution is prepared by dissolving 1 gram of soluble starch in 150 cc. of water.
Copper Percentage = No. of cc. Thiosulphate × Copper Value per cc. 
× 100 + Weight of Sample (2 grams).

Note. In case the residue has not been carefully washed or when the iron content is high, an additional amount of Na₃HPO₄ may be required, and must be added until all iron and aluminum salts have been precipitated.

Determination of Manganese

Sodium Arsenite Method: Mn up to 2%

Weigh out accurately a 0.2-gram sample and place in a 200-cc. Erlenmeyer flask. Add 15 cc. of acid mixture No. 2 (400 cc. conc. H₂SO₄—400 cc. conc. HNO₃—200 cc. H₂O). Place upon a hot plate and boil until solution is complete. Add 5 cc. more of acid mixture No. 2 and boil for 2 or 3 minutes to drive off nitrous fumes. Remove from the source of heat, cool, add 10 cc. of AgNO₃ solution (3 grams per liter) and 90 cc. of warm water containing 1 gram of ammonium persulphate. Heat gently until the permanganic acid is fully developed as indicated by a ring of bubbles forming around the surface. Cool to room temperature and titrate with standard sodium arsenite solution, the approximate value of 1 cc. being equal to 0.00052 gram or 0.10% Mn.

If desired, the silver may be precipitated before titration by adding 5 cc. of NaCl solution (2 grams to 1 liter). The titration in standardizing must be done the same way as in working the samples.

Preparation of Standard Arsenite Solution

For standardizing the sodium arsenite solution for the determination of manganese a standard alloy of known manganese content must be used.

Procedure. (1) Stock Solution — stock solution is prepared by dissolving 10 grams As₂O₃ and 30 grams Na₂CO₃ in a small amount of hot water, filtering and making up to 1000 cc.

(2) Standard Solution — the standard solution is prepared by taking required amount of stock solution (about 65 cc.) and diluting to 1000 cc. After 24 hours, this solution is carefully standardized by using it to titrate the manganese in the standard sample. Three determinations should be made using exact procedure as given above.

Note. (1) By adding the acid mixture in two portions it is made more certain that the proper amount is present when peroxodizing the manganese.

(2) When dissolving the sample it should not be allowed to go to dryness, as some manganese oxide might be made insoluble.

Determination of Zinc—0.50% or Less

ZnO Method

Place 2 grams of sample in a 400-cc. beaker or casserole with 10 grams NaOH and 50 cc. water. When violent reaction is over, wash down and heat to near boiling till no more action can be seen. Add boiling water to make 200 cc. and bring to boil. Let settle, then filter. The filtrate is allowed to stand for several hours or is boiled a few minutes with about 5 gram Na₂O₃ to insure removal of manganese. If any precipitate forms, it is filtered out. 5 grams NaOH is added to the filtrate which is then heated to boiling and treated with H₂S for about 3 minutes. The solution is boiled for 10 minutes.
and filtered through a dry double filter, keeping the filter full. Do not wash. The zinc sulphide is then dissolved off the filter with warm dilute hydrochloric acid (1:10) and the filter washed three times with hot water. The filtrate is boiled free from hydrogen sulphide, a few drops of bromine water are added to oxidize any iron present and the solution is made slightly alkaline with ammonia, boiled and filtered. Hydrogen sulphide is then passed into the filtrate until saturated. The solution is then boiled for ten minutes and filtered through a small filter without washing. The filter is burned at low temperature in a porcelain crucible. Dissolve the residue using HCl and transfer to a beaker. Make just ammoniacal to methyl red, filter and wash. Add 10 drops of ammonia to the filtrate, heat solution to near boiling, saturate with H2S, filter, burn the paper and precipitate in a weighed porcelain crucible. Calculate the weight of zinc oxide to zinc.

\[ \text{ZnO} \times 0.8034 = \text{Zn}. \]

**Determination of Calcium and Magnesium**

**Calcium: Permanganate Method**

Place one gram of the alloy together with 5 grams of solid sodium or potassium hydrate in a porcelain dish and add just enough water to cover; when violent action has ceased, dilute to 200-250 cc. with hot water and boil until solution is complete. Filter while hot and wash the residue until free from alkali. The aluminum and most of the zinc dissolve, while the other metals remain in the metallic state.

Using a few drops of nitric acid and 40 cc. of hot 1:1 hydrochloric acid completely dissolve the residue obtained from the sodium hydrate solution into a 250-cc. beaker, or flask. Neutralize with ammonia and add 5 cc. excess. Precipitate with hydrogen sulphide. Filter and wash with hot water. Discard the precipitate.

**Note.** The hydrogen sulphide metals which are here discarded can be used for the determination of copper by the isonicl phosphate method.

Boil off the hydrogen sulphide from the filtrate, adding a little bromine water toward the latter part of the boiling to oxidize the sulphur. Boil off the excess of bromine. Add methyl red indicator and then ammonia drop by drop until the solution is just ammoniacal; then add 2 drops excess. Add 10 cc. of saturated solution of ammonium oxalate, allow the solution to digest for 5 minutes, remove from the hot plate and filter. Wash eight times with hot water.

More or less magnesium will be precipitated with the calcium oxalate depending on the ratio in which these metals are present. If very accurate results are desired, it will be necessary to reprecipitate the calcium oxalate.

Return the paper containing the thoroughly washed calcium oxalate to the original beaker. Add 150 cc. of boiling water and 10 cc. (1:1) sulphuric acid and titrate with standard potassium permanganate.

Potassium permanganate in the presence of sulphuric acid reacts with calcium oxalate thus:

\[ 5\text{CaC}_2\text{O}_4 + 2\text{KMnO}_4 + \text{8H}_2\text{SO}_4 = 5\text{CaSO}_4 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}. \]

The iron value \( \times 0.3588 \) = the calcium value.
Magnesium: Mg₃P₂O₇ Method

The filtrate from the calcium oxalate which has been received into a 250-cc. beaker is made just acid with hydrochloric acid. Add 30 cc. of a saturated solution of microcosmic salt. Add ammonia drop by drop, stirring vigorously to make the precipitate crystalline. Then add an excess of ammonia equal to ten per cent by volume, and let stand for at least three hours. Filter, wash with cold water containing 5% of strong ammonia, and 5% of ammonium nitrate. Ignite until completely white, weigh as Mg₃P₂O₇.

$$\text{Mg₃P₂O₇} \times 0.2185 = \text{grams Magnesium.}$$

For very accurate results the Mg₃P₂O₇ precipitate should be dissolved and reprecipitated, and the final precipitate should be examined for manganese or other impurities and corrected accordingly.

ANALYSIS OF SILICON ALLOYS

Determination of Silicon

Place convenient weight (1.0 gram up to 10% Si, 0.5 gram above 10% Si) of well-mixed drillings in a 250-cc. casserole and cover with a watch glass. Add 25 cc. of acid mixture No. 1 (1200 cc. 25% sulphuric acid, 600 cc. conc. hydrochloric acid, 200 cc. conc. nitric acid) from an acid burette, keeping the casserole covered and adding the acid very slowly at first until violent action has subsided. Digest on the hot plate and evaporate to dryness, taking care to prevent spattering. Cool, moisten with 5 cc. of 1:1 sulphuric acid, add 100 cc. water, and boil to solution of soluble salts. Filter, using a double quantitative filter paper, and filter pulp. Wash the residue six times in hot water to insure the removal of all iron salts.

Ignite the residue in a large platinum crucible. Cool. Add 5-8 grams of a mixture of 1:1 anhydrous sodium carbonate and sodium bicarbonate. Stir thoroughly and cool with a layer of the fusion mixture. Fuse the mixture over a Meker flame, keeping the crucible covered, until reaction is complete. This will require about 15 minutes. Cool. Place the crucible in a casserole and add 60 cc. of 1:3 sulphuric acid. When the fusion cake has dissolved, remove the crucible. Evaporate to heavy fumes. Cool. Take up with 100 cc. water. Heat to complete solution of soluble salts.

Filter through a quantitative paper, wash thoroughly, dry and ignite in a small platinum crucible. Weigh, moisten the residue with water, treat with a drop of H₂SO₄, and then with an excess of HF. Take down to dryness, ignite, cool, weigh again. The loss in weight is SiO₂, which multiplied by 0.4670= Silicon.
ANALYSIS OF BAUXITE (R. Z. Method)

Methods used by the Aluminum Company of America, Technical Direction Bureau, Standard Methods of Analysis

Determination of Moisture

If the bauxite has not been previously dried, the moisture is determined at 105° C.

Determination of Loss on Ignition

Place one gram of dried sample in a weighed crucible and cover with platinum lid. Heat slowly to a red heat for one hour. Remove cover and heat for one hour at the hottest temperature obtainable on a blast lamp. Cool and weigh. The loss in weight represents combined water and organic matter.

Determination of SiO₂

Place in a 250-cc. casserole one gram of dried sample and moisten with 5 cc. of water. Add 90 cc. of acid mixture (900 cc. water, 300 cc. H₂SO₄, 600 cc. HCl and 200 cc. H₂O₂) and 10 cc. concentrated H₂SO₄. Cover with watch glass and boil until H₂SO₄ fumes are given off copiously. Cool, and dilute carefully to 150 cc. volume, washing cover glass and sides of dish. Replace cover glass and boil the solution carefully until the solution has a clear appearance. Filter the solution through an ashless filter into a 250-cc. flask and wash the residue with hot water until free from acid. Ignite the filter in a platinum crucible, cool in desiccator and weigh. Moisten the residue in crucible with two or three drops of water, 3 drops conc. H₂SO₄ and 2–3 cc. HF. Evaporate slowly to dryness to avoid spattering, ignite, cool and weigh. The difference between the two weights obtained gives the silica content of sample.

Determination of Fe₂O₃

If any appreciable residue remains in the crucible, it is brought into solution by fusing it with a little potassium bisulphate and dissolving the resultant fusion in very dilute sulphuric acid. This solution is then added to the original filtrate, the whole cooled to room temperature and made up to a volume of 250 cc.

25 cc. of this solution is then transferred with a pipette to a 100-cc. Nesher comparison tube for use in the determination of titanium.

The remainder of the solution is transferred to a 400-cc. beaker and evaporated to approximately 100 cc., 20 cc. of conc. HCl are then added and the solution brought to boiling. The iron is reduced by adding drop by drop to the boiling hot solution a concentrated solution of stannous chloride until the solution is colorless. The end point is sharp and not more than two drops of stannous chloride should be added in excess. Cool the solution to the room temperature and add while stirring 5 cc. of a saturated solution of
mercuric chloride. Stir solution for about thirty seconds. The iron must be titrated either with bichromate solution, using potassium ferriyanide as an external indicator, or with permanganate solution according to the Reinhart-Zimmerman method which is as follows:

Place 50 cc. of a preventative solution in a wide neck liter flask containing 350 cc. water. Pour the reduced iron solution into the flask and while swirling the flask, titrate with permanganate solution to the appearance of a pink tinge. The end point is sharp, but only lasts for a moment.

The preventative solution contains:

1750 cc. water,
160 grams manganous sulfate,
330 cc. 85% phosphoric acid,
320 cc. H₂SO₄ sp.gr. 1.84.

Determination of TiO₂

To the 25-cc. solution in the Nessler comparison tube add 20 cc. 25% H₂SO₄ and 3 cc. 3% hydrogen peroxide, fill to the mark with water and mix. In a similar tube place 20 cc. 25% H₂SO₄, 3 cc. hydrogen peroxide and water to slightly below the mark. To this tube add standard titanic acid solution from a burette, mixing and comparing after each addition, and continue till its color matches that of the tube containing sample. From the amount of the standard used the titanium content of the sample may be calculated, remembering that the sample taken for the titanium determination represents one-tenth of the entire sample.

If a colorimeter is at hand, it may be used in place of the second Nessler tube for comparison.

Determination of Al₂O₃

The alumina is obtained by the difference between the sum of the silica, titanium oxide, iron oxide and loss on ignition calculated as percentages and 100%.

When it is required to determine whether a material is bauxite or not, some modifications are necessary. If the unvolatilized residue from silica determination amounts to more than a few milligrams, it should be fused with sodium carbonate and examined for additional silica. Absence of any considerable amount of phosphate in the sample should be established. Also the alumina should be determined in a portion of the filtrate from silica by precipitation with ammonia, deducting from the ignited oxides the iron and titanium oxides which have been directly determined.
ANALYSIS OF ALUMINUM HYDRATE

Determination of Loss on Ignition

A one-gram sample is weighed into a platinum crucible and placed over a
low flame of the bunsen burner. The temperature is gradually raised until
the crucible is a bright red, when it is transferred to a muffle furnace at 1100°
C. for one hour. Place in desiccator, cool and weigh. The loss in weight
equals the per cent loss on ignition. This value of loss on ignition is the total
of free and combined water.

Note. A great deal of care is necessary when starting to heat the hydrate. The
temperature should be slowly increased because if the hydrate is heated too rapidly,
the high rate at which the moisture is driven off will force the particles of hydrate out
of the crucible.

Determination of SiO₂

A ten-gram sample is weighed into a casserole. Enough H₂O is added to
make a thin paste, then 25 cc. conc. H₂SO₄ are quickly added and casserole
covered. Casserole is placed on the hot plate and taken down to considerable
fuming. Allow contents to cool and dilute with 150 cc. H₂O, boil until clear.
Filter and wash with hot water. Place the filter paper in a platinum crucible
and ignite. Cool and weigh. Add a few drops of conc. H₂SO₄ and 1 cc. of
HF. Heat on hot plate until SO₃ fumes have disappeared. Then ignite for
15 minutes; cool and weigh. Difference in weight×10 = per cent SiO₂.

Note. Considerable attention is required in placing the hydrate in a solution of
H₂SO₄. When the mixture of hydrate and H₂SO₄ is heated slightly, violent action
takes place which is caused by the reaction of hydrate of alumina and H₂SO₄ to form
aluminum sulphate. After this reaction, continue to heat for one minute and cool.
on taking up with water it seems to go in solution quite readily.

Determination of Fe₂O₃

To the filtrate from the silica determination add 5 cc. of conc. HCl; cool
to room temperature. Make up a solution of 0.5 gram sample of cupferron
in 25 cc. H₂O. Filter and add filtrate slowly to the acidified filtrate from the
silica determination, stirring well. Set aside to complete precipitation for
30 minutes. Filter precipitate with gentle suction and be sure the filtrate is
crystal clear. Wash 1 : 1 HCl solution; ignite, precipitate and weigh.

Per cent Fe₂O₃ = 10×weight of ppt.

Note. It is important that the solution be thoroughly cooled before adding the
cupferron. Also in making the cupferron solution cool water is necessary. After
adding the cupferron, place the solution in a cool place such as a vessel containing
circulating tap water for at least 30 minutes to complete the precipitation.
Determination of Na₂O

Weigh a 10-gram sample into a platinum dish and add 30 cc. conc. HCl. Take to dryness on a steam bath or in a hot oven 110° C. Remove to muffle furnace at 500° C. to burn off free HCl. Cool and add 50 cc. hot water; boil ten minutes and add 25 cc. saturated ammonium carbonate solution; allow to stand for one hour or longer on hot plate but not boiling; filter and wash residue with hot water. Transfer filtrate to platinum dish, cover with watch glass and evaporate to dryness. Place in muffle at 500° C. to drive off NH₄ salts. Remove, cool, and add 5 cc. hot water. Filter contents of dish, catching filtrate in a 250-cc. beaker, wash to a volume of 25 cc. of filtrate; allow to cool and add a crystal of potassium chromate and titrate with N/20 silver nitrate.

Cc. N/20 AgNO₃ × value of AgNO₃ solution in grams Na₂O per cc. × 10 = per cent Na₂O in hydrate.

Note. When taking the hydrate sample down to dryness with HCl, caution has to be taken so as not to heat it at too high a temperature. The use of a muffle furnace at 500° C. will prevent this. The same precaution is necessary when driving off the NH₄ salts. Too high a temperature will volatilize some of the NaCl. Always have a solution cool before titrating with N/20 silver nitrate.

Determination of Insoluble

Weigh a 10-gram sample into a casserole and add 50 cc. H₂SO₄ 50° Be. and boil until solution is clear. Be careful not to boil down until fumes come off. Filter and place filter paper in: platinum crucible and ignite for one hour in muffle furnace at 1100° C. Cool and weigh. This weight less weight of crucible × 10 = per cent of insoluble.
ANALYSIS OF CALCINED ORE

Bisulphate Fusion Methods

Preparation of Sample

The portion of ore collected is well mixed and cut down to the amount which it is wished to reserve for the determination of impurities, ordinarily about 4 oz. A separate part should be kept for mesh test, and may be used also for loss on ignition. The 4-oz. lot is quickly sifted through a 60-mesh sieve, the part retained ground till it passes the sieve and the whole thoroughly remixed. In the above grinding it is well to cover the coarse particles with a little of the sifted ore to prevent flying out and also to rinse the mortar with some of this fine part. No further grinding is to be done on the sample as there is danger of disproportionate contamination.

Determination of SiO₂

"A" (General Laboratory). Twenty-two grams of bisulphate are considered ample to make the fusion by this procedure. Weigh two-gram sample into 50 cc. platinum crucible, add about 17 grams of bisulphate and carefully fuse until violent action is over. Cool the fusion, running it up the sides of the crucible. Add the remaining 5 grams of bisulphate to be used and continue fusion until decomposition of the ore is complete.

Using procedure "A" continue from this point by cooling the crucible with air blast. Place the fused cake, which is easily removed, in a 250-cc. casserole and add 25 cc. concentrated sulfuric acid. Heat gently until the fused cake is completely broken up and copious fumes are evolved. Cool and take up with about 200 cc. of hot water. Heat gently to complete solution of soluble salts. Filter off the SiO₂, using approved quantitative filter paper, and wash with a small amount of hot water. Set aside the strong filtrate and wash the SiO₂ thoroughly until washings give no test for sulfate with barium chloride.

Ignite the filter paper in a platinum crucible at approximately 950° C. for one hour. Cool and weigh accurately on an approved balance. Treat with HF, a few drops of H₂SO₄, and evaporate to dryness. Ignite and weigh. Loss in weight is SiO₂. Corrections must be made for SiO₂ derived from reagents or apparatus.

\[
\text{Per cent SiO₂} = \frac{\text{Loss in Weight} \times 100}{\text{Weight of Sample (2 grams)}}
\]
Determinations of Fe₂O₃ (Cupferron Method)

Receive the filtrate from SiO₂ determination in a 600-cc. beaker and bring to a volume of 250 cc. to 300 cc. The solution must have sufficient volume to prevent any crystallization of salts upon cooling. Add 10 cc. concentrated HCl. To the cold solution add drop-wise—at the same time stirring vigorously—30 cc. of a 1% water solution of "Cupferron." The cloudy brown solution is filtered. Wash with 20 per cent cold HCl until the paper is free from soluble salts, then wash with cold water. Ignite the paper in platinum crucible, cool and weigh. All results must be corrected by running blank.

\[
\text{Per cent Fe₂O₃} = \frac{\text{Weight of Residue} \times 100}{\text{Weight of Sample}}
\]

Determination of Na₂O

Weigh 5 grams from sample which has been pulverized in an agate mortar into a 250-cc. casserole. Add 20 cc. of concentrated HCl and evaporate on hot plate to dryness. Care should be taken at this point not to heat the residue too high so that a minimum amount of cake will be formed. Take up with hot water and digest until all soluble salts are in solution. This operation should be assisted by thoroughly breaking up any cake that has formed. Add 50 cc. of saturated (NH₄)₂CO₃. Let stand for half an hour and filter with suction. Transfer the filtrate to casserole, evaporate to dryness and heat until all white fumes of (NH₄)₂CO₃ are driven off (500° C. to 600° C.). Cool, take up with hot water, add 5 cc. of saturated solution of (NH₄)₂CO₃, filter and wash into a platinum dish of 125-150 cc. capacity. Evaporate to dryness and ignite at 500° C. until all ammonium salts are driven off. Cool. Dissolve in a little water, filter and wash into a 200-cc. Erlenmeyer flask. Bring volume of solution to 150 cc. Add 6 to 8 drops of saturated solution of K₂CrO₄ and titrate with standard silver nitrate solution.

Determination of Loss on Ignition

Prepare a 10 or 15 cc. platinum crucible provided with a close-fitting cover by igniting, cooling in desiccator and weighing. Weigh into it one gram of ore. Place in an electric furnace heated to 1050-1100° C. or in a flame giving that temperature for 45 minutes. Transfer to a sulphuric acid desiccator and as soon as cool weigh quickly. The loss in weight \( \times 100 = \) per cent loss on ignition.
Estimating Metallic Aluminum in Aluminum Dust

The value of aluminum dust for technical purposes depends chiefly upon the amount of metallic aluminum contained. A rapid method of estimating this constituent is therefore highly desirable. A modification of Wahl's method for the determination of metallic zinc by the reduction of ferric sulphate in cold neutral aqueous solution has been found to be rapid and simple. It does not require special skill in manipulation and gives results that are of value for comparative purposes at least.

The reduction of ferric sulphate by metallic aluminum does not take place in cold neutral aqueous solution. If, however, sufficient free sulphuric acid be added and the liquid be heated, ferric sulphate is formed proportionally to the amount of metallic aluminum present.

The results obtained with samples of known composition were usually about 5% lower than those indicated by the supposed reaction

\[ 3\text{Fe}_2\text{(SO}_4\text{)}_3 + 2\text{Al} = \text{Al}_2\text{(SO}_4\text{)}_3 + 6\text{FeSO}_4 \]  

so that for accurate results it is necessary to standardize on a sample of pure metallic aluminum or on a sample of which the aluminum contents have been exactly determined by some other method. From equation (1) above, it follows that 1 part Al = 6.182 parts Fe reduced from ferric to ferrous iron, or 1 part Fe = 0.16177 parts Al, assuming Al = 27.1 and Fe = 55.84.

The test as generally made is as follows: 100 mg. of the aluminum dust is accurately weighed and placed in a conical flask provided with stopper and Bunsen valve to reduce risk of oxidation, together with 50 cc. of a standard solution of acid ferric sulphate and the mixture heated gradually until the liquid is boiling gently. If the aluminum dissolves completely with moderate heat, it is not essential to boil. The flask is then cooled to room temperature by placing under a running tap, and 50 cc. of cold distilled water is added. The liquid is then titrated with standard permanganate.

A convenient standard solution contains 3.35 grams KMnO₄ per liter of this solution: 1 cc. = 1/17. Al, approximately.

With samples of ordinary aluminum dust the reaction takes place without visible evolution of hydrogen. When the powder contains coarse flakes or granules, some effervescence can be observed. In such cases it would seem that the titration must indicate a result too low, as the part of the Al has been dissolved according to the reaction

\[ 3\text{H}_2\text{SO}_4 + 2\text{Al} = \text{Al}_2\text{(SO}_4\text{)}_3 + 6\text{H}_2\text{O} \]  

without reducing its equivalent of ferric sulphate.

Another source of error, which acts in the opposite direction, is the presence of iron, zinc or other metal capable of reacting with ferric sulphate. For accurate work, therefore, these metals must be determined and their effect allowed for. When, however, comparative results only are required, as in checking the quality of factory products from day to day, the rapid test described is sufficient. For some purposes also metallic iron, zinc, etc., would be as effective as their equivalent of aluminum, in which case no correction ought to be applied.

The reactions in the case of iron and zinc are presumably:

\[ \text{Fe} + \text{Fe}_2\text{(SO}_4\text{)}_3 = 3\text{FeSO}_4 \]  
\[ \text{Zn} + \text{Fe}_2\text{(SO}_4\text{)}_3 = 2\text{FeSO}_4 + \text{ZnSO}_4 \]  

Assuming Al = 27.1; Fe = 55.84; Zn = 65.37, 1 part metallic Fe has the same reducing power as 0.4863 part metallic Al, and 1 part metallic Zn has the same reducing power as 0.2763 part metallic Al.

In making the ordinary tests for controlling plant operations, a sample of the purest obtainable aluminum dust is accepted as a standard. Tests are then made concurrently with the standard dust and with the sample to be examined, the result of the latter being expressed as a percentage of the standard.

1 By J. E. Clennell, Eng. and Mining Journal, May 6, 1916.

2 To 100 grams of pure ferric sulphate distilled water is added, then 250 cc. of concentrated sulphuric acid. This mixture is heated to boiling until the ferric sulphate has completely dissolved, then cooled and finally made up to a liter with distilled water.

The revised atomic weights of Al and Zn changes slightly the ratios above.—Editor.
ANTIMONY

Sb, at.wt. 121.77; sp.gr. 6.63; m.p. 630°C; b.p. 1440°C; oxides, Sb₂O₃, Sb₂O₅.

DETECTION

Hydrogen Sulphide precipitates the orange-colored sulphide of antimony from fairly strong hydrochloric acid solutions (1:4) in which several members of the group remain dissolved. Arsenic is also precipitated. The latter may be removed by boiling the solution containing the trichloride, AsCl₃, being volatile.

If antimony is already present as a sulphide, together with other elements of the hydrogen sulphide group, it may be dissolved out by treating the precipitate with sodium hydroxide, potassium hydroxide, sodium sulphide, ammonium polysulphide in solution. Antimony sulphide is reprecipitated upon acidifying the filtrate. Arsenic and tin will also be precipitated with antimony if they are present in the original precipitate. Should a separation be necessary, the precipitate is dissolved with hot concentrated hydrochloric acid, with the addition of crystals of potassium chlorate, from time to time, until the sulphides dissolve. The solution is placed in a Marsh apparatus, pure zinc added and the evolved gases passed into a neutral solution of silver nitrate. The black precipitate of silver antimonide and metallic silver are filtered off, washed free of arsenous acid, and the antimonide dissolved in strong hydrochloric acid (silver remains insoluble). The orange-colored antimony sulphide may now be precipitated by diluting the solution with water and passing in H₂S gas to saturation.

Minerals which contain antimony, when heated alone or with 3 to 4 parts of fusion mixture (K₂CO₃ and Na₂CO₃), on charcoal, yield dense white fumes, a portion of the oxide remaining as a white incrustation on the charcoal. A drop of ammonium sulphide placed upon this sublimate gives a deep orange stain.

Hydrolysis. Most of the inorganic antimony salts are decomposed by water, forming insoluble basic salts, which in turn break down to the oxide of antimony and free acid. An excess of tartaric acid prevents this precipitation.

Traces of Antimony. Nascent hydrogen liberated by the action of zinc and hydrochloric or sulphuric acid reacts upon antimony compounds with the formation of stibine. This gas produces a black stain on mercuric chloride or silver nitrate paper. Details of the procedure are given under the quantitative method for determining minute amounts of antimony.

Distinction between Antimonous and Antimonic Salts.

Chromates form with antimonous salts green chromic salts and antimonic salts.

Potassium Iodide reduces antimonic salts, free iodine being liberated.

¹ Van Nostrand's Chem. Annual, Olsen, 3d Ed.
² Cir. 35, U. S. Bureau of Standards.
Contributed by Wilfred W. Scott.
ANTIMONY

ESTIMATION

The determination of antimony is required in the evaluation of antimony ores—stibnite, Sb₂S₃; valerinite, Sb₂O₃; etc. It is generally required in the complete analysis of minerals of nickel, lead, copper, silver, in which antimony generally occurs as a sulphide. The determination is required in the analysis of Britannia metal, bearing and antifriction metals, type metal and hard lead; in the analysis of certain mordants, antimony salts, vulcanized rubber, etc. It is looked for as an undesirable impurity in certain food products.

Preparation and Solution of the Sample

In dissolving the substance containing antimony it must be remembered that metallic antimony is practically insoluble in cold dilute hydrochloric, nitric or sulphuric acid and the oxides, Sb₂O₃ or Sb₂O₅, are precipitated in strong nitric acid. The element, however, is readily soluble in hydrochloric acid containing an oxidizing agent, such as nitric acid, potassium chlorate, chlorine, bromine, etc. The oxides of antimony are soluble in hydrochloric acid and the caustic alkalis.

Solution of Sulphide Ores, Low-grade Oxides, etc.¹

0.5 to 1 gram of the finely ground ore, placed in a Kjeldahl flask, is mixed with 5 to 7 grams of granular or powdered potassium sulphate, and 10 cc. of strong sulphuric acid. About 0.5 gram of tartaric acid, or a piece of filter paper, is added to reduce arsenic and antimony and the mixture heated, gradually at first, and then with the full Bunsen flame. The heating is continued until the carbon is completely oxidized and most of the free acid driven off, leaving a clear fusion but not to complete expulsion of H₂SO₄. The melt is now cooled over the bottom and sides of the flask by gently rotating during the cooling.

About 50 cc. of dilute hydrochloric acid (1 : 1) are added and the melt dissolved by warming gently. The contents of the Kjeldahl flask are transferred to an Erlenmeyer flask, the Kjeldahl being rinsed out with 25 cc. of strong hydrochloric acid. Arsenic sulphide may now be precipitated with H₂S from the strongly acid solution, whereas antimony, etc., remain in solution. The sulphide is filtered off through a double filter, that has been moistened with hydrochloric acid (2 : 1), a platinum cone supporting the filter to prevent its breaking. The flask is rinsed out with hydrochloric acid (2 : 1). The precipitate is washed at least six times with the acid. Antimony passes into the filtrate together with other elements of the ore.

The filtrate is diluted with double its volume of warm water and then is saturated with hydrogen sulphide. Antimony sulphide, together with other elements of the Hydrogen Sulphide Group, will precipitate. These are washed with hydrogen sulphide water. Antimony sulphide may now be dissolved by addition of sodium sulphide and caustic solution (separation from Cu, Pb, Cd, Bi, etc.) (5 to 10 cc. of a mix of 60 grams Na₂S with 40 grams of NaOH diluted to 1000 cc.).

¹ Method of A. H. Low modified.
The solution containing the antimony is treated with about 2 grams of potassium sulphate and 10 cc. of strong sulphuric acid and heated as before, to destroy liberated sulphur and expel most of the free acid. The melt is dissolved in hydrochloric acid, and the antimony titrated according to one of the volumetric procedures given under "Volumetric Methods."

Norr. An insoluble residue remaining from the acid extraction of the first melt may be dissolved by fusion with sodium hydroxide and extraction of the melt with hot water. If a precipitate forms when this alkaline solution is acidified with hydrochloric acid, the presence of barium sulphate is indicated.

**Decomposition of the Ores by Fusion with Sodium Hydroxide.**

Oxides. 0.5 to 1 gram of the powdered ore is mixed with about 10 grams of sodium hydroxide and placed in a thin-walled iron crucible of 60 cc. capacity. It is advisable to fuse a portion of the alkali hydroxide in the crucible with a pinch of potassium nitrate and then add the ore mixed with the remainder of the sodium hydroxide. The covered crucible is heated until the fusion becomes homogeneous. The melt is poured out on a large nickel crucible cover or shallow dish. On cooling, the cake is detached and placed in a casserole containing water, any adhering cake on the cover, or melt remaining in the iron crucible, being dissolved with dilute hydrochloric acid and added to the sample in the casserole. About 30 to 40 cc. of strong hydrochloric acid are now added and the mixture heated (casserole covered) until the melt has dissolved. Two to 3 grams of tartaric acid having been added to keep antimony dissolved, the solution is diluted to about 300 cc., and antimony is then precipitated as the sulphide with hydrogen sulphide. The treatment of the precipitate at this stage has been given in the "Solution of Sulphide Ores."

**Sulphides.** Howard and Harrison recommend the following procedure for fusion of sulphide ores with caustic: 0.5 gram of the powdered ore is fused with a mixture of 8 grams of sodium carbonate and sodium peroxide, 1:1, in a nickel crucible. The cooled melt is dissolved with sufficient hydrochloric acid to neutralize the alkali and about 15 cc. of strong acid added in excess. The solution is diluted to 250 cc., antimony being kept in solution by addition of potassium chlorate. An aliquot portion of the solution is taken, antimony reduced by metabisulphite and titrated with iodine.

**Treatment of Speisses, Slags, Mattes, etc.** 0.5 to 2 grams of the sample is treated with 10 to 15 cc. of strong nitric acid and the mixture taken to dryness. Fifteen cc. of strong hydrochloric acid are added and the sample transferred to a 350-cc. flask, additional hydrochloric acid being used to wash out the beaker. Arsenic is precipitated from the strong acid solution as the sulphide, and antimony determined in the filtrate.

**Solution of Alloys.** Alloys are generally decomposed by treatment with mixtures of hydrochloric acid together with an oxidizing agent—nitric acid, potassium chlorate, bromine, etc. The subject is taken up in detail in the chapter on alloys.

The alloy drillings are treated with strong hydrochloric acid, a little bromine added, and the mixture heated until the alloy dissolves, additional bromine being added from time to time if necessary. The excess bromine is removed by heating gently to boiling. The higher oxides are reduced by addition of

2 H. E. Hooper's method.
sodium metabisulphite and the sulphides precipitated, as usual, with hydrogen sulphide. Arsenic may now be volatilized by boiling, and antimony titrated with iodine or potassium bromate.

**Alloys of Antimony, Lead and Tin.** 0.5 to 1 gram of the finely divided alloy is warmed with 100 cc. of strong hydrochloric acid until the action subsides. Solid iodine is now added, in small quantities at a time, until the alloy completely dissolves. The excess of iodine is now removed by boiling and the small amount of free iodine remaining neutralized with a few drops of a weak solution of sodium thiosulphate. Although tin is oxidized to the higher state, antimony is not oxidized by iodine in acid solution beyond the trivalent form. The solution may now be titrated with standard iodine in presence of an excess of sodium bicarbonate according to the procedure given under the volumetric methods.

**Hard Lead.** The method of solution and titration are given under “Potassium Bromate Method for Determining Antimony.”

**Antimony in Rubber Goods.** Three grams of the finely rasped rubber are treated in a Kjeldahl flask with 40 to 45 cc. of strong sulphuric acid. A small quantity of mercury or mercury salt is added, together with a small piece of paraffine wax. The mixture is heated until the rubber is dissolved and the black liquid begins to clear. Two to 4 grams of potassium sulphate are then added and the heating continued until a colorless or pale yellow liquid is obtained. After cooling, 1 to 2 grams of potassium metabisulphate are added and an excess of tartaric acid. The liquid is diluted sufficiently to prevent the charring of the tartaric acid and boiled until the odor of sulphurous acid has disappeared. A few cc. of dilute hydrochloric acid are added, the liquid diluted to 200 cc., filtered through a dry filter, and 195 cc. titrated either with iodine or with potassium bromate (the latter in acid solution), as described under the volumetric procedures.

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ANTIMONY

SEPARATIONS

Separation of Antimony (together with Members of the Hydrogen Sulphide Group), from Iron, Chromium, Aluminum, Cobalt, Nickel, Manganese, Zinc, the Alkaline Earths, and Alkali. The acid solution of the elements is saturated with hydrogen sulphide, the elements of the Hydrogen Sulphide Group are precipitated as sulphides, the other elements remaining in solution. Antimony sulphide may be precipitated from an hydrochloric acid solution containing 15 cc. of strong acid per 100 cc. of solution; lead and cadmium are incompletely precipitated.

Separation of Antimony (together with Arsenic and Tin), from Mercury, Copper, Bismuth, Cadmium and Lead. The sulphides of antimony, arsenic, and tin are soluble in a mixture of sodium hydroxide and sodium sulphide, the soluble sulpho salts being formed, mercury, copper, bismuth, cadmium, and lead remaining as insoluble sulphides. The following procedure may be used for alloys free from members of other groups. The acid solution is treated with 3 to 5 grams of tartaric acid and diluted slightly (more tartaric acid being added if the solution becomes turbid), then poured into 300 cc. of a mixture of sodium sulphide and sodium hydroxide (150 cc. of the mix described under "Solution of Sulphide Ores" diluted to 300 cc.). The mixture is warmed and the insoluble sulphides allowed to settle out. The solution is filtered free of the precipitate and the latter washed. The filtrate is acidified with hydrochloric or sulphuric acid and saturated with hydrogen sulphide. The sulphides of arsenic, antimony and tin are now filtered off and treated as described later.

Separation of Arsenic, Antimony, and Tin. The sulphides may be dissolved in concentrated hydrochloric acid by addition of potassium chlorate to oxidize the sulphur to sulphuric acid. This oxidation may be effected in the alkaline solution of the sulpho salts by addition of 30% hydrogen peroxide in small portions until the yellow solution is completely decolorized and then 1 to 2 cc. in excess, the solution then boiled to completely oxidize the sulphides to sulphates and to remove the excess of peroxide. The solution is then acidified, the precipitation of the sulphides and the subsequent filtration and resolution being avoided.

Removal of Arsenic. This may be accomplished by volatilizing arsenic as arsenic trichloride in a strong hydrochloric solution by boiling. If arsenic is to be determined the procedure given under the chapter on arsenic is followed, the arsenic being distilled in a current of hydrochloric acid gas. If arsenic is not desired it may be expelled by reducing the solution with sodium metabisulphite or potassium iodide and boiling. Antimony and tin remain in the concentrated acid solution.

The separation of arsenic from antimony and tin may be effected by removal of the former in a strong hydrochloric acid solution as described under the section "Preparation and Solution of the Sample," arsenic being precipitated by hydrogen sulphide, whereas antimony and tin remain in solution.

Separation of Antimony from Tin. Upon the removal of arsenic, antimony may be determined directly in the presence of tin by one of the volumetric methods given later. If a gravimetric separation is desired, it may be made according to a modification of Clark's method, which depends upon the
The fact that antimony is completely precipitated from a solution containing oxalic acid, by hydrogen sulphide, whereas tin is not. The tin must be in the stannic form, otherwise the insoluble crystalline stannous oxalate will form.

If the mixture is acid, it is neutralized with caustic and twenty times the weight of the Sn and Sb present added in excess, e.g., 2 grams potassium hydroxide in excess for every 0.1 gram of tin and antimony present in the solution. About ten times as much of tartaric acid is now added as the maximum weight of the two metals, followed by 30% hydrogen peroxide to oxidize the tin. The excess of peroxide is removed by boiling. To the slightly cooled solution a hot solution of pure oxalic acid is added, 5 grams of oxalic acid for each 0.1 gram of the mixed elements. CO$_4$+O$_2$ are evolved. The solution is boiled for about ten minutes and the volume made up to about 100 cc. Hydrogen sulphide is rapidly passed into the boiling solution until a change from a white turbidity to an orange color takes place and antimony begins to precipitate. The passage of the gas is continued for fifteen minutes, the solution diluted with hot water to a volume of 250 cc. and hydrogen sulphide passed into the boiling solution for another fifteen minutes. The flame is now removed and the H$_2$S "gasing" continued for ten minutes longer. The precipitated antimony pentasulphide is filtered off in a weighed Gooch crucible. It may be determined gravimetrically as Sb$_2$S$_5$, according to the procedure given later, by washing with 1% oxalic acid and dilute acetic acid, by decantation, the solutions being hot and saturated with hydrogen sulphide. The precipitate washed into the crucible is dried in a current of CO$_2$ at a heat of 280 to 300° and weighed as Sb$_2$S$_5$.

Tin may be determined electrolytically in the filtrate evaporated to about 150 cc., the oxalic acid being nearly neutralized with ammonia. See Electrolytic Determination of Tin.

Antimony may be separated from tin in a hot hydrochloric acid solution by addition of pure iron. The iron and tin sulphiides are dissolved in concentrated hydrochloric acid plus a few crystals of potassium chlorate. The solution should contain about 10% hydrochloric acid, more hydrochloric acid being added as the iron dissolves. Antimony is precipitated as a metal.

1 The Original procedure may be found in Chem. News, Vol. XXI, p. 124.
ANTIMONY

GRAVIMETRIC METHODS FOR THE DETERMINATION OF ANTIMONY

The accuracy and rapidity of volumetric methods for the determination of antimony leave little to be desired in the estimation of this element, so that the more tedious gravimetric methods are less frequently used. The following procedures are given in view of possible utility in certain analyses.

Determination of Antimony as the Trisulphide, $\text{Sb}_2\text{S}_3$ \(^1\)

Although hydrogen sulphide passed into a cold solution tends to precipitate $\text{Sb}_2\text{S}_3$, in hot strongly acid solutions, the lower sulphide, $\text{Sb}_2\text{S}_3$, tends to form. The higher sulphide is decomposed at 230° C. with formation of $\text{Sb}_2\text{S}_3$ and the volatilization of sulphur. A temperature of 280 to 300° C. is even more favorable for this transformation. The method takes advantage of these conditions for formation of antimony trisulphide, in which form it is weighed.

Procedure. The solution of antimony, free from arsenic, is treated in an Erlenmeyer flask with strong hydrochloric acid until the solution contains about 20% of the concentrated acid. The mixture is heated to boiling and a slow current of hydrogen sulphide is passed into the hot solution until the precipitate passes from a yellow color through an orange and finally becomes a dark red to black color. The flask is agitated gently to coagulate the precipitate, which settles in a crystalline form. The solution is diluted with an equal volume of water, washing down the walls of the flask. A slight turbidity is generally seen, due to precipitation of a small amount of antimony that remains in solution in a strong acid solution. $\text{H}_2\text{S}$ is now passed into the diluted solution until it becomes clear, thirty-five to forty minutes are usually sufficient to precipitate all of the antimony. The precipitate is transferred to a weighed Gooch crucible, washed with small portions of water containing hydrogen sulphide, and finally with pure water.

It is a common practice, at this juncture, to wash the precipitate with carbon disulphide or carbon tetrachloride to remove precipitated sulphur. Alcohol is now used, followed by ether, and the precipitate sucked dry.

The Gooch crucible is placed in a large combustion tube and heated in a current of dry, pure $\text{CO}_2$ at 130° C. for an hour. The temperature is now raised to 280 to 300° C. and the heating continued for two hours. The residue will consist of pure $\text{Sb}_2\text{S}_3$.

$$\text{Sb}_2\text{S}_3 \times 0.7142 = \text{Sb}_2 \text{ or Sb}_2\text{S}_3 \times 0.8568 = \text{Sb}_4\text{O}_3.$$  

Notes. Antimony may be determined by oxidation of the sulphide precipitate by means of fuming nitric acid. The mixture evaporated to dryness is ignited and the residue weighed as $\text{Sb}_4\text{O}_3$. The temperature of the ignition should be between 750 to 800° C. The volatile trioxide forms at a little above 950°. The procedure requires greater care than the sulphide method and possesses no advantages.

Pure carbon dioxide may be obtained from limestone placed in a Kipp generator. The gas is dried by passing it through strong sulphuric acid. It should be free from oxygen of the air. It is advisable to sweep out the air from the generator before attaching it to the combustion train. The air in the tube is swept out with carbon dioxide before heating the sample.

Property of $\text{Sb}_2\text{S}_3$, m.r., 330.61; sp.gr., 4.65; fusible and volatile; solubility, 0.000175 gram per 100 cc. $\text{H}_2\text{O}$; decomposed by hot $\text{H}_2\text{O}$; soluble in alkalies, $\text{NH}_4\text{HS}$, $\text{K}_2\text{S}$, conc. $\text{HCl}$.

\(^1\) Method of Vortmann and Metzel modified.
Electrolytic Determination of Antimony

The chief condition for the success of the electrolytic deposition of antimony in metallic form is the absence of polysulphides, since these substances prevent the element from being deposited, \(2\text{Sb} + 3\text{Na}_2\text{S}_2 = 2\text{Na}_2\text{SbS}_3\). The formation of polysulphides may be prevented during electrolysis by addition of potassium cyanide to the solution, \(\text{Na}_2\text{S}_2 + \text{KCN} = \text{Na}_2\text{S} + \text{KCN}\).

The results of this method, according to F. Heinz, are invariably 1.5 to 2% too high of the total antimony present in the solution. The sample for analysis should contain not over 0.2 gram antimony.

**Procedure.** Antimony precipitated as the sulphide is washed and then dissolved off the filter by pouring pure sodium sulphide solution (sp.gr. 1.14) over the precipitate, the solution being caught in a weighed platinum dish, with unpolished inner surface. The total volume of the solution should be not over 80 cc. (if less than this, additional \(\text{Na}_2\text{S}\) solution is added to make up to 80 cc.). Sixty cc. of water followed by 2 to 3 grams of potassium cyanide (C.P.) are added and the cyanide dissolved by stirring with the rotating anode. The solution heated to 60 to 70° is electrolyzed with a current of 1 to 1.5 amperes, E.M.F. = 2 to 3 volts. Two hours are generally sufficient to deposit all the antimony. The light-gray deposit adheres firmly upon the cathode. Without breaking the current the solution is siphoned off, while fresh water is being added, until the current ceases to flow through the liquid. The cathode is washed thoroughly with water, followed by alcohol and ether and then dried at about 80°, cooled in a desiccator and weighed.

The antimony deposits may be removed by heating with a solution of alkali polysulphide or by a mixture of equal parts of saturated solution of tartaric acid and nitric acid.

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1 Method first proposed by Parrodi and Mascuzzini, Z. anal. Chem., 18, 587 (1879), modified by Luckow, Z. anal. Chem., 19, 13 (1880), and later improved by Chassen and Reise, Berichte, 14, 1029 (1881); 17, 2474 (1884); 18, 408 (1885); 27, 2074 (1894).

VOLUMETRIC METHODS

Potassium Bromate Method for Determining Antimony

Outline. This method is of special value in determining antimony in hard lead and alloys. It was first suggested by Györy and later modified by Siedler, Nissensen and Rowell. The process is based upon the oxidation of antimony from the trivalent to the pentavalent form by potassium bromate, the following reaction taking place:

\[ \text{KBrO}_3 + 3\text{SbCl}_3 + 6\text{HCl} = 3\text{SbCl}_4 + \text{KBr} + 3\text{H}_2\text{O} \]

Standard Solutions.

Antimony Chloride Solution. Six grams of the C. P. pulverized metal are dissolved in 500 cc. of concentrated hydrochloric acid together with 100 cc. saturated bromine solution, more acid and bromine added if necessary to effect solution. After expelling the bromine by boiling, about 200 cc. concentrated hydrochloric acid are added and the whole made up to one liter. Fifty cc. = 0.3 gram antimony.

N/10 Potassium Bromate Solution. 2.82 grams of C. P. salt are dissolved in water and made up to 1 liter. Theoretically 2.7852 grams are required, but the salt invariably contains potassium bromide as an impurity. The solution is standardized against 50 cc. of the antimony chloride solution, which has been reduced with sodium sulphite according to the standard scheme. One cc. of N/10 KBrO\textsubscript{3} = 0.006 gram Sb.

Methyl Orange. 0.1 gram M. O. per 100 cc. of distilled water. The indicator should be free from sediment.

Saturated Bromine Solution. 500 cc. concentrated hydrochloric acid saturated with 70 cc. of bromine.

Procedure. Solution. One gram of the finely divided alloy is brushed into a 500-cc. beaker, 100 cc. of concentrated hydrochloric acid and 20 cc. of saturated bromine solution are added. The beaker is covered and placed on the steam bath until the metal dissolves. It may be necessary to add more bromine and acid to effect complete solution. In case the oxides of antimony and tin separate out and do not redissolve, fusion with sodium hydroxide may be necessary. Bromine is now expelled by boiling the solution down to about 40 cc.

Reduction. One hundred cc. of concentrated hydrochloric acid and 10 cc. of a fresh saturated solution of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} are added and the solution boiled down to 40 cc., on a sand bath, to expel arsenic and the excess of normal sodium sulphite. Samples high in arsenic may require a repetition of the reduction.

Titration. The cover and sides of the beaker are rinsed down with 20 cc. of hydrochloric acid (sp.gr. 1.2) followed by a few cc. of hot water and the solution heated to boiling on a sand bath. The standard bromate solution is now run into the hot solution of antimony to within 2 to 3 cc. of the end.
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point, this having been determined in a preliminary run with methyl orange added in the beginning, 4 drops of methyl orange are added and the titration completed cautiously until the color of the indicator is destroyed. If iron or copper is present the final product will appear yellow. Since the end-reaction is slow the last portion of the reagent should be added drop by drop with constant stirring.

1 cc. N/10 KBrO₃ = 0.006 gram Sh.

Notes. Since antimony chloride begins to volatilize at 195° C. and boils at 220° C. it is advisable not to carry the concentration too far while expelling arsenic.

Lead, copper, zinc, tin, silver, chromium, and sulphuric acid have no effect upon the determination, but large quantities of calcium, magnesium, and ammonium salts tend to make the results high. Low found that copper produced high results, approximately .012% too high for every 0.1% of copper present. The author (W.W.S.) finds, however, that with the procedure given above, amounts of copper as high as 15% produced no difficulty beyond a yellow coloration of the solution. With larger amounts of copper, the end-point became difficult to detect owing to the depth of this yellow color, so that in case of brass and copper alloys, the method must be modified by a procedure for removal of the copper. Lead up to 95% caused no difficulty. Iron, in amounts such as are commonly met in alloys of lead, does not interfere.

During the course of analysis antimony may be isolated as the sulphide; this is dissolved in strong hydrochloric acid, and reduced and concentrated to expel arsenic that may be present as a contamination, and the resulting solution titrated with potassium bromate as directed above.

Sources of Error. (a) Imperfect volatilization of arsenic. (b) Incomplete expulsion of SO₃. (c) Over-titration if insufficient hydrochloric acid is present.

No loss of antimony occurs at temperatures below 120° C.

Potassium Iodide Method for Determining Antimony

Procedure. To 1 gram of fine sawings or filings in a 10-oz. Erlenmeyer flask add 60 cc. of concentrated hydrochloric acid and heat on an asbestos board or on the water bath just below boiling. When hydrogen is no longer evolved, decant the liquor and wash twice with concentrated hydrochloric acid, retaining the antimony in the flask. Now dissolve the antimony by adding 15 cc. of concentrated hydrochloric acid and solid potassium chlorate, a few crystals at a time, until the antimony is in solution, the liquid being kept hot. Expel chlorine by boiling, add 50 cc. of concentrated hydrochloric acid and again bring to boiling. Cool and add 20 cc. of 20% potassium iodide solution and 1 cc. of carbon disulphide or tetrachloride. Titrate the liberated iodine with tenth-normal sodium thiosulphate. The brown color will gradually disappear from the solution and the last traces of free iodine will be collected in carbon disulphide or carbon tetrachloride, giving a pink color. When this pink color disappears the end-point has been reached.

One cc. N/10 Na₂S₂O₃ = .006 gram of Sh.

Na₂S₂O₃ is standardized against .3 gram antimony as in case of Potassium Bromate Method, the above procedure, however, being followed. Antimony must be free from copper and arsenic.

Notes. The following reversible reaction is of interest: “R” representing a trivalent metal with oxidation to pentavalent form.

\[ \text{R}_2\text{O}_7 + 2\text{I}^- + 2\text{H}_2\text{O} = 2\text{RO}_4^- + 4\text{H}^+ \]

The reaction goes to the right when an alkali is present to neutralize the free acid formed; e.g., Mohr’s process for determining arsenic by titration of the lower

1 A. H. Low, “Technical Methods of Ore Analysis.”
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oxide with iodine in presence of sodium bicarbonate. The reaction goes to the left in presence of strong acid; e.g., Weller's process for the determination of antimony in an acid solution.

The solution should not contain more than \( \frac{1}{2} \) of its volume of hydrochloric acid (sp.gr. 1.16), since too much hydrochloric acid gives high results, owing to the action of hydrochloric acid on potassium iodide. Too little acid leads to the separation of basic iodides and chlorides of antimony. The solution is best boiled down to 20% hydrochloric acid (above strength).

Stannous chloride may be used in place of thio-sulphate in titration of iodine.

\[
\text{SbCl}_4 + 2\text{KI} = \text{SbCl}_3 + 2\text{KCl} + \text{I}_2 \quad \text{and} \quad \text{I}_2 + 8\text{NaCl} + 2\text{HCl} = 8\text{NaCl}_4 + 2\text{HI}.
\]

Determination of Antimony by Oxidation with Iodine

The procedure originated by Mohr and modified by Clark, depends upon the reaction \( \text{Sb}_2\text{O}_3 + 2\text{I}_2 + 2\text{H}_2\text{O} = 2\text{Sb}_2\text{O}_5 + 4\text{HI} \).

The reaction takes place when iodine is added to a solution of antimonous salt in presence of an excess of alkali bicarbonate. In an acid solution oxidation with iodine does not go beyond \( \text{Sb}_2\text{O}_3 \).

Procedure. Solution. The sample is brought into solution by one of the procedures given under "Preparation and Solution of the Sample." Alloys of antimony, lead, and tin are treated according to directions given for this combination.

Titration. To the hydrochloric acid solution of antimony is added tartaric acid or Rochelle salts, the excess of the acid neutralized with sodium carbonate, the solution made barely acid with hydrochloric acid and a saturated solution of sodium bicarbonate added in the proportion of 10 cc. bicarbonate solution for each 0.1 gram of \( \text{Sb}_2\text{O}_3 \). Starch is added as an indicator and the solution titrated with \( \text{N}/10 \) iodine.

1 cc. \( \text{N}/10 \) iodine = 0.005 gram \( \text{Sb} \).

Note. The titration should be made immediately upon addition of the sodium salts.

Antimony in Solder Metal and Alloys with Tin and Lead

Procedure. Dissolve 2 grams of the sample of alloy in concentrated hydrochloric acid. When the metal is all in solution, add crystals of iodine until the solution is thoroughly permeated. The color at this point should be a deep purple. Boil until all of the iodine fumes have been driven out. The metallic antimony which did not go into solution in the hydrochloric acid should now be all dissolved. If it is not, add more iodine until the solution is complete. When all is in solution and the color changes to a straw yellow, cool, add a few cc. of starch solution. If a blue color appears, due to an excess of iodine, run in \( \text{N}/10 \) sodium thiosulphate solution until colorless. In case there is no blue color developed, add \( \text{N}/10 \) iodine until a faint blue appears. Now add 50 cc. of a saturated solution of Rochelle salts. Make alkaline to litmus by adding 25\% sodium hydrate solution. Then make slightly acid with HCl and finally alkaline with sodium bicarbonate. Cool and titrate with \( \text{N}/10 \) iodine.

Note. "The method gives very good results. I have checked it up when there was one-tenth of a gram known antimony present and the results were within a reasonable limit of accuracy." 1

1 Method communicated to author by Mr. R. S. Clark.
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Other Procedures

Permanganate Method

Antimonous salts may be titrated with standard potassium permanganate. The iron value for the permanganate multiplied by 1.075 or the oxalic acid (C₂H₂O₄·2H₂O) value multiplied by 0.9532, will give the antimony value.

Indirect Evolution Method

The method depends upon the evolution of H₂S from the sulphides of antimony decomposed by strong hydrochloric acid, the amount of hydrogen sulphide being the same for either Sb₂S₅ or Sb₂S₃, the following reactions taking place:

1. Sb₂S₅ + 6HCl \rightarrow 2SbCl₃ + 3H₂S.
2. Sb₂S₃ + 6HCl \rightarrow 2SbCl₅ + S₂ + 3H₂S.

The details of the method are practically the same as determination of sulphur by the evolution method in the analysis of iron and steel. See Chapter on Sulphur. The antimony sulphide precipitate is placed in the evolution flask, strong hydrochloric acid added with an equal volume of water and the evolved hydrogen sulphide absorbed in an ammoniacal solution of cadmium chloride. The precipitated cadmium sulphide is then titrated with iodine in an acid solution.

One cc. N/10 I = 0.001604 gram S, since 3S = 2Sb, therefore Sb = S × 2.499, hence, 1 cc. N/10 I = 0.00401 gram Sb.

Preparation of Standard Iodine Solution. An approximate tenth normal solution is made by dissolving 12.7 grams of commercial iodine, roughly weighed on a watch-glass, in 200 cc. of water containing about 25 grams of potassium iodide, solution being effected in a graduated liter flask. After making up to 1000 cc. with distilled water, the reagent is transferred to a dark-colored bottle, to protect it from light. It is advisable to make up 5 to 10 liters at a time for laboratories where the solution is in constant demand. After standing several hours, the reagent is standardized by running a portion from a burette into 100 cc. of tenth normal arsenious acid (see page 240) until a faint yellow color is perceptible. In presence of starch indicator a faint blue color is obtained.

100 divided by the cc. of iodine required gives the factor for a N/10 solution.

Example. If 98.5 cc. of iodine are required, 100 ÷ 98.5 = 1.0152 N/10 or .10152 normal.

Tenth normal arsenious acid solution contains 4.953 grams of As₂O₃ per liter, dissolved in sodium hydroxide and made up according to directions given on page 204. The oxide is seldom pure, so that allowance must be made for impurities. For example, the acid containing 99.56 per cent As₂O₃ would require 4.953 ÷ .9956 = 4.97 grams per liter of solution.

Commercial iodine may contain chlorine, bromine, cyanogen and water. It may be purified by repeated sublimation ("Analytical Chemistry," Treadwell and Hall, IV Ed., page 646, or "A Treatise on Quantitative Inorganic Analysis" (1913), by J. W. Mellor, page 288). There is no advantage in taking the theoretical amount of purified iodine, however, since the reagent changes in strength on standing.

Potassium iodide augments solution of iodine, which is sparingly soluble in water. The iodine may be standardized by titrating a definite volume with N/10 sodium thiosulphate. See page 240.
Determination of Antimony in Brass-Permanganate Method

Reagents. Potassium Permanganate. 0.3 g. of KMnO₄ is dissolved in water and made to 1000 cc. The reagent is standardized against 25 mg. of pure antimony that has been dissolved in 15 cc. of boiling sulphuric acid and treated as described in the procedure below, under 4 and 5.

Procedure. 1. A sample of 5 grams of brass is dissolved in a 250 cc. beaker in 25 cc. of strong nitric acid (d. 1.42), and after the action has ceased the solution is boiled to expel the oxides of nitrogen. Now 125 cc. of boiling water are added and the solution allowed to settle for an hour or more, keeping the temperature just below boiling. The tin and antimony precipitates are filtered on double 9 cm. closely woven filter papers, keeping the solution hot, and then washed with boiling water. The filtrate is discarded.

2. The papers and residue, transferred to a 350 cc. beaker, are treated with 25 cc. of strong nitric acid (d. 1.42), 5 grams of ammonium persulphate, and 15 cc. of strong sulphuric acid (d. 1.84) and boiled down to strong fumes. (The reaction may be conveniently carried out in a "copper flask" of pyrex glass.) If the solution is brown, 5 cc. of strong nitric acid are added to the cooled solution and about 1 gram additional of persulphate and the boiling to fumes repeated.

4. When the solution is colorless, it is cooled, 20 cc. of water added, together with 20 cc. strong hydrochloric acid (d. 1.20) and (cautiously) 1 gram of sodium sulphite and the SO₂ completely expelled by gentle heating for 10 minutes, or longer.

5. The solution is diluted with 200 cc. of water, and cooled under running water to 10° to 12° C., then titrated with the standard potassium permanganate solution to a decided pink color.

Notes. Antimony is precipitated quantitatively with meta-stannic acid in alloys containing a large amount of tin.

The filter paper is destroyed by ammonium persulphate and nitric acid, while tin and antimony go into solution with the sulphuric acid. Fuming nitric and sulphuric acids may be used, in place of the persulphate and nitric acid, but are not so efficient.

The solution is kept hot to prevent solution of the meta-stannic acid.

Arsenic in the alloy necessitates a correction.

In case of alloys containing considerable amounts of tin and antimony, smaller samples should be taken and stronger potassium permanganate solution than is recommended for brass.

Should the oxides remain undissolved upon fuming with sulphuric acid, a small piece of filter paper added (1/8 inch square) will effect reduction and solution of the oxides. The solution should be heated until the carbon of the filter is destroyed and the solution clears and becomes colorless.
Determination of Small Amounts of Antimony

Details of this procedure were worked out by Mr. W. Shelton, under the direction of Mr. W. C. Ferguson, chief chemist, and Mr. E. Fitzpatrick, first assistant chemist, Nichols Copper Company. The method is accurate and is of special value in determining traces of antimony in copper and in alloys. Since arsenic may also be determined a separation by distillation is necessary if the latter is present. (See pages 32, 37.)

Description of Generator

The generator consists of three separate parts:

1. Glass cap which is placed over funnel A, to hold the disc of test paper in place.
2. F-G, this part of the apparatus has two small parts: F, which is a tube of glass \( \frac{1}{4} \)" long, \( \frac{1}{4} \)" wide, fitted into a rubber tube G, \( \frac{1}{4} \)" wide which in turn is fitted into the lower part of funnel A. The part F is a very important one and care should be taken to have exactly the same size glass tubing and that distance from the top of A to top of F is \( \frac{1}{4} \)".

The entire apparatus consists of parts: A, B, C, D, E, F, G.

A. The funnel for test paper.
B. Bulb for holding cotton saturated with lead acetate to absorb any \( \text{H}_2\text{S} \) gas. Should any be present when generator is operating. Use 0.5 gms. of cotton.
C. This part extends to E, which has two purposes: No. 1. For introducing acid, \( \text{H}_2\text{O} \), the test, etc., without opening the apparatus. No. 2. As a safety valve, should the apparatus become clogged or stopped up the pressure will exert itself in this direction.
D. Upper part acts as condenser. The lower part is ground to fit the bottle No. 3.
E. This part is explained in C.

Note: All generators must be made and assembled as nearly uniform as possible to assure concordant results.

4. This figure shows the manner in which the test is placed on funnel A, Fig. 2, and how the cap, Fig. 1, fits over and holds the test paper in position.

![Fig. 1a. Fitzpatrick Apparatus for Determining Traces of Antimony.](image-url)
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Chemicals and Solutions

All chemicals and solutions must be previously tested for arsenic and antimony before using.

HCl—C.P. Conc. redistilled. As and Sb free.
HN03—C.P. Conc.
NH4OH—C.P. Conc.
Fe(NO3)3—5 lbs. to 9 liters, about 3% solution.
KClO4—use dry crystals.
FeCl3—2 lbs. to 2 liters.
ZnCl2—20 lbs. to 9 liters HCl (purified by dissolving 15 gms. zinc in 500 cc. of the above stock solution).

Zinc Shot—Wash in dilute HCl before using.
SnCl2 solution—52.5 gms. per liter.
5% HgCl2 used for test paper. 5 gr. to 100 cc. H2O. (Cut with die into circles of 14" in diameter.)
10% Pb. (CeH4O2h for cotton. 10 gms. to 100 cc. H4) 5% NH4OH for developer of test paper, 200 cc. NH4OH per liter.
1% AuCl3 solution.

Preparation of Test Paper. The paper used must be selected, when purchased, for evenness of thickness and texture in sheets of 24" x 40".
The above sheets are cut in half and saturated with a 5% HgCl2 solution—the wet sheet is then placed on a glass plate and the surplus solution is squeezed out with a 10" rubber roller, which is rolled over the paper twice. Care must be exercised to roll the paper evenly and with good pressure using the same conditions for each sheet. The sheet is now hung over a line to dry, in a warm place away from the sunlight or any influence of hydrogen sulphide. Do not dry paper in oven. When dry the paper is cut with die into pieces of 14" in diameter. Keep the dies of test paper in a dark-brown bottle and away from the light until used.

Each test paper should be made at one time to last for about 3 months.
Each new lot made should be tested with known amounts of As and Sb and compared with standards, before using. Should they not check close it is advisable to make a new set of standards from the test paper just made.

Preparation of Lead Acetate Cotton. A roll of absorbent cotton is opened and saturated with a 10% solution of lead acetate and surplus drained off, then hung on a line to dry in a warm place away from the influence of hydrogen sulphide. Do not dry in oven. When dry, place in stoppered bottle until used.

Precautions

Blank. A blank test should be run with each day's work, using all the reagents used in actual tests.
The stain obtained on test paper from blank is subtracted from the actual test.
Limits. The limits of As or Sb that can be determined by this method must be within the following figures:

As separately from .00002 gms. to .00010 gms.
Sb separately from .00002 gms. to .00015 gms.

Checks. A 10 gms. sample of standard copper known to be free from As or Sb is weighed out and known amounts of As and Sb are introduced.
Distillation. The distilling apparatus should not be used for any other tests when the As or Sb is known to be higher than the limits for this work.
Zinc. The zinc shot must be cleaned with dilute HCl and washed with distilled water each day to insure proper action in generator, and to expel any sulphide present which would spoil the test.
Generator. The presence of nitrates, chlorates, or compounds of copper interfere with generation of arsenic and stibine, so care must be exercised to have these compounds eliminated.

Large quantities of ferrous and ferric compounds interfere also in the generation of stibine. 10% solution. The small amount of Fe that gets into the test from the process of distillation is overcome by the addition of 2 cc. stannous chloride—at times more may be required.
Uniformity. Uniformity must be strictly adhered to throughout the test.
In the determination of antimony in presence of arsenic the removal of the latter is necessary. This is accomplished by distillation of AsCl₃ according to the procedure outlined on page 32, 37.

**Standard Antimony Solution and Standard Stains**

Antimony Solution. A stock solution is made up by weighing out 0.553 gms. K₂Sb₂O₄.C₂H₂O₆, which is dissolved in distilled water and made up to 2000 cc. which represents 1 cc. = .0001 g. Sb.

From the above stock solution take 100 cc. and make up to 1000 cc. this solution now equals 1 cc. = .00001 g. Sb, which is used for making the standard stains and introducing into checks.

**Outline of the Method**

Preparation of Standard Stains. Extreme care must be taken when preparing the standard stains.

Wash the generator thoroughly with distilled water, place freshly prepared lead acetate cotton in the bulb, B, No. 2, and see that the top of part F, No. 2, is exactly 1/4" from the top of part A, No. 2.

Now introduce into bottle of generator, No. 3, the required amount of As or Sb as desired and then add 50 cc. redistilled HCl, As free, 2 cc. stannous chloride solution and make up to 220 cc. with distilled water.

The disc of mercuric chloride test paper is now placed on top of funnel A, No. 2, and the glass cap, No. 1, is forced over the paper holding it in place.

Now introduce 15 gms. metallic zinc shot and place the No. 2 section with No. 1 attached into the No. 3 or bottle of generator. The apparatus now being assembled, observe that the apparatus is fitted together tightly, because as soon as the zinc is introduced, Arsine and Stibine is generated immediately. Place the generator into the water bath to maintain constant temperature which should be about 70° F. Allow the generator to operate for 1 hour.

The glass cap, No. 1, is now removed and the test paper is developed in a No. 2 beaker with 5% NH₄OH solution for three minutes, then washed 5 times with distilled water. The test paper is now toned with a 1% AuCl₃ solution by allowing the test paper to remain in solution for five minutes. The test paper will now have a violet or purple stain, the intensity depending on the amount of As or Sb introduced. Wash the paper 5 times with distilled water and preserve in 50 cc. glass stoppered bottles containing about 5 cc. water. Keep bottles in dark place, because the stains darken on exposure to light.

Duplicate tests are made, finally selecting of two the one which is the most uniform.

The stains are made to represent the following amounts:

<table>
<thead>
<tr>
<th>Sb</th>
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<tr>
<td>6</td>
<td>.00012</td>
</tr>
<tr>
<td>7</td>
<td>.00014</td>
</tr>
<tr>
<td>8</td>
<td>.00016</td>
</tr>
</tbody>
</table>
Procedure for Refined Copper

A blank is run with all tests. Weigh 10 gms. of the shot or drilled sample into a No. 3 beaker. Add 50 cc. Conc. HNO₃, C.P. As free, let stand covered with watch glass until the action has subsided. Now place beaker on wire gauze over Bunsen flame and heat until all the copper is dissolved.

Remove from flame, dilute to 150 cc. with distilled water (if too basic add a few drops of HCl to clear the solution). Add 2 cc. ferric nitrate solution, stir, then make ammoniacal by adding C.P. ammonium hydrate (As free). Bring to boiling. Remove from flame and filter through a 15 cm. fluted Perfection filter paper. Immediately wash the filter paper free from copper compounds with hot water, using dilute ammonia where necessary to wash out any copper salts that have crystallized.

The precipitate (which contains both As and Sb) is dissolved off the filter with hot dilute hydrochloric acid, by means of a wash bottle into a No. 4 casserole. Wash the filter three times with hot water.

Add a pinch of KClO₃ to the casserole, cover with watch glass, place the casserole in an asbestos cut out over Bunsen burner and boil the contents down to 10 cc., taking care that it does not roast on the sides.

Distillation. Transfer the contents of the casserole to the distilling apparatus. Add 20 cc. ferrous chloride and 20 cc. zinc chloride solution, and distill until the contents of flask begins to froth. Now add, drop at a time, 35 cc. HCl, through the dropping funnel which is connected to flask. Distill until all the HCl is out of the funnel and out of the flask.

The distillate is received in a No. 4 beaker having 40 cc. H₂O in which both the As and Sb is contained.

The above distillate is now transferred and washed from the beaker into the special designed generator. Add 2 cc. stannous chloride which insure a complete reduction of any ferric compounds present. Dilute the contents of generator to 220 cc. Place disc of HgCl₂ test paper on the funnel top, then put on cap to hold in place. Add 15 gms. metallic zinc or 1 No. 6 porcelain spoonful. Take care that the generating apparatus is properly closed, then place into water bath to maintain constant temperature which should be about 70° F. The apparatus is allowed to operate for one hour during which time the arsenic and stibine generated shall effect the HgCl₂ test paper, causing a yellow or orange colored spot which varies in color and size according to the amount of As and Sb present. The paper is now removed from the apparatus and developed in a No. 2 beaker containing 5% ammonium hydrate solution for three minutes. The color of the spot now changes to a brownish black. Wash test paper five times with distilled water. Now cover the test paper with 10 cc. of 1% gold chloride solution which tones the color of the spot to a violet or purple hue that fixes it so comparison can be made with the standard stains or spots to determine the amount of arsenic or antimony in the sample.
Determination of Antimony in Tartar Emetic

Iodine in the presence of sodium bicarbonate oxidizes trivalent antimony to the pentavalent form as shown by the reaction:

\[
\text{K(SbO)}\text{C}_8\text{H}_4\text{O}_4 + 6\text{NaHCO}_3 + \text{I}_2 \\
= \text{Na}_3\text{SbO}_4 + \text{KNaC}_4\text{H}_4\text{O}_4 + 2\text{NaI} + \text{H}_2\text{O} + 6\text{CO}_2.
\]

Procedure. 10 grams of tartar emetic are dissolved in water, the solution diluted to 500 cc. and 20 cc. taken for analysis. This is diluted to 100 cc. 25 cc. of 2 per cent sodium bicarbonate are added and the mixture titrated with \(\text{N/10 iodine reagent}\).

1 cc. \(\text{N/10 I} = 0.010617\) g. K(SbO)C\(_8\)H\(_4\)O\(_4\)·\(\frac{1}{2}\)H\(_2\)O
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\[ \text{As, at. wt. 74.90—cryst. sp.gr. 5.73 m.p. 850 b.p. subl. 554° amorp. 4.72 .... < 360°} \]

\text{Oxides, As}_2\text{O}_3, \text{As}_2\text{O}_5.1

DETECTION

Hydrogen sulphide precipitates the yellow sulphide of arsenic, As₂S₅, when passed into its solution made strongly acid with hydrochloric acid. If the solution contains more than 25% hydrochloric acid, (sp.gr. 1.126) the other members of the hydrogen sulphide group do not interfere, as they are not precipitated from strong acid solutions by hydrogen sulphide. Arsenic sulphide is soluble in alkaline carbonates. (Antimony sulphide, Sb₂S₅, reddish yellow, is insoluble in alkaline carbonates.)

Voluty of the chloride, AsCl₅, is a means of separation and distinction of arsenic. Details of the procedure are given under "Separations." The distillate may be tested for arsenic as directed above.

Traces of arsenic may be detected by either the Gutzzeit or Marsh test for arsenic. Directions for the Gutzzeit test are given at the close of the volumetric procedures.

Distinction between Arsenates and Arsenites. Magnesia mixture precipitates white, MgNH₄AsO₄, when added to ammonical solutions containing arsenates, but it produces no precipitate with arsenites.

Red silver arsenate and yellow silver arsenite are precipitated from neutral solutions by ammonium silver nitrate. An arsenate gives a yellow precipitate with ammonium molybdate solution.

ESTIMATION

The determination of arsenic is required in the valuation of native arsenic, white arsenic, As₂O₅; ores of arsenic—orpiment, As₂S₅; realgar, As₂S₃; pyrargyrite, As₂S₅; arsenopyrite, or mispickel, Fe₃As₅; cobaltite or cobalt glance, Co₂As₅; smaltite, Co₂As₅; niccolite, Ni₃As. The substance is estimated in copper ores, in spess, regulus; in iron precipitates (basic arsenate). It is determined in paint pigments, Scheel's green, etc. The element is determined in shot alloy and in many metals. It is estimated in germicides, disinfectants, and insecticides—Paris green, lead arsenate, zinc arsenite. Traces are looked for in food products and in substances where its presence is not desired.

Preparation and Solution of the Sample

In dissolving arsenic compounds it will be recalled that the oxide, As₂O₅, is not readily acted upon by dilute acids—hydrochloric or sulphuric. The compound is soluble, however, in alkaline hydroxides and carbonates. Nitric

\[ ^1 \text{Van Nostrand's Chem. Annual—O6en—3d Ed.} \]

\[ \text{Chapter contributed by Wilfred W. Scott.} \]

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acid oxidizes As₂O₃ to the higher oxide, As₂O₅, which is soluble in water. The sulphides As₂S₃ and As₂S₅ are practically insoluble in hydrochloric or sulphuric acids, but are dissolved by the fixed alkalies and alkali sulphides. All arsenites, with the exception of the alkali arsenites, require acids to effect solution.

Pyrites Ore and Arseno-pyrites. The amount of the sample may vary from 1 to 20 grams, according to the arsenic content. The finely ground sample in a large casserole is oxidized by adding 10 to 50 cc. of bromine solution (75 cc. KBr + 50 cc. liquid Br₂ + 450 cc. H₂O) covering and allowing to stand for fifteen minutes, then 20 to 50 cc. of strong nitric acid are added in three or four portions, allowing the action to subside upon each addition. The glass cover is raised by means of riddlers, and the sample evaporated to dryness on the steam bath; 10 to 25 cc. of hydrochloric acid are now added and the sample again taken to dryness. Again 10 to 25 cc. of hydrochloric acid are added and the sample taken to dryness. Finally 25 cc. of hydrochloric acid and 75 cc. of water are added, and the mixture digested over a low flame until all the gangue, except the silica, is dissolved. The solution is now examined for arsenic by distillation of the arsenic after reduction, the distillate being titrated with standard iodine solution according to directions given later.

Arsenous Oxide. The sample may be dissolved in caustic soda, the solution neutralized with hydrochloric acid, and the resulting sample titrated with iodine.

Fusion Method. One gram of the finely powdered mineral is fused in a nickel crucible with about 10 grams of a mixture of potassium carbonate and nitrate, 1 : 1, and the melt extracted with hot water. Two hundred cc. of a saturated solution of SO₂ is added to the filtrate to reduce the arsenic, the excess of SO₂ then expelled by boiling, the solution diluted with dilute sulphuric acid, and arsenic determined in the filtrate.

Arsenic in Sulphuric Acid. Arsenous acid may be titrated directly with iodine in a 20- to 50-gram sample, which has been diluted to 200 to 300 cc. with water and nearly neutralized with ammonium hydroxide and then an excess of sodium acid carbonate added, followed by the iodine titration.

Arsenic in Sulphuric Acid. Twenty-five cc. of the acid containing about 0.1% arsenic or a larger volume in case the percentage of arsenic is less than 0.1% As₂O₃ (the sp.gr. of the acid being known) are measured out into a short-necked Kjeldahl flask. About half a gram of tartaric acid and 2 grams of fused, arsenic-free potassium bisulphate are added and the acid heated over a low flame until the liberated carbon is completely oxidized and the acid again becomes clear, e.g., a pale straw color. It is not advisable to heat to violent fuming, as a loss of arsenic is then apt to occur. The cooled acid is poured into about 300 cc. of water, the excess acid nearly neutralized with ammonia, bicarbonate of soda added in excess and the arsenic acid titrated with standard iodine. Total arsenic as As₂O₃ minus arsenous arsenic as AsO₃ = arsenic arsenic in terms of As₂O₅. This result multiplied by 1.1616 = As₂O₅.

Arsenic in Hydrochloric Acid. The arsenic in 20 to 100 cc. sample is reduced by ferrous chloride, the arsenic distilled according to directions given later, and the distillate titrated with iodine.

1 0.1% arsenic determined on a 20-gram sample.

2 SO₃ should be expelled by heat or by a current of air before treating with the alkali.
Artsenic in Organic Matter.\(^1\) 0.2 to 0.5 gram of the sample finely powdered is oxidized by mixing with 10 to 15 grams of sodium carbonate and sodium peroxide, 1 : 1, in a nickel crucible, a portion of the fusion mixture being spread over the charge. After heating gently for fifteen minutes, the fusion is completed by heating to dull redness for five minutes longer. The contents of the crucible are rinsed into an Erlenmeyer flask after extraction with water, and the solution made acid with dilute sulphuric acid, 1 : 1. The mixture is boiled down to 100 cc., 1 to 2 grams of potassium iodide added and the solution further concentrated to about 40 cc. Iodine is reduced with sulphurous acid or thiosulphate, the solution diluted with hot water and saturated with hydrogen sulphide. Arsenous sulphide is filtered off, washed, dissolved in 15 to 20 cc. of half-normal sodium hydroxide and 30 cc. of hydrogen peroxide (30%) solution added, and the solution boiled. About 12 cc. of dilute sulphuric acid, 1 : 1, are added, together with 1 to 2 grams of potassium iodide, the solution concentrated to 40 cc. and free iodine reduced with thiosulphate as before. Arsenic is now titrated, with standard iodine, upon neutralization of the free acid with sodium hydroxide and sodium acid carbonate.

Lead Arsenate. Ten grams of the thoroughly mixed paste or 5 grams of the powder are dissolved by treating with 25 cc. of 10% hot sodium hydroxide solution, and diluted to 250 cc. An aliquot part, 50 cc. (=2 grams paste and 1 gram powder) is placed in an Erlenmeyer flask and 20 cc. of dilute sulphuric acid, 1 : 1, added, and the solution diluted to 150 cc. About 3 grams of solid potassium iodide are added and the solution boiled down to about 50 cc. (not to fumes). The liquor will be colored yellow by free iodine. Tenth normal sodium thiosulphate is added drop by drop until the free iodine is neutralized (solution loses its yellow color), it is now diluted to about 250 cc. and the free acid neutralized by ammonium hydroxide (methyl orange indicator), then made slightly acid with dilute sulphuric acid, and an excess of bichromate of soda added. The arsenic is titrated with standard iodine.

The arsenic may be reduced by placing the 50-cc. sample in a Kjeldahl flask, adding 25 cc. of strong sulphuric acid (1.84 sp.gr.), \(\frac{1}{2}\) gram tartaric acid and 2 grams acid potassium sulphate, KHSO\(_4\), and digesting over a strong flame until the organic matter is destroyed and the solution is a pale yellow color. The cooled acid is diluted and neutralized, etc., as directed above.

Water-soluble Arsenic in Insecticides. Rapid Works Test. Two grams of the paste is digested with 1000 cc. of water at 90° C, for five minutes, in a graduated 1000-cc. flask. An aliquot portion is filtered and the arsenic determined by the Gutzzeit method.

Water-soluble arsenite may be titrated directly with iodine in presence of sodium bichromate.

Zinc Arsenite. About 5 grams of powder or 10 grams of paste are taken and dissolved in a warm solution containing 300 cc. of water and 25 cc. of strong hydrochloric acid. The cooled solution is diluted to 500 cc. and 100-cc. portions taken for analysis. The acid is partly neutralized with ammonium hydroxide and 50 cc. of a saturated solution of ammonium oxalate added (to prevent precipitation of the zinc as Zn(O\(_4\)), and an excess of sodium bichromate, Na\(_2\)H\(_2\)O\(_4\). Arsenic is now titrated with iodine as directed later.

Soluble Arsenic in Zinc Arsenite. One gram sample is rubbed into an

\(^1\) Organic matter may be destroyed by heating the substance on addition of 10% \(\text{H}_2\text{SO}_4\) and solid \((\text{NH}_4)_\text{2}\text{SO}_4\).
Emulsion with several portions of water until the whole is in suspension. The cloudy liquor is diluted to 1000 cc. and a portion filtered through a ½-in. asbestos mat on a perforated plate, the asbestos being covered with a layer of filter paper. The first 50 cc. are rejected. One hundred cc. of the clear filtrate (= 0.1 gram) is treated with 10 cc. of strong sulphuric acid, 0.05 gram, Fe₂O₃ (use ferric ammonium sulphate) and ½ cc. of 80% stannous chloride solution and heated until colorless. Arsenic is now determined by the Gutmüh method, using the larger-sized apparatus.

**Arsenic Acid, Alkali Arsenates, etc.** The sample is dissolved in 20 to 25 cc. of dilute sulphuric acid, 1:1, in an Erlenmeyer flask, and reduced by addition of 3 to 5 grams of potassium iodide, the action being hastened by placing the mixture on a steam bath. The iodine liberated is exactly neutralized with thiosulphate and the arsenous acid titrated with iodine according to the procedure given later.

**Arsenic in Steel, Iron, Pig Iron, etc.** One to 50 grams of steel, etc., may be treated according to the scheme for pyrites. If a large sample is taken, it is advisable to treat it in a 500-cc. flask, connected with a second flask containing bromine, to guard against loss of arsenic by volatilization. When the sample has dissolved it is taken to dryness (the bromine in the second flask being combined with it) and treated as directed in pyrites. Arsenic chloride, AsCl₅, is transferred to the distilling flask with strong hydrochloric acid, and arsenic separated from the iron by volatilization of reduced chloride according to the procedure given below.

**Arsenic in Copper.** Arsenic is precipitated with iron by the basic acetate method, and thus freed from copper. Details of procedure are given under the determination of impurities in copper in the chapter on the subject.

Norrer. In the decomposition of the sample Low recommends the addition of a little sodium sulphide to ores containing oxides. To prevent loss of arsenic during the treatment with H₂S he uses a flask with a two-hole rubber stopper through which passes an inlet tube reaching to the bottom of the flask and an exit tube, the latter a thistle tube containing a little absorbent cotton soaked with dilute NaOH to retain any arsenic escaping from the flask.

Iron sulphate dissolves slowly, so that if much is present in the ore time must be allowed for this to dissolve.

As arsenous chloride is volatile, great care must be exercised in heating solutions containing HCl and arsenous salts as a loss will occur. B.p. 113.9°.

The ore may be brought into solution by fusion with a mixture of sodium carbonate, potassium nitrate and zinc oxide, 1:1:2. The fusion being made in a platinum dish. The potassium iodide procedure may be followed for reduction of arsenic. (See Lead Arsenate.)
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SEPARATIONS

Isolation of Arsenic by Distillation as Arsenous Chloride

By this method arsenic may be separated from antimony, tin, and from other heavy metals. It is of special value in the direct determination of arsenic in iron ores, copper ores, and like products and has a wide application. The procedure depends upon the volatility of arsenous chloride at temperatures lower than the other heavy metals. In a current of HCl gas, arsenous chloride begins to volatilize below 108° C., and is actively volatile at 120° C.; antimony starts to volatilize at 125° C., but is not actively volatile until a temperature of 180° has been reached. The boiling-point of arsenous chloride, AsCl₃, is 130.2°; antimony trichloride, SnCl₃, is 223.5°; and that of stannous chloride, SnCl₂, is over 603°; other chlorides having still higher boiling-points. Tin in its higher form, SnCl₄, is readily volatile, boiling-point is 114° C., so that it is necessary to have it in its divalent form to effect a separation from arsenic. When heavy metals are present in the residue running from the arsenic distillate, or when zinc chloride is added to raise the boiling-point, antimony may also be separated by distillation by carrying the solution to near dryness, adding concentrated HCl by means of a separatory funnel, drop by drop, during further distillation of the concentrate. Arsenic may be determined in the distillate (first portions) either gravimetrically or volumetrically.

Procedure. If arsenic is present as arsenic chloride, as prepared in the method for solution of iron ores, the sample may be transferred directly to the distillation flask by means of concentrated, arsenic-free hydrochloric acid. If a preliminary separation of other metals has been made and arsenic is present (along with antimony and tin) as a sulphide, it is oxidized by addition of concentrated HCl and sufficient potassium chloride to cause solution and oxidation of free sulphur, and the chlorate decomposed by evaporation to dryness; or if preferred, by evaporation of the alkaline solution to dryness, oxidation with fuming nitric and re-evaporation to dryness to expel the nitric acid. The residue is taken up with hydrochloric acid and washed into the flask with strong hydrochloric acid as directed above.

Distillation. The sample, in a half-liter distilling flask (Fig. 1, "5") is made up to about 150 cc. with concentrated hydrochloric acid and about 5 grams of cuprous chloride, Cu₂Cl₄, are added. The apparatus is connected up as shown in the illustration, Fig. 1. The end of the condenser dips into 400 cc. of cold water in a large beaker (1 liter) or flask ("4"). The solution is cooled by placing it in ice-water or cold running water. The sample is saturated with dry hydrogen chloride gas generated by dropping concentrated sulphuric acid into strong hydrochloric acid ("3") and passing the gas through

sulphuric acid (sp.gr. 1.84) as shown in cut. When the point of saturation is reached the gas begins to bubble through the solution instead of being absorbed by it. When this occurs, heat is applied and the solution brought to boiling, the current of HCl gas being continued. At a temperature of 108 to 110° C. the first 100 cc. will contain practically all of the arsenic. About

Fig. 1 — Apparatus for the Distillation of Arsenous Acid.

two-thirds of the solution is distilled off. It is advisable to add more hydrochloric acid to the residue in the flask, together with cuprous chloride, and repeat the distillation into a fresh lot of water. This may be done during the estimation of arsenic in the first distillate.

Arsenic may be determined in the distillates either gravimetrically or volumetrically. The volumetric procedures for arsenic, in this isolated form, are generally to be preferred, since they are both rapid and accurate. For amounts over 0.5%, arsenic, the iodine method is recommended, for smaller amounts (arsenic in crude copper), precipitation with silver nitrate and titration of the silver salt is best. Exceedingly small amounts are best determined by the Gutzeit method, page 46.

In place of the large bottle shown, a smaller wash bottle may be used filled with concentrated hydrochloric acid, the bottle contains an inlet tube dipping to the bottom and an exit tube connected to the distillation flask containing the arsenic. The receiving flask is connected with an aspirator and air drawn through the system. HCl is swept into the distillation flask during the arsenic distillation, keeping the solution concentrated with HCl gas.
The inlet funnel is filled about half full with hydrochloric acid (sp.gr. 1.2). The outlet of the condenser tube is caused to dip just beneath the surface of 100 cc. of distilled water, containing a lump of ice. The solution in the distillation flask is heated to boiling; concentrated hydrochloric acid is introduced through the funnel drop by drop at the rate sufficient to replace the evaporation. All the arsenic usually distils over in half an hour. At this time the beaker holding the condensate is replaced by another with 100 cc. of water. And the distillation continued about 15 minutes. Test this distillate to ascertain whether any arsenic is present. The arsenous chloride thus obtained is titrated with standard iodine according to the procedure described on page 44. The free HCl is first neutralized with a fixed alkali and then made faintly acid with HCl. Sodium bicarbonate is now added in excess and the titration with iodine made according to the customary procedure.

Commercial hydrochloric acid invariably contains arsenic, so this must be purified by redistillation in presence of an oxidizing agent to oxidize the arsenic to the non-volatile arsenic pentachloride, AsCl₅, form, (Fig. 5) or by treatment with H₂S and filtration. A blank run should be made on the reagents used, especially when traces of arsenic are to be determined.
Cuprous Chloride. This is used to reduce arsenic. At least 2 grams CuCl should be used per each gram of iron present. In the distillation, HCl gas (generated in a flask containing strong sulphuric acid by allowing hydrochloric acid to flow in through a thistle tube, drop by drop) may be passed into the solution containing the arsenic, in place of adding strong hydrochloric acid.

Hydrazine Distillation Method. Weigh a suitable amount of sample into a 275 cc. Pyrex sulphur flask. Treat with a small amount of HNO₃ (5-10 cc.), and a pinch of potassium chlorate. Take to dryness. Add 3-5 cc. HCl and take again to dryness. Add 20 cc. 1-1 HCl and boil several minutes. Filter, if insoluble is appreciable, into another flask, and wash. Add 30 cc. HCl, \frac{1}{2} gm. NaBr and \frac{1}{2} gm. hydrazine sulphate, (NH₃)₂SO₄. Set the flask on a small electric plate, and at the same time, insert in the flask a two-hole stopper, in one hole of which is a separatory funnel, and in the other a glass tube leading to an 8-in. Allihn condenser, set vertically. The lower end of the condenser is immersed in cold water contained in a No. 3 beaker, which sits on a block of wood. Have the cock of the funnel open. Have a good stream of cold water running through the jacket of the condenser.

Distill until the volume in the flask has been reduced to 20 cc. Close the cock of the funnel, add 20 cc. HCl, remove the block of wood from underneath the beaker and hold the beaker in one hand. Holding the beaker at such a height that no liquid may be sucked back into the flask, open the funnel cock and let the acid run into the flask. Now, place the block under the beaker, and distill until liquid in flask is again reduced to 20 cc.

Remove the flask from the plate, and disconnect it from the condenser. Wash the condenser, allowing washings to run into the distillate. Remove the beaker from under the condenser. Add 8-10 drops of methyl orange (1 gm. of salt per liter of water). Make the solution alkaline with NH₄OH, then just acid with HCl. Cool. Add 10 gm. NaHCO₃ and 10 cc. starch solution (10 gm. soluble starch boiled in a liter of water; cooled).

Titrated with iodine solution, one cc. of which equals about .005 gm. As₂O₃. Subtract a blank determination which amounts to .4 or .5 cc.
Separation of Arsenic from Antimony and Tin by Precipitation as Sulphide in a Strong Hydrochloric Acid Solution

This procedure for isolation of arsenic depends upon the insolubility of the sulphide of arsenic in strong hydrochloric acid, whereas that of antimony dissolves. The sulphide of tin is also soluble.

Procedure. The metals present in their lower conditions of oxidation are precipitated as sulphides in presence of dilute hydrochloric acid (5% solution) to free them from subsequent groups (Fe, Al, Cu, etc.). The soluble members of the hydrogen sulphide group are now dissolved and separated from copper, lead, etc., by caustic as follows: The greater part of the washed precipitate is transferred to a small cassepole, that remaining on the filter paper is dissolved off by adding to it a little hot dilute potash solution, catching the filtrate in the cassepole. About 5 grams weight of solid potassium hydroxide or sodium hydroxide is added to the precipitate. Arsenic, antimony, and tin sulphones dissolve. The solution is filtered if a residue remains, and the filter washed. This preliminary treatment is omitted if alkaline earths and alkalies are the only contaminating elements present.

The cassepole containing the sample is covered and placed on a steam bath. Chlorine is now conducted into the warm solution for an hour, whereby the alkali is decomposed and antimony and arsenic oxidized to their higher state. Sufficient hydrochloric acid is added to decompose the chlorate formed, and the uncovered solution evaporated to half its volume. An equal volume of hydrochloric acid is added and the evaporation repeated, to expel the last trace of chlorine. The acid solution is washed into an Erlenmeyer flask, cooled by ice to 0°C. and two volumes of cooled, concentrated, hydrochloric acid added. H₂S gas is rapidly passed into this solution for an hour and a half. The flask is now stoppered and placed in boiling water for an hour. The yellow arsenic sulphide, As₂S₃, is filtered through a weighed Gooch crucible, washed with hydrochloric acid, 2:1, until free from antimony, i.e., the washing upon dilution remains clear. The residue is now washed with water, followed by alcohol, and may be dried and weighed as As₂S₃ or determined volumetrically. Antimony and tin are determined in the filtrate. McCay recommends washing As₂S₃ with alcohol, CS₂, and finally alcohol.¹

The sulphide may be dissolved in concentrated sulphuric acid by heating to sulphuric acid fumes and until the solution becomes clear. No arsenic is lost, provided the heating is not unduly prolonged. Fifteen to twenty-five minutes is generally sufficient to dissolve the sulphide and expel SO₃, etc. The acid may be neutralized with ammonia or caustic, made again barely acid and then alkaline with bicarbonate of soda, and arsenous acid titrated with iodine.²

² J. and H. S. Pattinson, Jour. Soc. Chem. Ind., 1898, p. 211.
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GRAVIMETRIC METHODS FOR DETERMINATION OF ARSENIC

As in the case of antimony, the accuracy and rapidity of the volumetric methods for the determination of arsenic make these generally preferable to the more tedious gravimetric methods. The following methods, however, are of value in certain analytical procedures.

Determination of Arsenic as the Trisulphide, $\text{As}_2\text{S}_3$

Arsenic acid and arsenates should be reduced to the arsenous form before precipitation as the sulphide. The procedure is especially adapted to the isolation of arsenic from other elements, when this substance is present in the solution in appreciable quantities, advantage being taken of the extreme difficulty with which arsenous sulphide, $\text{AsS}_3$, dissolves in hydrochloric acid solution.

**Procedure.** The solution containing arsenic in the arsenous form is made strongly acid with hydrochloric acid and hydrogen sulphide passed into the cold solution to complete saturation. The hydrogen sulphide pressure generator is recommended for this treatment. Figs. 3 and 4. The precipitate is filtered into a weighed Gooch crucible (previously dried at 105° C.), the compound dried at 105° C. to constant weight and weighed as $\text{AsS}_3$.

**Factors.**

- $\text{AsS}_3 \times 0.6091 = \text{grams As}$
- $\text{AsS}_3 \times 0.8042 = \text{grams As}_2\text{O}_3$
- $\text{As}_2\text{O}_3 \times 1.1616 = \text{grams As}_4\text{O}_6$
- $\text{As}_4\text{O}_6 \times 1.3134 = \text{grams HA}_2\text{AsO}_4 \cdot \frac{3}{4}\text{H}_2\text{O}$
- $\text{AsS}_3 \times 1.2906 = \text{grams As}_2\text{S}_3$

**Note.** Arsenic may also be determined as arsenic sulphide by passing a rapid stream of $\text{H}_2\text{S}$ into a cooled solution of arsenic acid containing at least two parts of concentrated hydrochloric acid for each part of water present in the solution.

Determination of Arsenic as Magnesium Pyroarsenate

The method worked out by Levol depends upon the precipitation of arsenic as $\text{MgNH}_2\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, when magnesia mixture is added to an ammoniacal solution of the arsenate. Although 600 parts of water dissolve 1 part of the salt, it is practically insoluble in a 2½ per cent ammonia solution, 1 part of the anhydrous salt requiring 24.55 parts of the ammonia water according to Virgili. The compound loses $\frac{3}{4}$ molecules of water at 102° C. and all of the water when strongly ignited, forming in presence of oxygen the stable magnesium pyroarsenate, $\text{MgAs}_2\text{O}_6$, in which form arsenic is determined.

**Procedure.** The solution containing the arsenic, in the form of arsenate, and having a volume not exceeding 100 cc. per 0.1 gram arsenic present, is treated with 5 cc. of concentrated hydrochloric acid, added, with constant stirring, drop by drop. Ten cc. of magnesia mixture are added (Reagent = 55 grams $\text{MgCl}_2 + 70$ grams $\text{NH}_4\text{Cl} + 650$ cc. $\text{H}_2\text{O}$ and made up to 1000 cc. with $\text{NH}_4\text{OH}$, sp.gr. 0.96), for each 0.1 gram of arsenic present. Ammonia solution (sp.gr. 0.96) is added from a burette, with stirring, until the mixture is neutralized (a red color imparted to the solution in presence of phenolphthalein indicator), and

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then ammonia added in excess equal to one-third the volume of the neutralized solution. The precipitate is allowed to settle at least twelve hours and is then filtered into a weighed Gooch crucible and washed with 2.5% ammonia until free from chloride. After draining as completely as possible by suction the precipitate is dried at 100° and then heated to a dull red heat (400 to 500° C.), preferably in an electric oven, until free of ammonia. The temperature is then raised to a bright red heat (800 to 900° C.) for about ten minutes, the crucible then cooled in a desiccator and the residue weighed as Mg₃As₂O₇.

Factors, Mg₃As₂O₇×0.4827 = As₂, or ×0.6373 = As₂O₅, or ×0.7403 = As₂O₃, or ×0.7925 = As₂S₅.

Fig. 3.—Scott’s Hydrogen Sulphide Generator.
Notes. In place of an electric furnace the Gooch crucible may be placed in a larger non-perforated crucible, the bottom of the Gooch being 2–3 mm. above the bottom of the outer crucible. The product may now be heated in presence of a current of oxygen passed through a perforation in the covering lid of the Gooch, or

![Diagram of the hydrogen sulphide generator.]

**Fig. 4.**—Ursach's Hydrogen Sulphide Generator.

The apparatus designed by Ursach (Chem. Zeit. 1910, 34, 1088; The Analyst, 1910, 35, 558), shown in Fig. 2, enables a constant supply of gas and its saturated aqueous solution to be obtained. The bottle IV is charged with hydrochloric acid, and iron sulphide is placed in III. The hydrogen sulphide is passed through the water in II until a saturated solution is obtained. Water is placed in I and II. If gas is required the taps A and B are opened and H₂S drawn from A. Hydrogen sulphide-water is obtained by opening the pinch cock C of the burette, the liquid drawn off being simultaneously replaced from the vessel II. The container is made of dark-colored glass to protect the hydrogen sulphide-water from light. Water may be drawn into II, when required by opening the pinch cock leading to the bottle I.

In place of the oxygen, a thin layer of powdered NH₄NO₃ may be placed on the arsenate residue and the heat gradually applied until the outer crucible attains a light red glow.
VOLUMETRIC METHODS FOR THE DETERMINATION OF ARSENIC

Oxidation of the Arsenous Acid with Standard Iodine

This procedure is applicable for the determination of arsenic in acids, after reduction of arsenic to its arsenuous form, for valuation of arsenic in the trioxide, for determination of arsenic isolated by distillation as arsenuous chloride, for arsenic in arsenites and reduced arsenates in insecticides, etc. The method depends upon the reaction: \( \text{As}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{I}_2 = \text{As}_2\text{O}_4 + 4\text{HI} \). The liberated hydriodic acid is neutralized by sodium bicarbonate. The trace of excess iodine is detected by means of starch, a blue color being produced.

Procedure. If the solution is acid, it is neutralized by sodium or potassium hydroxide or carbonate (phenolphthalein indicator) then made slightly acid. If the solution is alkaline, it is made slightly acid. Two to 3 grams of sodium bicarbonate are added together with starch indicator and the solution titrated with tenth normal iodine solution, the iodine being added cautiously from a burette until a permanent blue color develops.

One cc. N/10 iodine = 0.00375 gram As, or 0.004948 gram As$_2$O$_3$.

\[
\text{As}_2\text{O}_3 \times 1.1016 = \text{As}_2\text{O}_4. \quad \text{As} \times 1.3201 = \text{As}_2\text{O}_4 \quad \text{or} \quad \times 1.5336 = \text{As}_2\text{O}_3.
\]

Potassium Iodate Method for Determining Arsenic

The method is specially applicable to determining arsenic in insecticides. The reaction is represented as follows:

\[
\text{As}_2\text{O}_3 + \text{KIO}_3 + 2\text{HCl} = \text{As}_2\text{O}_5 + \text{ICl} + \text{KCl} + \text{H}_2\text{O}.
\]

Procedure. In determining total arsenic the sample is placed in a distilling bulb, connected to a condenser, strong hydrochloric acid added together with cuprous chloride, and arsenuous chloride distilled over into an Erlenmeyer flask according to the standard procedure outlined on page 38. If arsenic is high, an aliquot portion of the distillate is taken and the titration made with standard iodate solution as stated later.

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For determining arsenious oxide in Paris Green or other arsenite 0.15 to 0.4 grams of the sample may be weighed directly into a glass-stoppered bottle (500 cc.) and the titration made.

**Iodate Titration.** 30 cc. of hydrochloric acid sp.gr. 1.19, 20 cc. of water and 6 cc. of chloroform are added to the solid arsenite. If the arsenic is in solution, sufficient HCl should be present to have the acidity between 11 and 20 per cent HCl. (If this falls below 11% HCl hydrolysis of the iodine monochloride will take place. If over 20% HCl the reaction proceeds very slowly.) Potassium iodate solution is now added, rapidly at first, shaking the contents of the bottle. When the iodine that has been liberated during the first part of the titration has largely disappeared from the solution, the stopper of the bottle is inserted and the contents thoroughly shaken. The titration is now conducted cautiously, shaking thoroughly with each addition of the reagent. The titration is complete when after shaking and allowing to stand 5 minutes no color is observed in the chloroform.

**Reagent.** Contains 3.241 g. of KIO₃ (dried at 140° C.) per 1000 cc. = 1 cc. = 0.003 g. As₂O₃.

**Volumetric Determination of Arsenic by Precipitation as Silver Arsenate**

Bennett's modification of Pearse's method, combining Volhard's, depends upon precipitation of arsenic, from a solution neutralized with acetic, by addition of neutral silver nitrate solution; the silver arsenate is dissolved in nitric acid, and the silver titrated with standard thiocyanate.

**Procedure.** 0.5 gram, or less, of the finely powdered substance is fused with 3 to 5 grams of a mixture of sodium carbonate and potassium nitrate (1:1) about one-third being used on top of the charge. The cooled mass is extracted with boiling water and filtered. The filtrate, containing the alkali arsenate, is strongly acidified with acetic acid, boiled to expel the carbon dioxide, then cooled and treated with sufficient sodium hydroxide solution to give an alkaline reaction to phenolphthalein indicator. The purple red color is now discharged from the solution by addition of acetic acid. A slight excess of neutral silver nitrate is vigorously stirred in and the precipitate allowed to settle in the dark. The supernatant liquid is poured off through a filter and the precipitate washed by decantation with cold distilled water, then thrown on the filter and washed free of silver nitrate solution. The funnel is filled with water and 20 cc. of strong nitric acid added. The dissolved silver arsenate is caught in the original beaker in which the precipitation was made, the residue on the filter washed thoroughly with cold water and the filtrate and washings made up to 100 cc. The silver is now titrated by addition of standard ammonium or potassium thiocyanate, until a faint red color is evident, using ferric ammonium alum indicator, according to the procedure described for determination of silver. (See Chlorine and Silver Chapters.)

One cc. N/10 thiocyanate = 0.010788 gram Ag.

Factor. Ag x 0.2316 = As.

**Note.** The silver arsenate salt is nearly six times the weight of arsenic, so that very small amounts of arsenic may be determined by the procedure, hence it is not necessary to use over 0.5 gram of the material. For traces of arsenic the Gutzeit method, following, should be used.
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DETERMINATION OF SMALL AMOUNTS OF ARSENIC

Modified Gutzeit Method

The following procedure furnishes a rapid and accurate method for determination of exceedingly small amounts of arsenic ranging from 0.001 milligram to 0.5 milligram As₂O₃. It is more sensitive and less tedious than the Marsh test. The details, given below with slight modifications, have been carefully worked out in the laboratories of the General Chemical Company and have proved exceedingly valuable in estimating small amounts of arsenic in acids, bases, salts, soluble arsenic in lead arsenate and zinc arsenite and other insecticides, traces of arsenic in food products, baking powders, canned goods, etc.

The method depends upon the evolution of arsine by the action of hydrogen on arsenic compounds under the catalytic action of zinc, the reaction taking place either in alkaline or acid solutions. The evolved arsine reacts with mercuric chloride, forming a colored compound. From the length and intensity of the color stain the amount of arsenic is estimated by comparison with standard stains.

Although the acidity of the sample and the amount of zinc shot should be kept within certain limits, the results are not effected by slight variation as was formerly thought. The physical characteristics of the zinc used rather than the surface exposed to acid action appears to have an effect on the evolution of arsine. The best results are obtained with zinc having a finely crystalline structure.

Iron present in the solution tends to prevent evolution of stibine, but has no apparent effect of arsine generation.

Stannous chloride is essential to the complete evolution of arsine, hence this reagent is added to the solution in which arsenic is determined.

Antimony present in the solution in amounts less than 0.0001 gram, does not interfere with the determination of arsenic. If a greater amount of antimony is present a separation of arsenic should be made by distillation. The following modification of the method given on page 38 is recommended. In place of the generator for HCl shown in Fig. 1, air saturated with HCl, by passing it through a gas wash bottle containing concentrated hydrochloric acid, is drawn through the boiling solution containing the sample in a saturated HCl solution, reduction of arsenic to arsenious chloride having been effected with cuprous chloride as prescribed. The air sweeps the arsine into the water in the receiving flasks (Fig. 1). It is advisable to have two flasks connected in series in place of one as shown. Gentle suction is applied at the receiving end of the train. The apparatus may be made in fairly compact form.

Nors. The above method was carefully investigated by R. M. Palmer and F. J. Selbert and found to be extremely accurate.
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- **Special Reagents. Standard Arsenic Solution.** One gram of resublimed arsenous acid, As$_2$O$_3$, is dissolved in 25 cc. of 20% sodium hydroxide solution (arsenic-free) and neutralized with dilute sulphuric acid. This is diluted with fresh distilled water, to which 10 cc. of 95% H$_2$SO$_4$ has been added, to a volume of 1000 cc. Ten cc. of this solution is again diluted to a liter with distilled water containing acid. Finally 100 cc. of the latter solution is diluted to a liter with distilled water containing acid. One cc. of the final solution contains 0.001 milligram As$_2$O$_3$.

**Standard Stains.** Two sets of stains are made, one for the small apparatus for determining amounts of As$_2$O$_3$ ranging from 0.001 to 0.02 milligram, and a second set for the larger-sized apparatus for determining 0.02 to 0.5 milligram As$_2$O$_3$. Stains made by As$_2$O$_3$ in the following amounts are convenient for the standard sets; e.g., small apparatus, 0.001, 0.002, 0.004, 0.006, 0.01, 0.15, 0.02 milligram As$_2$O$_3$. Large apparatus, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 milligram As$_2$O$_3$.

In making the stain the requisite amount of standard reagent, As$_2$O$_3$, solution, is placed in the Gutzeit bottle with the amounts of reagents prescribed for the regular tests and the run made exactly as prescribed in the regular procedure.

**Preservation of the Stains.** The strips of sensitized paper with the arsenic stain are dipped in molten paraffine (free from water), and mounted on a sheet of white paper, folded back to form a cylinder. The tube is placed in a glass test-tube containing phosphorus pentoxide, which is then closed with a stopper. It is important to keep the stained strip dry, otherwise the stain soon fades, hence the paper on which the strips are mounted and the glass test-tube, etc., must be perfectly dry. It is advisable to keep the standard in a hydrometer case, while not in use, as light will gradually fade the color.

**Sensitized Mercuric Chloride (or Bromide) Paper.** 20×20 in. Swedish Filter Paper No. 0 is cut into four equal squares. For use in the large Gutzeit apparatus the paper is dipped into a 3.25% solution of mercuric chloride (mercuric bromide may be used in place of the chloride) or if it is to be used in the small Gutzeit apparatus it is dipped into a 0.35% mercuric chloride solution. (The weaker the solution, the longer and less intense will be the stain.) The paper should be of uniform thickness, otherwise there will be an irregularity in length of

---

1. The accuracy of the method is within 10% of the truth.

Evolution of arsine by the electrolytic method, in place of the method outlined, proved to be unreliable. The evolution of arsine is effected by the slightest variation in conditions so it is extremely difficult to obtain concordant results.

In the **Merek** test arsine is passed through a glass tube constricted to capillarity. By application of heat the arsine is decomposed and metallic arsenic deposited. The tube is heated just before the capillary constriction so that arsenic deposits in the drawn out tube. Comparison is made with standards, the length of the stain being governed by the amount of arsenic in the evolved gas. Slight variations in the size of the capillary tube and rate of evolution make a notable variation in length of stain.
stain for the same amounts of arsenic. (The thicker the paper the shorter the stain. The paper is hung up and dried in the air, free from gas fumes, $\text{H}_2\text{S}$ being particularly undesirable.) When dry, half an inch of the outer edge is trimmed off (since this is apt to contain more of the reagent), and the paper cut into strips. The paper with more concentrated reagent is cut into strips 13 cm. by 5 mm. and that with 0.5% mercuric chloride into strips 7 cm. by 4 mm. The paper is preserved in bottles with tight-fitting stoppers. Standards should be made with each batch of paper. Paper with a white deposit of $\text{HgCl}_2$ should not be used.

**Ferric Ammonium Alum.** Eighty-four grams of the alum with 10 cc. of mixed acid is dissolved and made up to a liter. Ten cc. of this solution contains approximately 0.5 gram $\text{FeCl}_3$.

**Lead Acetate.** One per cent solution with sufficient acetic acid to clear the solution.

**Zinc.** Arsenic-free zinc shot, 3 to 6-in. mesh. The zinc is treated with C. P. hydrochloric acid, until the surface of the zinc becomes clean and dull. It is
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bom washed, and kept, in a casserole, covered with distilled water, a clock-glass keeping out the dust.

**Mixed Acid.** One volume of arsenic-free H₂SO₄ is diluted with four volumes of pure water and to this are added 10 grams of NaCl per each 100 cc. of solution.

**Stannous Chloride.** Eighty grams of stannous chloride dissolved in 100 cc. of water containing 5 cc. arsenic-free hydrochloric acid (1.2 sp.gr.).

**Arsenic-free Hydrochloric Acid.** The commercial acid is treated with potassium chloride to oxidize the arsenic to its higher form and the acid distilled. The distilling apparatus may be arranged so that a constant distillation takes place, acid from a large container dropping slowly into a retort containing potassium chloride, fresh hydrochloric acid being supplied as rapidly as the acid distills. See Fig. 5 on page 48.

**Lead Acetate Test Paper for Removal of H₂S.** Large sheets of qualitative filter paper are soaked in a dilute solution of lead acetate and dried. The paper is cut into strips 7x5 cm.

Blanks should be run on all reagents used for this work. The reagents are arsenic-free if no stain is produced on mercuric chloride paper after forty-five minutes' test.

**Special Apparatus.** The illustration, Fig. 6 (page 52), shows the Gutzeit apparatus connected up, ready for the test. The dimensions on the left-hand side are for the small apparatus and those on the right for the large form. Rubber stoppers connect the tubes to the bottle. The apparatus consists of a wide-mouth 2-oz. or 8-oz. bottle according to whether the small or large apparatus is desired, a glass tube (see Fig. 6) containing dry lead acetate paper and moist glass wool for removal of traces of hydrogen sulphide and a small-bore tube containing the strip of mercuric chloride paper.

**Preparation of the Sample**

The initial treatment of the sample is of vital importance to the Gutzeit Method for determining traces of arsenic. The following procedures cover the more important materials or substances in which the chemist will be called upon to determine minute amounts of arsenic.

**Traces of Arsenic in Acids.** The acid placed in the Gutzeit apparatus should be equivalent to 4.2 grams of sulphuric acid or 3.1 grams of hydrochloric acid and should contain 0.05 to 0.1 gram Fe₂O₃ equivalent. If large samples are required for obtaining the test it is necessary either to expel a portion of the acid in order to obtain the above acidity or to make standard stains under similar conditions of acidity. It must be remembered that arsenous chloride is readily volatile, whereas the arsenic chloride is not, hence it is necessary to oxidize arsenic before attempting to expel acids. If nitric acid or bromine or chlorine (chlorate) be added for this purpose, it must be expelled before attempting the Gutzeit test. Nitric acid may be expelled by adding sulphuric acid and taking to SO₂ fumes. Free chlorine, bromine, or iodine will volatilize on warming the solution. Chlorine in a chlorate is expelled by taking the sample to near dryness in presence of free acid. Sulphurous acid or hydrogen sulphide, if present, should be expelled by boiling the solution, then making faintly pink with KMnO₄ and destroying the excess with a drop or so of oxalic acid. SO₂ is reduced by zinc and hydrogen to H₂S, which forms black HgS with
mercuric chloride, hence removal of \(\text{SO}_2\) and \(\text{H}_2\text{S}\) are necessary before running the test.

**Sulphuric Acid.** With amounts of arsenic exceeding 0.00005% \(\text{As}_5\text{O}_8\), 5 to 10 grams of acid, according to its strength, are taken for analysis and diluted to 15 or 20 cc. If \(\text{H}_2\text{S}\) or \(\text{SO}_2\) are present, expel by boiling for fifteen or twenty minutes. Prolonged fuming of strong acid should be avoided by previously diluting the acid with sufficient water. In mixed acid containing nitric acid the sample is taken to \(\text{SO}_3\) fumes to expel nitric acid. The procedure given later for the regular determination is now followed.

For estimating very minute amounts of arsenic, 0.000005 to 0.00005% \(\text{As}_5\text{O}_8\), it is necessary to take a 25- to 50-gram sample for analysis. The acid is treated as directed above for removal of \(\text{H}_2\text{S}\) or \(\text{SO}_2\) or nitric acid and diluted in the Gutzzeit apparatus to at least 150 cc., using the large apparatus. Upon the addition of iron and stannous chloride as directed in the procedure described on page 52 for large Gutzzeit test. The stains are compared with standard stains produced by known amounts of arsenic added to 50-gram portions of arsenic-free sulphuric acid of strength equal to that of the sample. The stains are longer and less intense than those produced by less acid.

**Hydrochloric Acid.** Twenty cc. is taken for analysis (sp.gr. being known); the sample should contain an acid equivalent of about 3.1 grams of hydrochloric acid. Chlorine is expelled by bubbling air through the acid before taking a sample. The procedure is given for further treatment of the sample following the section on preparation of the sample.

**Nitric Acid.** One hundred cc. of the acid (sp.gr. being known) is evaporated with 5 cc. of concentrated sulphuric acid to \(\text{SO}_3\) fumes, to expel nitric acid. Arsenic is determined in the residue by the standard procedure.

**Iron Ores, Pyrites, Burnt Pyrites, Cinders, etc.** One gram of the finely ground ore is oxidized by treating with 5 cc. of a mixture of 2 parts liquid bromine and 3 parts of carbon tetrachloride. After fifteen minutes, 10 cc. of concentrated nitric acid are added and the mixture taken to dryness. Five cc. of concentrated sulphuric acid (95°C) are added and the mixture taken to \(\text{SO}_3\) fumes to expel the nitric acid. The cooled sample is taken up with 50 cc. of water and digested until all of the iron sulphate has dissolved; it is now washed into a 100-cc. flask, made to volume, and arsenic determined in an aliquot portion in the usual way, given later. Insoluble \(\text{Fe}_2\text{O}_3\), briquettes, etc., is best dissolved by fusion with potassium bisulphate, \(\text{K}_2\text{H}_2\text{SO}_4\). The fused mass is dissolved in warm dilute hydrochloric acid, and then washed into the Gutzzeit bottle.

**Alumina Ores. Bauxite.** One gram of bauxite is treated with one part of concentrated nitric acid and 6 parts of concentrated hydrochloric acid, and taken to dryness on the water bath. The residue is taken up with an equivalent of 4.7 grams of hydrochloric acid or 6.3 grams of sulphuric acid in a volume of 25 cc. and the mix heated until the material has dissolved. The sample is diluted to exactly 100 cc. and arsenic determined on an aliquot portion.

**Phosphates, Phosphoric Acid.** Arsenic, in phosphoric acid, combined or free, cannot be determined in the usual way, as \(\text{P}_4\text{O}_6\), has a retarding effect upon the evolution of arsine, so that the results are invariably low, and small amounts of arsenic escaping detection. Arsenic, however, may be volatilized from phosphates and phosphoric acid, as arsenous chloride, \(\text{AsCl}_3\), in a current of
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hydrogen chloride by heating to boiling. One gram or more of the phosphate is placed in a small distilling flask, connected directly to a 6-in. coil condenser dipping into the Gutzeit bottle, containing 20 to 30 cc. of cold distilled water. A second bottle connected in series may be attached for safeguarding loss (this seldom occurs). Fifty cc. of concentrated hydrochloric acid are added to the sample and 5 grams of cuprous chloride. Arsenic is distilled into the Gutzeit bottle by heating the solution to boiling and passing a current of air through strong hydrochloric acid into the distilling flask by applying suction at the receiving end of the system. All of the arsenic will be found in the first 10 or 15 cc. of the distillate. Arsenic may now be evolved after addition of iron, stannous chloride and zinc, as directed in the procedure.

Salts, Sodium Chloride, Magnesium Sulphate, etc. One-gram samples are taken and dissolved in a little water and an equivalent of 0.3 grams of sulphuric acid added. The solution of iron and stannous chloride having been added, the run is made with 5 cc. of zinc shot, placed in the Gutzeit bottle.

Baking Powder, Other than Phosphate Baking Powder. A 10-gram sample is heated with 10 cc. hydrochloric acid, 10 cc. of ferric ammonium alum and 30 cc. of distilled water, until the starch hydrolyzes. 0.5 cc. of stannous chloride is added to the hot solution and the mixture washed into the Gutzeit apparatus. The required amount of zinc is added and the arsenic determined as usual.

Phosphate Baking Powders. Ten grams of the material mixed to a paste with about 50 cc. of hydrochloric acid are transferred to a small distilling flask with a few cc. of HCl. A tube, connected to a bottle of strong hydrochloric acid, passes into the mixture in the flask through a ground glass stopper. The flask is attached to a tube, which dips into water in a Gutzeit bottle. Two grams of cuprous chloride are added, the apparatus made tight and the flask immersed in boiling hot water. By aspirating air through the system into the Gutzeit bottle, which is water cooled, arsenic distills into the bottle and may be determined by the procedure outlined.

Arsenic in Organic Matter, Canned Goods, Meat, etc. The finely chopped, well-mixed sample is placed in a large flask and enough water added to produce a fluid mass. An equal quantity of concentrated hydrochloric acid and 1 to 2 grams of potassium chlorate are added. The flask is shaken to mix the material and it is then placed on the steam bath. Upon becoming hot, nascent chlorine is evolved and vigorously attacks the organic matter. Half-gram portions of potassium chlorate are added at five-minute intervals, shaking the flask frequently. When the organic material has decomposed and the solution becomes a pale yellow color, the mass is diluted with water and filtered. Arsenic will be found in the filtrate. A white, amorphous substance generally remains on the filter, when cadaver is being examined. The filtrate is diluted to a given volume and an aliquot portion taken for analysis. This is evaporated to near dryness to expel excess of acid and decompose chlorates. An equivalent of 4.7 grams of hydrochloric acid is added (three times this amount for the large apparatus), the volume of the solution made to about 30 cc., 10 cc. of ferric ammonium alum and 0.5 cc. of stannous chloride added, and the solution poured into the Gutzeit apparatus for the test as given below.
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Procedure for Making the Test

For amounts of arsenic varying from 0.001 milligram to 0.02 milligram As\textsubscript{2}O\textsubscript{3}, a small apparatus is used. The volume of the solution should be 50 cc. It should contain an equivalent of 4.2 to 6.3 grams sulphuric acid and should have about 0.1 gram equivalent of FeO\textsubscript{4} reduced by 0.5 cc. of stannous chloride solution. Arsine is generated by adding one 5-cc. crucible of arsenic-free zinc shot, \(\frac{1}{4}\) to \(\frac{1}{8}\)-inch mesh. Temperature 75 to 80\(^\circ\) F.

For amounts ranging from 0.02 to 0.5 milligram As\textsubscript{2}O\textsubscript{3}, the large apparatus is used. The volume of the solution should be about 200 cc. and should contain an equivalent of 18.5 grams of sulphuric acid and should have 0.1 gram equivalent of FeO\textsubscript{4}, reduced by 0.5 cc. stannous chloride solution. Arsine is generated by adding one 12-cc. crucible of zinc shot (\(\frac{1}{4}\) to \(\frac{1}{8}\)-inch mesh.) The temperature should be 105\(^\circ\) F. The sample taken should be of such size that a stain is obtained equivalent to that given by 0.1 to 0.5 milligram As\textsubscript{2}O\textsubscript{3}.

Lead acetate paper is placed in the lower portion of tube \(B\); the upper portion of \(B\) contains glass wool moistened with lead acetate solution; the tube \(A\) contains the test strip of mercuric chloride paper. See Fig. 6. Immediately upon adding the required amount of zinc to the solution in the bottles, the connected tubes are put in position, as shown in the illustration, and the bottle gently shaken and allowed to stand for one hour for the small apparatus, forty minutes for the large. The test paper is removed, dipped in molten paraffine and compared with the standard stains. See Plate I.

Estimation of Per cent.

\[
\text{The milligram As}_2\text{O}_3 \text{ stain} \times 100 = \frac{C}{W} \text{ As}_2\text{O}_3.
\]

\(W\) is weight of sample taken.

1 It is advisable to use smaller samples when the arsenic content is over 0.3 milligram As\textsubscript{2}O\textsubscript{3}, as the longer stains are unreliable.

In the analysis of baking powders, bauxite, sodium or similar salts, the distillation method is recommended. See pages 60 and 51, "Phosphates," and "Phosphate baking water."

Hydrochloric acid is used in place of sulphuric acid in cases where complete solution by the latter acid cannot be effected.

Standards and samples should be run under similar conditions, temperature, dity, amount of zinc, volume of solution, etc. In place of zinc shot, zinc rods, cubes discs may be used for generating arsine and hydrogen.
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METHOD FOR ANALYSIS OF COMMERCIAL "ARSENIC,"
ARSENIOUS OXIDE, $\text{As}_2\text{O}_3$

The following constituents may be commonly present as impurities, $\text{SiO}_2$, $\text{Sb}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{NiO}$, $\text{CoO}$, $\text{CaO}$, $\text{SO}_3$, $\text{Cu}$, $\text{Pb}$, and $\text{Zn}$.

Determination of Moisture

Two 10-gram samples are dried to constant weight in the oven at 100° C. Loss in weight = moisture.

Sulphuric Acid, $\text{H}_2\text{SO}_4$

The samples from the moisture determination are dissolved in concentrated hydrochloric acid, heating to boiling if necessary, and the samples diluted to 300 to 400 cc. Barium chloride solution is added in slight excess to the hot solution, the precipitate, $\text{BaSO}_4$, allowed to settle and filtered and the sulphate dried and ignited as usual.

$\text{BaSO}_4 \times 0.343 = \text{SO}_3$.

Determination of Arsenic as $\text{As}_2\text{O}_3$

Duplicate 5-gram samples are dissolved in 20 grams potassium carbonate in 60 cc. of hot water, by boiling until solution is effected. The samples are made up to 1 liter and aliquots of 100 cc. (=0.5 gram) taken for analysis. The solution is made faintly acid with hydrochloric acid, testing the solution with litmus paper or by adding methyl orange directly to the solution. An excess of bicarbonate is added and the arsenic titrated with thiosulfate-normal iodine according to the standard procedure for arsenic. One cc. N/10 I = .004948 gram $\text{As}_2\text{O}_3$.

Residue upon Sublimation of $\text{As}_2\text{O}_3$. $\text{SiO}_2$, $\text{Pb}$, $\text{Cu}$, $\text{Fe}_2\text{O}_3$, $\text{NiO}$, $\text{CoO}$, $\text{Zn}$

Two 5-gram samples are weighed into tared porcelain crucibles and heated gently on sand baths with the sand banked carefully around the crucible so as to heat the entire receptacle. After the greater part of the arsenious oxide has volatilized, the crucible is ignited directly in the flame to a dull red heat, until fumes are no longer given off. The residue is weighed as total non-sublimable residue.

Silica

The residues are transferred to beakers and treated with aqua regia, taken to dryness, and the silica dehydrated at 110° C. for an hour or more. The residue is taken up with hot dilute hydrochloric acid, boiled, and the silica filtered off, ignited, and weighed.

Lead and Copper

The filtrate from the silica is "gassed" with $\text{H}_2\text{S}$ and the precipitate filtered off. The filtrate is put aside for determination of iron, etc. The precipitate is dissolved in hot dilute nitric acid, 2 to 3 cc. of concentrated sulphuric acid added,
the solution taken to SO₂ fumes, the cooled concentrate diluted to 20 or 30 cc., and the lead sulphate filtered off, ignited, and weighed as PbSO₄.

The filtrate from the lead sulphate containing the copper is treated with aluminum powder and the copper thrown out of solution; the excess of aluminum is dissolved with a few cc. of hydrochloric acid. The filtrate should be tested for copper with H₂S and the precipitate added to the copper thrown out by the aluminum. The copper on the filter is dissolved in hot dilute nitric acid, the extract evaporated to 2 or 3 cc., the acid neutralized with ammonia and then made acid with acetic, potassium iodide added and the liberated iodine titrated with standard thiosulphate solution according to the regular scheme for copper.

Iron, Nickel, Cobalt, and Zinc

The filtrate from the H₂S Group is boiled to expel the H₂S and the iron oxidized by addition of nitric acid and boiling. The iron (and alumina) is precipitated with ammonium hydroxide and the precipitate filtered off and washed several times with hot water. If alumina is suspected (light-colored precipitate) it may be determined by the difference method—ignition of the precipitate, weighing, and finally substracting the iron found by titration with standard stannous chloride solution. The iron is dissolved in hydrochloric acid and titrated hot with stannous chloride solution.

The filtrate from the iron is boiled and a 1% alcoholic solution of dimethylglyoxime added to precipitate the nickel. The salt is filtered on a tared Gooch, the precipitate dried at 100° C., and weighed. The weight of the salt × 0.2032 = Ni.

The filtrate from the nickel is boiled until all the alcohol has been driven off and the cobalt precipitated by addition of sodium hydroxide in excess filtered, ignited, and weighed as CoO.

The filtrate is made acid with hydrochloric acid, and then alkaline with ammonium hydroxide and colorless sodium sulphide solution added to precipitate the zinc. The mixture is boiled five to ten minutes, the precipitated ZnS allowed to settle, filtered off, and washed once or twice and then dissolved in hydrochloric acid and the zinc determined by titration directly with potassium ferrocyanide, or by converting to the carbonate by addition of potassium carbonate, filtered and washed free of alkali, the precipitate dissolved in a known amount of standard acid, and the excess acid titrated with standard caustic (methyl orange indicator) according to the procedure given for zinc. H₂SO₄ × 0.06065 = Zn.

Antimony and Calcium Oxides

Two 15-gram samples are treated with 300 cc. of concentrated hydrochloric acid, boiled down to 50 cc. to expel the arsenic as AsCl₃, an equal amount of concentrated hydrochloric acid is added, and the last traces of arsenic precipitated into the hot concentrated hydrochloric acid solution. The arsenous sulphide, As₂S₃, is filtered off. Antimony is precipitated by diluting the solution with an equal volume of water, the solution having been concentrated by boiling down to about 50 cc. The Sb₂S₃ is filtered off, washed several times with hot water, dissolved by washing through the filter with concentrated hydrochloric acid, and antimony determined in the strong hydrochloric acid solution by the potassium bromate method—addition of methyl orange indicator.
and titration with standard potassium bromate added to the hot solution to the disappearance of the pink color of the indicator.

The filtrate from the antimony is concentrated, made slightly alkaline with ammonium hydroxide, and gased with hydrogen sulphide to remove iron, nickel, cobalt, zinc, chromium, and last traces of lead, etc. The filtrate is then concentrated and made acid with crystals of oxalic acid, boiled and methyl orange added and then ammonia drop by drop slowly until the indicator changes to an orange color. An excess of ammonium oxalate is now added and the beaker placed on the steam bath until the calcium oxalate has settled. The lime is now determined by filtering off the precipitate and washing, drying and igniting to CaO, or by titration with standard permanganate, according to the regular procedure for calcium.

**Arsenic in Iron and Steel.** Ten grams of sample are placed in a distillation flask and dissolved in dilute HNO₃, the solution evaporated to dryness and heated to expel oxides of nitrogen, 100 cc. of HCl and 20 grams of CuCl are added and the arsenious acid distilled and determined by the iodine method.

**Arsenic in Copper.** Since arsenic impairs the electrical conductivity of copper, its determination is required. One gram of the sample is placed in a distillation flask with 10 cc. FeCl₃ and 100 cc. HCl and 5 grams KCl and the arsenious acid distilled and determined by titration with iodine.