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GRAVIMETRIC ANALYSIS

Part III

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CHAPTER 48

CHLORINE – Cl – 35·453

Cl_2, HCl, HClO, $HClO_2$, $HClO_3$, $HClO_4$

GASEOUS chlorine can be obtained from the liquid form which is available commercially in steel containers. Chlorine is used in the textile industry for decolourization and whitening. The insecticide industry (DDT), and also the plastic industry (polyvinyl chloride, chlorinated rubber) use large amounts of chlorine. Chlorine is also used to disinfect water, and can be absorbed in calcium hydroxide or other alkalies and used as hypochlorite in decolourization and the production of chloroform. It occurs naturally most often as chloride, together with sodium, potassium and magnesium. These salts are found in sea water and in salt mines. Soil water, streams and rivers also contain small amounts of dissolved chlorides. Chloride ions are also found in plants and animal tissues. The following minerals contain chloride: rock salt (halite, NaCl); sylvine (KCl); ammonium chloride (NH_4Cl); chlorocalcite ($CaCl_2$); chloromagnesite ($MgCl_2$); lawrencite [$(Fe,Ni)Cl_2$]; scacchite ($MnCl_2$); molizite ($FeCl_3$); carnallite ($KCl{\cdot}MgCl_2{\cdot}6\,H_2O$); tachidrite ($CaCl_2{\cdot}2\,MgCl_2{\cdot}12\,H_2O$); matlochite (PbClF); cotumnite ($PbCl_2$); chlorargyrite (AgCl); atacamite [$CuCl_2{\cdot}3Cu(OH)_2$].

Chlorine may be present in analytical samples as elementary chlorine (Cl_2); hydrochloric acid (HCl); hypochlorous acid (HClO); chlorous acid ($HClO_2$); chloric acid ($HClO_3$); and perchloric acid ($HClO_4$); or as the salts of these acids or organic substances containing chlorine. Of the methods shown in Table 48.1. only some are suitable for the gravimetric determination of chlorine, and of these the silver chloride method is usually preferred. A number of fairly accurate volumetric methods (argentimetric), however, are available for the determination of chloride ions.[1] Redox titrations are usually used for the determination of hypochlorite, chlorite and chlorate ions. Perchlorate ions can also be determined by direct gravimetric methods ($KClO_4$, nitron perchlorate).

The preparation of samples containing chlorine thus consists of the following operations: (a) dissolution of the sample, and (b) transformation to chloride.

Dissolution of the sample. Most inorganic chlorine compounds, particularly chlorides, are easily soluble in water. The chlorides of the following

[1] I. M. KOLTHOFF and V. A. STENGER, *Volumetric Analysis* II. 2 Ed. Interscience, New York, London (1947), p. 256. – L. ERDEY, *Bevezetés a kémiai analízisbe II. Térfogatos analízis.* (Introduction to Chemical Analysis II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest, p. 268. (1965).

ions are insoluble, or slightly soluble: Ag, Hg(I), Cu(I), Pb, Tl(I), Au(I), Pt(II), and also the following basic chlorides: BiOCl, SbOCl and Hg_2Cl_2O. Hygroscopic chlorides ($CaCl_2$, LiCl), and mercury(II) chloride are soluble in absolute ethanol, and even in higher alcohols (amyl alcohol). KCl, NaCl and $BaCl_2$ are only slightly soluble in concentrated hydrochloric acid, and thus can be separated from other chlorides if their aqueous solution is saturated with gaseous hydrogen chloride and the solution is filtered. Most metal chlorides are insoluble in ether; the chlorides of Fe(III), Hg(II), Sn(II, IV) and Au(III), however, are soluble. All chlorides, with the exception of silver chloride, can be dissolved in *aqua regia*.

TABLE 48.1. Forms of determination of chlorine
(for References see p. 15)

Ref. Number	Ions	Forms of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	Cl^-	AgCl	$AgNO_3$	nitric acid	AgCl	143·337	70–600
2.	Cl^-	Hg_2Cl_2	$Hg_2(NO_3)_2$	nitric acid	Hg_2Cl_2	472·13	< 130
3.	ClO_2^-	$Pb(ClO_2)_2$	$Pb(NO_3)_2$	weak nitric acid	$Pb(ClO_2)_2$	342·124	< 77
4.	ClO_3^-	$C_{20}H_{16}N_4 \cdot HClO_3$	nitron (1-4-diphenyl endanilo triazole)	weak sulphuric acid	$C_{20}H_{16}N_4 \cdot HClO_3$	396·845	105
5.	ClO_4^-	$KClO_4$	KCl	hydrochloric acid	$KClO_4$	138·557	110
6.	ClO_4^-	$C_{20}H_{16}N_4 \cdot HClO_4$	nitron (1-4-diphenyl endanilo triazole)	weak sulphuric acid	$C_{20}H_{16}N_4 \cdot HClO_4$	412·845	105 (40–232)

Most minerals containing chloride are insoluble in water, but can be fused with a five-fold excess of chloride-free sodium carbonate. The cold melt must be leached in water, filtered, and the filtrate made just acid to methyl orange with nitric acid. If the solution also contains silicate it must be made alkaline with ammonia, and a small amount of zinc nitrate added. The solution must then be boiled and filtered. The precipitate is washed with hot water and the filtrate is acidified with nitric acid.

Lead chloride can be decomposed by boiling with sodium carbonate or sodium bicarbonate solution.

Silver chloride can be decomposed by igniting the material with a three-fold excess of chloride-free sodium carbonate until sintering occurs.

When the cold melt is leached with water, sodium chloride dissolves; the residue consists of silver carbonate and silver metal. The filtrate can then be acidified with nitric acid and the chloride can be determined by one of the recommended methods.

Mercury(I) chloride can be decomposed by boiling with sodium hydroxide, and after the mercury(I) oxide has been filtered off, the solution may be acidified with nitric acid, and the chloride determined.

Gaseous chlorine (Cl_2), is quite soluble in water; at 10°C, 1 volume of water dissolves 3 volumes of chlorine at 1 atmosphere pressure. The vapour pressure of the chlorine above the chlorine water, however, is considerable. Chlorine can be removed completely from the solution by boiling. Chlorine is absorbed in alkalis with the formation of chloride and hypochlorite. In the cold, hypochlorite is slowly converted to chlorate; the reaction is rapid in hot solution. Hypochlorites, chlorites, chlorates and perchlorates can be dissolved in water. When silver nitrate is added to the solution of chlorine, only part of the chlorine is precipitated:

$$3\ Cl_2 + 6\ AgNO_3 + 3\ H_2O = 5\ AgCl \downarrow + AgClO_3 + 6\ HNO_3$$

Thus, when chlorine is to be determined gravimetrically, the solution must be made alkaline with ammonia and boiled. Chlorine reacts with ammonia with the formation of chloride and hypochlorite:

$$Cl_2 + 2\ NH_4OH = NH_4Cl + NH_4OCl + H_2O$$

Ammonium hypochlorite decomposes on boiling:

$$3\ NH_4OCl + 2\ NH_3 = 3\ NH_4Cl + N_2 + 3\ H_2O$$

After acidification with nitric acid the chlorine can be precipitated quantitatively as silver chloride.

Chlorine cannot be precipitated quantitatively from a solution containing *hypochlorite* (ClO^-) and *chlorite* (ClO_2^-) with silver nitrate, because partly soluble silver chlorate is formed. If hydrogen peroxide is added to the alkaline solution, however, and the mixture is boiled until the liberation of gas ceases, the hypochlorite and chlorate are reduced to chloride. Aged hypochlorite and chlorite solutions, however, always contain chlorate also, and it is advisable first to add sulphurous acid or sodium hydrogen sulphite to the solution.

Chlorates (ClO_3^-) do not form precipitates with silver nitrate in dilute aqueous solutions, because silver chlorate is partly soluble in water. Chlorates can be reduced by iron(II) sulphate, sulphurous acid or metallic zinc. Dry alkali chlorates, when evaporated several times with ammonium chloride, form chlorate-free alkali chlorides.

(a) *Reduction with iron(II) sulphate.* To 100 ml of the solution, containing about 0·2 g of chlorate, add 50 ml of 10% iron(II) sulphate solution, and boil for 15 min with constant stirring. Cool the solution, dissolve the precipitate of basic iron(III) sulphate in nitric acid, and precipitate chloride with silver

nitrate. If the solution contains sufficient excess of nitric acid there is no danger of the reduction of silver ions by iron(II) sulphate.

(b) *Reduction with sulphurous acid.* Add excess sulphurous acid to the slightly acidic or neutral solution of the chlorates, and boil the solution until the smell of sulphur dioxide disappears. Acidify the solution with nitric acid and precipitate the chloride with silver nitrate.

(c) *Reduction with metallic zinc.* Make the solution of the chlorates strongly acid with acetic acid, add excess of cut or granulated zinc to the solution, and boil for 1 hr. Dissolve the excess zinc in nitric acid and precipitate the chloride in the filtrate with silver nitrate.

Perchlorates (ClO_4^-) cannot be reduced using the above reducing agents, but reduction can be effected with titanium(III) sulphate. A much easier method, however, is to ignite the solid alkali perchlorates with ammonium chloride in a platinum crucible:

$$3\ KClO_4 + 8\ NH_4Cl = 3\ KCl + 8\ HCl \uparrow + 4\ N_2 \uparrow + 12\ H_2O \uparrow$$

Platinum also acts as a catalyst in the reaction.

Procedure. Take about 0·40 g of the solid alkali perchlorate, or evaporate to dryness a solution containing the same amount, add 1·5 g of analytically pure ammonium chloride, mix well, cover the crucible with a watch-glass, and heat on an air-bath for about 1 hr. Repeat the evaporation with 1·5 g of ammonium chloride. When the ammonium salts have been completely removed dissolve the residue in a small volume of water, remove any traces of platinum by filtration on a small filter paper, acidify the filtrate with a small volume of nitric acid, and precipitate the chloride with silver nitrate.

48.1. DIGESTION OF ORGANIC HALOGEN-CONTAINING SUBSTANCES

In organic chlorine compounds chlorine is usually bound covalently in the molecule and cannot therefore be precipitated with silver nitrate. Organic acid chlorides decompose with water, while most organic chloro-compounds of low molecular weight can be hydrolysed by boiling with alcoholic potassium hydroxide; chlorine is then converted to the ionic state. Usually, however, especially with aromatic chloro-compounds, the chlorine is difficult to convert to the ionic state. The following methods of decomposition can be used:

(1) Decomposition by the method of Carius in a bomb using concentrated nitric acid.

(2) Pyrolytic decomposition with calcium oxide, according to the method of Liebig for non-volatile solid samples.

(3) Fusion with sodium peroxide in a Parr bomb.

(4) Decomposition by metallic sodium in alcoholic solution (method of Stepanow).

The last method has the advantage that special apparatus is not required.

On the semimicro- and micro-scale, organic halogen compounds can be combusted in an oxygen atmosphere by the method of Hempel as modified by various later investigators such as Novak or Schöniger. The methods mentioned are also suitable for the decomposition of organic bromo- and iodo-substances.

48.1.1. *Digestion of organic halogen substances in the bomb by the method of L. Carius*[1]

Organic compounds can be completely digested with fuming nitric acid at 200–300°C when sealed into a thick-wall glass tube. If the destruction is carried out in the presence of silver nitrate, the halogens bound in the organic compound are converted to silver halides, which can be weighed after filtration. During the Carius process the sulphur content of the organic compounds is converted to sulphuric acid, and can then be determined in the form of barium sulphate. The method can be used generally for the destruction of organic substances, but aromatic compounds must be destroyed at higher temperatures (300°C). Although the method does not give satisfactory results in some special cases, particularly for aromatic compounds which are difficult to digest, owing to its simplicity it can be used very effectively for a series of analyses. The method requires some skill in glass blowing, and explosion of the bomb may result from the incorrect use of the procedure. This contingency must be considered during the heat-treatment and when the bomb is opened. For a bomb of volume 50 ml, not more than 4 g of fuming nitric acid should be used, otherwise explosion may result.

The bomb is made of glass tubing, 50 cm long, 2 cm in diameter and 2 mm thick, which has a round sealed end. Hard glass must be used. No 20 Jena glass, Supremax glass or potassium glass is suitable for the construction of Carius tubes. The tube must be clean and dry.

Procedure. Transfer 0·5–1·0 g of powdered silver nitrate and 2–3 ml of fuming nitric acid (sp. gr. 1·5) carefully to the tube through a long-stemmed funnel, and ensure that the wall of the tube does not become wet. Weigh 100–200 mg of the organic material into a hard glass test tube of length 4–5 cm and diameter 5 mm. Cautiously slide the test tube into the Carius tube, and ensure that the organic material does not come into contact with the nitric acid before the tube is sealed. Melt the end of the tube in a blowpipe flame, and seal it so that a capillary 8 cm long is formed at the end of the tube. The wall of the capillary must not be less than 2 mm thick. Seal the end of the capillary.

Cool the tube, wrap it in asbestos paper, and place it in the iron sheet of the furnace.

The electrical furnace, equipped with a regulator, shown in Fig. 48.1. can be used. A perforated aluminium cover can be screwed on to the upper end of the open tube to avoid explosions. The furnace must stand somewhat

[1] L. Carius, *Ann. d. Chem.* **136**, 129 (1865).

obliquely, and its open end should be turned towards the wall or surrounded by bricks.

The tube must be heated very carefully. The temperature should be raised by not more than 50 °C in 1 hr. Aliphatic compounds can usually be decomposed in 4 hr at 170–200 °C, while aromatic compounds require 6–10 hr at 250–300 °C.

During the decomposition, pressures in excess of the safety limit may often develop in the tube. When this occurs, therefore, periodically stop the heating at 200 °C, and release the pressure by opening the sealed capillary. Reseal the tube and continue the decomposition at the required higher temperature.

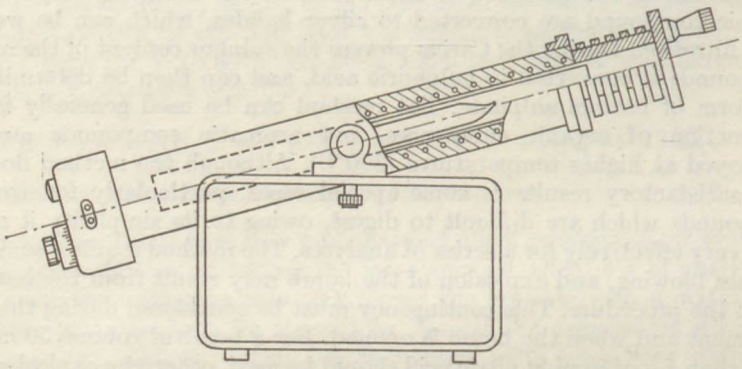

Fig. 48.1. Bomb furnace for digestion of organic halogen compounds

Allow the tube to cool to room temperature. Remove the tube and iron sheet from the furnace, wrap in cloth, and withdraw the tube from the iron tube until the capillary is showing (using protective screen and spectacles). Drive back the drop of liquid which condenses in the capillary into the body of the tube by cautious heating. Heat the capillary until the glass softens. The gas pressure then blows out the end of the capillary and the gas escapes.

Scratch the thicker tubing and remove the capillary using a hot glass rod. Rinse the contents of the tube into a beaker with water, remove the test tube, and dilute the solution to 300 ml.

Heat the solution to boiling, place it on a water bath for 1 hr, and if the original substance contained iodine, reduce silver iodate to silver iodide with a small amount of sulphurous acid. Cool, collect the silver halide on a glass filter, wash with water, dry at 130 °C, and weigh. When the presence of pieces of glass in the precipitate is suspected, silver chloride or bromide can be dissolved from the filter with hot ammonia and the filter weighed after being washed and dried. Silver iodide can be dissolved from the filter with hot potassium cyanide solution.

Notes. (1) The Carius method can also be used for the determination of the *sulphur content* of organic compounds. For this determination 100–300 mg of the organic substance and 1–3 ml of fuming nitric acid must be weighed into the bomb. If the

substance is difficult to digest 1–2 drops of bromine must also be placed in the tube. Carry out the digestion for 3–6 hr at 250–300°C. After digestion the solution must be evaporated to dryness with concentrated hydrochloric acid several times on a water bath, to remove completely the nitric acid. Dissolve the residue in a small volume of water, filter, dilute to 100 ml, add 1 ml of N hydrochloric acid, and precipitate barium sulphate with barium chloride in hot solution. Weighing form: $BaSO_4$.

(2) The digestion is complete when neither crystal formation nor oil drops can be observed in the residue.

48.1.2. *Decomposition of organic halogen compounds with calcium oxide according to J. Liebig and R. Piria*[1]

The pyrolytic decomposition of organic halogen compounds with calcium oxide can be used as widely as the Carius digestion for the conversion of their halogen content to the ionic form. When an organic substance is ignited with calcium oxide, the organic substance decomposes, and its halogen content is converted to calcium halide. When water is added to the ignited mixture and the solution acidified with nitric acid the calcium halide dissolves. The solution must be filtered to remove carbon particles formed during the ignition. Silver halide can then be precipitated from the filtrate.

Procedure according to Liebig. Take a Supremax glass heating tube 1 cm in diameter and 35–40 cm long, which is sealed at one end. Add a layer of calcium oxide powder 5–6 cm thick. Weigh in to the tube by difference 100–500 mg of the organic substance to be determined, cover it with a layer of calcium oxide 5 cm thick and mix with a spiral of copper wire. Add sufficient calcium oxide powder to three-quarters fill the tube. Place the tube horizontally into a heating furnace, and make a small channel through the whole length of the filling by gentle tapping. Heat the calcium oxide nearest the open end of the tube to a slight red glow, and then heat stepwise towards the substance to be analysed. Finally heat the whole contents of the tube to a slight red glow for 1 hr. Ensure that the substance does not explode, otherwise losses may occur. Cool, and cautiously pour the contents of the tube into 300 ml of water.

If the organic compound also contains sulphur, calcium sulphide is formed. This must be oxidized by adding chloride-free hydrogen peroxide to the alkaline solution and boiling. When the organic compound contains nitrogen the residue also contains calcium cyanide. This can be decomposed by boiling the solution with nitric acid.

Rinse the heating tube with chloride-free nitric acid, and cautiously acidify the calcium hydroxide solution with nitric acid. Filter the solution to remove carbon and insoluble material, and precipitate the silver halide by the addition of a slight excess of 5% silver nitrate solution to the filtrate. Coagulate the precipitate by boiling for a short period, and filter on a G4 glass filter after cooling and standing for 2–3 hr. Wash with water acidified with nitric acid. Dry at 120 °C for 2 hr. Weighing form: Ag-halide.

[1] R. Piria, *Nuovo Cimento* **5**, 321 (1857).

Note. When organic iodine compounds are digested, calcium iodate is also formed, and on acidification this reacts with iodide with the liberation of iodine. After acidification, therefore, the iodine must be reduced with a small amount of sulphurous acid or sodium bisulphite.

Procedure according to Piria. In the Liebig method the tube often becomes temporarily blocked on ignition, and later the pressure blows the filling out of the tube. When the ignition is carried out in a crucible, however, according to the method of Piria, there is no danger of this happening. Two platinum, nickel or porcelain crucibles, which fit together as shown in Fig. 48.2., must be used.

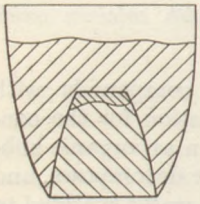

Fig. 48.2. Decomposition of organic halogen compounds in crucible according to Piria

Weigh 100–200 mg of the substance to be determined into the smaller crucible, and add a small amount of calcium oxide powder. Mix the substance well with the calcium oxide using a glass rod, rinse the rod with calcium oxide powder and add the powder to the crucible. Pack down the contents of the crucible using a flat-ended glass rod, and then fill the crucible with calcium oxide. Cover the smaller crucible with the larger crucible, fit the crucibles firmly together and rapidly invert them. Add sufficient calcium oxide to the empty part between the crucibles so that the compact filling completely covers the smaller crucible, but the larger one is not filled completely. Heat the crucible gently at first, and then more strongly to the temperature corresponding to a red glow, and maintain this temperature for 1–2 hr.

Allow the crucibles to cool after the ignition, place them into a beaker, add water, remove the crucibles after careful rinsing, and then follow the procedure given for the Liebig method.

48.1.3. *Destruction of organic halogen compounds with sodium peroxide in a Parr bomb*[1]

Organic halogen compounds can be digested with sodium peroxide in a Parr bomb in the same way as organic compounds containing sulphur. The method is described in Chapter 54.9. The aqueous solution from the sodium peroxide smelt must be acidified with nitric acid, and the halates formed must be reduced by heating with sulphurous acid. Sulphur dioxide must be removed by boiling the filtered solution, and silver halide can then be precipitated with 5% silver nitrate solution and weighed.

48.1.4. *Combustion of organic halogen compounds in oxygen according to Hempel*[2]

A 1 litre flask with a glass stopper must be used for the combustion.

[1] T. Parr, *J. Am. Chem. Soc.* **30**, 764 (1908).

[2] W. Hempel, *Z. angew. Chem.* **13**, 393 (1892); O. Mikl and J. Pech, *Chem. Listy*, **46**, 382 (1952); W. Schöniger, *Mikrochim. Acta* **1**, 123 (1955); W. Böttger, *Physikalische Methoden der analytischen Chemie.* II. 2 Ed. Akad. Verlag, Leipzig (1949), p. 254.

For a history of this long-neglected procedure, see the paper of A. M. G. Macdonald, *Analyst*, **86**, 3 (1961).

A platinum wire, on the end of which a 3×3 cm platinum net is soldered, should be sealed into the stopper of the flask (see Fig. 48.3.).

Procedure. Weigh not more than 150 mg of the organic material on to an ash-free filter paper of the shape shown in Fig. 48.3b., and wrap the substance in the paper so that a small tag of the paper protrudes. Moisten this part of the paper with paraffin, and wrap the whole paper in the platinum net. Add 20 ml of 2 N sodium hydroxide to the bottom of the flask and fill the vessel with oxygen. Light the paper and rapidly close the flask. The compound combusts rapidly in the oxygen atmosphere. The water in the combustion products condenses rapidly, and the acidic gases are absorbed in the alkaline solution. After $\frac{1}{2}$–1 hr rinse the contents of the flask into a large beaker, add 1 ml of 30% hydrogen peroxide, and boil until the liberation of oxygen ceases. Hypohalites are then converted to halides. Acidify the solution with nitric acid, add 10–15 ml of saturated sulphurous acid solution, boil and pass carbon dioxide into the solution for 30 min to remove the excess sulphur dioxide. Halates are reduced to halides. Add 5% silver nitrate solution to about 200 ml of the cold solution, coagulate the precipitate by boiling, allow the solution to cool and stand for 2–3 hr, and filter the solution on a G4 glass filter. Wash with water containing nitric acid. Dry at 120°C for 2 hr. Weighing form: Ag-halide.

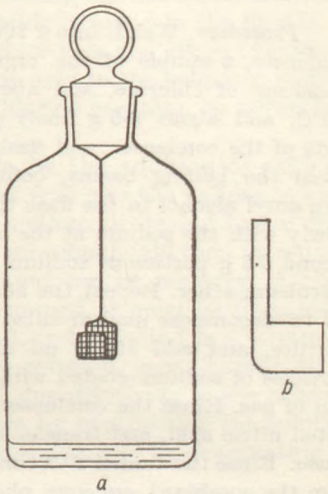

Fig. 48.3. Device for combustion of organic halogen compounds

Note. The method is useful mainly for the determination of the halogen content of non-volatile organic substances.

48.1.5. *Decomposition of organic chlorine compounds with metallic sodium according to A. Stepanow* (1906)[1]

Procedure. Weigh the substance to be determined into a small Erlenmeyer flask, add 20–40 ml of 96% alcohol, fit the flask with a reflux condenser, and heat on a water bath. Add a 25–30 fold excess of small pieces of cut sodium metal in small portions to the flask, via the condenser. After each piece is added allow the sodium to dissolve completely in the alcohol. When all the sodium has been added add 20–40 ml of water to the flask, exchange the reflux con-

[1] A. Stepanow, *Ber.* **39**, 4056 (1906).

denser for an obliquely fastened Liebig condenser, and distil off the alcohol from the sample. Acidify the aqueous solution with nitric acid and precipitate chloride with silver nitrate.

Note. According to G. Vastagh and E. Varga (1948)[1] even organic compounds which are difficult to decompose [e.g. DDT, 1-trichloro-2-2'bis (*p*-chlorophenyl) ethane, hexachlorobenzene, etc.] can be decomposed if the organic substance is treated with sodium metal in the presence of amyl alcohol diluted with petroleum ether.

Procedure. Weigh into a 200-ml Erlenmeyer flask, equipped with a reflux condenser, a sample of the organic compound containing the equivalent of 15–20 mg of chlorine, add about 10 ml of petroleum ether of boiling point 100°C, and about 0·5 g finely powdered sodium metal. Moisten the polished parts of the condenser and flask with paraffin and boil the mixture gently. When the boiling begins, before the sodium metal has melted, add 5 ml of pure amyl alcohol to the flask through the condenser. The amyl alcohol reacts slowly with the sodium at the boiling point of the mixture. After 2 hr add a second 0·5 g portion of sodium metal through the condenser and rinse with petroleum ether. Repeat the addition of sodium after 2 hr; 5–6 hr are required to decompose nuclear-substituted aromatic chlorine compounds. Cool the mixture, and add 15–20 ml of water to the flask through the condenser. Particles of sodium coated with a layer of salt then dissolve with the evolution of gas. Rinse the condenser with water. Acidify the residue with concentrated nitric acid, and transfer it to a separating funnel. Run off the aqueous phase. Rinse the funnel 2–3 times with 5 ml of water, and precipitate chloride from the combined aqueous phase with silver nitrate or titrate argentimetrically.

48.1.6. *Removal of interfering ions*

The heavy metal cations interfere in the determination of chloride as AgCl, because they contaminate the precipitate as their basic chlorides. Hg(II), Au(III), Pt(IV) and Cr(III) ions form complexes with chloride ions and prevent their precipitation with silver nitrate. The anions bromide, iodide, thiocyanate, cyanide, sulphide, thiosulphate, ferrocyanide and ferricyanide interfere.

Heavy metal ions can be precipitated from hot solution with sodium carbonate. Iron, aluminium and chromium(III), however, are better precipitated from cold solution with ammonia, and the solution filtered after boiling. The precipitate remaining on the filter must be dissolved in nitric acid; precipitation must then be repeated. Excess ammonia can be removed from the filtrate by boiling.

Mercury(II), bismuth, copper(II) and antimony(III) ions can be precipitated from cold solution containing 2–3% of nitric acid using gaseous hydrogen sulphide. The precipitate must be washed with hydrogen sulphide water containing 1–2% of acetic acid after filtration. Excess hydrogen sulphide can be removed from the filtrate in a current of carbon dioxide.

[1] G. Vastagh and E. Varga, *Magy. Kém. Lapja* **3**, 89 (1948).

Tin(II) or tin(IV) ions can be removed by the following method:

Dilute the solution to 200–300 ml, make just alkaline with ammonia in the presence of methyl orange, add 2–3 g of ammonium nitrate to the solution, and boil for 1–2 min. (See Chapter 13.1.). Collect the precipitate on a filter and wash with 1% ammonium nitrate solution.

Platinum(IV) chloride must be evaporated to dryness with a slight excess of sodium carbonate, and the residue just melted with a small flame. The melt must be leached with water after cooling and the solution filtered. Platinum remains on the filter and the chloride is found in the filtrate.

Chloride ions can be separated from silver ions and silver cyanide by adding a small amount of zinc and sulphuric acid to the solution; metallic silver and hydrogen cyanide are formed. Chloride can then be determined in the filtrate.

Iodide can be separated from chloride by the addition of sufficient water to the nearly neutral solution of about 0·25 g of the halides to make the volume about 700 ml, followed by 3 g of sodium nitrite and 3 ml of diluted sulphuric acid (1 : 1). The volume of the solution should then be reduced to about 500 ml by boiling. The iodine liberated can be removed in about 45 min. When the iodine is also to be determined, it must be liberated in a glass distillation apparatus (see Fig. 49.1.), and collected in a mixture of sodium carbonate and hydrogen peroxide solution, (see Chapter 50.3.). Chloride, and also bromide, remain behind quantitatively in the solution.

Bromide can be removed from chlorides by neutralizing the solution, after the removal of iodine, with sodium hydroxide, and by evaporating the solution to 50 ml.

Add 65 ml of diluted acetic acid (1 : 2), and about 1·5 g of solid potassium permanganate to the solution, and distil off the bromine with water vapour in a glass distillation apparatus (see Fig. 49.1.). When bromine is to be determined in the distillate it must be collected in sodium hydroxide or in ammonia solution.

Cyanide does not usually require separation from chloride, because silver cyanide and silver chloride can be precipitated from one aliquot of the sample and weighed; the cyanide alone can be determined in a second aliquot by the Liebig titration.[1]

48.2. DETERMINATION OF CHLORIDE IN THE FORM OF SILVER CHLORIDE (AgCl)

(according to L. W. Winkler)

This method is a reversal of the determination of silver described in Chapter 5.1. The solution must be acidified with nitric acid and excess silver nitrate added. The precipitate must be filtered, washed, dried, and weighed. The solubility and morphological structure of the precipitate has already been discussed in Chapter 5.1. An important difference, however, is that

[1] L. Erdey, *Bevezetés a kémiai analizisbe II. Térfogatos analizis.* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest (1965), p. 279; I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis* II. 2 Ed. Interscience, New York, London, (1947), p. 282.

the silver chloride precipitate coagulates more easily in the presence of excess silver than in that of chloride.

Procedure. Acidify 100 ml of the cold solution containing 0·01–0·40 g chloride with 5 ml of 1 N nitric acid — in the presence of iron(III) ions, 10–20 ml of acid must be added — and add a slight excess of 5% silver nitrate solution. (1 ml of the precipitant is required for the precipitation of 10 mg of Cl^-). Allow the mixture to stand in the dark for 1 hr, especially when small amounts of chloride are present, and then heat to boiling. Leave the mixture to stand overnight and collect the precipitate on a weighed G3 glass, A 2 porcelain filter-crucible or No. 4 glass texture filter-funnel. Wash with 50 ml of cold water to which 2–3 drops of concentrated nitric acid have been added. Finally, wash the precipitate with 1% acetic acid.

Water cannot be used for washing the precipitate as it peptizes slightly. The filtrate from the first portion of the washing solution then develops a turbidity.

Remove the washing solution thoroughly at the pump, and dry the filter-crucible and precipitate for 2 hr at 130 °C. Cool and weigh. Apply the following corrections to the weight of the precipitate:

Weight of AgCl precipitate, g:	1·50	1·00	0·50	0·40	0·30	0·02
Correction, mg:	−0·9	−0·8	−0·3	−0·1	+0·1	+0·2

Stoichiometric factors: $Cl/AgCl = 0{\cdot}24737$; $ClO_3/AgCl = 0{\cdot}58224$; $ClO_4/AgCl = 0{\cdot}69387$.

Notes. (1) The bulk of the precipitate must be removed from the filter mechanically. Traces of AgCl which remain in the pores can then be reduced with alkaline formaldehyde solution (see note in Chapter 5.1.). Metallic silver can then be dissolved from the filter using hot nitric acid. The filter must finally be rinsed with water.

(2) The accuracy of the method can be judged from the data of Table 48.2. (measurements of Z. Rády).

TABLE 48.2. Determination of chloride ions in the form of silver chloride

Number of measurements	Mean of precipitate weights mg	Corrected precipitate weight mg	True value mg	Deviation from true value Δ%	Standard deviation	
					mg	%
6	513·3	513·0	512·6	+0·08	±0·80	±0·15

(3) If filter paper is used for the filtration it must be combusted separately from the precipitate, according to the procedure of Chapter 5.1.

(4) Fairly accurate results can be obtained, even in the presence of iron(III) ions, if the precipitation is carried out in the presence of sufficient nitric acid. The danger of precipitation of basic iron(III) salts is then eliminated, and a preliminary separation of iron is not necessary. When iron(II) ions are present, 1–2 ml

of 30% hydrogen peroxide must also be added to 100 ml of the solution, which contains 10–20 ml of 1 N nitric acid, before precipitation.

(5) The precipitate is light-sensitive, and must not be exposed to direct sunlight, but in diffuse daylight photochemical decomposition causes no appreciable error.

48.3. DETERMINATION OF PERCHLORATE IONS IN THE FORM OF POTASSIUM PERCHLORATE ($KClO_4$)

The determination is a reversal of the determination of potassium with perchlorate (see Chapter 44.4). The heavy metal perchlorates are not completely soluble, and therefore heavy metal ions must first be removed by boiling the solution with a slight excess of sodium carbonate.

Procedure. Evaporate the filtrate, which contains sodium perchlorate, to dryness. Extract the cold residue 6–8 times with 5 ml of anhydrous ethyl acetate, and evaporate the filtrate to dryness. Dissolve the residue in 20 ml of water and precipitate potassium perchlorate as follows:

Heat not more than 25 ml of the solution containing 0·4 g of perchlorate to 80–90 °C, add a slight excess of saturated potassium acetate, and allow the mixture to cool. After 1 hr collect the precipitate on a G3 glass, A 2 porcelain filter-crucible or No. 3 sintered glass filter-funnel, wash twice with 0·05 M potassium acetate solution and four times with anhydrous ethyl acetate, and finally dry at 110 °C to constant weight (1–2 hr). Cool and weigh. Stoichiometric factor: $ClO_4/KClO_4 = 0{\cdot}71781$.

Note. Perchlorate ions can also be precipitated in the form of nitron perchlorate according to the procedure described for the determination of nitrate with nitron (see Chapter 55.1). The nitron perchlorate precipitate, however, is appreciably water-soluble, even at 20 °C, and therefore the mixture and washing solution must be cooled in ice-water. Nitron perchlorate should not be dried at temperatures higher than 105 °C because it explodes easily.

Separation Methods

It has already been mentioned that apart from the heavy metal ions, other halide and pseudo halide ions interfere in the determination of chloride as silver chloride. The solubilities of the silver halides, however, are not sufficiently different to enable Cl^-, Br^- and I^- to be separated by fractional precipitation. Such a separation can only be made by potentiometric argentimetric titration of the three anions (see Chapter 3.1.). The ease of oxidation of the different halides, however, is sufficiently different to enable their separation by fractional oxidation. The indirect analysis of silver halide mixtures, if the mixing ratio is favourable, yields satisfactory results.

48.4. Cl^- — ClO_3^-

Chlorate ions can be reduced to chloride by one of the methods described in the introduction to Chapter 48., using iron(II) sulphate, sulphurous acid, metallic cadmium or zinc, and can then be precipitated as silver

chloride and weighed. When chloride ions are also present in the solution the following two methods can be used:

(a) Acidify one aliquot of the solution with nitric acid and precipitate chloride ions with silver nitrate. Collect the precipitate in a porcelain crucible, and wash with water acidified with nitric acid. Weighing form: AgCl. From a second aliquot of the solution reduce chlorate ions with iron(II) sulphate, sulphurous acid, metallic cadmium or zinc (see introduction to Chapter 48), and precipitate the total chloride from strongly acidic, nitric acid solution. Weighing form: AgCl.

The chloride and chlorate content of the sample can then be determined from the two results.

(b) Chloride and chlorate can also be determined in the sample. Under these conditions the reduction must be effected in the filtrate with sulphurous acid or metallic cadmium: Precipitate silver chloride by the addition of silver nitrate to the solution of the weighed sample. Add 5–10 ml of saturated sulphur dioxide solution and 1 ml of 2 N nitric acid to the filtrate, and heat the mixture on a water bath for 30 min:

$$AgClO_3 + 3\,H_2SO_3 = AgCl\downarrow + 3\,H_2SO_4$$

Confirm the presence of excess precipitant by the addition of a small amount of silver nitrate. Collect the precipitate on a porcelain filter and wash thoroughly with water containing nitric acid to remove any silver sulphate which may be present. Weighing form: AgCl.

Note. Chlorate ions can be reduced quite easily if 1–2 g of finely divided electrolytic cadmium powder is added to the 1 N sulphuric acid solution of the sample, and the solution is heated on a water bath for 30 min.

48.5. ClO_4^- — ClO_3^-, Cl^-

(a) *Cl^-:* Precipitate chloride ions from an aliquot of the solution using silver nitrate and weigh in the form of AgCl.

(b) *ClO_3^-:* Reduce the chlorate in a second aliquot of the 1 N sulphuric acid solution of the sample by the addition of 5–10 ml of saturated sulphur dioxide water. Heat on a water bath, and remove excess sulphur dioxide from the hot solution in a current of carbon dioxide.

The reduction can also be carried out with 1–2 g of cadmium powder from a 1 N sulphuric acid solution. The reduction is complete after 30 min if the solution is heated on a water bath. Chloride ions can then be precipitated with silver nitrate. Weighing form: AgCl.

(c) *ClO_4^-:* In a third aliquot of the sample reduce perchlorate ions to chloride. Add to 100 ml of the solution, which should be 2 N in sulphuric acid, 1–2 g of cadmium powder and 0·2 g of titanium metal powder [or 1 g of titanium(III) sulphate], and boil the solution under reflux for 1 hr. After complete reduction dilute the solution to 200 ml, oxidize any violet titanium(III) ions present using nitric acid, and precipitate chloride ions with silver nitrate. Wash the precipitate thoroughly with water acidified with nitric acid to remove any silver sulphate which may be present. Weighing form: AgCl.

(d) *ClO_4^-: Precipitation with nitron acetate (W. Geilmann and A. Voight, 1930)*[1] Reduce chlorate ions with sulphurous acid according to procedure (b). Neutralize the solution with ammonia and dilute until it contains about 0·1 g ClO_4^- ion per 50–100 ml of solution. Acidify with 1 ml of 2 N sulphuric acid. Heat the solution to boiling and add 10–15 ml of 10% nitron acetate precipitant dropwise (10 g nitron dissolved in 5 ml glacial acetic acid and 95 ml water). Allow the mixture to cool in ice-water and maintain the solution at this temperature for 2 hr, stirring occasionally. Collect the precipitate on a G4 glass filter, wash with 20–50 ml of concentrated nitron perchlorate solution and then 3 times with 3 ml of ice-water, and dry for 1–2 hr at a temperature not higher than 100°C (!). The temperature must not be allowed to exceed 105°C, otherwise the precipitate may explode! Weighing form: $C_{20}H_{16}N_4 \cdot HClO_4$; Stoichiometric factor: $ClO_4^-/C_{20}H_{16}N_4 \cdot HClO_4 = 0{\cdot}24091$.

Note. The precipitate is appreciably soluble, even at 20°C. Nitrate and perrhenate ions interfere.

(e) *ClO_4^-:* Perchlorates can also be converted to chlorides by evaporation with ammonium salts. Add a threefold excess of ammonium chloride to the solid sample in a platinum crucible and evaporate slowly at 350–400°C. Platinum catalyses the reaction. Dissolve the residue in water and remove the contaminating platinum by filtration.

(f) *ClO_4^-:* Alkali perchlorates can be reduced to chlorides by fusion with sodium carbonate and sodium nitrate. This method is of most importance in the analysis of Chile saltpetre: Mix 10–20 g of saltpetre with the same amount of chloride-free sodium carbonate, and fuse the mixture in a porcelain crucible. Dissolve the residue in water. Acidify the solution with nitric acid and precipitate the chloride with silver nitrate. Weighing form: AgCl.

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to Table 48.1.

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CHAPTER 49

BROMINE — Br — 79·909

HBr, HBrO, $HBrO_3$

ELEMENTARY bromine is a dark brown liquid of high specific gravity. It fumes strongly in air. Bromine is used mostly for the production of organic compounds and for analytical purposes. Bromine only occurs naturally in the form of its compounds. Bromine compounds are found in the presence of chlorine compounds, and are therefore present in sea water and many mineral waters. Considerable amounts of alkali and alkaline earth bromides are found in some rock salt mines. Alkali bromates are found in natural saltpetre. Some sea plants and animals are able to concentrate bromine in their bodies. Alkali bromides and some organic compounds containing bromine are used as drugs.

Dissolution of the sample. Elementary bromine is quite soluble in organic solvents (alcohol, ether, chloroform, carbon disulphide). Saturated bromine water contains about 4% of bromine. The solubility of bromine in water is increased in the presence of alkali bromides, hydrochloric acid, barium chloride, strontium chloride etc. When aqueous bromine solutions are made alkaline, hypobromites are formed. Hypobromites are converted to bromides on heating with ammonia. Bromides are easily soluble in water, with the exception of silver, mercury, lead and copper(I) bromides. Most bromates, except silver, barium, thorium and some basic bromates, are water-soluble. Insoluble bromides can be decomposed with metallic zinc in sulphuric acid medium; heavy metals are then reduced and the bromides dissolve. Bromates can be reduced to bromide with iron(II) sulphate or sulphurous acid by a method similar to that described for chlorates (introduction to Chapter 48.). Organic compounds containing bromine can be decomposed by the Carius method with concentrated nitric acid in the presence of silver nitrate (see Chapter 48.1.1.). The other methods of decomposition described for chlorine (Chapter 48.1.), particularly the method utilizing alcohol and metallic sodium (Chapter 48.1.5.), can also be used for the decomposition of organic bromine compounds.

Forms of determination. Bromide is almost always weighed in the form of silver bromide. Elementary bromine, hypobromites and bromates must first be reduced to bromides, by methods similar to those described for chlorine (see the introduction to Chapter 48.). Silver bromide is less soluble in water than silver chloride. The value of its solubility product at 18°C is $L = [Ag^+] \cdot [Br^-] = 4 \cdot 1 \cdot 10^{-13}$.

Removal of interfering ions. Bromide ions can be separated from interfering heavy metal ions by boiling with sodium carbonate. The heavy metal ions are precipitated as their carbonates or hydroxides, and sodium bromide remains in solution. Silver halides can be decomposed with zinc and sulphuric acid. Bromide ions can be separated from iodide ions by the method described for the separation of chloride ions (Chapter 48.1.6.), i.e. the iodide must be oxidized to iodine with sodium nitrite in dilute sulphuric acid solution. Elementary iodine can be distilled with water vapour.

TABLE 49.1. Forms of determination of bromine
(for References see p. 27)

Ref. Number	Ions	Form of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	Br^-	AgBr	$AgNO_3$	weak nitric acid	AgBr	187·796	130
2.	BrO_3^-	AgBr	$AgNO_3$	weak nitric acid	AgBr	187·796	130

The separation of chloride and bromide ions from each other is somewhat more difficult; the two halides are usually precipitated together as the mixed silver halide. The ratio of the weights of the two halides is then usually determined by indirect analysis. Alternatively bromine can be liberated with a slight excess of potassium permanganate (or telluric acid) and distilled from a glass apparatus. It can be collected in a mixture of sodium hydroxide and hydrogen peroxide. Small amounts of chlorine also distil, and the bromine should be redistilled from a strongly acidic sulphuric acid solution with a slight excess of potassium permanganate (or telluric acid). Bromide can be completely separated from chloride by this method. It is advisable, however, to combine the distillation method with a permanganometric titration of bromide.[1]

49.1. DETERMINATION OF BROMIDE IN THE FORM OF SILVER BROMIDE (AgBr)

(according to L. W. Winkler, 1918)

Procedure. Add 5 ml of 1 N nitric acid to 100 ml of the solution containing 0·01–0·7 g of bromide. When iron(III) ions are present, the solution must be acidified with 10–20 ml of 1 N nitric acid. Add a slight excess of 5% silver nitrate solution dropwise with constant stirring (1 ml of 5% $AgNO_3$ is required for the precipitation of 23·5 mg Br^-). Allow the mixture to stand in the dark for 1 hour, and then heat until the precipitate coagulates. Allow the solution to stand overnight and filter on a G 3 glass, A 2 porcelain or No. 2 glass texture

[1] L. ERDEY, *Bevezetés a kémiai analizisbe II. Térfogatos analizis.* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest (1965), p. 127; I. M. KOLTHOFF and R. BELCHER, *Volumetric Analysis* III. 2 Ed. Interscience, New York, London (1957), p. 62.

filter funnel. Wash with 50 ml of cold water to which 2–3 drops of concentrated nitric acid have been added. Rinse with 50 ml of 1% acetic acid. Dry the filter and precipitate at 130°C for 2 hr. Cool and weigh. Correct the weight of precipitate by the following factors:

Weight of AgBr precipitate g:	1·50	0·00	0·50	0·40	0·30	0·02
Correction mg:	−0·6	−0·5	−0·3	−0·2	−0·1	±0·0

Stoichiometric factors: $Br/AgBr = 0{\cdot}42555$; $BrO_3/AgBr = 0{\cdot}68114$.

Notes. (1) Traces of precipitate on the filter which cannot be removed mechanically can be reduced with hot alkaline formaldehyde solution. The filter can then be washed and the metallic silver dissolved with hot nitric acid.

TABLE 49.2. Determination of bromide ions in the form of silver bromide

Number of measurements	Mean of AgBr precipitate weights mg	True value AgBr mg	Deviation from true value Δ%	Standard deviation	
				mg	%
6	96·3	96·6	−0·3	±0·18	±0·19
6	193·0	193·2	−0·1	±0·24	±0·12
6	482·5	482·9	−0·08	±0·40	±0·08

(2) The accuracy of the method can be assessed from the data in Table 49.2. (measurements of Z. Rády). The method yields fairly accurate results, especially for large samples. For six measurements the corrections of L. W. Winkler are lower than the standard deviation of the method, and therefore need only be used for very precise determinations if the result is obtained from more than six simultaneous determinations.

(3) The precipitate is light-sensitive, and the operations must if possible be carried out in a dark or shaded place.

Separation Methods

49.2. THE SEPARATION OF Br^- FROM LARGE AMOUNTS OF Cl^-

(a) *Determination of the bromide content of sea water and natural rock salt, according to L. W. Winkler* (1915)[1]. Bromine can be distilled from a strongly acid sulphuric acid solution to which a slight excess of potassium permanganate has been added. The apparatus used (see Fig. 49.1.) is made entirely of glass. When large amounts of chloride (> 20 mg) are present, small amounts of chlorine also distil with the bromine. The halogens can be absorbed in sulphurous acid or sodium pyrosulphite solution. The solution obtained can then be redistilled with potassium permanganate in the pre-

[1] L. W. WINKLER, *Z. angew. Chem.* **28**, 477, 532 (1916).

sence of sulphuric acid and manganese(II) sulphate. The bromine which distils may be absorbed in hydrogen peroxide solution.

Procedure. Weigh an amount of the alkali halide mixture which contains not more than 0·15 g of bromide and 5–10 g of sodium chloride or potassium chloride into the distillation flask. Dissolve the salt in 100 ml of water, acidify

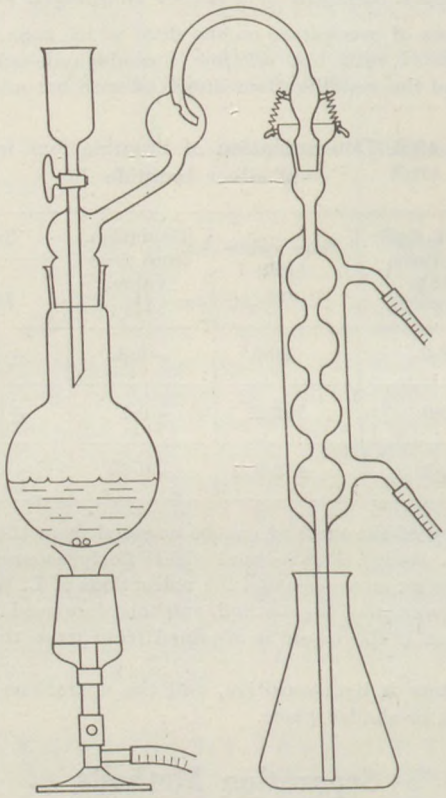

Fig. 49.1. Distillation apparatus

the solution with 2 N hydrochloric acid in the presence of methyl orange, and add 25 ml of 50% sulphuric acid. Add 1 g of pure sodium chloride to the solution when the sample contains only a small amount of salt. Add two glass beads to the solution to promote smooth boiling, and assemble the distillation apparatus. Lubricate the ground glass joints with syrupy phosphoric acid. A 200-ml Erlenmeyer flask, containing 5 ml of water and 1 ml of saturated sulphurous acid solution (or 0·3 g $K_2S_2O_5$) is used as a receiver. The tube from the condenser must reach the bottom of the flask. Heat the solution in the flask and boil until the air in the flask has been displaced by water vapour. Add 0·1 N potassium permanganate solution dropwise to the flask through the dropping

funnel, until the colour of permanganate fades slowly and the liberation of bromine ceases. Continue the distillation until the bromine has completely distilled into the receiving flask. It is usually sufficient to collect 25 ml of the distillate.

Clean the distillation flask, and transfer the solution in the receiving flask (containing the hydrogen bromide and excess sulphurous acid) back into the distillation flask. Dilute to 120 ml with water. Add 5 ml of 50% sulphuric acid to the solution and distil 20 ml of solution to remove the excess sulphurous acid. Add a further 20 ml of 50% sulphuric acid and 0·1 g of crystalline manganese(II) sulphate, and reassemble the apparatus. Lubricate the glass joints with syrupy phosphoric acid.

Collect the distillate in a 100-ml Erlenmeyer flask containing 5 ml of distilled water and 2–3 ml of 30% hydrogen peroxide. Boil the solution in the distillation flask until the air is displaced, and then add 0·1 N potassium permanganate solution dropwise with stirring until the solution becomes a definite pink and the colour remains stable for 1–2 min.

Large amounts of permanganate should not be used, even if the colour disappears completely before the end of distillation.

Distil a further 20 ml of the solution over a small flame and collect the bromine in the receiving flask. The colourless distillate contains excess hydrogen peroxide as well as hydrogen bromide. Silver bromide can be precipitated from the solution after dilution and acidification with nitric acid (see Chapter 49.1.). Place the covered beaker on a water bath and heat until the liberation of oxygen ceases. Allow the mixture to stand in a dark place for several hours. Weighing form: AgBr.

Notes. (1) When the solution to be determined also contains iodide, add several drops of hydrochloric acid and iron(III) chloride solution to 100 ml of the solution, and remove the liberated iodine by distilling 10 ml of the solution. The bromine can then be distilled after the addition of 25 ml of 50% sulphuric acid.

(2) The bromine which distils can also be collected in chloride-free 0·1 N sodium hydroxide solution. The sodium hypobromite formed can be decomposed by the addition of several millilitres of 30% hydrogen peroxide solution. Hypobromite can also be titrated iodimetrically.

(3) In the presence of ammonium salts, add 5 ml of 1 N sodium hydroxide solution to 100 ml of the neutral solution and evaporate the solution to two-thirds of its volume. The ammonia is then quantitatively removed. Dilute the residue to 100 ml again and distil the bromine by the above procedure.

(4) When the bulk of the original sample consists of alkali bromide, and contains less than 1% of alkali chloride, a single distillation effects a satisfactory separation.

(5) Carbonate, sulphate and nitrate ions do not interfere in the separation.

(b) *The separation of Br^- from large amounts of Cl^-.* Add 5 g of chromium(VI) oxide to 80–100 ml of the solution of the neutral salts in a distillation apparatus and bubble a slow current of air through the solution (2–3 bubbles/sec.). Collect the distillate in 1 N ammonia. The bromine is collected quantitatively in the receiver in 60–90 min. Evaporate the ammoniacal solution to dryness on a water bath. Ammonium bromide remains behind. Dissolve the residue

in 100 ml of water, make the solution slightly acid with nitric acid, and precipitate silver bromide with silver nitrate.

Note. When the bromine is present in the form of bromate it must be reduced with a few drops of sulphurous acid before the addition of chromic acid.

49.3. INDIRECT DETERMINATION OF BROMIDE AND CHLORIDE

Precipitate the two halides together in the form of AgBr and AgCl, and weigh the precipitate.

(a) Convert the precipitate to silver chloride in a current of chlorine and re-weigh. The original weights of chloride and bromide present can then be calculated.

(b) Alternatively reduce the mixed precipitate to silver by heating in an atmosphere of hydrogen in a Rose crucible. Weigh the metallic silver.

(c) The silver halide mixture can also be reduced with metallic cadmium. The metallic silver can then be dissolved in nitric acid, and silver chloride can be precipitated with 0·1 N sodium chloride solution.

(d) The silver halide mixture may be evaporated with ammonium bromide and the weight of AgBr formed can be determined.

(a) *Determination by heating in an atmosphere of chlorine.* Precipitate AgBr and AgCl according to the procedure described in Chapter 49.1., and weigh after drying in a filter-crucible. Let its weight be (A).

Place the filter-crucible into a Stähler aluminium block (see Fig. 2.98.), and transfer the block to a well-ventilated fume-cupboard. Cover the glass tube inside the aluminium block with a watch glass, and connect the side tube to a source of gaseous chlorine via a washing tower containing sulphuric acid. Prepare the chlorine from concentrated hydrochloric acid and solid potassium permanganate. PVC tubing should be used for the connections.

The reaction, $2\,AgBr + Cl_2 = 2\,AgCl + Br_2$, begins at 250–300 °C.

Heat the aluminium block to 430–450 °C for 10–15 min, then remove the crucible holding the side tube of the crucible holder, and allow it to cool on an asbestos plate. The current of chlorine should be turned off at the same time.

When the smell of chlorine has disappeared, place the crucible in a desiccator filled with solid potassium hydroxide. Cool and weigh (B). Repeat the heating in chlorine and check for constant weight.

If x g of AgCl and y g of AgBr are present in the mixed halide precipitate,

$$x + y = A.$$

After heating in a current of chlorine the silver bromide is converted into silver chloride, therefore

$$x + y\frac{\text{AgCl}}{\text{AgBr}} = B.$$

From this

$$y = \frac{A - B}{1 - \frac{\text{AgCl}}{\text{AgBr}}} = \frac{A - B}{0{\cdot}23675} = 4{\cdot}2240\ (A - B)$$

$$x = A - y.$$

Error calculation. It is necessary to estimate how the relative errors $\Delta A/A$ and $\Delta B/B$ in weighing A and B influence the relative error of the results $\Delta x/x$ and $\Delta y/y$. The error can be calculated using the principles detailed in Chapter 3.10.1. For the relative error of x and y we obtain:

$$\frac{\Delta x}{x} = \left(3{\cdot}22 + 3{\cdot}22\,\frac{y}{x}\right)\frac{\Delta A}{A} + \left(4{\cdot}22 + 3{\cdot}22\,\frac{y}{x}\right)\frac{\Delta B}{B}$$

$$\frac{\Delta y}{y} = \left(4{\cdot}22 + 4{\cdot}22\,\frac{x}{y}\right)\frac{\Delta A}{A} + \left(3{\cdot}22 + 4{\cdot}22\,\frac{x}{y}\right)\frac{\Delta B}{B}.$$

The sum of the relative errors in x and y is a minimum at the following mixing ratio $(x/y)_{\text{min}}$.

$$\left(\frac{x}{y}\right)_{\text{min}} = \sqrt{\frac{\text{AgCl}}{\text{AgBr}}} = \frac{5{\cdot}4}{4{\cdot}6} = 0{\cdot}87.$$

The error therefore is least for both components when the mixture of the silver halides contains 54% of silver chloride and 46% silver bromide. Table 49.3. summarizes the relative errors in x and y when the relative errors in A and B are 0·1% i.e.

$$\frac{\Delta A}{A} = \frac{\Delta B}{B} = 0{\cdot}1\%.$$

TABLE 49.3. Relative errors of indirect determinations of chloride and bromide ions

(a) Determination by heating in chlorine gas current

Relative content of the precipitate		Relative error of AgCl determination	Relative error of AgBr determination
AgCl = x	AgBr = y	$\frac{\Delta x}{x}$ %	$\frac{\Delta y}{y}$ %
1 wt about 10%	10 wt about 90%	7·1	0·83
5·4 wt 54%	4·6 wt 46%	1·49	1·49
10 wt about 90%	1 wt about 10%	0·81	9·28

From the data of Table 49.3. it is evident that the relative error of the result, even for the most favourable mixing ratio, is about 15 times as great as the error produced in the measurements. The method can therefore only be used when great accuracy is not required.

(b) *Determination by heating in an atmosphere of hydrogen.* After the determination of the weight of the mixed AgBr and AgCl precipitate (A), place the bulk of the precipitate in a weighed Rose crucible and determine the weight of precipitate transferred (B). Cover the crucible with a lid fitted with a porcelain tube. Pass *oxygen-free* hydrogen into the crucible via the pipe. Ignite the hydrogen after it has displaced the air from the crucible. Heat the crucible to a red glow with a gas flame. Remove the burner after 20 min heating and after a further 10 min interrupt the current of hydrogen momentarily to extinguish the hydrogen flame. Pass hydrogen for several minutes more, and then allow the crucible to cool in a desiccator for 10 minutes and weigh (C). Check for constant weight after repeating the heat treatment. The weight of metallic silver (D) in the original precipitate must be calculated $(A/B)\,C = D$.

If x g of AgCl and y g of AgBr is present in the original silver halide mixture, the sum of the two precipitate weights:

$$x + y = A.$$

After reduction the weight of silver metal:

$$x \cdot \frac{\text{Ag}}{\text{AgCl}} + y \cdot \frac{\text{Ag}}{\text{AgBr}} = D.$$

The amount of chloride present is $u = x \cdot \frac{\text{Cl}}{\text{AgCl}}$, while that of bromide, $v = y \cdot \frac{\text{Br}}{\text{AgBr}}$. When these values are substituted in the above equations we obtain

$$u = 1{\cdot}3883 \cdot D - 0{\cdot}7975 \cdot A, \quad \text{g chloride}$$

$$v = 1{\cdot}7975 \cdot A - 2{\cdot}3883 \cdot D, \quad \text{g bromide}$$

The *errors* can be calculated by the method described in Chapter 3.10.1. The following results are obtained for the relative error of chloride (u) and bromide (v) in the determination of

$$\frac{du}{u} = \left(3{\cdot}21\,\frac{v}{u} \cdot 1{\cdot}86\right)\frac{\Delta A}{A} + \left(4{\cdot}18 + \frac{v}{u} \cdot 1{\cdot}86\right)\frac{\Delta D}{D}$$

$$\frac{dv}{v} = \left(4{\cdot}18\,\frac{u}{v} \cdot 7{\cdot}25\right)\frac{\Delta A}{A} + \left(3{\cdot}21 + \frac{u}{v} \cdot 7{\cdot}25\right)\frac{\Delta D}{D}$$

where $\Delta A/A$ is the relative error in the weighing of the silver halides and $\Delta D/D$ is the relative error in weighing the metallic silver.

The sum of the relative errors shows a minimum at the following mixing ratio:

$$\left(\frac{u}{v}\right)_{\text{min}} = \frac{\text{Cl}}{\text{Br}}\sqrt{\frac{\text{AgBr}}{\text{AgCl}}} = 0{\cdot}51.$$

The sum of the errors is a minimum when the sample contains 34% of Cl^- and 66% of Br^-. Table 49.4. shows the relative errors in u and v for various mixing ratios when the relative errors

$$\frac{\Delta A}{A} = \frac{\Delta D}{D} = 0{\cdot}1\%.$$

From the data in Table 49.4 it can be seen that the relative errors of the results, even at the most favourable mixing ratio, are 15 times greater than the errors produced in the measurements. Great accuracy cannot be obtained by this method.

(c) *Determination by reduction with cadmium.* Take an aliquot of the sample and precipitate AgBr + AgCl with silver nitrate, according to the procedure of Chapter 49.1. Weigh the mixed silver halides (A).

TABLE 49.4. Relative errors of indirect determinations of chloride and bromide ions

(b) Determination by heating in hydrogen gas current

Relative content of the precipitate		Relative error of Cl^- determination $\frac{\Delta u}{u}$ %	Relative error of Br^- determination $\frac{\Delta v}{v}$ %
$Cl^- = u$	$Br^- = v$		
1 wt about 10%	10 wt about 90%	4·46	0·88
3·4 wt 34%	6·6 wt 66%	1·48	1·48
1 wt 50%	1 wt 50%	1·11	2·19
10 wt about 90%	1 wt about 10%	0·78	15·24

From a second aliquot precipitate the mixed silver halides with excess of silver nitrate. Collect the precipitate on a filter paper, wash the precipitate, and rinse it with a fine jet of water into a porcelain dish. Combust the filter paper and add the traces of precipitate which adhered to it to the main part of the precipitate. Pour 1–2 g of finely divided cadmium powder on to the precipitate and acidify the solution with 2 N sulphuric acid. Cover the dish with a watch glass and heat on a water bath until the precipitate is completely reduced to metallic silver. Collect the silver, and the cadmium residue, on a filter paper, wash thoroughly with hot water, and dissolve it in hot 2 N nitric acid. Rinse the filter paper thoroughly with water, and precipitate silver ions with 0·1 N sodium chloride solution. Weighing form: AgCl. Weight of AgCl precipitate: (B) g.

The weight of AgCl in the original precipitate should be x g, while that of AgBr should be y g. Then

$$y = \frac{A - B}{0{\cdot}23675} = 4{\cdot}2240\ (A - B) \qquad \ldots \text{AgBr g}$$

$$x = A - y \qquad \ldots \text{AgCl g}$$

CHAPTER 50

IODINE — I — 126·90

I_2, HI, HIO, HIO_3, HIO_4

IODINE is a volatile steel-grey solid. It is a rarer element than the other halogens, but is fairly widely distributed in nature, where it occurs as iodide. Sea water contains small amounts of iodine, and some mineral waters contain considerable amounts of iodide. Some algae can accumulate large amounts of iodide in their organisms. In the human body, especially the thyroid gland, iodine can accumulate bound with proteins. In some rare minerals iodine can be found with silver, copper(I) and lead in the form of its salts with these ions. Chile saltpetre also contains about 0·1% of iodate. Apart from elementary iodine, large amounts of potassium iodide, potassium iodate, potassium biiodate (Than-salt) and iodoform are used commercially. Iodine is mainly used for pharmaceutical purposes and as a reagent chemical.

Dissolution of the sample. Elementary iodine is only slightly soluble in water. At 11°C, 1 litre of water dissolves 182 mg of iodine. Iodine is easily soluble in potassium iodide solutions, however, and can also be dissolved in organic solvents (alcohol, ether, chloroform, benzene). With the exception of silver, mercury(I, II), copper(I), lead, thallium(I) and palladium(II) iodides, all the metal iodides are easily soluble in water. The iodides of bismuth, tin and antimony are acid-soluble. The iodates of silver, barium, lead, mercury(I, II), thorium, zirconium, cerium(IV), titanium(IV), the rare earths, bismuth, tin, iron(III) and chromium(III) are difficultly soluble in water. Insoluble iodides and iodates can be decomposed with zinc in sulphuric acid solution; iodate is then reduced to iodide.

Mineral waters which contain iodide must first be evaporated to one-quarter of their original volume, and calcium and magnesium carbonate must be precipitated with sodium carbonate. The filtrate must be evaporated until crystallization occurs, and the hot halide solution must be treated with three times its volume of 96% ethyl alcohol. The solution must then be filtered, and the residue washed with alcohol. Most of the sodium chloride remains on the filter, while the alkali iodides and bromides are quantitatively extracted into the alcoholic solution. The solution must then be made alkaline with potassium hydroxide solution, evaporated to crystallization again, and the extraction with alcohol repeated. After the alcohol has been removed, the dry substance must be cautiously ignited, dissolved in a small volume of water, and filtered. The iodide in the filtrate can then be oxidized

to iodate by the method of L. W. Winkler and titrated iodometrically, or weighed as PdI_2.

The iodine can also be separated by distillation, and must then be reduced to iodide with sulphurous acid and weighed in the form of silver iodide.

Organic iodine compounds can be fused with potassium hydroxide, or can be decomposed with metallic sodium in alcoholic medium by a similar method to that described for chlorine compounds (see Chapter 48.1.5.).

TABLE 50.1. Forms of determination of iodine
(for References see p. 41)

Ref. Number	Ions	Forms of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	I^-	AgI	$AgNO_3$	weak nitric acid	AgI	234·79	60–900
2.	I^-	CuI	$CuSO_4$	weak sulphuric acid	CuI	190·45	60–296
3.	I^-	TlI	$TlNO_3$	nitric acid	TlI	331·30	60–473
4.	I^-	PbI_2	$Pb(NO_3)_2$	weak nitric acid	PbI_2	461·03	60–370
5.	I^-	PdI_2	$PdCl_2$	weak hydrochloric acid	PdI_2	360·52	80–365
6.	IO_3^-	$AgIO_3$	$AgNO_3$	neutral	$AgIO_3$	282·79	80–410

Forms of determination. Iodine and its compounds are usually determined by titrimetric methods (iodimetry). Suitable gravimetric forms of determination are shown in Table 50.1. Of these methods, precipitation in the form of silver iodide is the most frequently used. This method, however, has the disadvantage that it is subject to interference by the other halides. Iodide must first be separated from chloride and bromide, or an indirect analytical method must be used. Precipitation in the form of palladium(II) iodide is not affected by chloride and small amounts of bromide ions, but the precipitant is rather expensive. However, the palladium used can be regenerated by reduction with zinc.

Iodate ions can be determined most conveniently and rapidly by iodimetric titration. If a gravimetric determination is required it is advisable first to reduce iodate to iodide with zinc or sulphurous acid, and to precipitate the iodide in the form of silver iodide.

Removal of interfering ions. Interfering heavy metal ions must be precipitated in the form of carbonates before the determination. The

solution is made alkaline with sodium carbonate and the heavy metal carbonates filtered off. The iodide dissolves as sodium iodide. Silver, mercury and copper iodides can be decomposed with zinc in sulphuric acid medium. The iodide solution must be filtered off from the mixed metal precipitate. Iodate must be reduced to iodide with sulphurous acid, and the excess of sulphurous acid evaporated in a current of carbon dioxide. Periodate ions are reduced more slowly with sulphurous acid, and the solution must also be heated during the reduction. Iodide ions can be separated from chloride and bromide ions according to the methods described for the separation of chlorine (Chapter 48.1.6.).

50.1. DETERMINATION OF IODIDE IN THE FORM OF SILVER IODIDE (AgI)

Silver iodide is the least soluble silver halide. Its solubility product at 25°C is: $L = [Ag^+] \cdot [I^-] = 1{\cdot}5 \cdot 10^{-16}$. The precipitate tends to adsorb silver nitrate and other accompanying substances. These contaminations are much more difficult to remove than in the case of silver chloride, because the silver iodide precipitate is not soluble in ammonia and thus cannot be purified by reprecipitation. A fairly pure precipitate can be obtained by the addition of excess, very dilute (0·05 N) silver nitrate solution with constant stirring to the ammoniacal solution of iodide ions. The solution should then be acidified with a 1% excess of 2 N nitric acid related to the volume of the solution. The precipitate must be washed with very dilute nitric acid and then with water. Nitric acid which adheres to the surface of the precipitate partly decomposes the precipitate on drying.

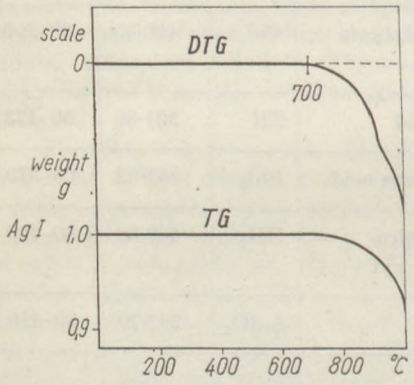

Fig. 50.1. Thermoanalytical curves of silver iodide precipitate

A second precipitation procedure, the method of L. W. Winkler, attempts to ensure ease of filtration of the precipitate whilst it avoids coprecipitation errors by the application of corrections.

Thermal investigation of the precipitate (see Fig. 50.1.) has shown that the precipitate has constant weight and stoichiometric composition in the range 60–700°C. The precipitate decomposes at higher temperatures. Similarly shaped curves are obtained when the ignition is carried out in an atmosphere of nitrogen which contains 5% of hydrogen. C. Duval (1953) found that the decomposition of AgI only begins above 900°C in air. The lower decomposition temperature which we have observed results from the presence of traces of silver, formed by photodecomposition and reduction, which catalyse the decomposition of the precipitate. Silver iodide melts at 552°C. When the precipitate is collected on a filter paper it must be sepa-

rated and the paper must be ignited alone. Small amounts of silver which are occasionally formed by reduction can be converted to silver iodide by the addition of a small piece of iodine, 2–3 drops of ammonia and hydrogen peroxide, and evaporating the residue to dryness.

Precipitation by the precision method of L. W. Winkler. Add excess 5% silver nitrate solution with constant stirring to 100 ml of solution containing 0·01–0·8 g of iodide (for the precipitation of 38 mg I^-, at least 1 ml of 5% silver nitrate solution is required). Allow to stand for 30 min and acidify the solution with 5 ml of 1 N nitric acid. Allow to stand for a further 30 minutes, heat the mixture to boiling, and leave the mixture overnight. Collect the precipitate on a G 3 glass, A 2 porcelain or No. 4 glass texture filter-funnel, wash with 50 ml of water containing 2–3 drops of concentrated nitric acid, and then with 50 ml of 1% acetic acid. Remove the washing solution thoroughly at the pump, and dry the filter-crucible at 130°C for 2 hr. Cool and weigh. Correct the weight of the precipitate by the following factors:

Precipitate weight g:	1·50	1·00	0·50	0·40	0·30	0·02
Correction mg:	−0·6	−0·2	+0·2	+0·3	+0·4	+0·6

Stoichiometric factors: $I/AgI = 0{\cdot}54053$; $IO_3/AgI = 0{\cdot}74496$; $I_2O_5/2\,AgI = 0{\cdot}71089$.

Note. The precipitate is very sensitive to light, and must not be exposed to sunlight or strong diffuse light, especially when wet. According to the data of Table 50.2. the results agree quite closely with the true values even without the application of the corrections (measurements of Z. Rády).

TABLE 50.2. Determination of iodide ions in the form of silver iodide

Number of measurements	Mean of AgI precipitate weights mg	True value AgI mg	Deviation from true value Δ%	Standard deviation	
				mg	%
6	100·4	100·4	±0·0	±0·1	±0·1
6	202·9	203·4	−0·2	±0·13	±0·06
6	507·2	508·5	−0·2	±0·67	±0·13

50.2. DETERMINATION OF IODIDE IN THE FORM OF PALLADIUM(II) IODIDE (PdI_2)

(according to L. W. Winkler, 1918)

Palladium(II) iodide is practically insoluble in water, diluted hydrochloric acid and alkali chloride solutions. Reducing agents (alcohol) reduce the precipitate to metallic palladium. The solution should not contain sulphide and cyanide ions, because they also form precipitates with palladium(II) ions. Large amounts of bromide interfere by coprecipitation.

Tetravalent palladium forms a precipitate in the presence of ammonium chloride or potassium chloride. According to the thermoanalytical curves of Fig. 50.2. (measurements of G. Liptay) palladium(II) iodide has constant weight in the range 100–280°C; at higher temperatures, however, it decomposes with the liberation of iodine. The metal which remains behind takes up small amounts of oxygen between 680–780°C, but loses it again at higher temperatures. The palladium iodide precipitate must therefore be dried at 100–280°C, or must be decomposed at 650°C in an atmosphere of hydrogen and the equivalent amount of iodide calculated from the weight of metallic palladium obtained.

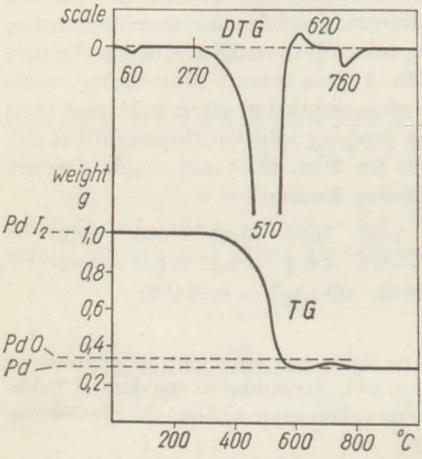

Fig. 50.2. Thermoanalytical curves of palladium iodide precipitate

According to Winkler a colloidal precipitate which is difficult to filter is obtained when palladium(II) chloride is added to a dilute solution of alkali iodide when chloride is absent. From hot solutions the precipitate is obtained in a powdery, easily filtered form, while from cold solutions a flocculent precipitate which may block the filter may be obtained. When the amount of palladium(II) iodide to be obtained is relatively high (about 0·1 g), therefore, the precipitation must be carried out from hot solutions, but when small amounts (several milligrams) of palladium iodide are to be precipitated, it is advisable to conduct the precipitation from a cold solution. Small amounts of the precipitate do not block the filter appreciably.

Preparation of palladium(II) chloride precipitant. Dissolve 0·5 g of palladium metal in 5 ml of concentrated nitric acid with gentle heating, and evaporate the solution in a small glass dish. Dissolve the dry residue in 10 ml of diluted hydrochloric acid (1 : 1), and evaporate to dryness again. Repeat the evaporation with hydrochloric acid twice. Dissolve the nitric acid-free residue in 10 ml of 10% hydrochloric acid to which 1 ml of alcohol has been added to reduce any chlorine present. Dilute the solution to 100 ml, leave overnight, and filter.

Procedure. Two procedures are described, depending on the amount of iodide present relative to the chloride content.

When *large amounts of iodide* are present relative to the chloride content, dilute the neutral solution so that the amount of palladium iodide present per 100 ml will be about 0·1 g. Add 1 g of sodium chloride for each 100 ml of the solution, and when it has dissolved add 20 ml of the palladium chloride reagent. Boil the mixture on a small flame until the precipitate, which is flocculent initially, becomes powdery. Collect the precipitate after 24 or 48 hr on a G 4 glass, A 1 porcelain or No. 4 glass texture filter-funnel, wash with 50 ml cold water, and dry at 130°C to constant weight (2 hr). Cool and weigh

the palladium iodide precipitate. For very accurate measurements add 0·1 mg to the weight of the precipitate as a correction.

When the *amount of iodide* present *is small* (several mg) compared to the chloride content, the precipitation must be effected from cold solution. To 100 ml of the neutral solution, containing large amounts of chloride, add 5 ml of the palladium(II) chloride precipitant. Mix and allow to stand for 24–48 hr. Collect the flocculent precipitate on an A 1 porcelain, G 4 glass or No. 4 glass texture filter-funnel, wash with 25 ml of cold water, and dry at 130°C for two hr. Cool and weigh.

Stoichiometric factors: $2\,I/PdI_2 = 0{\cdot}70462$; $2\,IO_3/PdI_2 = 0{\cdot}97113$; $I_2O_5/PdI_2 = 0{\cdot}92671$.

Notes. (1) The second method can usually be used for the determination of small amounts of iodide in the presence of large amounts of chloride. The correction used must be determined from the following table according to the amount of chloride present:

Chloride content in 100 ml solution	g:	0·5–5·0	8·0	10·0	12·0
Correction	mg:	+0·1	+0·2	+0·4	+0·6

(2) Sulphates and nitrates have no appreciable affect on the accuracy of the method when less than 1 g/100 ml of anion is present. Accurate results can only be obtained in the absence of bromide ions. Small amounts of bromide (several tenths of 1 g in 100 ml) give results which are just acceptable. When large amounts of bromide are present (several g in 100 ml) the method cannot be used.

Separation Methods

50.3. I^-—Cl^-, Br^-

(a) Iodide ions can be oxidized to elementary iodine with nitrous acid, and the iodine can then be distilled with water vapour from a glass apparatus (Fig. 49.1.).

Procedure. Transfer the mixed halide solution to a 1·5 litre distillation flask and dilute to about 700 ml with water. Connect the dropping funnel and condenser to the neck of the flask, and lubricate the ground glass joints with syrupy phosphoric acid. Add 25 ml of 10% sodium nitrite solution and 3 ml of diluted sulphuric acid (1 : 1) to the flask from the funnel, and turn on the condenser water. Distil the liberated iodine. Two flasks connected in series, which each contain 50 ml of a 1 : 1 mixture of chloride-free 5% sodium carbonate solution and 3% hydrogen peroxide solution should be used as receiver flasks. Cool the flasks in ice-water. The iodine distils completely in 30–50 min and the solution which remains in the distillation flask is decolourized.

Continue the distillation for 30 min after the solution becomes decolourized. Heat the solutions in the receiver flasks to boiling to decompose the hydrogen peroxide. Acidify the cooled solution with sulphuric acid. If elementary iodine is liberated it must be reduced with sulphurous acid.

Note. Occasionally, if the solution in the receiver flask is not adequately cooled, the hypoiodite formed in the sodium carbonate solution is partly converted to iodate. Hydrogen peroxide will not reduce iodate to iodide. On acidification, iodate and iodide ions then react to form elementary iodine. Any iodine liberated can be reduced quantitatively to iodide with sulphurous acid. Silver iodide can be precipitated from the solution with silver nitrate after acidification with 5 ml of 1 N nitric acid.

(b) A mixture of the three silver halides can be precipitated from one aliquot of the sample solution (see Chapter 50.1.) and can be weighed. Let the weight of AgCl + AgBr + AgI be *A*. The weighed precipitate can then be converted to silver chloride by heating in an atmosphere of chlorine. The operations must be carried out according to the procedure described for separation (a) bromide-chloride (Chapter 49.3.). Let the weight of silver chloride obtained after heating in chlorine be *B*.

Palladium(II) iodide should be precipitated from a second aliquot of the sample solution, according to the method of L. W. Winkler (see Chapter 50.2.). Let the weight of palladium(II) iodide be *C*. The equivalent amount of silver chloride can be calculated from the weight of the palladium(II) iodide: $0{\cdot}795 \cdot C =$ $= \text{AgCl}$. Similarly the amount of silver iodide equivalent to the palladium(II) iodide can be calculated: $1{\cdot}303 \cdot C = \text{AgI}$. These values can then be substituted into the corresponding equations:

$$\begin{array}{rcl} \underset{x}{\text{AgCl}} + \underset{y}{\text{AgBr}} & = & A - 1{\cdot}303 \cdot C \\ x + 0{\cdot}7633\ y & = & B - 0{\cdot}795 \cdot C \end{array}$$

$$\begin{array}{ll} y = 4{\cdot}224\ (A - B - 0{\cdot}508 \cdot C) & \ldots \text{AgBr g} \\ x = A - 1{\cdot}303 \cdot C - y & \ldots \text{AgCl g.} \end{array}$$

Note. The method only gives accurate results if less than 0·1 g of bromide is present in 100 ml of the solution from which the palladium(II) iodide is precipitated.

(c) *By indirect analysis according to H. Baubigny, 1898 and J. Beck, 1915.*[1] The three halides must be precipitated as their silver salts and weighed. The precipitate must then be heated to 95°C with a mixture of potassium dichromate and concentrated sulphuric acid; silver chloride and silver bromide decompose with the formation of chromyl chloride and bromine; silver iodide is converted to non-volatile iodic acid:

$$6\,\text{AgCl} + \text{K}_2\text{Cr}_2\text{O}_7 + 7\,\text{H}_2\text{SO}_4 = 3\,\text{Ag}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \\ + 7\,\text{H}_2\text{O} + 3\,\text{Cl}_2\uparrow$$

$$6\,\text{AgBr} + \text{K}_2\text{Cr}_2\text{O}_7 + 7\,\text{H}_2\text{SO}_4 = 3\,\text{Ag}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \\ + 7\,\text{H}_2\text{O} + 3\,\text{Br}_2\uparrow$$

$$2\,\text{AgI} + 2\,\text{K}_2\text{Cr}_2\text{O}_7 + 9\,\text{H}_2\text{SO}_4 = \text{Ag}_2\text{SO}_4 + 2\,\text{K}_2\text{SO}_4 + 2\,\text{Cr}_2(\text{SO}_4)_3 + \\ + 8\,\text{H}_2\text{O} + 2\,\text{HIO}_3$$

[1] H. Baubigny, *Compt. rend.* **127**, 1219 (1898); J. Beck, *Chemiker Z.* **39**, 405 (1915).

When the chlorine and bromine have been removed, the iodic acid can be reduced with sulphurous acid; silver iodide is then reprecipitated and can be filtered and weighed. Silver ions which remain in solution must then be precipitated with potassium iodide, and the amounts of each halide present calculated from the data obtained.

Procedure. Prepare a stock solution of the alkali halides. Take two aliquots which contain not more than the equivalent of 0·4 g of silver halide precipitate (*A* g). Precipitate the halides from each solution with a slight excess of silver nitrate, wash the first precipitate, dry it at 130°C, and weigh (*B*). Filter the other silver halide precipitate through a layer of asbestos, wash with 1% acetic acid, and then loosen the asbestos layer and transfer it to an Erlenmeyer flask. For each 0·3–0·4 g of the silver salt, add 2 g of potassium dichromate and 30 ml of concentrated sulphuric acid to the flask through the filter, and heat at 95°C on a water bath for 2 hr. Near the end of the reaction, bubble air through the solution to remove the last traces of chlorine. Cool the solution, dilute cautiously to 300–400 ml with water, filter off the asbestos, and add a slight excess of saturated sodium bisulphite solution dropwise to the filtrate until the smell of sulphur dioxide is noticeable. Collect the silver iodide precipitate on the filter, wash, dry at 130°C, and weigh. Let the weight of the precipitate be *C*. Precipitate the silver from the filtrate of the silver iodide precipitation using a slight excess of potassium iodide, and weigh the silver iodide (*D*) which is equivalent to the chlorine and bromine content in the original aliquot. The percentage halide content of the substance can be calculated from the data obtained.

Sample weight: *A*, AgCl + AgBr + AgI: *B*, AgI: *C*, AgI equivalent to AgCl + AgBr: *D*, AgCl + AgBr: $B - C$.

$$\% \text{ chloride: } [2{\cdot}57865 \cdot D - 3{\cdot}2340\ (B - C)]\ \frac{24{\cdot}7384}{A}$$

$$\% \text{ bromide: } [4{\cdot}22398\ (B - C) - 2{\cdot}57865\ D]\ \frac{42{\cdot}556}{A}$$

$$\% \text{ iodide: } \frac{54{\cdot}05{\cdot}C}{A}$$

50.4. $I^- — Cl^-$ AND $I^- — Br^-$ BY INDIRECT ANALYSIS

In these methods the two halides are precipitated together as their silver salts. After weighing, the precipitate is converted to silver chloride or metallic silver, as described for the indirect determination of $Br^- — Cl^-$ ions (see Chapter 49.3.). The precipitate is then reweighed. From the data obtained the weights of each halide present can be calculated.

(a) *Determination of iodide in the presence of chloride.* If the weight of the AgI + AgCl precipitate is *A*, and the weight of AgCl obtained from the precipitate after treatment with chlorine is *B*, and if the AgCl present in the original precipitate-mixture is x and the AgI present, y, the following equations can be derived:

$$x + y = A$$

$$x + \frac{\text{AgCl}}{\text{AgI}} y = B$$

From this we obtain:

$$y = \frac{1}{1 - \frac{\text{AgCl}}{\text{AgI}}} (A - B)$$

$$y = 2{\cdot}5673\ (A - B) = \text{AgI g}$$

$$x = A - y \qquad\qquad = \text{AgCl g}$$

The *relative error* in x and y can be calculated from the following equations:

$$\frac{\Delta x}{x} = \left(1{\cdot}57 + 1{\cdot}57 \cdot \frac{y}{x}\right)\frac{\Delta A}{A} + \left(2{\cdot}57 + 1{\cdot}57 \cdot \frac{y}{x}\right)\frac{\Delta B}{B}$$

$$\frac{\Delta y}{y} = \left(2{\cdot}57 + 2{\cdot}57 \cdot \frac{x}{y}\right)\frac{\Delta A}{A} + \left(1{\cdot}57 + 2{\cdot}57 \cdot \frac{x}{y}\right)\frac{\Delta B}{B}.$$

The sum of the relative errors shows a minimum at the following mixing ratio:

$$\left(\frac{x}{y}\right)_{\text{min}} = \sqrt{\frac{\text{AgCl}}{\text{AgI}}} = 0{\cdot}79\,.$$

The sum of the errors is therefore least when the precipitate contains 44% of silver chloride and 56% of silver iodide. The values of the relative errors in x and y as a function of the mixing ratio are shown in Table 50.3. The values of the error in measurements are:

$$\frac{\Delta A}{A} = \frac{\Delta B}{B} = 0{\cdot}1\%.$$

TABLE 50.3. Relative errors of indirect determinations of iodide and chloride ions

(a) Determination by heating in chlorine gas current

Relative content of the precipitate		Relative error of AgCl determination	Relative error of AgI determination*
AgCl = x	AgI = y	$\frac{\Delta x}{x}$ %	$\frac{\Delta y}{y}$ %
1, wt about 10%	10, wt about 90%	3·56	0·48
4·4, wt 44%	5·6, wt 56%	0·82	0·82
1, wt 50%	1, wt 50%	0·74	0·94
10, wt about 90%	1, wt about 10%	0·46	5·56

* $\frac{\Delta A}{A} = \frac{\Delta B}{B} = 0{\cdot}1\%$

According to these data, the relative error of the result is about eight times as great as the error in the actual measurements even at the optimum mixing ratio.

TABLE 50.4. Relative errors of indirect determinations of iodide and bromide ions

(b) Determination by heating in chlorine gas current

Relative content of the precipitate		Relative error of AgI determination*	Relative error of AgBr determination*
AgI = x	AgBr = y	$\frac{\Delta x}{x}$ %	$\frac{\Delta y}{y}$ %
1, wt about 10%	1, wt about 90%	10·9	0·98
1, wt 50%	1, wt 50%	1·9	1·7
5·3, wt 53%	4·7, wt 47%	1·8	1·8
10, wt about 90%	1, wt about 10%	1·0	8·9
		$^*\frac{\Delta A}{A} = \frac{\Delta B}{B} = 0{\cdot}1\%$	

(b) *Determination of iodide in the presence of bromide.* Let A represent the sum of the weights of the precipitate AgI + AgBr, x the weight of AgI in the precipitate, and y the weight of AgBr present. Let the weight of AgCl obtained after heating in an atmosphere of chlorine be B. The following equations can then be derived:

$$x + y = A$$

$$\frac{\text{AgCl}}{\text{AgI}}\,x + \frac{\text{AgCl}}{\text{AgI}}\,y = B\,.$$

From this

$$x = 4{\cdot}9958\,A - 6{\cdot}5453\,B = \text{AgI g}$$

$$y = A - x \qquad\qquad = \text{AgBr g}$$

The *relative errors* in x and y can be calculated from the following equations:

$$\frac{\Delta x}{x} = \left(5 + 5\cdot\frac{y}{x}\right)\frac{\Delta A}{A} + \left(4 + 5\cdot\frac{y}{x}\right)\frac{\Delta B}{B}$$

$$\frac{\Delta y}{y} = \left(4 + 4\cdot\frac{x}{y}\right)\frac{\Delta A}{A} = \left(5 + 4\cdot\frac{x}{y}\right)\frac{\Delta B}{B}\,.$$

The sum of the relative errors shows a minimum at the following mixing ratio:

$$\left(\frac{x}{y}\right)_{\min} = \sqrt{\frac{\text{AgI}}{\text{AgBr}}} = 1{\cdot}11\,.$$

The sum of the errors is therefore least when the precipitate contains 53% of silver iodide and 47% of silver bromide. Table 50.4. shows the values of the relative errors as a function of the mixing ratio when the measurements are carried out with errors:

$$\frac{\Delta A}{A} = \frac{\Delta B}{B} = 0{\cdot}1\% .$$

According to these data, the relative error of the results is 18 times that of the measurements even at the most favourable mixing ratio. The accuracy of the determination therefore is not very high.

(c) *Determination after evaporation with ammonium iodide.* Precipitate the mixture of silver halides according to the procedure of Chapter 50.1., and weigh AgCl + AgI or AgBr + AgI. Transfer most of the precipitate to a weighed porcelain crucible and weigh (A). Add 3–4 times its bulk of solid ammonium iodide to the precipitate, andevaporate cautiously at 500°C in an electric furnace. Cool and weigh the silver iodide (B). The calculations can be carried out using the following equations:

Indirect analysis of $I^- — Cl^-$

$$x = 1{\cdot}5674\ (B - A) \quad \ldots\ldots \text{ AgCl g}$$
$$y = A - x \quad \ldots\ldots \text{ AgI g}$$

Relative errors in x and y:

$$\frac{\Delta x}{y} = \left(1{\cdot}57 + \frac{y}{x} \cdot 1{\cdot}57\right)\frac{\Delta A}{A} + \left(2{\cdot}57 + \frac{y}{x} \cdot 1{\cdot}57\right)\frac{\Delta B}{B}$$

$$\frac{\Delta y}{y} = \left(2{\cdot}57 + 2{\cdot}57\,\frac{x}{y}\right)\frac{\Delta A}{A} + \left(1{\cdot}57 + \frac{x}{y} \cdot 2{\cdot}57\right)\frac{\Delta B}{B} .$$

The mixing ratio which corresponds to the minimum of the sum of the errors $\left(u = \frac{\Delta x}{x} + \frac{\Delta y}{y}\right)$:

$$\left(\frac{x}{y}\right)_{\min} = \sqrt{\frac{\text{AgCl}}{\text{AgI}}} = 0{\cdot}79 .$$

Composition of the precipitate corresponding to the minimum sum of the error: AgCl: 44%; AgI: 56%. Table 50.5. shows the values of the relative errors if the errors in the measurements are:

$$\frac{\Delta A}{A} = \frac{\Delta B}{B} = 0{\cdot}1\% .$$

The error of the results is therefore 8 times as great as that of the measurement even at the most favourable mixing ratio.

Indirect analysis of $I^- — Br^-$

$$x = 3{\cdot}9968\ (B - A) \quad \ldots \text{ AgBr g}$$
$$y = A - x \quad \ldots \text{ AgI g.}$$

TABLE 50.5. Relative errors of indirect determinations of iodide and chloride ions

(c) Determination by evaporation with ammonium iodide

Relative content of the precipitate		Relative error of AgCl determination*	Relative error of AgI determination*
AgCl = x	AgI = y	$\frac{\Delta x}{x}$ %	$\frac{\Delta y}{y}$ %
1, wt about 10%	10, wt about 90%	3·56	0·46
4·4, wt 44%	5·6, wt 56%	0·82	0·82
1, wt 50%	1, wt 50%	0·74	0·94
10, wt about 90%	1, wt about 10%	0·47	5·56
		$^{*}\frac{\Delta A}{A} = \frac{\Delta B}{B} = 0{\cdot}1\%$	

TABLE 50.6. Relative errors of indirect determinations of iodide and bromide ions

(c) Determination by evaporation with ammonium iodide

Relative content of the precipitate		Relative error of AgBr determination*	Relative error of AgI determination*
AgBr = x	AgI = y	$\frac{\Delta x}{x}$ %	$\frac{\Delta y}{y}$ %
1, wt about 10%	10, wt about 90%	8·90	1·00
4·7, wt 47%	5·3, wt 53%	1·80	1·80
1, wt 50%	1, wt 50%	1·70	1·90
10, wt about 90%	1, wt about 10%	0·98	10·90
		$^{*}\frac{\Delta A}{A} = \frac{\Delta B}{B} = 0{\cdot}1\%$	

Relative errors in x and y

$$\frac{\Delta x}{x} = \left(4 + 4\frac{y}{x}\right)\frac{\Delta A}{A} + \left(5 + 4\frac{y}{x}\right)\frac{\Delta B}{B}$$

$$\frac{\Delta y}{y} = \left(5 + 5\frac{x}{y}\right)\frac{\Delta A}{A} + \left(4 + 5\frac{x}{y}\right)\frac{\Delta B}{B}.$$

The mixing ratio which corresponds to the minimum of the sum of the errors $\left(u = \frac{\Delta x}{x} + \frac{\Delta y}{y}\right)$:

$$\left(\frac{x}{y}\right)_{\min} = \sqrt{\frac{\text{AgBr}}{\text{AgI}}} = 0{\cdot}88\,.$$

Composition of the precipitate corresponding to the minimum sum of the error: AgBr: 47%; AgI: 53%. Table 50.6. shows the values of the relative errors if the errors in the measurements are:

$$\frac{\Delta A}{A} = \frac{\Delta B}{B} = 0{\cdot}1\%\,.$$

The error of the result is therefore about 18 times as great as that of the measurements, even at the most favourable mixing ratio.

50.5. I^-—IO_3^- DETERMINATION IN THE PRESENCE OF EACH OTHER

Acidify an aliquot part of the solution with 5 ml of 2 N sulphuric acid, dilute to about 200 ml and add a saturated solution of sulphur dioxide dropwise until the iodate is reduced quantitatively to iodide. This can be determined by observation of the disappearance of iodine colour which appears transitionally.

Pass carbon dioxide into the boiling solution until the excess sulphur dioxide is removed. Evaporate the solution to about two-thirds of its volume. Dilute the solution with water to about 200 ml and precipitate silver iodide by the addition of a slight excess of 5% silver nitrate solution with constant stirring. After about 30 min, acidify the solution with 5 ml nitric acid, and heat to boiling after further 30 min standing. Cool, collect the precipitate on a G 4 glass filter-crucible, wash with 50 ml of water containing nitric acid and then with 50 ml of 1% acetic acid. Dry the precipitate at 130 °C for 2 hr. Cool and weigh. Weighing form: AgI.

The total amount of iodine present can be calculated from the weight of the precipitate.

Take a second aliquot of the sample, dilute to 200 ml with water, acidify with 2 N sulphuric acid, and boil to remove iodine liberated by the reaction

$$IO_3^- + 5\,I^- + 6\,H^+ = 3\,H_2O + 3\,I_2\uparrow\,.$$

(a) After the removal of iodine, acidify the solution with several drops of sulphuric acid and test whether further liberation of iodine occurs. If not, add 1 drop of saturated sulphurous acid solution to the cold solution. If iodine is liberated excess iodate was present in the sample. Add excess sulphurous acid to the solution to reduce iodate quantitatively to iodide. Remove the excess sulphur dioxide by heating while carbon dioxide is passed into the solution. Cool, and precipitate silver iodide with silver nitrate solution, acidify the mixture with nitric acid and after 30 min heat the mixture to boiling. Collect the precipitate on a filter after several hours standing, wash, and dry as described above. Weighing form: AgI.

From the weight of the precipitate the amount of iodine corresponding to the excess iodate can be calculated. This value must be subtracted from the total amount of iodine. One-sixth of the residue corresponds to iodate, and the remaining five-sixths corresponds to the iodide present.

(b) If, after the removal of iodine, further iodine liberation does not occur when sulphurous acid is added, the sample contains excess iodide. Precipitate silver iodide with silver nitrate, and weigh according to the former procedure. The amount of iodine can be calculated from the weight of the precipitate. This value must be subtracted from the total amount of iodine present. One-sixth of the residue corresponds to iodate, while the remaining five-sixths was present as iodide in the original sample.

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to Table 50.1.

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CHAPTER 51

FLUORINE — F — 18·998

F_2, H_2F_2, H_2SiF_6

BECAUSE of its high chemical activity, elementary fluorine does not occur naturally. Hydrogen fluoride is present in some volcanic gases. In aqueous solution it is used for etching glass and as a laboratory reagent. It is stored in a plastic vessel or vessels coated with paraffin wax. The most important minerals of fluorine are fluorite (CaF_2), cryolite (Na_3AlF_6) and apatite [Ca_3(Cl, F) $(PO_4)_3$]. Small amounts of fluorite are also found in some pyrites, zinc and lead sulphides, as well as in some silicates (topaz, lepidolite, opal). Small amounts of fluorine are present in almost all soils, from which part of it passes into springs and soil waters. River water contains about 0·6 mg of fluorine per litre while sea water contains 0·2—0·3 mg/l. Fluorine is a constituent of animal and plant tissues. Plant ash contains 0·03—0·1 per cent, and teeth and bone ashes contain about 0·04—0·4 per cent of fluorine. Opal glasses and enamels also contain fluorine.

Forms of determination. Fluorine and fluorine compounds are always determined as fluoride. The most important forms of determination of fluoride are summarized in Table 51.1. The most frequently used forms of determination are calcium fluoride and lead chlorofluoride. Argentimetric titration of lead chlorofluoride is a rapid method of determination. Accurate results can also be obtained by titration with thorium nitrate. This last method, primarily when used in conjunction with the separation by distillation according to H. H. Willard and O. B. Winter, has been developed into a highly accurate determination. The hexafluosilicate anion is not usually determined directly, but the silicic acid and fluoride content of the solution are most frequently determined. If the hydrogen ion concentration is known, the equilibrium between fluoride and hexafluosilicate ions can then be estimated from the data obtained:

$$[SiF_6]^{2-} + 2\,H_2O \rightleftharpoons SiO_2 + 4\,H^+ + 6\,F^-$$

$$H^+ + F^- \rightleftharpoons HF.$$

The pH of 0·05—0·025 M alkali hexafluosilicate solutions is 3·5, a relatively stable value for this rather wide concentration interval.

Preparation and fusion of the sample. The alkali fluorides, silver and mercury(I) fluoride are easily soluble in water. The normal fluorides of Cu(II), Zn, Pb and Fe(III) are slightly soluble in water, while the solu-

bilities of the alkaline earth fluorides are the smallest (100 ml of water dissolves 163 mg BaF_2, 12 mg SrF_2 and 1·6 mg CaF_2). Potassium, sodium and barium silicofluorides are slightly soluble in water, but are practically insoluble in the presence of alcohol. In practice, therefore, most samples must be fused before analysis, or the interfering ions must first be removed. The following chapters detail the most important methods of fusion and separation of the more important types of sample.

TABLE 51.1. Forms of determination of fluorine
(for References see p. 62)

Ref. Number	Forms of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	CaF_2	$CaCl_2$	neutral	CaF_2	78·08	400–950
2.	PbClF	$PbCl_2$	pH 4·1–4·8	PbClF	261·67	70–540
3.	BiF_3	$Bi(NO_3)_3$	CH_3COOH	BiF_3	266·00	50– 93
4.	LaF_3 + + 2 $La(OH)_3$	$(CH_3COO)_3La$	CH_3COOH + + CH_3COONa	$LaF_3 \cdot La_2O_3$	521·76	475–946
5.	$(C_6H_5)_3SnF$	$(C_6H_5)_3SnCl$	neutral	$(C_6H_5)_3SnF$	369·02	< 158
6.	$UOF_2 \cdot 2\,H_2O$	$UOSO_4$	neutral or slightly acidic	U_3O_8	842·21	812–945

Seldom used forms of determination: 7. potassium fluorosilicate $K_2[SiF_6]$, 8. barium fluorosilicate $Ba[SiF_6]$, 9. barium fluoride (BaF_2).

51.0.1. *Fusion of calcium fluoride, cryolite and silicates, and preparation of the solution for precipitation (J. J. Berzelius, 1816)*

Calcium fluoride and cryolite cannot be converted completely to sodium fluoride when fused with sodium carbonate because an equilibrium is established. In the presence of excess of silica, however, silicates containing fluorine are formed which can easily be fused with sodium carbonate. When the melt is leached with water, calcium carbonate and part of the silicic acid remains behind, while sodium fluoride dissolves completely. If the pH is reduced by the addition of ammonium carbonate, most of the colloidal silicic acid is also precipitated, and only a small amount of silicic acid remains behind in the filtrate with the alkali fluoride. When the neutralized solution is boiled with ammoniacal zinc oxide solution, zinc silicate is precipitated and the alkali fluoride can be separated from it by dissolution in water. Any phosphate in the solution must be precipitated with silver nitrate in neutral medium, and the excess silver in the filtrate must be precipitated with sodium chloride. Calcium fluoride or lead chlorofluoride can then be precipitated from the silicic acid-free fluoride solution.

This method can also be used for the fusion of silicates which contain fluoride, e.g. topaz, lepidolite, mica, slags, glasses and enamels. For these samples additional silicic acid need not be added to the sample before fusion with sodium carbonate.

Ammoniacal zinc oxide solution. Reagent. 1: Dissolve analytical-grade zinc metal in hydrochloric acid, and precipitate zinc hydroxide with sodium hydroxide, taking care that excess sodium hydroxide is not added. Wash the precipitate with water, and dissolve in the minimum volume of concentrated ammonia; 2–5 ml of this solution must be used for each determination.

Reagent 2: Zinc hydroxide can also be prepared from analytical-grade zinc nitrate. This reagent does not contain traces of chloride.

Reagent 3: Pure zinc oxide does not dissolve in ammonia. Concentrated ammonium carbonate solution, however, dissolves it easily (M. Kleinstück, 1911)[1]; 0·5 g of zinc oxide must be dissolved in 2 ml of 10% ammonium carbonate and 3 ml of 20% ammonia. This reagent can be prepared more rapidly and does not contain traces of chloride. When the solution also contains phosphate, therefore, it is advisable to use the chloride-free zinc oxide reagent because it does not form a precipitate with the silver nitrate reagent used for the precipitation of phosphate ions. This reagent should also be used if the chloride content of the solution is to be determined after the silicic acid has been precipitated.

Procedure. Add 2·5 times its bulk of pure finely powdered quartz and 6 times its bulk of a 1 : 1 mixture of potassium and sodium carbonates to the finely powdered sample in a platinum crucible. Cover the crucible with a lid, and heat cautiously.

The fusion must be carried out slowly at the sintering temperature, because otherwise the contents may foam out owing to the liberation of carbon dioxide. The easily flowing melt becomes viscous and pasty during the heating. The melt must not be heated too strongly otherwise losses may occur from the volatilization of alkali fluoride. It is not necessary to melt the dense reaction products because the fusion is complete when the liberation of carbon dioxide ceases.

Cool, place the crucible in a large beaker, add water, and dissolve the residue from the crucible by heating on a water bath. Filter the solution on filter paper, and wash the residue thoroughly with 1% sodium carbonate solution.

The alkaline filtrate contains some silicic acid and the fluorine content of the sample is present quantitatively in the form of alkali fluoride.

Neutralize the filtrate with hydrochloric or nitric acid so that the solution just shows a yellow colour to methyl orange. Cover the beaker with a watch glass during neutralization to minimize any loss caused by the vigorous evolution of carbon dioxide. Dissolve 4 g of ammonium carbonate in the nearly neutral solution, place the beaker on a water bath at 40 °C for 1–2 hr, and allow to stand overnight. Collect the silicic acid on a filter paper, and wash with water containing ammonium carbonate. Only a small amount of silicic acid should then remain in the filtrate with the alkali fluoride.

To precipitate silicic acid quantitatively, evaporate the solution almost to dryness in a platinum or porcelain dish. Dissolve the residue in a small

[1] M. Kleinstück, *Z. anal. Chem.* **50**, 697 (1911).

volume of water, and neutralize in the presence of phenolphthalein with 2 N hydrochloric or nitric acid until the faint pink colour disappears. To remove carbon dioxide and any alkali salt adsorbed on the silicic acid, heat the solution to boiling so that the phenolphthalein exhibits an alkaline reaction again. Cool, neutralize the solution again by the cautious addition of hydrochloric or nitric acid. Repeat the boiling and neutralization until the solution does become pink on repeated boiling. The addition of 1–2 ml of 2 N hydrochloric or nitric acid is usually required. Add 2–5 ml of ammoniacal zinc oxide reagent to the solution, and boil until the smell of ammonia completely disappears. Filter the precipitate on a filter paper, wash the precipitate with water, and precipitate the fluoride from the filtrate in the form of CaF_2 or PbClF according to the procedures described below (see Chapters 51.1. and 51.2.).

Notes. (1) When the fluoride is to be determined in the form of PbClF, or when the solution also contains phosphate ions, nitric acid must be used for acidification and a chloride-free ammoniacal zinc oxide reagent must be employed.

(2) In the presence of pyrites and sulphides it is advisable also to add a small amount of sodium peroxide to the fusion mixture.

(3) When silicates are fused, additional silicic acid must not be added with the sodium carbonate.

51.0.2. *Fusion of samples containing phosphate and preparation of the solution for the precipitation of fluoride (H. Rose, 1849; A. A. Koch, 1904)*[1]

After the separation procedure, phosphate or chromate in the sample remain with fluoride ions and interfere in the gravimetric determination of fluoride. These interfering ions can be removed by precipitation with silver nitrate in neutral medium. In the initial precipitation of silicic acid, however, nitric acid must be used instead of hydrochloric acid so that the solution does not contain large amounts of chloride.

Procedure. Neutralize the filtrate obtained after fusion with silicic acid and the removal of silicate with ammoniacal zinc oxide reagent, using 2 N nitric acid and phenolphthalein, rinse into a 250-ml volumetric flask and precipitate phosphate and chromate ions with a slight excess of 5% silver nitrate. Dilute the mixture to volume, shake thoroughly, and allow the precipitate to settle. Filter the supernatant solution through a filter paper into a dry beaker. Pour off the first 10 ml of the filtrate, and from the next fraction remove 200 ml with a pipette and transfer the solution to a 250-ml volumetric flask. Precipitate the excess silver ions with a slight excess of 5% sodium chloride solution, dilute the mixture to the mark, shake thoroughly, and allow the precipitate to settle. Filter the solution through a filter paper into a dry beaker, discard the first 10 ml and precipitate fluoride from a 200-ml aliquot as calcium fluoride or lead chlorofluoride.

The amount of fluoride obtained must be multiplied by 1·563 to obtain the fluoride content of the original sample.

[1] H. Rose, *Liebigs Ann.* **72**, 343 (1849), A. A. Koch, *Z. anal. Chem.* **43**, 469 (1904).

Notes, (1) Beryllium fluoride and cerium(III) fluoride can also be prepared for analysis by this method.

(2) When the sample contains small amounts of phosphate and silicate (plant ashes, concentrates of natural waters) 100–150 ml of the solution must be made slightly alkaline with sodium hydroxide, 1 g of freshly precipitated cadmium hydroxide must be added,[1] and the solution must be boiled for 30 min and filtered. Fluoride can be determined in the filtrate in the form of calcium fluoride or lead chlorofluoride or by a volumetric or colorimetric method. Cadmium hydroxide retains phosphate and silicate ions quantitatively and does not itself dissolve appreciably.

51.0.3. *Separation of fluorine by distillation of silicon tetrafluoride (S. Penfield, 1882)*

Hydrogen fluoride evolved by the action of concentrated sulphuric acid on fluorides reacts with silicic acid with the formation of gaseous silicon tetrafluoride, SiF_4. When silicon tetrafluoride is absorbed in 50% alcohol saturated with potassium chloride it hydrolyses to form hexafluorosilicic acid:

$$3\,SiF_4 + 3\,H_2O \rightleftharpoons 2\,H_2[SiF_6] + H_2SiO_3,$$

the potassium salt of which is immediately precipitated:

$$H_2[SiF_6] + 2\,KCl \rightleftharpoons K_2[SiF_6]\downarrow + 2\,HCl.$$

The hydrochloric acid formed can be titrated with sodium hydroxide in the presence of methyl orange.

This method can be used for the analysis of insoluble fluorides (CaF_2, apatite), as well as for the separation of fluorine from interfering ions (Al^{3+}, SO_4^{2-}, PO_4^{3-}). The distillation is rather difficult, because completely dry glass vessels and rinsing gases must be used. Silicates containing fluorine must first be fused, and the fluoride must be separated from silicic acid. Gelatinous silicic acid reacts with hydrogen fluoride with the formation of non-volatile $SiOF_2$, and thus in the presence of silicic acid the results are lower than the true values. Although the separation of silicic acid by the method of Berzelius can be carried out quite reliably, it is difficult to convert fluoride to the anhydrous form after the separation to ensure quantitative liberation of SiF_4. Owing to this difficulty fluoride is often now distilled as hexafluorosilicic acid with superheated steam.

[1] *Preparation of cadmium hydroxide pulp.* Dissolve about 2 g of crystalline cadmium sulphate $CdSO_4 \cdot 8/3\,H_2O$ in 100 ml of distilled water by heating, and precipitate cadmium hydroxide from the hot solution with about 15 ml of 1 N sodium hydroxide solution. Collect the rapidly settling precipitate on a white-band filter paper, and wash with about 100 ml of water to remove alkali (test the filtrate for alkali with phenolphthalein). Make a hole in the filter paper with a glass rod and rinse the precipitate into a beaker with 20 ml distilled water added from a pipette. This suspension may then be added to the solution to be analysed.

51.0.4. *Distillation in the form of hexafluorosilicic acid (H. H. Willard, O. B. Winter, 1933)*

This method is usually used when insoluble fluorides (CaF_2) and interfering ions (aluminium, phosphate, sulphate) are present. Silicates or samples containing silicic acid must first be fused with sodium carbonate. Silicic acid must then be separated with ammonium carbonate and ammoniacal zinc oxide according to the method of Berzelius, and the alkali fluoride solution evaporated to small volume. The sample, however, must not be made anhydrous.

The hexafluorosilicic acid must be distilled from a perchloric acid solution of boiling point 135 $\pm$ 10°C in the presence of quartz or glass. The distillate must be collected in slightly alkaline solution. Perchloric acid has the advantage over sulphuric or phosphoric acids, which can also be used, in that it does not form precipitates with other ions present in the solution because most perchlorates are easily soluble in water and perchloric acid. At 135°C perchloric acid is able to fuse most insoluble fluorides.

In the presence of phosphates (fertilizers, apatite, food ashes) and sulphates, phosphoric acid or sulphuric acid are collected in the distillate and interfere. When this happens the distillate must be made slightly alkaline and evaporated, and the distillation must be repeated with perchloric acid. The distillation must be repeated when pyrites and sulphides are present. In the presence of organic substances, perchloric acid cannot be used because of the danger of explosion. When organic material is present the distillation must be effected in the presence of sulphuric acid at 160—170°C, and the fluoride in the distillate weighed as $CaF_2 + CaSO_4$.

Organic fluorine substances can be decomposed in a sealed tube or in a Parr bomb with metallic potassium. It is advisable, however, to combust fluorine compounds by the method of L. Mázor in a 15 cm (alundum) tube. The end 5–6 cm of the tube which is in contact with the pyrolysis products must be coated with aqueous red lead pulp and dried. The organic fluorine compound is placed into a platinum vessel in the other end of the tube, and heated in a current of oxygen or air. The organic material is evaporated and decomposed, and the decomposition of the products becomes complete on the surface coated with red lead where carbon dioxide and water are formed at 550–570°C. At the same time fluorine remains bound on the surface of the red lead as lead fluoride. When the combustion is completed the layer of red lead can be dissolved from the tube with nitric acid which contains hydrogen peroxide. Fluoride can then be precipitated from the solution in the form of PbClF and weighed, or the tube can be placed directly into the flask of the distillation apparatus and the fluorine distilled in the form of H_2SiF_6. Fluorine in the distillate can be determined by a gravimetric, titrimetric or colorimetric method.

Amorphous silicic acid, aluminium and boric acid retard the distillation; when these substances are present a higher volume (300–500) ml of distillate must be collected. In the presence of aluminium, distillation must be made at 162 $\pm$ 2°C with sulphuric acid, and must then be repeated with sulphuric acid at 132–142°C.

For mineral waters, a sample which contains at least 0·2 mg of fluorine must be taken. This sample must be made slightly alkaline and evaporated to 50 ml. The distillation of fluorine can then be carried out on this solution.

Any steam distillation apparatus which permits measurement of the temperature of the solution in the distillation flask can be used. A suitable apparatus is shown in Fig. 51.1. The 150 ml distillation flask (1) is fitted with a capillary funnel (2) on to which a thermometer (4) is fastened by means of platinum wire. The thermometer should be able to measure temperatures between 100–200°C. Steam must be passed through the tube, or water must be added through the funnel (3). The bottom of the flask must be heated with a gas flame, and an asbestos ring must be placed around the flask to avoid overheating of the upper parts of the flask. Drops of liquid are retained by a layer of silver wool 4 cm thick (6), which can be placed in the side arm of the flask through the stopper (5). A spiral condenser (8) must be connected to the side-arm (7) by a rubber stopper. The distillate is collected in a 300—700 ml Erlenmeyer flask (9).

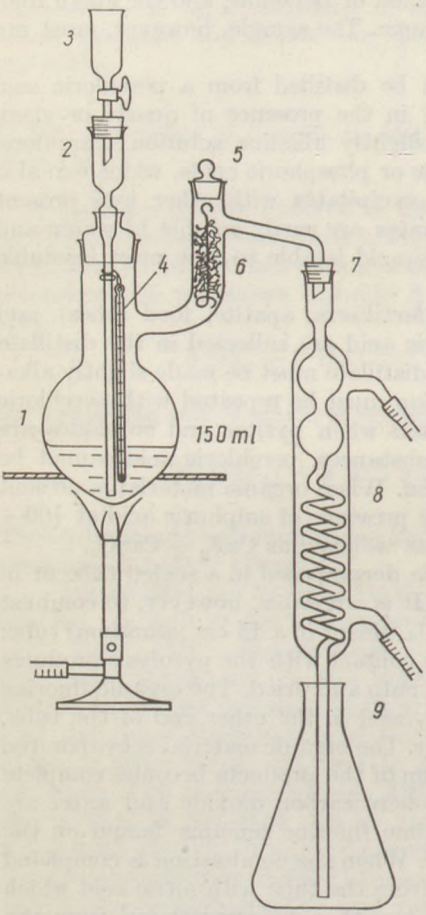

Fig. 51.1. Vapour distillation apparatus for fluorine determination

Procedure. Place 2–3 g of broken quartz or pieces of window glass into the distillation flask.[1] Place the sample, containing 4–100 mg fluorine, into the flask, either as a solid sample or in solution. Add 10 ml of 60% perchloric acid (or 15 ml 50% sulphuric acid) and sufficient water to make the boiling point of the solution lower than 110°C. Assemble the apparatus, and place the flask in the asbestos ring so that only one third of the flask is in contact with the flame. Begin the distillation, and when the temperature of the flask reaches 135°C pass steam into the flask or add water dropwise through the funnel. Control the heating and addition of water so that the temperature of the solution

[1] Laboratory equipment glass is not suitable for this purpose, because it is chemically resistant and its boron content may cause interference.

remains between 130–140 °C. When interfering ions are not present, fluorine distils quantitatively with the first 75–100 ml of distillate. When interfering ions are present it is advisable to collect 300–500 ml of distillate.

Owing to the silicic acid content of the distillate, it is not suitable for the direct determination of more than 4 mg of fluorine. Therefore, make the distillate slightly alkaline, evaporate nearly to dryness, add 20 ml of water and 1–2 ml of ammoniacal zinc oxide reagent (or 1 g of freshly prepared cadmium hydroxide), boil for 30 min, and filter. Precipitate calcium fluoride or lead chlorofluoride from the filtrate. If less than 4 mg of fluorine is present the silicic acid must not be removed.

Note. The precipitation of the silicic acid content of the filtrate can be avoided if the fluoride is determined by one of the titrimetric methods. Sulphate and phosphate ions, however, interfere in these determinations.

Titration of fluoride ions with standard thorium nitrate solution. If thorium nitrate is added to a solution containing fluoride, thorium fluoride, which is insoluble in 50% alcohol is formed:

$$Th^{4+} + 4\,F^- = ThF_4\downarrow .$$

The reaction also takes place when hexafluosilicate ions are present, but in this case the hydrogen ions formed during the reaction must be neutralized, otherwise an equilibrium is established:

$$3\,Th^{4+} + 2\,[SiF_6]^{2-} + 4\,H_2O \rightleftharpoons 3\,ThF_4\downarrow + 8\,H^+ + 2\,SiO_2.$$

The end point of the reaction can be detected by the zirconium alizarin dye lake. Fluoride ions form a very stable complex with zirconium $[ZrF_6]^{2-}$; thus, in the presence of fluoride ions, the reddish-violet lake decomposes:

Zr-alizarin sulphonic acid + 6 F^- = $[ZrF_6]^{2-}$ + alizarin sulphonic acid
(reddish-violet) (yellow)

The yellow alizarin sulphonic acid which is liberated forms a reddish-violet lake with the excess thorium:

alizarin sulphonic acid + Th^{4+} = Th-alizarin sulphonic acid
(yellow) (reddish-violet)

The free alizarin sulphonic acid is also a sensitive acid–base indicator which shows a yellow colour in acidic medium and a red colour in alkaline medium. The pH region corresponding to the colour change is 3·7–4·2. Fluoride must therefore be titrated in slightly acidic solution, because only under these conditions can the colour change of the indicator be easily observed.

Reagents. (1) *Zirconium nitrate solution:* Dissolve 1 g of crystalline $Zr(NO_3)_4 \cdot 5H_2O$ in 250 ml water.

(2) *Alizarin red solution:* Dissolve 1 g of sodium alizarin sulphonate in 100 ml of ethyl alcohol and filter the solution. Add a further 150 ml of ethanol to the filtrate. Use a 3 : 2 mixture of reagents 1 and 2 respectively as an indicator.

(3) *Standard thorium nitrate solution (ca. 0.02 N):* Dissolve 2·76 g of $Th(NO_3)_4 \cdot 4H_2O$ or 3·48 g of $Th(NO_3)_4 \cdot 12\,H_2O$ in 1 litre of water, and determine

the titre of the solution containing a known amount of fluoride (e.g with pure 0·02 N Na_2SiF_6 or 0·02 N LiF solution).

(4) *Dilute hydrochloric acid* (1 : 50).

Procedure. Add a small amount of sodium hydroxide to the silicic-acid free distillate, and evaporate to 20–50 ml. Add 3 drops of alizarin–zirconium indicator and add dilute hydrochloric acid dropwise to the solution, until the colour of the indicator just disappears. Dilute the solution with an equal volume of ethanol, and titrate with standard 0·02 N thorium nitrate solution against a white back ground until the colour of the indicator is permanent.

The reaction is slow near the end point, and therefore the titration must be carried out slowly.

Notes. (1) The indicator itself consumes fluoride. The indicator blank can be determined by a blank titration. The amount of indicator used in the titrations is titrated with 0·02 N sodium fluoride solution until the colour of the indicator disappears.

(2) The accuracy of the method can be judged from the data of H. H. Willard and O. B. Winter (see Table 51.2). From this data it is evident that this method gives good results even for very small amounts (0·017 mg) of fluoride.

(3) The titration can also be carried out with 4–5 drops of zirconium salt-free 0·1% aqueous sodium alizarin sulphonate solution.

(4) In *technical analyses* the silicic acid need not be removed from the distillate. In such cases a buffer solution must be added to adjust the solution to a favourable pH. The monochloracetic acid-acetate Roweley-Churchill buffer is usually suitable. This can be prepared by dissolving 23·62 g of monochloracetic acid and 5·0 g of solid sodium hydroxide in 250 ml of water. In technical practice a factorized standard solution is usually used; each millilitre is equivalent to about 2 mg of fluorine (a little more dilute than 0·1 N). To prepare such a solution dissolve 13·75 g of $Th(NO_3)_4 \cdot 4\ H_2O$ or 17·30 g of $Th(NO_3)_4 \cdot 12\ H_2O$ in one litre of water and standardize the solution against analytical grade sodium fluoride.

Procedure. Add 4–5 drops of an aqueous 0·1% sodium alizarin sulphonate solution to the distillate, and add 1 N sodium hydroxide solution dropwise to the yellow solution until it becomes permanently red. Acidify the solution with 0·5 N hydrochloric acid until the yellow colour of the indicator appears, add 1 ml of monochloracetic acid-acetate buffer, and titrate slowly with standard thorium nitrate solution to pink colour.

51.0.5. *Distillation of fluorine in the form of H_2SiF_6 from drinking waters (E. Schulek and P. Rózsa 1947)*

Schulek and Rózsa have developed a micro-gravimetric method by which more than 5 mg of lead chlorofluoride can be weighed. The steam distillation can be carried out at 160—180°C from concentrated zinc chloride solution in the apparatus shown in Fig. 51.2. They found that when less than 10 mg of fluoride is present, it can be distilled easily in the form of H_2SiF_6.

The apparatus consists of a 70—80 ml Kjeldahl flask with a short neck to which a condenser is connected by a ground glass joint. A small funnel fitted with a long tube and stopcock is connected to the flask stopper via a ground glass joint. A small thermometer can be fixed on the tube with a platinum wire to observe the temperature of the liquid.

Procedure. Take 100–1000 ml of the water, according to its fluoride content, make alkaline, and evaporate it in a large platinum dish. Dissolve the residue in concentrated hydrochloric acid and rinse the solution into the distillation apparatus. Make the solution alkaline with 10% sodium hydroxide solution and then make just acid with 10% hydrochloric acid. The final volume of the solution is then about 10 ml.

TABLE 51.2. Distillation of fluorine in the form of H_2SiF_6 according to H. H. Willard and O. B. Winter, 1933

Substance	Distillate ml	F^- true value mg	F^- found mg	Deviation from true value Δ%
NaF	50	7·34	7·37	+ 0·4
,,	50	7·37	7·43	+ 0·8
,,	30	0·167	0·167	± 0·0
plant ash + NaF	50	7·37	7·37	± 0·0
,,	50	7·37	7·40	+ 0·4
,,	30	0·167	0·171	+ 2·4
,,	30	0·017	0·019	+11·8
100 mg amorphous silicic acid + NaF	50	9·73	8·96	− 8·0
100 mg amorphous silicic acid + NaF	100	9·73	9·27	− 4·7
100 mg amorphous silicic acid + NaF	150	9·73	9·73	± 0·0
50 mg amorphous silicic acid + NaF	50	9·73	9·64	− 0·9
10 mg boric acid + NaF	150	9·73	9·68	− 0·5
1 g $AlCl_3$ + NaF	250	9·50	5·14	−45·0
250 mg $AlCl_3$ + NaF	225	9·50	9·34	− 1·7
100 mg ,, ,,	50	9·50	9·47	− 0·3
50 mg ,, ,,	50	9·50	9·45	− 0·5
Na_2SiF_6	50	7·54	7·51	− 0·4

Insoluble fluorides mg	Found F^- mg	F^- true value %	F^- found %	Deviation from true value Δ%
50 mg fluorite	24·45	48·70	48·90	+ 0·4
	24·24		48·48	− 0·4
250 mg apatite	9·78		3·91	
	9·83		3·93	
250 mg rock phosphate	8·68	3·52	3·47	− 1·4
	8·75		3·50	− 0·5
50 mg cryolite	29·09	54·20	54·18	− 0·04
	27·18		54·36	+ 0·3

Add 15 g of anhydrous zinc chloride and 20 mg of finely powdered quartz to the solution, and lubricate the ground glass joints with a little phosphoric acid. Add 20 ml of methyl alcohol to the solution and distil below 100 °C. Repeat the distillation nine times after the addition of 10 ml portions of methyl alcohol. Collect methyl alcohol in a large silver dish containing 1–2 grains of solid potassium hydroxide, and determine the boric acid after evaporation, gentle ignition and neutralization with standard 0·01 N sodium hydroxide solution in the presence of mannitol.[1]

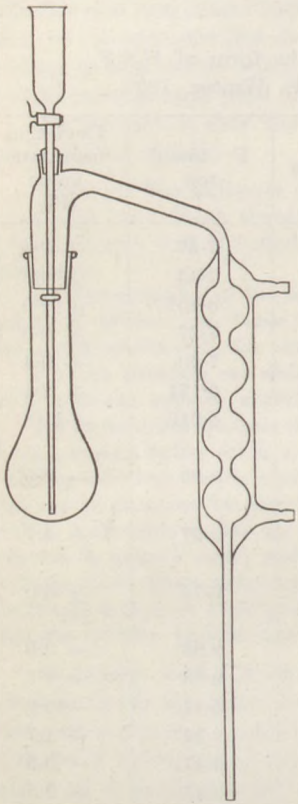

Fig. 51.2. Distillation apparatus for hydrogen silicofluoride according to Schulek and Rózsa

To the boric acid-free residue in the flask add 5–6 ml of water, connect the funnel of the apparatus with a steam source and begin the distillation of H_2SiF_6. Heat the flask with a small flame until the temperature of the solution is 160 °C, and steam distil 300 ml of water at 160–180 °C. This amount of liquid is necessary for the quantitative distillation of fluorine. Make the distillate alkaline in a platinum dish, evaporate to 10 ml and repeat the distillation with 15 g of zinc chloride. Take at least 300 ml of the distillate into a platinum dish, make alkaline, and evaporate to dryness. Finally add a small amount of sodium bicarbonate to precipitate as zinc carbonate and zinc silicate traces of zinc chloride which distil with the fluoride. Dissolve the dry residue in a small volume of water and filter into a small beaker.

Evaporate the solution to 4–5 ml, make the solution just acid in the presence of methyl red using 10% and then 0·5% nitric acid, dilute the solution to 10 ml and precipitate lead chlorofluoride by the dropwise addition of 5 ml of 1% lead chloride solution. Leave the mixture overnight. Collect the precipitate on a glass filter, wash four times with 3 ml of saturated lead chlorofluoride solution and then with 1 ml of water, and finally 3 times with 3 ml alcohol, and dry in a current of air for 40 min. Weigh after 10 min.

Stoichiometric factor: F/PbClF = 0·072611.

Notes. (1) The result of the gravimetric measurement can be checked by a titrimetric method. Dissolve the lead chlorofluoride precipitate with five 1 ml portions of hot sodium acetate-acetic acid solution (0·4 g crystalline sodium acetate + 4 ml water + 5 drops of glacial acetic acid) into a small flask, wash three times

[1] L. Erdey, *Bevezetés a kémiai analizisbe II. Térfogatos analizis.* (Introduction to Chemical Analysis. II. Volumetric analysis). 8. Ed. Tankönyvkiadó, Budapest (1965), p. 64.

with 1·5 ml of water, and titrate the chloride with standard 0·01 N silver nitrate solution in the presence of 1 drop of 5% variamine blue acetate indicator.

(2) The hydrochloric acid distilled can be titrated with 0·1 N sodium hydroxide. If the amount of sodium chloride formed during the titration is greater than 0·10–0·15 g it must be precipitated with silver nitrate; 0·15 g of sodium chloride does not decrease the solubility of lead chloride to such an extent that precipitation occurs, but larger amounts do.

51.0.6. *Cyclic steam distillation method for the determination of small amounts of fluorine (G. Pietzka, P. Ehrlich, 1933, and L. Mázor 1957)*

The distillation methods for the determination of fluorine detailed above have the common disadvantage that even if small amounts of fluorine are to be determined, rather large volumes of distillate must be collected, and therefore the solution must later be evaporated after the addition of alkali. Losses may occur under these conditions because the walls of glass vessels may adsorb fluorine in the form of calcium fluoride. The cyclic distillation apparatus modified by L. Mázor enables the distillation to be carried out with 20—30 ml of water, and the distillate can be absorbed in water made alkaline with 2—3 drops of sodium silicate. Sodium silicate prevents the adsorption of fluoride ions on the walls of the vessel.

Figure 51.3. shows a cyclic distillation apparatus. Steam is introduced through the tube into the bottom of the distillation flask *A*. Between the walls of the double-walled flask a liquid with constant boiling point is placed (isoamyl ether B.P: 172°C, or anisole B.P: 154°C). This is heated electrically by the element fixed to the flask. The optimum heating temperature is thus maintained without special attention to the apparatus. Perchloric acid cannot be used for the distillation because if the flask breaks a dangerous explosion may occur. For distillation with sulphuric acid anisole can be used as a heating liquid, while if phosphoric acid is used, isoamyl ether is suitable.

During distillation the vapour from the heating liquid condenses in the tube connected to the outer flask and flows back into the apparatus. H_2SiF_6 and steam pass from the flask into the condenser *C* through a layer of silver wool. The silver wool prevents small amounts of sulphuric or phosphoric acid from passing from the flask to the distillate. The solution to be distilled can be introduced through the stopper of the flask *A*, after removing the layer of silver wool. Steam is produced in flask *B*, which is heated electrically, and is carried to the bottom of the flask in a slow current of nitrogen or oxygen which is introduced into the bottom of the steam flask. The heating must be regulated so that 4–5 ml of water per minute distil into the flask. The distillate passes back into the steam-producing flask via a thin tube from the collector cup. The lowest part of this tube is fitted with a stop-cock for the removal of the distillate from the flask.

Procedure. Into the distilling flask *A* place a few pieces of quartz or broken window glass to serve as a source of silicon for the generation of H_2SiF_6. Introduce the sample, which contains about 0·10–4·0 mg of fluoride, into the flask after the removal of the silver wool trap. Add 10 ml of diluted sulphuric acid (1 : 1) for samples of alkali or alkaline earth fluorides, or 10 ml of diluted

phosphoric acid (1 : 1) for samples which are difficult to decompose (thorium fluoride), replace the silver wool trap, and stopper the flask using spring fasteners. Start the flow of carrier gas and heat the distillation flask. When the heating solution begins to boil, switch on the steam generator and adjust the rate of

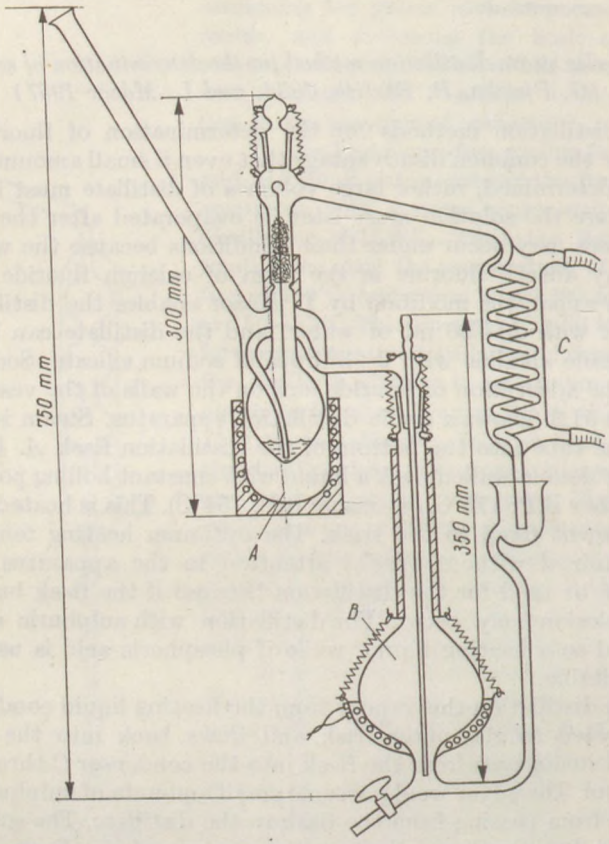

Fig. 51.3. A recycling distillation apparatus for fluorine

distillation. Place one drop of sodium silicate solution into the collector solution. Take care that the solution does not become very diluted in the distillation flask, otherwise the solution may foam over into the condenser. Distil for 40–60 minutes, stop heating and open the stopper. Place a receiving vessel under the outlet tube and collect the distillate. Rinse the steam generating flask twice with 5 ml of water, and titrate the fluoride content of the distillate with 0·02 N thorium nitrate solution.

Before gravimetric determination evaporate the solution almost to dryness in a platinum dish, and precipitate silicic acid by boiling with freshly prepared cadmium hydroxide or ammoniacal zinc oxide reagent.

Notes. (1) There is no need to change the acid in the distillation flask after each determination; this is only necessary when the distillation is not uniform because of the salt accumulation. When the acid is used for the first time it is advisable to pass steam through it to remove any volatile impurities.

(2) The accuracy of the method can be judged from the data of Table 51.3. (measurements of L. Mázor). The accuracy of the method, as it is a micro method, is very good.

TABLE 51.3. Determination of fluoride with cyclic steam distillation

Substance	Sample mg	F^- found mg	F^- true value mg	Deviation Δ%
Calcium fluoride	5·246	2·516	2·553	−1·81
	3·128	1·506	1·522	−0·52
	4·826	2·304	2·350	−0·95
Lead fluoride	5·440	0·815	0·843	−0·52
	4·282	0·691	0·664	+0·67
	5·100	0·851	0·790	+1·20
Lead chlorofluoride	10·216	0·801	0·742	+0·58
	8·412	0·581	0·611	−0·36
	13·110	1·010	0·952	+0·44

51.1. DETERMINATION IN THE FORM OF CALCIUM FLUORIDE (CaF_2)

(J. A. Berzelius, 1816; H. Rose, 1849)

Fluoride can be precipitated with calcium chloride from neutral or slightly acidic, acetic acid solution as well as from slightly alkaline solution. The calcium fluoride precipitate can be weighed in this form after washing and gentle ignition, or by evaporation with sulphuric acid and gentle ignition; the fluoride content can be calculated from the weight increase:

$$2\ NaF + CaCl_2 = 2\ NaCl + CaF_2 \downarrow .$$

Calcium fluoride is obtained as a white, gelatinous precipitate which becomes crystalline on gentle heating. Calcium fluoride is not completely insoluble in water. The value of the solubility product at 18°C, $L = [Ca^{2+}]\,[F^-]^2 = 3 \cdot 4 \cdot 10^{-11}$. At room temperature, 1 litre of water dissolves 16 mg of calcium fluoride. The solubility is greatly affected by the grain size of the precipitate. Gelatinous calcium fluoride is inclined to form a fairly stable colloidal solution. The presence of excess of calcium ions can decrease the solubility of the precipitate to one quarter of its solubility in water (4 mg/l). Acetic acid 0·5–2·0 N dissolves between 150–300 mg of calcium fluoride per litre, depending on its concentration. The solubility

of calcium fluoride increases considerably even in slightly acidic medium in the presence of ions which form stable fluoride complexes, e.g. in the presence of Al, Fe(III), Be, Zr, SiO_3^{2-} and BO_3^{3-} ions.

On heating, the calcium fluoride precipitate loses its water content up to 400°C. On further heating in dry air its weight is constant up to 950°C. On prolonged heating at a slight red glow hydrogen fluoride is evolved owing to the effect of water vapour in the air from the combustion products of the gas flame. Thus, if calcium fluoride is heated on a gas flame for 1 hour at a red glow its weight decreases by 2 mg.

Apart from its appreciable solubility the calcium fluoride precipitate has a further disadvantage from the analytical point of view that it is difficult to filter. Owing to the gel structure and ease of peptization of the precipitate, it can only be filtered without loss and blocking of the filter paper after the addition of other substances. In practice, therefore, calcium fluoride must always be precipitated with some other easily filtered precipitate, or it must be coagulated with a colloid of opposite characteristics. The following coprecipitation methods are generally used in practice.

(1) *Precipitation in the form of* $CaF_2 + CaCO_3$ *(J. Berzelius, H. Rose).* Add 1 ml of 2 N sodium carbonate solution to the neutral or neutralized solution of alkali fluoride, and precipitate calcium fluoride and calcium carbonate by the addition of excess calcium chloride solution. The mixture of the two precipitates is more easily filtered than calcium fluoride alone.

Heat gently and dissolve the calcium carbonate from the calcium fluoride with dilute acetic acid. Remove the excess of acetic acid by evaporation and extract the calcium acetate with water. Ignited calcium fluoride can be easily filtered. Wash, ignite the precipitate, and weigh.

The disadvantage of the method is that acetic acid dissolves some of the calcium fluoride and therefore losses occur. This error may cause a 15–25% decrease in the weight of the precipitate when small amounts of fluoride ($F^- < 0{\cdot}1\%$) are determined.

(2) *Precipitation in the form of* $CaF_2 + CaSO_4$ *(F. L. Hahn, 1926).* When fluoride is precipitated with excess calcium chloride in the presence of sulphate, calcium sulphate is precipitated with the calcium fluoride and facilitates the filtration of the calcium fluoride. The mixture can be weighed after gentle ignition, and hydrogen fluoride can then be removed with a few drops of sulphuric acid. The calcium sulphate which remains behind can then be weighed. The fluoride content of the original precipitate can be calculated from the weight increase. One gram of CaF_2 is equivalent to 1·7436 g of $CaSO_4$, and thus each 0·7436 g increase in weight is equivalent to 1 g of CaF_2; 1 mg increase in weight thus corresponds to 0·654 mg of F^-, 0·698 mg of HF or 1·344 mg of CaF_2. This method yields the best result and can be regarded as the most reliable. The details of the procedure are given below.

(3) *Precipitation in the form of* $CaF_2 + HgS$ *(I. Sarudi, 1947).*[1] When 0·5–1 ml of saturated mercury(II) chloride solution is added to the

[1] I. Sarudi, *Szervetlen mennyiségi analizis* I. *(Inorganic quantitative analysis* I.) (1947), p. 212.

calcium fluoride precipitate obtained from a solution which is free of alkali carbonate and sulphate, and the solution is saturated with hydrogen sulphide, the precipitate of mercury(II) sulphide obtained facilitates quantitative precipitation of calcium fluoride. The precipitate can be filtered and ignited; mercury(II) sulphide volatilizes and calcium fluoride remains behind.

(4) *Precipitation in the presence of gelatin or tannin.* The calcium fluoride precipitate can be more easily filtered after the addition of 10 drops of 1% gelatin solution or 2—3 ml of 3% tannin solution to each 100 ml of the solution. When the solution is boiled the precipitate coagulates and the colloid obtained on precipitation can be easily filtered. The organic material is combusted on ignition.

Removal of interfering ions. Only alkali metal ions, and zinc and cadmium ions, may be present during the precipitation of fluoride as calcium fluoride. Phosphate, silicate, sulphate and borate ions interfere. The fluoride must be distilled in the form of H_2SiF_6 before determination, and silicic acid must be removed from the solution with ammoniacal zinc oxide or freshly precipitated cadmium hydroxide. When the sample is free of phosphate, the interfering ions can also be removed by the method of Berzelius. Phosphate ions can be separated from fluoride by the method of Rose and Koch (see Chapter 51.0.2.). Part of the boric acid is precipitated with the calcium fluoride in the form of calcium metaborate. Calcium borate can be removed with acetic acid after the precipitate has been ignited.

Procedure. Take 100 ml of solution containing 20–200 mg of fluoride and which is free of silicate and interfering ions. Neutralize the solution with sodium hydroxide in the presence of phenolphthalein, and then add dilute acetic acid until the red colour of the phenolphthalein just disappears. Add sodium sulphate to the solution until at least 0·2 g of sulphate ion (0·67 g of $Na_2SO_4 \cdot 10\,H_2O$) is present per 100 ml of solution. When large amounts of fluoride are present a greater amount of sulphate is required. Add excess 10% calcium chloride solution to the cold solution with constant stirring, and filter the precipitate on paper after several hours standing. Wash the precipitate with hot water until chloride can no longer be detected in the washings. Dry the precipitate in a drying oven, remove the precipitate from the filter paper, and combust the filter paper in a weighed platinum crucible. Transfer the main part of the precipitate to the crucible, and ignite at 500–700 °C in an electric muffle furnace or on a gas flame for 15 minutes. Allow the crucible to cool in a desiccator and weigh. Check for constant weight, and then add a few drops of concentrated sulphuric acid to the precipitate, remove excess sulphuric acid on an air bath, and ignite the residue at 500–700 °C for 15 min. Allow the crucible to cool in a desiccator and weigh. An increase in weight of 1 mg is equivalent to 0·654 mg of F^-, 0·689 mg of HF or 1·344 mg of CaF_2.

Notes. (1) The results are 0·5–2% lower than the true values owing to the solubility of calcium fluoride. Better results are obtained if a loss of 1·6 mg of calcium fluoride is allowed for every 100 ml of mother liquor and washing solution and then applied as a correction. Errors caused by the presence of silicic acid cannot be eliminated.

(2) It is not advisable to ignite the whole precipitate with the filter paper because the calcium sulphate may be partly reduced.

(3) The accuracy of the method can be judged from the data of Table 51.4. (Measurements of M. Pápay).

TABLE 51.4. Determination of fluoride ions in the form of calcium fluoride

Number of measurements	Weight increase after evaporation with H_2SO_4 mean mg	Weighed fluoride ion mean mg	F^- true value mg	Deviation from true value Δ%	Standard deviation		Mother liquor + wash solution ml	Correction CaF_2 resp. F mg	Corrected value mg	Deviation of corrected value from true value Δ%
					mg	%				
6	85·9	56·2	57·2	−1·75	±2·5	±4·3	200	CaF_2 = +3·2	57·8	+1·0
6	207·0	139·4	142·1	−1·9	±2·0	±1·4	200	F^- = +1·6	141·0	−0·8

51.2. DETERMINATION IN THE FORM OF LEAD CHLOROFLUORIDE (PbClF)

(G. Starck, 1911; W. H. Adolph, 1913)

When a solution of lead chloride is added to a neutral or slightly acidic solution containing fluoride the double halide, lead chlorofluoride, PbClF, is slowly precipitated. The precipitate can be washed with saturated lead chlorofluoride solution, dried and weighed. The weight of precipitate obtained is about 14 times the weight of the fluoride, and therefore the method can also be used for the micro determination of fluoride ions (E. Schulek and P. Rózsa, Chapter 51.0.5.).

Lead chlorofluoride is quite soluble in water. At 18°C 1 litre of water dissolves 325 mg of lead chlorofluoride. The solubility increases to about three times this value in hot water. At 18°C the solubility product,

$$L = [Pb^{2+}]\cdot[Cl^-]\cdot[F^-] = 2{\cdot}3\cdot10^{-9}.$$

The lead chloride precipitant contains two ions common to the precipitate, and thus the use of excess precipitant depresses the solubility of the precipitate to a lower value than that of calcium fluoride. Thus 100 ml of 0·01 M lead chloride solution dissolves 2·0 mg of lead chlorofluoride, while the same volume of 0·05 M lead chloride solution only dissolves 0·2 mg. The solubility and composition of the precipitate also depend on the pH of the solution. The most favourable pH range for the precipitation is 4·1–4·8. At lower pH values the precipitate is appreciably soluble, and at higher pH values it becomes contaminated with basic salts (PbClOH). The precipitate should be washed with water saturated with lead chlorofluoride. The surface of the precipitate, however, must first be rinsed with

a small volume of water (4 ml), because any lead chloride which adheres to the surface may precipitate lead chlorofluoride from the washing solution.

The thermogravimetric investigations of Duval[1] (1953) have shown that the precipitate has constant weight between 66–538°C. At higher temperatures lead chlorofluoride decomposes more rapidly and partly sublimes. According to Duval the precipitate should be dried at 130–150°C. Our own thermogravimetric investigations which are shown in Fig. 51.4. (measurements of I. Markovits), however, have revealed that the weight of the precipitate increases by about 12% up to 450°C. Above 450°C there is a stepwise decrease in weight. The rate of decomposition shows a maximum about at 800°C, and the decomposition is complete at 950°C. Thus the curve does not exhibit a horizontal portion corresponding to a suitable weighing temperature range. The results of test analyses, however, have shown that when the precipitate is dried at 100–130°C its weight deviates from the true value by not more than 1%. Thus the loss owing to the solubility of the precipitate and the weight increase on heating almost compensate each other.

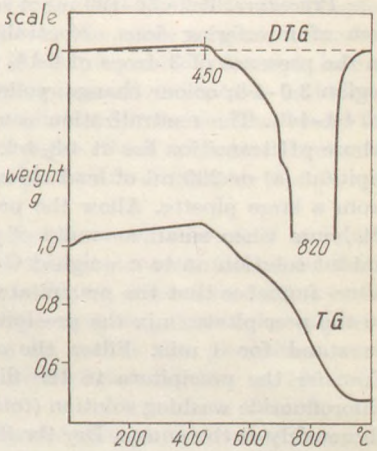

Fig. 51.4. Thermoanalytical curves of lead chlofluoride precipitate

The determination can be carried out in solutions of soluble fluorides which do not contain anions which form precipitates with lead (SO_4^{2-}, S^{2-}, PO_4^{3-}). Acetate and tartrate ions interfere, because they tend to form complexes with lead ions, and also change the pH of the solution. Chloride ions show less interference. If the mole ratio of chloride ions to fluoride ions is not greater than 1 : 17 the error is less than 1%. Alkali nitrates retard the formation of the precipitate, and large amounts interfere (foreign salt effect). When the amount of fluoride present is less than 4 mg, i.e. for the micro determination of fluoride, small amounts of sodium silicate which pass into solution during distillation in the form of H_2SiF_6 do not interfere. When the amount of fluoride present is greater than 4 mg, silicic acid must be removed from the solution with freshly precipitated cadmium hydroxide or ammoniacal zinc oxide reagent (Chapter 51.0.1.). Calcium ions interfere.

Fluoride can be separated from interfering ions by distillation (Chapters 51.0.3–6.) or by the method of Berzelius (Chapter 51.1.).

Precipitant. (a) *Saturated (ca.* 0·04 M*) lead chloride solution :* Shake 12 g of crystalline lead chloride with 1 litre of water for 1 hour. Allow the residue to settle and filter the solution. (The residue cannot be used for the preparation of further

[1] Cl. Duval, *Inorganic Thermogravimetric Analysis.* Elsevier, Amsterdam (1953), p. 89.

precipitant because it also contains basic salt.) 300 ml of saturated lead chloride solution is required for the precipitation of 100 mg of fluoride.

(b) *Saturated lead chloronitrate solution :* Dissolve 20·5 g of lead nitrate and 15 g potassium chloride in 1 litre of water; 200 ml of this solution is required for precipitation.

Washing solution : Shake 0·5 g of filtered lead chlorofluoride precipitate with 1 litre of water for about 1 hr. Allow the precipitate to settle and filter the solution.

Procedure. Take 50–100 ml of solution containing 4–100 mg of fluoride and free of interfering ions. Neutralize the solution with 0·5 N nitric acid in the presence of 3 drops of 0·1% bromophenol blue indicator (transition pH region 3·0–4·6; colour change: yellow-blue) until a blue colour appears (pH = = 4·1–4·6). The neutralization can also be checked with an indicator paper whose pH transition lies at 4·3–4·6. Add 300 ml of saturated lead chloride precipitant (a) or 200 ml of lead chloronitrate solution (b) with constant stirring from a large pipette. Allow the precipitate to settle for several hours, or for 24 hours when small amounts of precipitate are formed. Decant the supernatant solution on to a weighed G 4 glass, A 1 porcelain or No. 4 glass texture filter- funnel so that the precipitate remains in the beaker. Add 4 ml of water to the precipitate, mix the precipitate with the water, and allow the mixture to stand for 1 min. Filter the original supernatant solution at the pump. Transfer the precipitate to the filter with small volumes of saturated lead chlorofluoride washing solution (total volume 30–40 ml), and remove the liquid thoroughly at the pump. Dry the filter and precipitate at 100–130 °C for 1 hr, cool and weigh.

Stoichiometric factor: F/PbClF = 0·072611.

TABLE 51.5. Determination of fluoride ions in the form of lead chlorofluoride

Number of measurements	Mean of PbClF precipitate weights mg	True value PbClF mg	Deviation from true value Δ%	Standard deviation	
				mg	%
6	49·1	49·5	−0·8	±0·2	±0·4
6	491·9	494·7	−0·6	±0·4	±0·08

Notes. (1) The precipitate can be dissolved from the filter with hot nitric acid.

(2) Results which are accurate to 0·02–1 % can be obtained by this method, as shown in Table 51.5. (measurements of Z. Rády).

(3) The precipitate can be dissolved from the filter with nitric acid or hot acetate buffer, and its chloride content can be titrated by the Volhard method. Alternatively the chloride can be titrated directly with silver nitrate in the presence of Variamin Blue indicator, (see Chapter 51.0.5).

(4) When smaller volumes of solution are used the method is suitable for the micro determination of fluorine (see Chapter 51.0.6).

Separation Methods

51.3. $F^- - Cl^-, PO_4^{3-}$

When chloride and phosphate are also to be determined in the sample the method of sample preparation recommended by Rose and Koch (see Chapter 51.0.2.) must be supplemented by the following procedure.

Procedure. After fusion with sodium carbonate and silicic acid (see Chapter 51.0.1.) remove the silicic acid with ammoniacal zinc oxide reagent, neutralize the solution accurately with 2 N nitric acid in the presence of phenolphthalein, and dilute the solution to about 150 ml. Precipitate silver chloride and silver phosphate with a slight excess of 5% silver nitrate, let the solution stand for 2–3 hr, and filter the precipitate on filter paper. Wash with small volumes of water (treat the filtrate according to the procedure of Chapter 51.0.2. and determine fluoride as described therein).

Dissolve the pure AgCl and Ag_3PO_4 precipitate with hot 2 N ammonia and rinse the filter paper with water. Dilute the ammoniacal filtrate to about 100 ml, and precipitate silver chloride with sufficient 2 N nitric acid to make the solution strongly acidic. Boil for a few minutes to coagulate the precipitate. Cool the mixture, allow to stand for 2–3 hr, collect the precipitate on a glass filter, and wash with water acidified with nitric acid. Dry at 130 °C for 2 hr. Weighing form: AgCl.

Precipitate the silver in the filtrate from the chloride determination using hydrochloric acid, filter, and determine phosphate in the filtrate with magnesia mixture (Chapter 56.1.2.2.). Weighing form: $MgNH_4PO_4 \cdot 6\,H_2O$ or $Mg_2P_2O_7$.

51.4. $F^- - BO_3^{3-}$

(a) Distil boric acid as methyl borate by the method of E. Schulek and P. Rózsa (Chapter 51.0.5.) from slightly acid concentrated zinc chloride solution using methyl alcohol. Collect the methyl alcohol in a large silver dish containing 1–2 grains of solid potassium hydroxide, evaporate cautiously to dryness, ignite the residue gently, dissolve it in water, neutralize the solution in the presence of methyl red, and finally titrate with 0·1 N sodium hydroxide solution in the presence of mannitol and phenolphthalein indicator.

(b) Precipitate calcium fluoride in the presence of borate ions from 100 ml of the slightly acidic solution with a slight excess of calcium acetate. Rinse the precipitate into a distillation flask and distil methyl borate by the dropwise addition of methyl alcohol to the boiling solution (Chapter 59.1.). Collect the distillate in a large platinum dish which contains a known amount of calcium oxide. Evaporate the methyl alcohol, ignite the residue, and weigh. The increase in weight is equivalent to the boric acid content of the sample.

Fluoride can be precipitated as calcium fluoride together with calcium car onate from a second aliquot of the sample. Ignite the precipitate and dissolve calcium oxide and metaborate from the sample with diluted acetic acid (see Chapter 51.1.). Ignite and determine the weight of the CaF_2.

51.5. $F^- — SiF_6^{2-}$

Accurately neutralize a 10–15 ml aliquot of the solution of alkali fluoride and alkali silicofluoride by the addition of 0·1 N sodium hydroxide or hydrochloric acid in the presence of bromocresol purple indicator (pH 5·7). Add 10–25 ml of 4 N calcium chloride solution which has also been accurately neutralized in the presence of bromocresol purple. Hydrochloric acid is liberated according to the following equation:

$$Na_2SiF_6 + 3\ CaCl_2 + 3\ H_2O = H_2SiO_3 + 3\ CaF_2 + 2\ NaCl + 4\ HCl.$$

The hydrochloric acid can be titrated with carbonate-free 0·1 N sodium hydroxide, and from the amount of standard solution consumed the SiF_6^{2-} content can be calculated. Silicic acid, H_2SiO_3, is a weak acid and consumes no alkali under these circumstances.

Add freshly precipitated cadmium hydroxide to a second aliquot of the sample, make slightly alkaline, and boil. Silicic acid is precipitated and the fluorine is quantitatively dissolved. Determine fluoride in the filtrate by a suitable gravimetric or titrimetric method.

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9. A. Gautier and P. Clausmann, *Bull. soc. chim. France* [4] **11**, 872 (1912); *Compt. rend.* **154**, 1469 (1912).

CHAPTER 52

CYANIDE — CN^- — 26·018

HYDROGEN cyanide is found in combined form in the stones of some fruits (bitter almond, plum, peach). Benzaldehyde cyanide hydrate is produced from the kernel of bitter almond by hydrolysis, and "bitter almond water" used in pharmacy is produced from this by steam distillation. Pure hydrogen cyanide is a colourless, volatile liquid (B. P. 26·5°C), which smells of bitter almond. It is miscible with water and alcohol in all proportions. Alkali cyanides are used in the processing of gold ores. Large amounts of complex metal cyanides are used for the preparation of electroplating baths.

The salts of hydrocyanic acid are extremely poisonous!

Dissolution of the sample. The alkali and alkaline earth cyanides, and also mercury cyanides, are easily soluble in water. The heavy metal cyanides are slightly soluble in water or are practically insoluble. The complex alkali cyanides of iron(II), iron(III), mercury(II) and cobalt(III) are soluble in water but cyanide ions cannot be detected in their solutions with silver nitrate. Hydrogen cyanide is a very weak acid ($K_s = 7{\cdot}2 \cdot 10^{-10}$), and therefore most cyanides are decomposed with acid (carbonic, tartaric, sulphuric acid) and hydrogen cyanide can be distilled. The distillate can be absorbed in silver nitrate solution made slightly acid with nitric acid.

TABLE 52.1. Forms of determination of cyanide ions
(for References see p. 68)

Ref. Number	Forms of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	AgCN	$AgNO_3$	slightly alkaline	AgCN	133·899	110
2.	AgCN	$AgNO_3$	w. r. t. ammonia	Ag	107·880	700–900

Form of determination. Cyanide, like chloride, can be precipitated with silver nitrate, and the silver cyanide precipitate can be dried and weighed. Owing to the interference from halide ions, cyanide is usually determined by the titrimetric method of Liebig–Deniges in which halide does not

interfere[1]. The iodometric bromine cyanide method of E. Schulek can also be applied successfully. This method can also be used in the presence of reducing substances.[2]

52.1. DETERMINATION IN THE FORM OF SILVER CYANIDE (AgCN)

(R. Fresenius, 1870)

When a small amount of silver nitrate is added to a solution containing cyanide, a white precipitate which dissolves in the excess cyanide is formed:

$$Ag^+ = 2\,CN^- \rightleftharpoons [Ag(CN)_2]^-.$$

The complex silver cyanide ion formed is fairly stable (stability constant $p_k = 20{\cdot}9$). A permanent precipitate is only formed when all the cyanide ions are converted to complex silver cyanide:

$$Ag^+ + [Ag(CN)_2]^- \rightleftharpoons Ag[Ag(CN)_2] \downarrow .$$

At 20°C the solubility product of the precipitate

$$L = [Ag^+] \cdot [CN^-] = 2{\cdot}2 \cdot 10^{-12}.$$

Thus the precipitate does not dissolve in cold slightly acidic, nitric acid solution. In boiling solution hydrogen cyanide may be lost.

According to the thermoanalytical data of Fig. 52.1. the wet precipitate loses its water content at a maximum rate at 110°C; between 210–400°C it decomposes with the formation of metallic silver and cyanogen. The latter is combusted slowly and the metal has constant weight up to 1000°C. Thus when the precipitate is dried at less than 200°C it can be weighed as AgCN, and when the ignition is effected above 520°C it can be weighed as metallic silver.

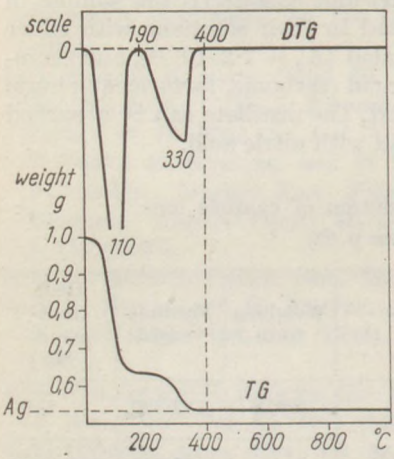

Fig. 52.1. Thermoanalytical curves of silver cyanide precipitate

The method is subject to interference from those anions whose silver salts are insoluble in nitric acid.

Procedure. Add excess of 5% silver nitrate solution to 100 ml of the cold slightly alkaline or ammoniacal solution containing 20–100 mg of cyanide ions. Stir the solution thoroughly and make the solution strongly acid with 2 N nitric acid.

[1] L. Erdey, *Bevezetés a kémiai analizisbe II. Térfogatos analizis.* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest (1965), p. 279.

[2] *ibid* p. 217.

The volume of silver nitrate solution required is easily estimated when the reagent is added dropwise to the solution from a measuring pipette. Slightly more than a two-fold excess of silver nitrate over that required to produce a permanent precipitate is required.

Test for complete precipitation by adding a drop of silver nitrate solution to the supernatant liquid. Allow the precipitate to settle, and filter on a G 4 glass, A 1 porcelain or No. 4 sintered glass filter-funnel. Wash with cold water until silver can no longer be detected in the washings, dry at 110°C for 2 hr, cool and weigh. Stoichiometric factors: $CN^-/AgCN = 0{\cdot}19432$, $KCN/AgCN = 0{\cdot}48633$.

Notes. (1) The precipitate can be dissolved from the filter with concentrated potassium cyanide solution. The filter must then be washed with water.

(2) The precipitate can also be collected on a filter paper. Transfer the bulk of the dry precipitate to a weighed porcelain crucible, and combust the filter paper above it so that the ash falls into the crucible. Ignite the crucible at 700—900°C in a well ventilated fume-cupboard for 30 min. Cool and weigh the metallic silver. Stoichiometric factors: $CN^-/Ag = 0{\cdot}2418$; $KCN/Ag = 0{\cdot}60362$.

(3) Bitter almond water contains some free hydrogen cyanide and ammonium cyanide, although most of the cyanide is present as benzaldehyde cyanohydrin [C_6H_5—CH(OH)CN]. The following equilibrium is established in solution:

$$C_6H_5CHO + HCN \rightleftharpoons C_6H_5CH(OH)CN.$$

In benzaldehyde cyanohydrin the cyanide is bound covalently to the rest of the molecule and therefore cannot be precipitated with silver nitrate. In ammoniacal medium, however, benzaldehyde cyanohydrin decomposes rapidly and cyanide ions pass into solution. On storing, however, ammonium cyanide is converted into ammonium formate and its cyanide content thus decreases. The total cyanide content of bitter almond water must therefore be determined as follows (S. Feldhaus, 1864):

Add 20 ml of 5% silver nitrate solution and 2—3 ml of concentrated ammonia to 100 ml of bitter almond water. Acidify immediately with nitric acid. Allow the precipitate to settle and filter. The remaining procedure is then similar to that above.

(4) When water-soluble cyanides are dissolved, a small amount of hydrogen cyanide is always lost. Silver nitrate solution should therefore be added to the solid salt, the mixture diluted with water, and nitric acid added. The above procedure can then be adopted.

(5) The complex cyanides of nickel and zinc are decomposed completely by silver nitrate with the formation of silver cyanide. Copper(I) cyanide decomposes only slowly. The more stable complex cyanides however, e.g. mercury(II) cyanide, ferricyanide and ferrocyanide ions, do not decompose with silver nitrate. The cyanide content of these ions can be determined by the method of H. Rose according to the following procedure.

52.2. DETERMINATION OF CYANIDE IN MERCURY(II) CYANIDE

(according to H. Rose and R. Finkener)

Mercury(II) cyanide does not dissociate into its ions, and therefore the silver cyanide precipitate cannot be obtained with silver nitrate. Owing to the very low solubility of mercury(II) sulphide it can be precipitated

with hydrogen sulphide even from mercury(II) cyanide solutions, while hydrogen cyanide is formed:

$$Hg(CN)_2 + H_2S = HgS \downarrow + 2\,HCN.$$

The precipitation must be conducted in ammoniacal medium because of the volatility of hydrogen cyanide. Excess hydrogen sulphide also forms a precipitate with silver and must therefore first be removed from the solution using ammoniacal zinc nitrate (or sulphate) solution.

Procedure. Add a solution of zinc nitrate or zinc sulphate in concentrated ammonia to the mercury(II) cyanide solution. For each part of the solid mercury salt add two parts of solid zinc nitrate (or sulphate). If the solution becomes turbid add sufficient ammonia to make the solution completely clear. Add a slight excess of hydrogen sulphide water or freshly prepared ammonium sulphide solution with constant stirring. A reddish-brown precipitate is formed and this becomes black when further sulphide is added and the solution is stirred. Continue the addition of sulphide solution until a white precipitate of zinc sulphide is formed. This indicates that the precipitation of mercury(II) sulphide is complete.

Filter the precipitate of mercury(II) sulphide and zinc sulphide by decantation on a filter paper and wash with 1% ammonia solution. The filtrate contains the cyanide. Add 5% silver nitrate solution to the filtrate, acidify the solution with nitric acid, allow the silver cyanide precipitate to settle, and filter by decantation so that the precipitate remains in the beaker. Add silver nitrate solution to the precipitate, heat to boiling to decompose any zinc cyanide which adheres to the precipitate, allow to cool and transfer to the filter. Wash the precipitate with cold water, dry, and weigh according to the procedure above

Notes. (1) Several simple and complex cyanides can be decomposed and converted to soluble mercury(II) cyanide by boiling the substance with excess mercury(II) oxide. Metals are then precipitated as their hydroxides. After filtration the cyanide can be determined in the filtrate by the method of H. Rose. The method is particularly useful for the determination of Berlin blue, potassium ferrocyanide, potassium ferricyanide and complex nickel and copper cyanides. The cobalticyanide complex, however, cannot be decomposed with mercury(II) oxide.

(2) Mercury(II) cyanide can also be decomposed by the following alternative method:

Reduce mercury to the metal from a neutral or alkaline solution with powdered cadmium or zinc, filter, precipitate silver cyanide in the filtrate with 5% silver nitrate, and acidify the solution with nitric acid. The filtration and washing of the solution can be carried out as in the above procedures.

Separation Methods

52.3. CN^- — Cl^-, Br^-, I^-, SCN^-

(a) Cyanide ions can be titrated by the method of Liebig–Denigès with standard 0·1 N silver nitrate solution in slightly ammoniacal medium in the presence of iodide ions.[1]

[1] L. Erdey, *Bevezetés a kémiai analízisbe II. Térfogatos analízis.* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest

When only a single halide is present as well as cyanide, the titration can be carried by the method of Liebig with standard 0·1 N silver nitrate solution in alkaline medium. The permanent appearance of a precipitate corresponds with the end point of the titration.

Excess silver nitrate solution must then be added to the titrated solution, the solution acidified with nitric acid, and the precipitate of silver cyanide + silver halide collected on a filter, washed with water and dried at 110°C. Weighing form: AgCN + Ag halide.

Note. The accompanying halide can also be titrated in neutral medium by Mohr's method with 0·1 N silver nitrate in the presence of potassium chromate indicator, or according to the method of Erdey in sodium acetate–acetic acid solution (pH 3·8–4·6) in the presence of variamine blue acetate indicator.[1]

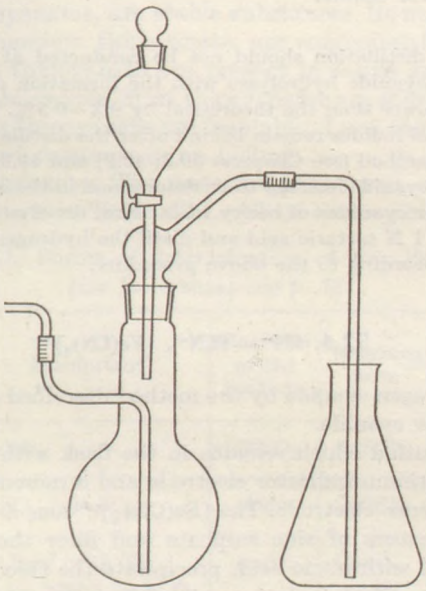

Fig. 52.2. Apparatus for separation of cyanide ions

(b) *Procedure.* Place the sample of about 0·2 g of alkali cyanide into the flask of Fig. 52.2., dissolve it in 25–30 ml of water, add 2 drops of methyl red indicator, and assemble the apparatus. Lubricate the joints with a small amount of vaseline. Place 50 ml of about 0·1 N silver nitrate solution into the receiving flask and acidify with 2 ml of 2 N nitric acid. Add 2 N sulphuric acid to the flask from the dropping funnel until the indicator shows an intermediate

(1965), p. 279; I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis.* II. 2 Ed. Interscience, New York, London (1947) p. 282.

[1] L. Erdey, I. Buzás and K. Vigh, *Talanta* **1**, 377 (1958).

colour. Heat the flask to 40–70 °C and over 1–2 hr expel the hydrogen cyanide which is liberated using a slow current of carbon dioxide (1–2 bubbles/second) into the receiving flask. Lower the receiving flask, rinse the tube with water, and test a portion of the liquid in the decomposition flask in a test tube with silver nitrate to check the quantitative removal of the hydrogen cyanide. Allow the precipitate in the receiving mixture to settle, test for complete precipitation with 1–2 drops of silver nitrate, and collect the precipitate on a G 4 glass filter. Wash with cold water and dry at 110 °C for 2 hr. Weighing form: AgCN.

Rinse the contents of the round-bottomed flask into a beaker, precipitate the halide ions with 5% silver nitrate solution, acidify the solution with 2 N nitric acid, and collect the precipitate, after coagulation by boiling, on a G 4 glass filter. Wash with water acidified with nitric acid. Dry at 130 °C for 2 hr. Weighing form: Silver halide.

Notes. (1) The distillation should not be conducted at higher temperatures, otherwise hydrogen cyanide hydrolyses with the formation of ammonium formate and the results are lower than the theoretical by 0·3 – 0·5%.

(2) When several halides remain behind after the distillation they can be separated by a suitable method (see Chapters 50.3; 49.2; and 49.3).

(3) When only cyanide ions are to be determined in the sample, in the presence of halides or complex cyanides of heavy metal ions, dissolve the sample in 5 ml of water, add 30 ml of 1 N tartaric acid and distil the hydrogen cyanide in a current of carbon dioxide according to the above procedure.

52.4. CN^- — SCN^-, $[Fe(CN)_6]^{4-}$

Distil the hydrogen cyanide by the method described above and determine in the form of silver cyanide.

Titrate the solution which remains in the flask with 0·1 N zinc sulphate solution using a platinum indicator electrode and a mercurous sulphate–potassium sulphate reference electrode. The $[Fe(CN)_6]^{4-}$ ions are titrated as follows:

Add a slight excess of zinc sulphate and filter the solution. Make the filtrate slightly acid with nitric acid, precipitate the thiocyanate with a slight excess of 5% silver nitrate solution, allow the mixture to stand for several hours, collect the precipitate on a G 4 glass filter, wash with cold water and dry at 100–130 °C for 2 hr. Weighing form: AgSCN.

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to Table 52.1.

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2. H. Rose and R. Finkener, *Z. anal. Chem.* **1**, 288 (1862).

CHAPTER 53

THIOCYANATE IONS — SCN^- — 58·084

FREE anhydrous hydrogen thiocyanate is an unstable, colourless liquid of unpleasant odour. In aqueous solution it behaves like a rather strong acid. Its salts, thiocyanates, are stable substances. Its most important salts, potassium and ammonium thiocyanate, are commercially available. Small amounts of sodium thiocyanate are present in saliva and urine.

Dissolution of the sample. Most thiocyanates are soluble in water. Silver, mercury and copper thiocyanate are insoluble. Lead thiocyanate is slightly soluble in water, and decomposes on boiling.

Forms of determination. The most frequent forms of determination of thiocyanate are shown in Table 53.1. All of these yield accurate results.

TABLE 53.1. Forms of determination of thiocyanate ions
(for References see p. 73)

Ref. Number	Forms of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	AgSCN	$AgNO_3$	HNO_3	AgSCN	165·965	< 224
2.	CuSCN	$CuSO_4 + H_2SO_3$	acidic	CuSCN	121·625	< 300
3.	$BaSO_4$	oxidised with Br_2, conc. HNO_3 or H_2O_2 to sulphate and precipitated with $BaCl_2$	acidic	$BaSO_4$	233·42	600–800

In practice the most suitable method must be chosen according to the other ions present so that they do not interfere. When interfering heavy metal ions are present they can be separated by boiling with sodium carbonate; these ions are then precipitated as their hydroxides or carbonates. Thiocyanate can be determined most rapidly by argentimetric titration according to the method of Volhard.[1]

[1] L. ERDEY, *Bevezetés a kémiai analízisbe II. Térfogatos analízis.* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest (1965), p. 272; I. M. KOLTHOFF and V. A. STENGER, *Volumetric Analysis* II. 2 Ed. Interscience, New York, London (1947), p. 278.

53.1. DETERMINATION IN THE FORM OF SILVER THIOCYANATE (AgSCN)

(G. van Name, 1900)

Thiocyanate forms a precipitate with silver ions in a solution acidified slightly with nitric acid. The solubility product of silver thiocyanate at 18°C,

$$L = [Ag^+] \cdot [SCN^-] = 4{\cdot}9 \cdot 10^{-11}.$$

Thus the losses due to the solubility of the precipitate are negligible. The silver thiocyanate precipitate has a constant weight up to 140°C (see the

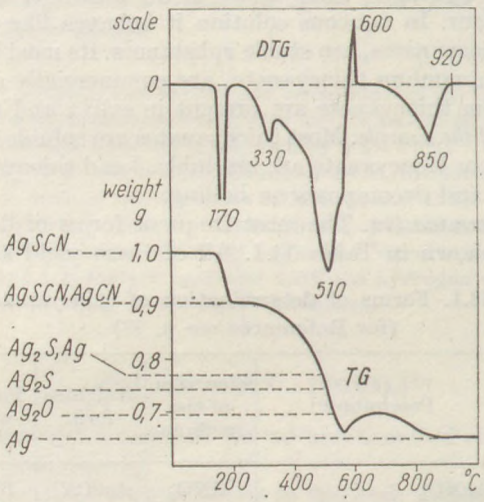

Fig. 53.1. Thermoanalytical curves of silver thiocyanate precipitate

thermoanalytical curves of Fig. 53.1., measurements of F. Paulik and G. Liptay). The precipitate can therefore be dried below this temperature without decomposition. At 170°C two molecules of silver thiocyanate lose one atom of sulphur and a double salt, AgSCN · AgCN, is formed. This compound has constant weight up to 230°C; on further heating silver sulphide is formed. Above 570°C the silver sulphide is partly oxidized to silver sulphate and silver peroxide; above 850°C these compounds decompose and metallic silver remains behind.

The determination can only be carried out in the absence of halide and cyanide ions. Sulphide ions can be separated with zinc sulphate in acidic solution. Ferrocyanide ions can be precipitated in the presence of thiocyanate ions with thorium nitrate in slightly acidic solution. Ferricyanide ions can be precipitated with cadmium ions.

Procedure. Add a small volume of nitric acid to 100 ml of the dilute solution of alkali thiocyanate. Add a slight excess of 0·1 N silver nitrate solution while

stirring. (17·2 ml of 0·1 N silver nitrate solution is required for the precipitation of 100 mg of SCN^-.) The precipitate coagulates on further stirring and becomes flocculent.

Allow the mixture to stand for 2 hr, collect the precipitate on a weighed G 4 glass, A 1 porcelain or No. 4 glass texture filter-funnel, and wash with cold distilled water until silver can no longer be detected in the washings. Dry at 100–130°C for 2 hr. Cool and weigh. Stoichiometric factor: SCN/AgSCN = 0·34998.

Note. The precipitate can be dissolved from the filter with hot ammonia.

53.2. DETERMINATION IN THE FORM OF COPPER(I) THIOCYANATE (CuSCN)

(M. L. Rivot, 1854)

This method is the reverse of the copper(I) thiocyanate method described for the determination of copper (see Chapter 8.2.). Nitrate, mercury(I) and lead ions interfere. Mercury(I) ions can be removed in the form of chloride, and lead ions as the sulphate. In the presence of iron(III) ions, a large excess of sulphurous acid must be added and the precipitation must be carried out in hot solution. In the presence of Bi, Sb and Sn ions, 1–1·5 g of tartaric acid must be added to the solution to avoid the precipitation of the basic salts of these ions. Co, Ni, Mn, Zn, Cd, Fe(II), As, alkali metals and also the alkaline earths in sulphate-free solution, do not interfere.

Procedure. To the neutral or slightly acidic solution (which may contain hydrochloric or sulphuric acid but not nitric acid) add 50–200 ml of freshly prepared saturated sulphur dioxide solution, or the same volume of 10% sodium or ammonium bisulphite solution. Add 60 ml of 0·1 N copper(II) sulphate solution dropwise with constant stirring. Add a further 10 ml of sulphurous acid or sulphite solution and allow the mixture to stand for several hours or overnight. Collect the precipitate on a weighed G 4 glass, A 1 porcelain or No. 4 glass texture filter-funnel, wash with diluted sulphurous acid solution until copper(II) can no longer be detected in the washings (test with potassium ferrocyanide), and finally rinse the precipitate with several millilitres of alcohol. Dry the precipitate at 110°C for 2–4 hr, cool and weigh. Stoichiometric factor: SCN/CuSCN = 0·47757.

Notes. (1) Dissolve the precipitate from the filter with hot dilute nitric acid (1 : 1).

(2) The precipitation can also be collected on filter paper and weighed in the form of copper(II) oxide after ignition to 900°C. The method yields fairly accurate results.

53.3. DETERMINATION IN THE FORM OF BARIUM SULPHATE ($BaSO_4$)

When sulphates and other sulphur compounds are absent, thiocyanate can be converted easily to sulphate by oxidation with strong oxidizing agents, and the sulphate ions can then be precipitated and weighed in the

form of barium sulphate. The oxidation can be carried out most conveniently with bromine water:

$$SCN^- + 4\,Br_2 + 4\,H_2O = SO_4^{2-} + 7\,Br^- + CNBr + 8\,H^+.$$

Procedure. Add excess bromine water to 100 ml of the neutral or slightly acidic solution containing not more than 100 mg of thiocyanate, and heat the solution on a water bath in a well-ventilated fume cupboard for 1 hour. Neutralize the solution with ammonia in the presence of methyl orange, and add 1 ml of 1 N hydrochloric acid and 1 g of solid ammonium chloride. Heat the solution to boiling and precipitate barium sulphate with 10 ml of 5% barium chloride solution. Boil for 2–3 min and allow the mixture to stand overnight. Filter the solution on a medium grade filter paper. Wash the precipitate with 25 ml of cold water and 25 ml of hot water, and heat in a weighed porcelain or platinum crucible together with the filter paper. When the paper has combusted ignite the precipitate at 620–800 °C for 10 min. Cool and weigh. For accurate measurements, if the weight of precipitate is greater than 0·1 g multiply the result by the correction factor of 1·0143 (correction method of L. W. Winkler, see Chapter 54.1.2.). Stoichiometric factor: $SCN/BaSO_4 = 0{\cdot}24884$.

Note. When *fuming nitric acid* is used as oxidant the reaction must be carried out in an all glass apparatus fitted with a reflux condenser, otherwise loss of thiocyanate may occur during the vigorous reaction. It is advisable, however, to follow the procedure of W. Brochers:

Precipitate the thiocyanate in the form of silver thiocyanate, collect the precipitate on a filter paper, wash with water, place the funnel into the neck of a flask and puncture the filter paper with a glass rod. Rinse the precipitate into the flask with concentrated nitric acid (sp. gr. approx. 1·4). The reaction is then not too vigorous and there is no danger of loss of hydrogen thiocyanate. Boil the solution in the flask for 45 min to effect complete oxidation of the silver thiocyanate. Evaporate the contents of the flask to small volume to remove excess nitric acid, dissolve in a small volume of water, and precipitate silver nitrate with hydrochloric acid. Precipitate the sulphate in the filtrate with barium chloride. This method enables thiocyanate to be determined in the form of barium sulphate even if sulphate is present in the original solution.

Hydrogen peroxide in ammoniacal solution is also suitable for the oxidation of thiocyanate to sulphate, but the reaction is very slow (24 hr). Commercially available hydrogen peroxide usually contains traces of sulphuric acid and should be tested for sulphate before use.

Separation Methods

53.4. SCN^- — Cl^-

Thiocyanate ions can be precipitated in the form of copper(I) thiocyanate (see Chapter 53.2.). Silver chloride can be precipitated from the filtrate with silver nitrate after the removal of sulphur dioxide.

53.5. $SCN^- - Cl^-, Br^-, I^-$

Precipitate silver thiocyanate and silver halides with excess silver nitrate solution. Collect the precipitate on a filter paper and wash with 1% nitric acid. Oxidize the sulphur of the thiocyanate to sulphate according to the method of W. Brochers (Chapter 53.3.) with concentrated nitric acid (sp. gr. 1·4) by boiling for 45 min. Remove the excess of nitric acid by boiling, dilute with water, and precipitate silver ions with hydrochloric acid. Evaporate the filtrate to dryness several times to remove nitrate ions. Dissolve the residue, and precipitate sulphate ions with barium chloride (see Chapters 54.1.1–2.). Weighing form: $BaSO_4$.

Note. The determination can also be carried out when the original sample contains sulphate.

53.6. $SCN^- - CN^-$

See the separation $CN^- - Cl^-$, Br^-, I^-, SCN^- in Chapter 52.3.

53.7. $SCN^- - CN^-, [Fe(CN)_6]^{4-}$

See the separation of $CN^- - SCN^-$, $[Fe(CN)_6]^{4-}$ in Chapter 52.4.

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to the Table 53.1.

1. G. van Name, *Am. J. Sci.* **10**, 451 (1900).
2. M. L. Rivot, *Compt. rend.* **38**, 868 (1864); G. Fenner and J. Forschmann, *Chemiker Z.* **42**, 205 (1918); I. M. Kolthoff and G. H. P. Meene, *Z. anal. Chem.* **72**, 337 (1927); J. Bodnár and V. Tolnay, *Z. anal. Chem.* **120**, 336 (1940); R. Belcher and T. S. West, *Anal. Chim. Acta* **6**, 337 (1952).
3. W. Brochers, *Repert. d. anal. Chem.* (1881) 130; L. W. Winkler, *Z. angew. Chem.* **33**, 160 (1920); *Ausgewählte Untersuchungsverfahren für das chemische Laboratorium.* Enke, Stuttgart (1931), p. 134; F. P. Treadwell, *Lehrbuch der analytischen Chemie II.* 11 Ed. Deuticke, Wien (1949) p. 291.

CHAPTER 54

SULPHUR — S — 32·064

S_x, H_2S, H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, H_2SO_4, $H_2S_2O_7$, $H_2S_2O_8$

ELEMENTARY sulphur occurs naturally in some volcanic areas. Purified mineral sulphur is commercially available in the form of bars or powder (flowers of sulphur). Commercial sulphur often contains traces of arsenic and selenium. Sulphur obtained from mineral oils and industrial gases may contain small amounts of organic substances. Sulphur is used for the vulcanization of rubber, the production of pesticides, drugs, sulphur dioxide and sulphuric acid. Hydrogen sulphide occurs in some volcanic gases, in mineral waters, in the decomposition products of organic substances, and in some industrial gases. Its dilute aqueous solution is used as an analytical reagent and as a reducing agent in preparative work. Pyrites (FeS_2), chalcopyrite ($CuFeS_2$), realgar (As_2S_2), auripigment (As_2S_3), sphalerite (ZnS) and cinnabar (HgS) are the most common natural sulphides. Artifically produced alkali and alkaline earth sulphides and polysulphides are used for industrial and agricultural purposes (leather processing, pesticides). Sulphur dioxide pollutes the air in towns as a combustion product of coals containing sulphur. Sulphur dioxide is used in industry mostly for bleaching textiles and in the removal of lignin in the processing of cellulose. In liquid form it is used as a selective solvent in the processing of mineral oil products and is also used in refrigerators. For these purposes it is usually stored in liquid form in steel cylinders. Sulphur dioxide is quite soluble in water, and is partly converted to sulphurous acid

$$SO_2 + H_2O \rightleftharpoons H_2SO_3.$$

The sodium and calcium salts of sulphurous acid are the most frequently encountered. Sulphuric acid is found in soil water where pyrites occurs and also in the water in pyrite mines. Sulphuric acid is produced by catalytic oxidation of the sulphur dioxide produced when pyrites are roasted. Sulphuric acid and oleum, which contains excess sulphur dioxide, are very important in the chemical industry. Most sulphuric acid is used for the production of phosphate fertilizers, in oil refining, and in the explosives industry. Gypsum ($CaSO_4 \cdot 2\,H_2O$), barytes ($BaSO_4$), celestine ($SrSO_4$), Epsom salt ($MgSO_4 \cdot 7\,H_2O$) and Glauber's salt ($Na_2SO_4 \cdot 10\,H_2O$) are the most important naturally occurring sulphates. Sulphides are usually present in silicate and carbonate rocks, and sulphates in natural waters. Thiosulphuric acid, pyro-

sulphuric acid and peroxidisulphuric acid are usually analysed in the form of their alkali salts.

Forms of determination. Elementary sulphur and substances containing sulphur can be determined by a number of specific titrimetric methods.

TABLE 54.1. Forms of determination of sulphur and its compounds
(For References see p. 116.)

Ref. Number	Constituents	Pretreatment	Forms of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	S_x	extraction with CS_2	S_x	after the evaporation of the solvent		S_x	32·066	< 135
2.	S_x	oxidize with Br_2	$BaSO_4$	$BaCl_2$	0·01 N HCl	$BaSO_4$	233·42	800–950
3.	S^{2-}	—	CuS	$CuSO_4$	neutral	CuO	79·54	> 940
4.	S^{2-}	distil H_2S in acidic medium and collect in $CdSO_4$	CdS CuS	$CuSO_4$	acetic acid	CuO	79·54	> 940
5.	S^{2-}	oxidize with Br_2, HNO_3 + + HCl, Na_2CO_3 + + $NaNO_3$ or Na_2CO_3 + + Na_2O_2	$BaSO_4$	$BaCl_2$	0·01 N HCl	$BaSO_4$	233·42	800–950
6.	SO_4^{2-}	separation of interfering ions	$BaSO_4$	$BaCl_2$	0·01 N HCl	$BaSO_4$	233·42	800–950
7.*	SO_4^{2-}	separation of interfering ions	benzidine sulphate $C_{12}H_{12}N_2 \cdot H_2SO_4$	$C_{12}H_{12}N_2 \cdot 2$ HCl	weak hydrochloric acid	benzidine sulphate $C_{12}H_{12}N_2 \cdot H_2SO_4$	282·33	72–130
8.	SO_3^{2-} $S_2O_3^{2-}$ $S_2O_4^{2-}$ etc.	oxidize previously with Br_2 or $H_2O_2 + NH_3$	$BaSO_4$	$BaCl_2$	0·01 N HCl	$BaSO_4$	233·42	800–950

Note:* The washed precipitate is usually titrated with NaOH

Titrimetric methods are usually used for the simultaneous determination of sulphur in various oxidation states, and in rapid technical analyses. The most important gravimetric forms of determination are shown in Table 54.1. In practice, the barium sulphate method is the most frequently employed. The sulphur in the sample must first be oxidized to sulphate, and the sulphate ions can then be precipitated with barium chloride. Sulphate can also be precipitated using benzidine hydrochloride, but it is advisable to titrate the precipitate after washing.[1] The most important form of determination for sulphur and all sulphur-containing materials is therefore barium sulphate, and the determination of sulphate ions in this form will first be described, followed by the determination of the other oxidation states of sulphur.

54.1. DETERMINATION OF SULPHATE IONS (SO_4^{2-})

When barium chloride solution is added dropwise to a solution of sulphuric acid, or a soluble sulphate in acidic medium, a precipitate of small crystals of barium sulphate is formed. The precipitate can be filtered, washed and dried, or ignited and weighed. The method is the reverse of the determination of barium described in Chapter 41.1.

The solubility of the precipitate and the difficulties encountered in this determination have already been detailed (Chapter 41.1.). It has been pointed out that the solubility of the precipitate increases in strongly acidic medium owing to the repression of the dissociation of sulphuric acid:

$$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^- \qquad (pK = 1{\cdot}92)$$

During the precipitation, therefore, the relative supersaturation is smaller in acidic medium, and under these conditions a well-developed, easily filtered, crystalline precipitate can be obtained. The precipitation should be effected from a hot solution containing hydrochloric acid, to facilitate the formation of an easily filtered precipitate. When barium sulphate is precipitated from a cold neutral solution, a very finely divided precipitate is formed and is difficult to filter. In neutral solution there is also danger of the coprecipitation of carbonates and basic sulphates. The barium sulphate precipitate has a strong tendency to collect foreign ions from the solution by adsorption, occlusion or mixed crystal formation. It is interesting, therefore, to examine the effect of acidity, foreign cations, rate of precipitation and foreign anions on the precipitation.

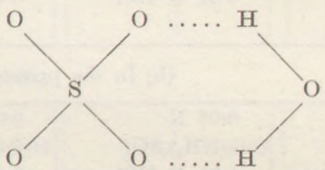
Effect of acidity on the contamination and morphological structure of the barium sulphate precipitate. The acidity of the medium influences not only the solubility of the precipitate, but also its morphological structure and

[1] L. Erdey, *Bevezetés a kémiai analizisbe II. Térfogatos analizis.* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8. Ed. Tankönyvkiadó, Budapest I1965), p. 102; I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis.* II. 2 Ed. (nterscience, New York, London (1947), p. 163.

the amount of bound volatile material it contains (H_2SO_4, HCl, H_2O; see Chapter 41.1.). From this point of view the acidic pH range can be divided into three regions (see Fig. 41.1.).

(a) Precipitates obtained from a solution whose pH is in the range 0–1·5 consist of large well shaped, orthorhombic crystals which contain a relatively small amount of volatile material (H_2SO_4 not more than 0·3%; HCl not more than 0·04%, H_2O not more than 0·12%). Although the solubility of the precipitate obtained at pH 0 is quite high, when excess barium chloride is used it is depressed so that loss due to solubility is only about 0·2%.

(b) Precipitates obtained at pH 1·5–3 consist of broken crystals of medium particle size, but are easily filtered. In this intermediate region the amount of water and hydrochloric acid bound by the precipitate and only removable by ignition increases rapidly with increase of the pH of the medium. At pH 3 the water content may be as high as 0·5%, and the hydrochloric acid content 0·15%. The amount of sulphuric acid removed on ignition shows a maximum at pH 2 (0·5%), while if the precipitation is effected at higher pH values the amount of volatile sulphuric acid present decreases. According to derivative thermoanalysis (Fig. 41.2.) these volatile substances are bound with well defined chemical bonds to the precipitate, as indicated by the well defined maxima at higher temperatures of the DTG curve. It is assumed that the water is bound to the sulphate ions by hydrogen bonding:



The amount of water bound by the precipitate is proportional to the sulphate ion concentration of the solution (see upper graph of Fig. 41.2.). Hydrochloric acid and chloride ions are probably bound to the barium ions as $Ba_2SO_4Cl_2$, while sulphuric acid is probably present as $Ba(HSO_4)_2$.

(c) Precipitates obtained from a medium of pH 3–7 consist of a mass of small, undeveloped crystals similar to gels. The crystals contain relatively large amounts of water, hence the precipitate is difficult to filter. The amount of volatile material present is constant in the pH range 3–7 (H_2O about 0·5%; H_2SO_4 about 0·25%; HCl about 0·18%).

Owing to the bisulphate content of the precipitate, its total weight is less than if the precipitate consisted entirely of barium sulphate. This decreased weight can be compensated for by the water and hydrochloric acid bound by the precipitate when the precipitate is ignited at temperatures lower than 180°C, and overcompensation may occur. After ignition, however, the weight of the precipitate may be smaller (occasionally by as much as 3%) than the expected weight of barium sulphate. This error can be overcome by two methods:

TABLE 54.2. Precipitation of sulphate ions with

(a) *In the presence*

Cations	The solutions contains		Weight of precipitate mg after drying at 180°C
	Before precipitation	After precipitation	
—	adding to pure water dropwise H_2SO_4 and $Ba(OH)_2$		100·37
0·05 N H^+	0·05 N H_2SO_4	0·05 N HCl 0·01 N $BaCl_2$	100·11
0·05 N Na^+	0·05 N Na_2SO_4 0·01 N HCl	0·05 N NaCl 0·01 N HCl 0·01 N $BaCl_2$	100·20
0·05 N NH_4^+	0·05 N $(NH_4)_2SO_4$ 0·01 N HCl	0·05 N NH_4Cl 0·01 N HCl 0·01 N $BaCl_2$	99·81
0·05 N K^+	0·05 N K_2SO_4 0·01 N HCl	0·05 N KCl 0·01 N HCl 0·01 N $BaCl_2$	99·40

(b) *In the presence of increasing amounts*

0·05 N NH^+	0·05 N $(NH_4)_2SO_4$ 0·01 N HCl	0·05 N NH_4Cl 0·01 N HCl 0·01 N $BaCl_2$	99·81
0·25 N NH_4^+	0·05 N $(NH_4)_2SO_4$ 0·01 N HCl 0·20 N NH_4Cl	0·25 N NH_4Cl 0·01 N HCl 0·01 N $BaCl_2$	99·60
2·05 N NH_4^+	0·05 N $(NH_4)_2SO_4$ 0·01 N HCl 2·00 N NH_4Cl	2·05 N NH_4Cl 0·01 N HCl 0·01 N $BaCl_2$	98·57

(c) *The influence of rate of precipitation*

Adding the $BaCl_2$ precipitant dropwise to the hot solution: *slow precipitation*	0·05 N Na_2SO_4 0·01 N HCl	0·05 N NaCl 0·01 N HCl 0·01 N $BaCl_2$	100·20
Pouring the hot $BaCl_2$ precipitant at once into the hot solution: *rapid precipitation*			101·13

barium ions. $BaSO_4$ true value 100·00 mg

of various cations

Weight of ignited precipitate mg	Amount of volatile substances removed at ignition mg			$BaSO_4$ remaining in solution mg	Note
	H_2SO_4	HCl	H_2O		
100·01	—	—	0·38		
99·72	0·14	0·04	0·17		
99·52	0·20	0·09	0·43		
99·25	0·26	0·04	0·33		
98·84	0·33	0·03	0·11		Small amounts of K_2SO_4 are built into the crystal lattice; the precipitate contains about 0·6% K_2SO_4

of NH_4Cl. Precipitant: $BaCl_2$

99·25	0·26	0·04	0·33	0·02	
98·80	0·49	0·08	0·29	0·04	The precipitate does not contain in either case weighable amounts of ammonium salts
97·07	0·82	0·13	0·43	0·96	

on the composition of $BaSO_4$ precipitate

99·52	0·20	0·09	0·39		
99·94	0·06	0·11	1·02		

(1) The precipitate can be obtained at a well defined acidity, dried at less than 180°C, and the error compensated for by application of corrections (compensation method of L. W. Winkler and E. Schulek).

(2) The barium sulphate can be precipitated at a well defined pH by the rapid addition of hot barium chloride precipitant to the sulphate solution. The precipitate then contains large amounts of water, but only small amounts of bisulphate and hydrochloric acid (see Table 54.2.(c.), and the precipitate can be ignited (compensation method of G. A. Hulett and L. H. Duschack). The sulphate losses are much lower in this procedure, and this error is compensated for by the adsorbed foreign salts present.

Effect of foreign cations on the contamination of the barium sulphate precipitate. Foreign cations may affect the composition of barium sulphate in three ways:

(1) The amount of volatile material present (H_2SO_4, HCl, H_2O) may vary in the presence of foreign cations and is dependent on their concentration. As shown in Table 54.2.(a), in the absence of foreign electrolytes the precipitate only contains about 0·4% water. In the presence of H^+, Na^+, NH_4^+ and K^+ ions the amount of bisulphate present increases in the order in which these ions are listed. When the concentration of the foreign cations present increases, the amount of volatile material present in the precipitate increases considerably (Table 54.2.(b.). Thus the difference in weight between the ignited and dried precipitate increases.

(2) The solubility of barium sulphate increases in the presence of foreign salts (foreign salt effect, see Chapter 2.7.1.3.). In 0·05 N binary electrolytes the increase in solubility is negligible, and even in 1 N hydrochloric acid solution there is no significant loss when excess precipitant is used. According to Table 54.2.(b). in 2·05 N ammonium chloride solution, 0·96% of the barium sulphate remains dissolved owing to the foreign salt effect.

(3) Foreign cations, according to their nature and size, may be present in the crystal lattice of barium sulphate. Of the cations shown in Table 54.2., at the concentrations given, only the occlusion of potassium ions causes appreciable errors. When barium sulphate is precipitated from 0·05 N potassium sulphate solution it contains 0·6% of potassium sulphate. Large errors may occur, therefore, in the presence of potassium ions owing to replacement of the heavy barium ions by light potassium ions. This error can be corrected as in the method of L. W. Winkler, or sulphuric acid can be removed from the precipitate with sodium metaphosphate by the Grote–Krekeler method, and the precipitation can be repeated in the sulphuric acid collected (L. Erdey and F. Paulik).[1]

The $BaSO_4$ precipitate adsorbs K, Ca, Fe(III), Cr(III), Al and Cd ions very strongly. These cations must therefore be separated by a suitable method before the precipitation of sulphate ions from the solution. Very large errors may occur in the presence of iron(III) ions. Barium sulphate which contains iron is pink or red in colour, and considerable amounts of sulphate are present as iron(III) sulphate. Iron(III) sulphate decomposes at

[1] L. Erdey and F. Paulik, *Acta Chim. Hung.* **4**, 97 (1954).

a relatively low temperature on ignition and in spite of the contamination of the precipitate by iron(III) oxide, a loss in weight occurs. Any traces of iron which remain in the precipitate act as catalysts in the thermal decomposition of barium sulphate. In solutions containing iron(III), chromium(III) and aluminium ions, sulphate complexes of various composition are formed and the effective sulphate content of the solution decreases. In the presence of these ions, therefore, the solubility of barium sulphate increases considerably. The interference of iron(III) ions can largely be eliminated by reduction to the bivalent form with metallic zinc or magnesium, or with hydroxylamine hydrochloride.

Na, Mg, Fe(II), Mn(II), Zn, Cu, Hg(II), Co and Ni ions interfere only slightly by coprecipitation. When only small amounts of these ions are present the precipitation can be carried out in strongly acidic solution (5 ml of 1 N HCl in 100 ml) but when large amounts are present they first must be removed. It is therefore not convenient to carry out the determination of sulphate in solutions which contain large amounts of alkali metal salts from fusion procedures. If the solution contains excess hydrochloric or nitric acid, it is advisable to remove the acid by evaporation rather than to neutralize the solution.

Effect of the rate of precipitation on the composition of the barium sulphate precipitate. The data of Table 54.2.(c). show that the weight of the dried precipitate obtained after slow precipitation is in good agreement with the theoretical weight, but the volatile sulphuric acid content is relatively high. When the precipitation is effected from hot solution by pouring hot barium chloride solution into the sulphate solution, the volatile sulphuric acid content of the precipitate decreases to a negligible value, but the amount of water in the precipitate increases. Thus under these conditions the weight of the dried precipitate differs markedly from the true value, but the weight of the ignited precipitate is in good agreement. The latter method of precipitation can be recommended when the solution contains cations which show little tendency towards coprecipitation [Na, Mg, Fe(II), Zn etc.]. It is then advisable to carry out the precipitation from a larger volume of solution, so that the error caused by the solubility is just compensated for by the coprecipitation error (E. Hintz and H. Weber, 1906).

Contamination of barium sulphate precipitate by foreign anions. It has already been mentioned (Chapter 41.1.), in connection with the determination of barium, that nitrate, nitrite, chlorate and permanganate ions contaminate the barium sulphate precipitate and cause large errors. These ions can be decomposed by several evaporations with hydrochloric acid. After the decomposition of nitrite, nitrate and chlorate ions the corresponding cation remains behind. As potassium ions interfere in the determination of sulphate, potassium chlorate should not be used for the initial oxidation. After the evaporation of permanganate ions with hydrochloric acid, manganese (II) ions remain behind. Moderate amounts of manganese(II) do not interfere, but if the solution contains potassium ions ($KMnO_4$), its interference must be considered.

In the presence of phosphate ions the precipitation must be carried out in strong hydrochloric acid solution, but even under these conditions

the precipitate will contain phosphate. This error can be compensated for by the application of a correction. When the precipitate is obtained in the presence of large amounts of phosphate, it is advisable to decompose the precipitate by fusion with a five-fold excess of sodium metaphosphate in a Grote–Krekeler apparatus, collect the sulphur trioxide in water, and finally precipitate the sulphate from this solution.

See the notes in Chapter 41.1. concerning the ignition of the barium sulphate precipitate.

Dissolution and fusion of the sample. Separations. $BaSO_4$, $SrSO_4$, $CaSO_4$ and $PbSO_4$ are insoluble; all other simple metal sulphates are soluble in water or dilute mineral acids. The three alkaline earth sulphates can be fused with a six-fold excess of anhydrous sodium carbonate:

$$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + Na_2SO_4.$$

When the melt is leached with water, barium, strontium and calcium carbonates remain behind undissolved. The residue must be washed free of sulphate with dilute sodium carbonate solution, and the filtrate acidified with hydrochloric acid. Barium sulphate can then be precipitated from the solution with barium chloride. In the presence of silicic acid, the filtrate must be acidified with hydrochloric acid and evaporated to dryness. The residue must be dehydrated (at 120°C for 1 hr), dissolved in water containing 1 ml of concentrated hydrochloric acid and the silicic acid filtered off. The filtrate must then be diluted to 300 ml and the sulphate precipitated as barium sulphate.

When the sample is fused with sodium carbonate an equilibrium is established; 0·1–0·3% of the barium sulphate remains behind with the barium carbonate. In accurate determinations, therefore, the residual barium carbonate must be dissolved in hydrochloric acid, and the insoluble material fused again with a small amount of sodium carbonate.

After fusion large amounts of alkali metal salts are present in the solution, and the barium sulphate precipitate is contaminated with an appreciable weight of alkali salts for which a correction must be applied. This error, and any error caused by loss during fusion, can be eliminated by the following procedure:

Decompose the original alkaline earth sulphate in a platinum vessel in a Grote–Krekeler apparatus, using a 4–6 fold excess of sodium metaphosphate. Collect the sulphuric acid in the absorption vessel and precipitate barium sulphate with barium chloride from this solution, which is now free of interfering ions.

If the sample also contains fluoride ions it must be fused with sodium metaphosphate in the presence of a small amount of boric acid.

Lead sulphate cannot be fused with sodium carbonate, because part of the lead dissolves when the melt is leached with water (lead salts should not be fused in a platinum vessel). The finely divided sample of lead sulphate must therefore be boiled with a concentrated solution of a twenty-fold excess of sodium bicarbonate for one hour, saturated with gaseous carbon

dioxide, and then boiled for a further 30–60 min. The mixture must then be filtered on a filter paper, and the basic lead carbonate precipitate washed on the filter with hot water containing a small amount of sodium bicarbonate, until sulphate can no longer be detected in the washings. Strontium and calcium sulphates can also be fused by this method.

When the solution is boiled, carbon dioxide is liberated from the sodium bicarbonate solution and the pH of the solution is adjusted to that corresponding to the minimum solubility of lead carbonate. It is, therefore, also necessary to wash the precipitate with hot sodium bicarbonate solution.

Separation from iron(III), aluminium and calcium ions. In the preceding discussion of the contamination of the barium sulphate precipitate, it was mentioned that not only the ions which form insoluble sulphates (Pb, Ca, Sr, Ba) interfere, but also that interference is encountered from those trivalent or higher valent ions which have a particular tendency towards coprecipitation [Fe(III), Al]. These ions must therefore be separated from sulphate ions even when less precise determinations are required.

The interference of moderate amounts of iron(III) ions can be minimized by reduction to the bivalent form with zinc, magnesium or hydroxylamine hydrochloride. When the original solution contains bivalent iron, it is also advisable to carry out the precipitation in the presence of hydroxylamine hydrochloride.

Before the precipitation of sulphate, large amounts of iron(III) or aluminium ions must be precipitated as their hydroxides with a slight excess of diluted ammonia (1 : 1) from 100–200 ml of hot solution. The solution must be filtered. Iron(III) and aluminium hydroxides may contain large amounts of sulphate ions, and the washed precipitate must be dissolved in hot diluted hydrochloric acid (1 : 1) and precipitation repeated with diluted ammonia (1 : 1). The sulphate can then be determined in the combined filtrates.

In the presence of *calcium ions*, a considerable amount of calcium sulphate may be precipitated with the barium sulphate and cause a negative error. Calcium ions must first be separated from the sulphate before precipitation:

Add a slight excess of sodium carbonate solution to the hot solution, which has been neutralized with ammonia, allow the mixture to stand for several hours, filter the precipitate through a filter paper, wash thoroughly with hot water, and determine sulphate ions in the filtrate after acidification with hydrochloric acid.

Removal of iron(III) and other interfering ions by ion exchange resin. Evaporate the sulphate solution to dryness several times with hydrochloric acid on a water bath to decompose any nitrate which is present. Remove the excess hydrochloric acid. Dissolve the residue in 100 ml of water and 1 ml of concentrated hydrochloric acid by heating, allow to cool, and transfer the solution to the strongly acidic cation exchange resin which has been converted to the H-form and covered with water. Rinse the column with 150 ml of water.

The first 50 ml of eluant can be discarded if it gives no reaction with barium chloride solution.

Data of the ion exchange resin. Resin: Dowex 50/H^+. Specific ion exchange capacity: 1·9 meq/ml, resin expanded with water. Ion exchange bed: 170 ml. Complete ion exchange capacity: about 320 meq. 1 g Fe(III) corresponds to 50 meq capacity (about 16% column capacity). Exchange process:

$$3\ \boxed{R^-}\ H^+ + FeCl_3 \rightarrow \boxed{R^-}_3\ Fe^{3+} + 3\ HCl.$$

Notes. (1) If the cations K, Na, Ca, Cu, Ni etc. are to be removed, it is advisable to neutralize the solution with ammonia in the presence of methyl red (pH 5·6–6), and to carry out the ion exchange in almost neutral solution. The washing can then be continued until the washings again become neutral. Phosphate ions can be precipitated in the form of magnesium ammonium phosphate, and magnesium and ammonium ions can be removed from the filtrate by ion exchange.

(2) After neutralization and removal of carbon dioxide, sodium ions can also be removed on a cation exchange resin from solutions obtained after fusion with sodium carbonate. Thus zirconium (titanium or thorium) salts containing sulphate can be prepared for the determination of sulphate by the following method:

Fuse about 2 g of zirconium salt (ZrO_2 containing sulphate) with a mixture of 5 g of sodium carbonate and 5 g of sodium hydroxide in a nickel crucible. Dissolve the melt in 100 ml of hot water, filter the mixture, and wash the filter with 50 ml of hot water. Neutralize the filtrate with hydrochloric acid, boil out the carbon dioxide, and adjust the pH of the solution to between 1 and 2. Transfer the solution to a strongly acidic cation exchange resin converted to the hydrogen form, and rinse with about 200 ml of water. The specifications of the ion exchange resin are the same as above.

The fusing agents correspond to

$$5\ g\ NaOH = 125\ meq$$

$$5\ g\ Na_2CO_3 = 94\ meq,$$

i.e. total 219 meq, which is approximately 68% of the ion exchange capacity.

Exchange process: $\boxed{R^-}\ H^+ + Na^+ \rightarrow \boxed{R^-}\ Na^+ + H^+$.

54.1.1. *Determination of sulphate ions in the form of $BaSO_4$ by the compensation method of E. Hintz and H. Weber*

This method is often used in the presence of the less contaminating ammonium and alkali metal salts. Barium sulphate is precipitated from a hot, dilute, slightly acidic solution by the rapid addition of hot barium chloride solution. Under these conditions the precipitate contains relatively little bisulphate, but appreciable amounts of water. The slight loss of sulphuric acid on ignition is just compensated for by the adsorption of alkali metal ions.

Calcium and iron(III) ions must first be removed from the solution, or iron(III) ions must be reduced to iron(II) with zinc, magnesium or hydroxylamine hydrochloride. Good results can also be obtained by complexing the iron(III) ions with disodium ethylenediaminetetraacetate (Na_2EDTA). Any nitrate, chlorate and permanganate which is present must be decomposed by repeated evaporation with hydrochloric acid.

Procedure. Neutralize the solution, which should contain sulphate equivalent to 0·5–2 g of barium sulphate, with ammonia or hydrochloric acid in the presence of methyl orange, add 1 ml of concentrated hydrochloric acid in excess, and dilute to 350–450 ml with water. Heat the solution to boiling.

Prepare the barium chloride precipitant. For each gram of barium sulphate transfer 10 ml of 1 N barium chloride solution into a 200 ml beaker (122 g of crystallized $BaCl_2$ dissolved in 1000 ml), dilute with water to 100 ml, and heat to boiling. Add the boiling barium chloride solution rapidly to the boiling sulphate solution with constant stirring. Heat the mixture to boiling, and allow it to stand for 2–3 hr covered with a watch glass (overnight when only a small amount of precipitate is obtained).

Filter the mixture through a medium grade ash-free filter paper, wash with cold water until chloride can no longer be detected in the washings, and place the wet precipitate and filter paper into a weighed platinum or porcelain crucible and dry on a small flame. Combust the filter paper on the same flame, taking care that the paper does not flame, and burn off the carbon on a higher flame. Ignite the precipitate at 800°C for 10–15 min, allow to cool, and weigh within 30 min of the completion of the ignition. Repeat the ignition and check for constant weight. Stoichiometric factors: $SO_4/BaSO_4 = 0{\cdot}41155$; $SO_3/BaSO_4 = 0{\cdot}34300$; $S/BaSO_4 = 0{\cdot}13737$.

Notes. (1) It is not advisable to carry out the precipitation by the slow or dropwise addition of the precipitant, because in the presence of alkali metal and ammonium salts the bisulphate content of the precipitate increases and a large negative error may occur. When pure sulphuric acid is precipitated, however, the precipitation can be effected by the dropwise addition of the precipitant. The precipitate should not be dried at less than 180°C, as below this temperature the water cannot be removed. Electric hot-plates should be used for the evaporation and boiling of solutions in the determination of sulphate, because the sulphur dioxide which is always present in the combustion products of gases may cause appreciable errors.

(2) The interference of iron(III) ions can be eliminated by the method of R. Přibil and D. Maričova (1952)[1] which involves the addition of a ten-fold excess of disodium ethylenediaminetetraacetate (Na_2EDTA) over the amount of iron(III) present before the precipitation. The precipitate must be washed with a 1% solution of Na_2EDTA. When larger amounts of iron(III) are present, the precipitate must be dissolved from the filter with hot, ammoniacal 5% Na_2EDTA solution, the filter washed with hot water, and the solution acidified in the presence of methyl red. Barium sulphate is then precipitated free of iron. A similar method can be employed in the presence of aluminium ions. The EDTA complex of chromium(III) ions is only formed in hot solution. In the presence of chromium(III) ions, however, the results are 1–2% lower than the true values.

(3) The dissolution of the barium sulphate precipitate in ammoniacal Na_2EDTA solution is a slow process; 500 mg of freshly precipitated barium sulphate must be boiled for more than six hours to be completely dissolved by ammoniacal Na_2EDTA solution. According to A. G. C. Morris,[2] by boiling in strongly alkaline solution containing sodium hydroxide (pH > 12) using a four-fold excess over the theoretically required amount of Na_2EDTA, large amounts (0·5 g) of barium sulphate can be

[1] R. Přibil and D. Maricova, *Chem. Listy* **46**, 542 (1952).
[2] A. G. C. Morris, *Chemist-Analyst* **48**, 76 (1959).

dissolved in 5–10 min. According to Morris, the barium sulphate precipitate can be most conveniently dissolved by the following method:

Collect the precipitate on a G 4 glass filter-crucible, wash, and transfer the precipitate into a good quality 500-ml glass beaker using a fine jet of water. Place the filter-crucible containing the traces of precipitate into the beaker and dilute the solution to about 200 ml with water. Add a four-fold excess of 0·1 M Na_2EDTA solution over that theoretically required for dissolution (for the dissolution of 100 mg of $BaSO_4$ theoretically 4·3 ml of 0·1 M Na_2EDTA solution is required). Neutralize the solution in the presence of phenolphthalein, and make alkaline with a further 5 ml of 0·5 N sodium hydroxide solution. Boil the mixture on an electric hotplate until the precipitate dissolves.

54.1.2. *Determination of sulphate ions by the correction method of L. W. Winkler*

In contrast to the method utilizing error compensation, Winkler has applied a correction for errors in his precision method. He recommended the experimental conditions suitable for the formation of an easily filtered precipitate of reproducible composition. His method attempts the elimination of the errors caused by solubility, coprecipitation and the removal of volatile substances by the application of corrections. Even under the most favourable conditions, however, the composition of the barium sulphate precipitate is affected by the presence and the nature of accompanying ions, and the correction factors had to be determined for each important accompanying ion. Using these corrections, which were determined by extremely accurate measurements, the results obtained are quite accurate and satisfy the most precise requirements, while the method itself is relatively simple.

The solution must be prepared for the determination in one of three ways, depending on the nature and quantity of the accompanying ions. In all three methods, however, calcium ions must be removed from the solution by precipitation with sodium carbonate, while nitrate, chlorate, and permanganate must be decomposed by evaporation with hydrochloric acid.

(1) When the solution contains only *alkali metal sulphates* or *magnesium sulphate*, neutralize 100 ml of the solution, containing sulphate ions equivalent to 0·01–0·10 g of sulphuric acid, using 1 N hydrochloric acid or 1 N ammonia in the presence of methyl red, and add 1 g of solid ammonium chloride and *1 ml* of *1 N hydrochloric acid.*

(2) When *small amounts of Zn, Cd, Cu, Hg, Al, Mn, Fe(III), Fe(II), Co* or *Ni* are present in the form of their sulphates or as their double salts formed with alkali sulphates, dissolve 0·25–0·30 g of the sample (corresponding to 0·10–0·30 g of $BaSO_4$) in 100 ml of water, and add 1 g of solid ammonium chloride and *5 ml* of *1 N hydrochloric acid.*

When the original sample contains mercury(I) ions they must be oxidized by evaporation to dryness with a small volume of nitric acid, and the evaporation must be repeated with a small volume of 10% hydrochloric acid until the nitric acid is completely decomposed.

When the solution also contains iron(III) ions, add 0·5 g of hydroxylamine hydrochloride to the solution. In the presence of iron(II) ions, 0·01–0·10 g of

hydroxylamine is sufficient to prevent the oxidation of iron to the trivalent state in the subsequent operations.

(3) When the original sample contains *large amounts of Zn, Cd, Cu, Hg(II), Fe(III), Fe(II), Ni* or *Co* (0·5–2·0 g) in the form of their chlorides, dissolve 1 g of the sample (corresponding to 0·10–0·30 g of $BaSO_4$) and 1 g of solid ammonium chloride in water and evaporate to dryness on a water bath. Dissolve the residue in *5 ml of 1 N hydrochloric acid* and 100 ml of water.

When the solution also contains iron(II) or iron(III) ions, add 0·5 g of hydroxylamine hydrochloride.

In the presence of aluminium chloride, evaporate the solution, which contains 1 g of ammonium chloride and 10% hydrochloric acid, so that the residue crystallizes on cooling. This must be dissolved in 100 ml of water without addition of hydrochloric acid.

Precipitation. Transfer 100 ml of the acidic solution to a beaker, cover with a watch glass which has a hole in its centre, and heat the solution to boiling. Add 10 ml of 5% barium chloride solution slowly from a precipitating burette, and ensure that the solution boils uniformly during the precipitation. Boil the solution for a further 2–3 min and allow the covered solution to stand overnight.

Filtration, washing. Wash a G 4 glass, A 1 porcelain or No. 4 glass texture filter-funnel with hydrochloric acid, water and alcohol, dry for 1 hour, and weigh. Collect the precipitate on the filter, and transfer the last traces of the precipitate to the filter by rinsing the walls with 1 ml of alcohol and by using a policeman. The traces of precipitate collect on the surface of the alcohol owing to their surface tension, and can then easily be transferred to the filter. This operation must be repeated several times with 1 ml of alcohol after washing with 2–3 ml of water. Wash the precipitate on the filter with 25 ml of hot water. The last traces of liquid must be thoroughly removed at the pump.

Drying, weighing. (a) After washing, dry the filter at 130°C for 2 hr, allow it to cool at the side of the balance in a small covered beaker, and weigh after 30 min.

(b) The precipitate can also be dried in a current of air according to E. Schulek and I. Boldizsár (see Chapter 2.10.1.).

Stir the washed precipitate on the filter with 2–3 ml of alcohol using a small glass rod, and remove the alcohol at the pump. Remove the traces of the precipitate which adhere to the rod using 2–3 ml of alcohol, and remove the alcohol at the pump again. Repeat the washing with alcohol until 10–12 ml of alcohol has been passed through the precipitate. Dry the outside of the filter, the rubber tube and the funnel using a linen cloth, and draw a current of air, filtered through cotton wool, through the precipitate for 40 min. Place the filter in the balance case for 5 min and weigh.

Ignition of the precipitate. The precipitate can be collected on a porcelain filter-crucible and ignited in a protecting crucible at 800°C for 15 minutes. The empty crucible must then also be ignited before the filtration. The precipitate can also be collected on a medium grade filter paper, and the filter paper can be combusted in a weighed platinum or porcelain crucible (see Chapter 2.10.4.). After the carbon has combusted the precipitate must be ignited at 800°C for 15 min. The filter must be allowed to stand for 30 min in a

small covered beaker by the balance and then weighed. Different corrections must be applied for ignited precipitates and precipitates which have only been dried.

TABLE 54.3. Values of correction factors as a function of the free hydrochloric acid concentration of the prepared solution, for precipitates larger than 0·1 g

Amount of free hydrochloric acid in 100 ml precipitation volume	HCl concentration of the solution	Correction factor for dried precipitate	Correction factor for ignited precipitate
1 ml N HCl	0·01 N	1·0061	1·0143
5 ml N HCl	0·05 N	1·0060	1·0115
10 ml N HCl	0·10 N	1·0058	1·0107

Corrections. When the precipitation is effected from alkali metal sulphate solution, after preparation (1) in the absence of alkali metal chlorides (NaCl, KCl), the weight of the precipitate must be multiplied by the following factors.

Dried precipitates: When more than 0·1 g of precipitate is obtained, its weight must be multiplied by 1·006 to obtain accurate results.

Ignited precipitates: When the weight of the precipitate is more than 0·1 g.

(a) When precipitation is effected after preparation of the solution by method (1), (i.e. in the presence of 1 ml of 1 N hydrochloric acid), the weight of the precipitate must be multiplied by 1·0143.

TABLE 54.4. Corrections valid for precipitates lower than 0·1 g

Weight of precipitate g	Corrections in mg		
	For dried precipitates a	For ignited precipitates a'	
		when precipitated in the presence of	
		1 ml N HCl	5 ml N HCl
0·10	+0·6	+1·4	+1·2
0·05	+0·5	+0·8	+0·8
0·01	+0·3	+0·3	+0·5

(b) When precipitation is effected after preparation of the solution by methods (2) or (3), (i.e. in the presence of 5 ml of 1 N HCl), the weight of the precipitate must be multiplied by 1·0115 to obtain the correct result.

When the weight of the precipitate is less than 0·1 g the additive corrections of Table 54.4. must be used.

Stoichiometric factors: $SO_4/BaSO_4 = 0{\cdot}41155$, $SO_3/BaSO_4 = 0{\cdot}34300$, $S/BaSO_4 = 0{\cdot}13737$.

Cleaning of filter-crucibles. Remove most of the precipitate mechanically using a jet of water. Draw water through the inverted filter in the reverse direction to normal filtration. Place the filter into a beaker, pour on 10–20 ml of hot, concentrated sulphuric acid, place the beaker on a water bath and allow the sulphuric acid to pass through the filter. It is often better to pour cold sulphuric acid on to the filter and mix it with 1–2 ml of 30% hydrogen peroxide. The sulphuric acid then becomes hot and oxidizes any organic material which is present on the filter. When the sulphuric acid has passed through the filter, wash thoroughly with tap water, and then pass lukewarm water and then a small volume of ammonia through the filter.

Barium sulphate can also be dissolved from the filter with 0·5 N sodium hydroxide solution containing 3% disodium ethylenediaminetetraacetate, by immersing the crucible in this solution and boiling for 10 min. Rinse several times with distilled water and dry the crucibles in a drying oven. The filter need not be cleaned after each determination. It is sufficient merely to remove most of the precipitate mechanically; after repeated drying and weighing, the crucible is then ready for use in a subsequent filtration.

Note. The validity of the Winkler correction factors has been verified by the author even for precipitates of 1g weight, although Winkler himself only applied the corrections to precipitates weighing between 0·1 and 0·3 g.

TABLE 54.5. Determination of sulphate ions in the form of barium sulphate according to L. W. Winkler

Number of measurements	Mean of $BaSO_4$ precipitate weights mg	Corrected value $BaSO_4$ mg (f = 1·0143)	True value $BaSO_4$ mg	Deviation from true value Δ%	Standard deviation	
					mg	%
6	121·7	123·4	123·2	+0·16	±0·30	±0·24
6	243·9	247·4	247·1	+0·12	±0·30	±0·12
6	610·2	619·0	619·3	−0·05	±0·30	±0·05

When sulphate is determined in pure sulphuric acid solutions which contain no foreign salts (i.e. no alkali metal sulphate) without the addition of ammonium chloride, the application of the corrections gives erratic results. Under these conditions, therefore, 1 g of ammonium chloride must be added and a correction applied to the weight of the precipitate obtained; accurate results can then be obtained.

The accuracy of the results can be judged from the data of Table 54.5. (measurements of Z. Rády). The determinations were effected from sodium sulphate solution after preparation of the solution according to method (1)

(1 g NH_4Cl + 1 ml of 1 N HCl); the precipitates were ignited (correction factor: 1·0143).

In the determination of sulphate in various metal salts, and double sulphates after preparation of the solution by method (2) (1 g NH_4Cl + 5 ml N HCl) Winkler obtained the results shown in Table 54.6. For dried and ignited precipitates he used the correction factors 1·0060 and 1·0115 respectively.

TABLE 54.6. Determination of various metal salts and double sulphates according to L. W. Winkler

Substance investigated	Found SO_4^{2-}		Corrected SO_4^{2-}		SO_4^{2-} true value %
	Dried precipitate %	Ignited precipitate %	Dried precipitate %	Ignited precipitate %	
$K_2SO_4 \cdot ZnSO_4 \cdot 6\,H_2O$	43·00	42·80	43·26	43·29	43·29
$3\,CdSO_4 \cdot 8\,H_2O$	37·27	37·06	37·49	37·49	37·45
$MnSO_4 \cdot 4\,H_2O$	42·80	42·51	43·05	43·00	43·07
$CuSO_4 \cdot 5\,H_2O$	38·24	38·05	38·47	38·49	38·47
$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6\,H_2O$	48·76	48·50	49·05	49·06	49·00
$(NH_4)_2SO_4 \cdot CoSO_4 \cdot 6\,H_2O$	48·28	48·04	48·57	48·59	48·61
$(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6\,H_2O$	48·39	48·14	48·68	48·69	48·64
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$	40·28	40·04	40·52	40·50	40·49

Magnesium salts do not affect the accuracy of results even if 5 g of crystalline magnesium chloride are present, and so the correction factors can be used. (The precipitation must be carried out after the addition of 1 g of ammonium chloride and 1 ml of 1 N hydrochloric acid as described in method 1).

If the amount of sodium and potassium chlorides present is less than 0·5 g in 100 ml of solution, their effect on the accuracy of the determination (i.e. for the values of the correction factors) is almost negligible. Ammonium chloride gives even less interference.

In the presence of large amounts (several grams) of alkali metal chloride, however, the precipitate becomes contaminated with alkali metal sulphates and the results are low. This error can be eliminated by the use of further additive corrections shown in Tables 54.7. (*a*) (*b*) and (*c*). These corrections are valid for both dried and ignited precipitates, and must be added to the values obtained after application of the correction factors described above. When the weight of precipitate is less than 0·1 g the corrections *a* and *a'* in Table 54.4., or correction *b* in Table 54.7. must be applied.

TABLE 54.7. Corrections for sulphate determinations in the presence of greater amounts of alkali chloride

(a) Corrections in the presence of potassium chloride (*b*) mg

Precipitate weight g	KCl content of 100 ml solution g					
	0·5	1·0	2·0	3·0	4·0	5·0
0·30	0·4	2·0	2·5	3·0	3·3	3·5
0·25	0·3	1·5	1·8	2·1	2·3	2·5
0·20	0·2	1·0	1·2	1·4	1·6	1·8
0·15	0·1	0·6	0·8	0·9	1·0	1·1
0·10	0·1	0·4	0·5	0·5	0·6	0·6
0·05	0·1	0·3	0·3	0·3	0·3	0·3
0·01	0·1	0·3	0·3	0·3	0·3	0·3

(b) Corrections in the presence of sodium chloride (*b*) mg

Precipitate weight g	NaCl content of 100 ml solution g					
	0·5	1·0	2·0	3·0	4·0	5·0
0·30	0·3	1·5	2·0	2·4	2·7	2·9
0·25	0·3	1·5	1·8	2·1	2·3	2·5
0·20	0·3	1·4	1·7	1·9	2·1	2·2
0·15	0·3	1·4	1·5	1·6	1·6	1·7
0·10	0·2	1·2	1·2	1·3	1·3	1·3
0·05	0·2	0·9	0·9	0·9	0·9	0·9
0·01	0·1	0·5	0·5	0·5	0·5	0·5

(c) Corrections in the presence of ammonium chloride (*b*) mg

Precipitate weight g	NH_4Cl content of 100 ml solution g, above 1 g					
	0·5	1·0	2·0	3·0	4·0	5·0
0·30	0·2	0·7	0·8	0·9	1·0	1·1
0·20	0·0	0·2	0·3	0·4	0·5	0·6
0·10	0·0	0·0	0·1	0·1	0·1	0·2
0·05	0·0	0·0	0·0	0·0	0·0	0·0

Example 1. If only *one alkali metal chloride* is present in the solution, correction *b* corresponding to the amount of alkali metal chloride present must be added to the weight of the precipitate obtained after application of the correction factor:

$BaSO_4$ = weight of dried precipitate · 1·006 + *b*

$BaSO_4$ = weight of ignited precipitate · 1·0143 + *b*.

If the weight of the precipitate is less than 0·1 g
$BaSO_4$ = weight of dried precipitate + a + b
$BaSO_4$ = weight of ignited precipitate + a' + b.

If *two alkali metal salts* (NaCl + KCl) are present together the correction (b) can be calculated as in the following example:

Example 2. The sulphate content of ammonium sulphate has been determined by the procedure described above. The solution contained, as well as ammonium sulphate, 1·0 g of potassium chloride and 4·0 g of sodium chloride. 100 ml of the solution therefore contained 5 g of foreign salt. The weight of the dried barium sulphate precipitate was 285·1 mg, while that of the ignited precipitate was 282·4 mg. For 5 g of potassium chloride, b = 3·2 mg should be added, but for 1 g only a fifth of this, 0·64 mg is added. For 5 g of sodium chloride, on the other hand, correction b = 2·8 mg and for the 4·0 g of sodium chloride 80% of this value, i.e. 2·24 mg must be added. The complete corrected value of the weight of $BaSO_4$ is therefore calculated as follows:

$BaSO_4 = 285{\cdot}1 \cdot 1{\cdot}006 + 0{\cdot}64 + 2{\cdot}24 = 289{\cdot}7$ mg.

$BaSO_4 = 282{\cdot}1 \cdot 1{\cdot}0143 + 0{\cdot}64 + 2{\cdot}24 = 289{\cdot}0$ mg.

Example 3. When the precipitation is carried out in the presence of 2·5 g of sodium chloride and 2·5 g of magnesium chloride the calculation of the correction should be made as follows:

Let the weight of the dried barium sulphate be 286·4 mg and the weight of the ignited precipitate 284·1 mg. The total weight of foreign salt present is 5 g. The value of correction (b) for the sodium chloride is thus half of that used for 5 g of sodium chloride, i.e. 1·4 mg. A correction is not required for the magnesium chloride content. The corrected weights of the precipitates are therefore:

$BaSO_4 = 286{\cdot}4 \cdot 1{\cdot}006 + 1{\cdot}4 + 0{\cdot}0 = 289{\cdot}5$ mg

$BaSO_4 = 284{\cdot}1 \cdot 1{\cdot}0143 + 1{\cdot}4 + 0{\cdot}0 = 289{\cdot}6$ mg.

The results agree within the limits of error. The corrected values are in better agreement with the true values when the precipitates are dried.

In the presence of phosphates or phosphoric acid, the weight of the barium sulphate precipitate is greater than the theoretical value, because the precipitate also contains barium phosphate. The following procedure should be adopted to reduce the error caused by coprecipitation when phosphates or phosphoric acid are present:

Procedure. Dissolve the sample and 0·5 g of ammonium chloride in 25 ml of 10% hydrochloric acid, heat to boiling, and add dropwise 5 ml of 10% barium chloride solution to the boiling solution. Dilute to 100 ml with water, heat the solution again, and allow it to stand overnight. Wash, filter and dry the precipitate by the recommended procedure.

When 0·05–0·50 g of phosphoric acid is present and the weight of the precipitate is 0·05–0·30 g, 1·1 mg must be subtracted from the weight of the dried precipitate or added to the weight of the ignited precipitate.

In the presence of chromium(III) salts only, the sulphate is incompletely precipitated with barium chloride, because part of the sulphate is com-

plexed by the chromium. This complex can only be decomposed by evaporating the solution to dryness with hydrochloric acid. The sulphate content of chrome alum can be determined by the following method:

Procedure. To 100 ml of the neutral solution add 1 g of ammonium chloride and 5 ml of 1 N hydrochloric acid, and precipitate barium sulphate by the recommended procedure. Evaporate the filtrate to dryness in a platinum dish after the addition of 10 ml of 10% hydrochloric acid. Add 1–2 drops of 10% hydrochloric acid to the residue and dissolve it in 20 ml of hot water. Filter off the barium sulphate precipitate and weigh. The weight of this precipitate must be added to the weight of the first precipitate.

For a sample of chromium alum, $KCr(SO_4)_2 \cdot 12\ H_2O$, L. W. Winkler obtained the following results:

Weighed salt:	I. 300·4 mg	II. 336·1 mg	III. 308·7 mg
First $BaSO_4$ precipitate	273·4 „	305·8 „	279·0 „
Second $BaSO_4$ precipitate	5·7 „	7·8 „	8·4 „

Thus after correction the sulphate content obtained:

Dried precipitates	(average)	38·55%
Ignited precipitates	(average)	38·40%
Theoretical value		38·47%

The ignited precipitate was slightly bluish-green in colour, i.e. it contained traces of chromium.

The method can also be used for the determination of the sulphate content of chromium-plating baths.

Procedure. From the 20–25% chromic acid solution, after filtration on a glass filter, take a 20-ml sample, or a smaller volume of a more concentrated solution. Add 15–20 ml of water, 7 ml of concentrated hydrochloric acid and 15 ml of ethyl alcohol. Boil the solution for 15–20 min. When the chromium is completely reduced, dilute the solution to 150 ml and precipitate the sulphate with barium chloride. Wash the precipitate with 1% hydrochloric acid, and evaporate the filtrate to dryness after the addition of 10 ml of 10% hydrochloric acid. Add 3–4 drops of 10% hydrochloric acid to the dry residue and dissolve it in 20 ml of water. Precipitate barium sulphate from this solution, filter, weigh, and calculate the total sulphate content from the sum of the weights of the two precipitates.

54.2. DETERMINATION OF SULPHIDE IONS (S^{2-})

The common and characteristic property of hydrogen sulphide and the soluble sulphides is that in neutral medium they form difficultly soluble precipitates with a series of heavy metal ions. Cadmium is the most frequently used heavy metal cation for the precipitation of sulphide ions. Cadmium has the advantage over the other heavy metal ions that it does not react with hydrogen phosphide or hydrochloric acid, which are almost always present with the hydrogen sulphide and cannot be reduced or oxidized

during the subsequent oxidation processes. Cadmium sulphide also has the advantage that it is soluble in strong acids, and the hydrogen sulphide evolved during the reaction can be titrated iodimetrically. The composition of cadmium sulphide, however, is not stoichiometric, and it changes according to the conditions of the precipitation. Thus, although it retains the sulphide quantitatively from the original sample, it cannot be weighed directly.

This error can be overcome by the addition of acidic copper(II) sulphate solution to the cadmium sulphide. Copper(II) sulphide is much less soluble than cadmium sulphide and a precipitate-exchange reaction takesplace. The copper(II) sulphide precipitate can be filtered, washed, and ignited to the oxide. Any copper sulphate formed on ignition must be decomposed by heating at 950°C. The copper oxide can then be weighed after cooling. Precipitation in the form of cadmium sulphide also has the advantage that sulphide can be precipitated selectively in the presence of sulphite, dithionite, thiosulphate and sulphate.

When no other sulphur compounds are present in the solution, or when the total sulphur content of the solution is to be determined, the sulphide can be oxidized to sulphate and precipitated in the form of barium sulphate.

Hydrogen sulphide can slowly be oxidized quantitatively to sulphate with bromine water. It is advisable to carry out the oxidation in alkaline solution to avoid the intermediate precipitation of sulphur. In alkaline medium, bromine water, sodium hypochlorite or hydrogen peroxide can be used as oxidant. As the determination of sulphate is not very accurate in the presence of large amounts of alkali metal salts, ammonia should preferably be used to make the solution alkaline. Hypochlorites and hypobromites, however, react with ammonia with the formation of nitrogen and are slowly decomposed. Under these conditions, therefore, when an alkaline hypohalite solution is used to absorb gaseous hydrogen sulphide (i.e. in gas absorption bottles), sodium carbonate or sodium hydroxide should be used to make the solution alkaline.

Commercial bromine and hydrogen peroxide often contain traces of sulphuric acid; hence a blank determination should be made using the same volume of bromine water or hydrogen peroxide as in the sulphide determination. Bromine can be made free of traces of sulphate by distillation in glass apparatus.

54.2.1. *Determination of water-soluble sulphides*

54.2.1.1. *Determination of the hydrogen sulphide content of industrial gases.* Collect a sample of the gas in a 5–10 litre glass flask fitted with a rubber stopper into which two holes are bored. Fit a long glass tube through the stopper so that it reaches the bottom of the flask, and fit a bent short tube through the stopper. Pass 30–40 litres of the gas to be analysed through the bottle and then clamp off the rubber tubes connected to the glass tube. When town gas is to be analysed, the absorbing apparatus can be connected directly to the gas tap with a rubber tube.

Reagent. Cadmium acetate solution. Dissolve 40 g of crystalline cadmium acetate in 900 ml of water and add 100 ml of glacial acetic acid.

Procedure. Connect the bottle containing the gas sample via a rubber tube to a ten-sphere absorption tube filled to the sixth or seventh bulb with cadmium acetate solution (see Fig. 54.1.). Connect a wash-bottle containing cadmium acetate to the other end of the absorption tube, and connect a 4–5 litre aspirator filled with water to the wash-bottle. Fasten a rubber tube to the free end of

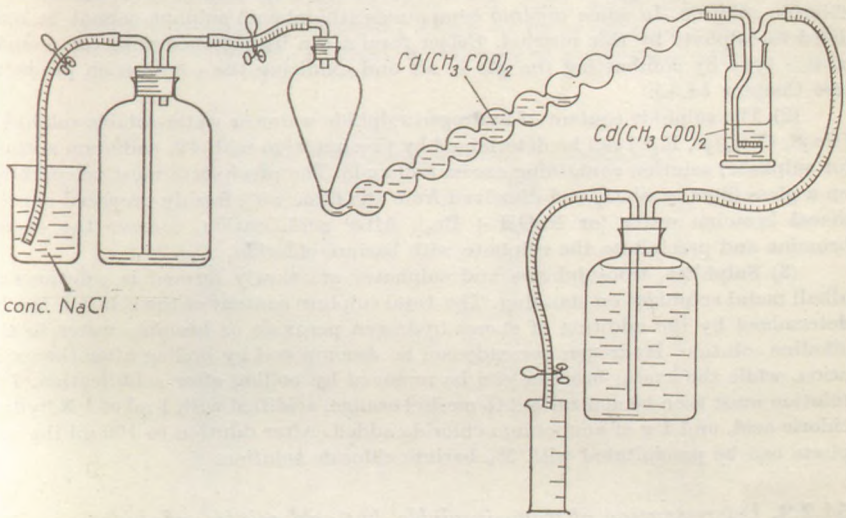


Fig. 54.1. Apparatus for determination of hydrogen sulphide content of industrial gases

the longer glass tube, and immerse its free end in a saturated sodium chloride solution. Open the clamp and draw the gas sample through the apparatus slowly (1 litre/hr) by running off water from the aspirator into a large measuring cylinder. Measure the volume of water collected. The volume of the gas sample to be drawn through the apparatus naturally depends on its hydrogen sulphide content.

The flow of gas must be stopped immediately when yellow cadmium sulphide begins to precipitate in the fifth and sixth bulbs. Rinse the absorbing liquid into a beaker, wash with water containing acetic acid, and add sufficient copper(II) sulphate solution to produce a noticeable blue colour of excess copper(II) sulphate in the supernatent liquid. Heat the mixture to boiling, filter on an ash-free filter paper, and wash the precipitate until sulphate can no longer be detected in the washings. Combust the filter paper in a weighed porcelain crucible, and ignite the residue in an electric furnace at 950°C for 1 hr. Cool and weigh the copper(II) oxide. Stoichiometric factor: $H_2S/CuO = 0{\cdot}42849$. Reduce the volume of the original gas to standard temperature and pressure using the air pressure and temperature data, and calculate the results in percentage by volume.

Notes. (1) When the total sulphur content of the gas is to be determined, i.e. its H_2S, SO_2, CS_2 and organic sulphur content, 0·5 N ammonia solution to which 2 ml of 30% sulphate-free hydrogen peroxide has been added must be used as absorbing liquid. When the absorption is complete, decompose the hydrogen peroxide which remains in the absorbing liquid by boiling, neutralize the solution to methyl orange with 1 N hydrochloric acid, add 1 ml of 1 N hydrochloric acid in excess, dilute to 100 ml, and precipitate the sulphate from the boiling solution with 5% barium chloride solution. In some organic compounds (thiophene) sulphur cannot be oxidized to sulphate by this method. Better results can be obtained with compounds of this type by combusting the gas in air and oxidizing the combustion products (see Chapter 54.5.).

(2) The sulphide content of hydrogen sulphide water or water-soluble sulphides [Na_2S, $(NH_4)_2S$, K_2S] can be determined by precipitation with 4% cadmium acetate (or sulphate) solution containing excess ammonia. The precipitate must be collected on a glass filter, washed, and dissolved from the filter with freshly prepared ammoniacal bromine water (or NaOH + Br_2). After acidification, remove the excess bromine and precipitate the sulphate with barium chloride.

(3) Sulphites, thiosulphates and sulphates are slowly formed in solutions of alkali metal sulphides on standing. The total sulphur content of the solution can be determined by the addition of excess hydrogen peroxide or bromine water to the alkaline solution. Hydrogen peroxide can be decomposed by boiling after the oxidation, while the excess bromine can be removed by boiling after acidification. The solution must then be neutralized to methyl orange, acidified with 1 ml of 1 N hydrochloric acid, and 1 g of ammonium chloride added. After dilution to 100 ml the sulphate can be precipitated with 5% barium chloride solution.

54.2.2. *Determination of water-insoluble, but acid soluble sulphides*

Sulphides which are insoluble in water, but which can be decomposed with hydrochloric acid or hydrochloric acid + zinc, include the simple sulphides of Fe(II), Zn, Cd, Pb, Sb(III), Cu(II) and Hg(II). Gaseous hydrogen sulphide can be liberated from these sulphides with hydrochloric acid, or hydrochloric acid and nascent hydrogen. The gas can be absorbed in cadmium acetate (or ammoniacal hydrogen peroxide) solution. The cadmium sulphide formed can be converted to copper(II) sulphide by the addition of copper sulphate to the solution, and can then be weighed after ignition to copper(II) oxide. Alternatively, the sulphide can be determined in the form of barium sulphate after oxidation. Cadmium sulphide can be titrated iodometrically.

Water-soluble sulphides (Na_2S, CaS, BaS) can, of course, also be determined by the gas evolution methods, and the method is preferable when accompanying ions interfere in the direct titration. The method is particularly suitable for the determination of the sulphur content of iron and steel samples which are soluble in hydrochloric acid.

54.2.2.1. *Determination of the sulphur content of iron and steel according to W. Schulte.* This relatively simple and quite rapid method utilizes the fact that when a sample of iron is dissolved in hydrochloric acid, the sulphur present is liberated in the form of hydrogen sulphide which can be absorbed in cadmium acetate solution, or in a mixture of cadmium acetate and zinc

acetate. Copper(II) or silver salt solutions are not suitable as absorbents, because when the sample of iron is dissolved, other gases which form precipitates with copper(II) ions or reduce silver to the metal are also evolved (hydrogen phosphide, acetylene). The cadmium sulphide can be converted to copper sulphide, which can then be weighed as copper(II) oxide.

Reagents. Hydrogen sulphide absorbent. (a) *Acetic acidic absorbent.* Dissolve 25 g of cadmium acetate, $Cd(CH_3COO)_2 \cdot 2\ H_2O$, or 5 g of cadmium acetate and 20 g of zinc acetate, $Zn(CH_3COO)_2 \cdot 2\ H_2O$, by warming in a mixture of 250 ml of water

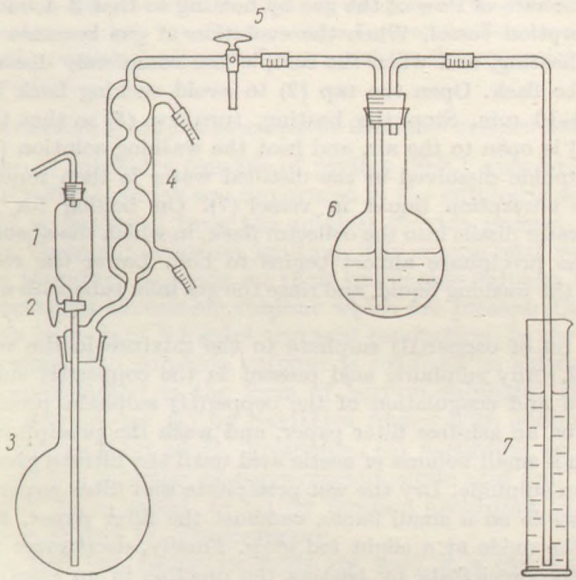


Fig. 54.2. Apparatus for determination of sulphur content of steels according to Schulte

and 250 ml of glacial acetic acid. Cool, dilute the solution to 4 litres with water, and filter through a filter paper. (b) *Ammoniacal absorbent.* Dissolve 10 g of cadmium sulphate, $CdSO_4 \cdot 8/3\ H_2O$, in 700 ml of water and add 300 ml of concentrated ammonia.

Copper(II) sulphate solution. Dissolve 120 g of crystalline copper(II) sulphate, $CuSO_4 \cdot 5\ H_2O$, in 800 ml of distilled water, and add 120 ml of concentrated sulphuric acid with constant stirring. Cool, dilute the solution to one litre, and filter on a filter paper.

Sample size : Weigh out 5–10 grams of samples containing 0·01–1·0% of sulphur. For other acid-decomposable sulphides:

weigh 1 g when the sulphur content is 1·0—10%,
„ 0·5 g „ „ „ „ „ 10 —30%,
0·25 g when the sample contains more than 30% of sulphur.

Procedure. Weigh 1–10 g of the finely cut iron or steel sample into the dry flask of the Schulte apparatus (Fig. 54.2 (3), and assemble the apparatus

Place 100 ml of concentrated hydrochloric acid into the dropping funnel (1), 160 ml of distilled water into the gas washing bottle (6), and 100 ml of cadmium acetate solution and 100 ml of water into the absorption vessel (7). Open the tap (2) of the dropping funnel and add one-quarter of the hydrochloric acid to the flask; add a further portion after 5 min. When the initial vigorous reaction has subsided add the remaining hydrochloric acid to the flask. It is essential that during the dissolution the hydrochloric acid remains cold, and that it is as concentrated as possible, because only under these conditions can the formation of organic sulphur compounds be avoided.

Adjust the rate of flow of the gas by heating so that 3–4 bubbles/sec pass into the absorption vessel. When the evolution of gas becomes less vigorous increase the heating, and when the sample has completely dissolved boil the mixture in the flask. Open the tap (2) to avoid sucking back and continue boiling for 8–10 min. Stop the heating, turn tap (5) so that the gas outlet from flask (3) is open to the air, and heat the washing solution (6) to boiling. Hydrogen sulphide dissolved in the distilled water is then removed and absorbed in the absorption liquid in vessel (7). On boiling for 5 min about 15–20 ml of water distils into the collector flask, in which the absorbing solution containing the precipitate almost begins to boil. Lower the receiving flask, finish boiling the washing liquid, and rinse the gas inlet tube with a small volume of water.

Add 10 ml of copper(II) sulphate to the mixture in the receiving flask and mix well. Any sulphuric acid present in the copper(II) sulphate assists the formation and coagulation of the copper(II) sulphide precipitate. Filter the mixture on an ash-free filter paper, and wash the precipitate with water acidified with a small volume of acetic acid until the filtrate gives no reaction with hydrogen sulphide. Dry the wet precipitate and filter paper in a weighed porcelain crucible on a small flame, combust the filter paper, and ignite the sulphide to the oxide at a slight red glow. Finally, decompose any traces of sulphate in the precipitate by heating the crucible in an electric furnace at 950°C for about 1 hour. Cool and weigh the copper(II) oxide.

Stoichiometric factor: S/CuO = 0·40314.

Notes. (1) The cadmium sulphide can also be titrated iodimetrically. Add excess standard iodine solution to the solution containing the precipitate, acidify the mixture with hydrochloric acid, and titrate the excess iodine with standard sodium thiosulphate solution.[1]

(2) The sulphur content of acid-insoluble sulphides (pyrites) can also be determined by this method after suitable reduction. According to Treadwell (1891), the reduction can be effected with iron powder: Weigh 0·3–0·5 g of the finely divided sulphide sample (pyrite) into a heat-resistant test tube of length 30 mm and diameter 10 mm which has a small rim. Mix the sample with 3 g of iron powder. Cover the mixture with a 2—3 mm layer of iron powder, and place the test tube into a hole cut in an asbestos sheet. Pass carbon dioxide into the tube, heat the mixture slowly to a red glow, and maintain it at this temperature for 10 minutes. Cool

[1] L. ERDEY, *Bevezetés a kémiai analizisbe II. Térfogatos analizis.* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest, (1965), p. 207.

in a current of carbon dioxide, place the test tube and contents into the flask of the Schulte apparatus, add 2—3 g of granulated zinc and proceed as described above. The iron powder also reduces part of the barium sulphate present in pyrites. Iron powder often contains sulphur and a blank should also be run on the iron powder at the same time.

(3) Iron ores which contain small amounts of sulphur can be reduced by ignition at a red heat in a nickel crucible with an equal weight of a mixture of 5 parts of sodium bicarbonate, 2 parts of powdered aluminium metal, and 1 part of pure charcoal. The combustion products of the gas flame, which often contain sulphur, must not come in contact with the mixture during its reduction. Place the crucible into a hole cut in an asbestos sheet and hold it obliquely in the flame. Cool, transfer the powdered substance into the decomposition flask of the Schulte apparatus, add several grams of granulated zinc, and carry out the determination according to the above procedure.

54.2.3. *Determination of sulphides which are insoluble in water and dilute acids*

This group of sulphides consists of pyrites (FeS_2), sphalerite (ZnS) and chalcopyrite ($CuFeS_2$), which are important in the sulphuric acid industry. Sulphuric acid is produced from the sulphur dioxide present in the gases liberated from these sulphides on ignition. The commercial value of these raw materials therefore depends on their oxidizable sulphur content, and any other substances containing sulphur which are present ($CaSO_4$, $BaSO_4$, $PbSO_4$) are less important for sulphuric acid production. In the gravimetric analysis, therefore, the sulphide sulphur is oxidized to sulphate and this can then be precipitated in the form of barium sulphate. The oxidative fusion can be carried out (a) by oxidative fusion with sodium carbonate according to the method of R. Fresenius, (b) according to the method of G. Lunge using a mixture of concentrated nitric acid and hydrochloric acid ("reversed" aqua regia), or (c) by ignition according to the method of B. Wurzschmitt and W. Zimmermann.

When the first two fusion methods are used, it is essential to remove iron from the solution before the precipitation of barium sulphate, or alternatively to reduce iron to the bivalent state to avoid interference on precipitation. Nitrates (and chlorates) must be decomposed by evaporation with hydrochloric acid. It is advisable to remove the sodium ions introduced by fusion with sodium carbonate on a cation exchange resin. The ignition method (c) has the advantage over methods (a) and (b) in that the sulphuric acid to be determined is separated in free form without any accompanying substances.

54.2.3.1. *Fusion of pyrites with sodium carbonate-potassium nitrate according to R. Fresenius.* During this alkaline oxidative fusion, sulphide sulphur is oxidized to sulphate and any insoluble sulphates present ($BaSO_4$, $PbSO_4$) are also fused. The total sulphur content of the sample is thus present as alkali sulphate in the aqueous solution of the melt. As lead carbonate is soluble in sodium carbonate solution, and the presence of alkali plumbites in the solution may interfere in the precipitation, the alkalinity of the solution must be buffered by the introduction of gaseous carbon dioxide. Lead carbonate is practically insoluble in sodium carbonate solution con-

taining bicarbonate. After the precipitation of lead carbonate the solution must be filtered immediately, otherwise considerable amounts of lead sulphate may be formed by exchange, and the recovery in the sulphate determination is then incomplete. The filtered sodium carbonate extract must be evaporated to dryness with hydrochloric acid to decompose nitrates and any silicic acid precipitated must be dehydrated and removed.

When the fusion is carried out using a mixture of sodium carbonate and sodium peroxide, instead of sodium carbonate and potassium nitrate, it is not necessary to evaporate the solution to remove nitrate ions. Sodium peroxide reacts explosively with pyrites, and it is advisable to dilute the sample with anhydrous sodium carbonate.

Pyrite samples must be powdered very finely and passed through a silk sieve. Larger particles which remain on the sieve must be powdered repeatedly until all the sample passes through the sieve.

Details of the fusion are given in Chapters 2.5.5. and 2.5.6.

Notes. (1) The combustion products of the gas flame must be carefully shielded from the sample during the fusion and evaporation, and it is advisable to use an alcohol-vapour burner or petrol flame instead of a gas flame. The evaporations should be carried out on an electrically heated water bath.

(2) Large amounts of sodium chloride can be removed from the neutralized solution, before the precipitation of barium sulphate, using a cation exchange resin converted to the hydrogen form (Dowex 50) (see Chapters 54.1. and 3.6.).

54.2.3.2. *Determination of the sulphur content of pyrites according to G. Lunge, using "reversed" aqua regia.* Reversed *aqua regia* consists of 3 volumes of concentrated nitric acid and 1 volume of concentrated hydrochloric acid. This acid mixture oxidizes the sulphur of pyrites to sulphate. The dissolution must be started in the cold, because sulphur may be precipitated from the hot solution produced by the vigorous reaction. The oxidation of sulphur is difficult, and therefore if sulphur precipitates it is advisable to repeat the determination on a fresh sample.

After dissolution the nitric acid solution must be evaporated several times on a water bath; nitrates are decomposed and silicic acid is precipitated. Iron(III) ions are precipitated from the filtrate with ammonia. The iron(III) hydroxide may contain a considerable amount of sulphate and the precipitation with ammonia must be repeated after dissolution of the precipitate in hydrochloric acid. Barium sulphate is precipitated from the filtrate by the compensation method of E. Hintz and H. Weber. If iron(III) ions are reduced to iron(II) with 0·5 g of hydroxylamine, the precipitation of barium sulphate can also be carried out by the method of L. W. Winkler.

Procedure. Weigh 0·3–0·5 g of the finely powdered sample, which has been sieved through a phosphor-bronze sieve of 0·06 mm mesh into a 200-ml beaker and place the beaker into ice-water. Mix 7·5 ml of concentrated nitric acid and 2·5 ml of concentrated hydrochloric acid in a test tube, cool the mixture in ice-water, and add it to the sample in the beaker. Cover the beaker with a watch glass, allow it to stand overnight, and then place it on a water bath and heat cautiously. Sulphur should not precipitate from the mixture.

When no more brown fumes are liberated, evaporate to dryness on a steam bath. Repeat the evaporation twice with 10 ml of hydrochloric acid (1 : 1), and then add 1 ml of concentrated hydrochloric acid to the cold residue and dissolve it in 100 ml of hot water. Filter the solution through an ash-free filter paper, and wash the precipitate with cold water and then hot water until the washings show a neutral reaction. Precipitate iron(III) ions from the hot filtrate (150 ml) with 20 ml of 10% ammonia. Heat the mixture on a water bath for 15 min, filter on an ash-free filter paper, and wash with hot water.

Rinse the precipitate back into the beaker with a fine water jet, dissolve it in a small volume of 10% hydrochloric acid by heating, and reprecipitate the iron(III) hydroxide with ammonia. Evaporate the filtrate carefully to remove the excess ammonia and add the solution to the first filtrate.

Remove the excess ammonia from the combined filtrates by boiling, neutralize the solution with hydrochloric acid in the presence of methyl orange, and acidify with 1 ml of concentrated hydrochloric acid. Dilute the solution to 350–450 ml and heat to boiling. Dissolve 2·4 g of crystalline barium chloride in 100 ml of water, heat to boiling and add the solution immediately to the boiling sulphate solution with stirring. Allow the mixture to stand for 2–3 hr (or overnight), filter on an ash-free filter paper, and wash the precipitate with cold water and then hot water until chloride can no longer be detected in the washings. Combust the filter paper, ignite the precipitate at 600–800 °C for 15 mins cool and weigh. Stoichiometric factor: $S/BaSO_4 = 0{\cdot}13737$.

Notes. (1) This method gives the most reliable results and should be used for accurate determinations.

(2) When the sample contains large amounts of lead and arsenic, fusion with sodium carbonate is preferred.

(3) If sulphur is precipitated after oxidation with the nitric acid–hydrochloric acid mixture, it can be oxidized by the addition of 0·5 ml of bromine (tested for sulphuric acid) and 2 ml of ether (or carbon tetrachloride) before heating (K. K. Järvinen, 1923).

(4) Unoxidized sulphur can also be dissolved easily with 1–2 ml of 18% iodine trichloride (E. Birk, 1928; E. Wilke-Dörfurt, 1930). Iodine trichloride can be prepared by the addition of 10 g of iodine to 100 ml of concentrated hydrochloric acid and then saturating the solution with gaseous chlorine.

54.2.3.3. *Determination of sulphur content of pyrites by ignition (H. Senf, A. Schöberl, 1937 ; B. Wurzschmidt, W. Zimmermann, 1938).* The Grote–Krekeler apparatus, equipped with a simple quartz tube (see Fig. 54.3.) can be used for the determination of the sulphur content of pyrites. The method has the advantage that the processes are similar to the processes used in industrial pyrite-roasting, and also that the sulphuric acid is collected free of accompanying ions and can be determined more easily. Considerable amounts of sulphur trioxide as well as sulphur dioxide are present in the gas produced on roasting. The sulphur trioxide forms an aerosol, and is difficult to absorb quantitatively. The absorbing vessels of the Grote–Krekeler apparatus (9 and 10) therefore contain fine-pored glass filter layers, through which the aerosol passes into the absorbing liquid. The diameter of the bubbles formed is hardly larger than that of the sulphuric acid

droplets, and therefore owing to the Brownian motion the aerosol droplet reaches the surface of the absorbing liquid quite fast. Traces of sulphuric acid which pass through the lower vessel (9) are absorbed in the upper vessel (10). The ignition tube of the apparatus *A* is a 50-cm quartz tube of 17 mm diameter, connected to the absorption vessel by ground glass joints (7). To the upper absorption vessel (10) a spray trap (11) connected

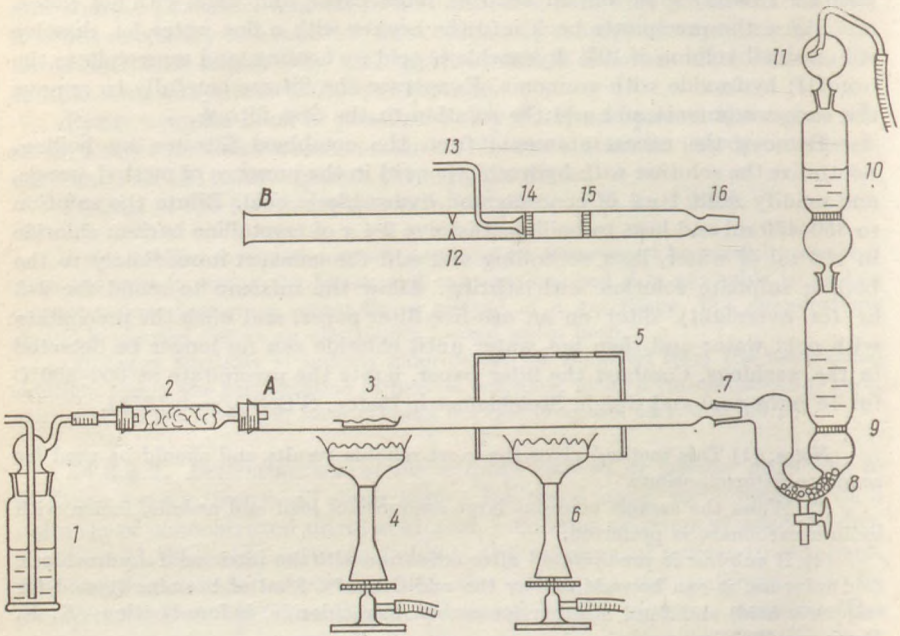


Fig. 54.3. Combustion apparatus according to Grote–Krekeler

to a water pump via pressure tubing is fitted. Sulphuric acid-free 3% hydrogen peroxide solution can be used as the absorbing medium. 50 ml of the solution must be placed in the upper vessel, and 100 ml in the lower vessel. Several millilitres of absorbing liquid can be transferred to the vessel (8) filled with glass beads by applying an inflated rubber balloon to the vessel (9).

Procedure. Weigh 0·3–0·5 g of the powdered pyrite sample into a small porcelain vessel, and place it in the quartz tube so that it is 15 cm from the end of the tube. Close the end of the tube with a rubber stopper into which a tube containing cotton wool (2) is fitted. Connect a washing bottle (1) filled with sodium hydroxide solution to this tube. Turn on the water pump and draw air through the apparatus at a rate of 2–4 bubbles/sec. Heat an 8-cm zone to 1000 °C with a Teclu burner, beginning the heating 5 cm from the porcelain vessel. The required temperature can be attained quite easily when the required part of the tube is covered with a suitable asbestos cover (5).

Begin heating the sample in the vessel from the side furthest from the furnace using a Teclu burner (4). Heat stepwise so that the substance is ignited slowly. The start of the roasting is indicated by the appearance of sulphuric acid fumes in the lower part of the absorbing vessel (8). The combustion must be regulated so that the absorption of the fumes is continuous. When the roasting is complete and the sulphuric acid fumes have disappeared from the absorber, move the asbestos sheath (5) to the end of the quartz tube, place both burners under it and heat the tube up to the ground glass joint. Volatilize sulphuric acid from the joint into the absorption vessel, and when the sulphuric acid fumes have been absorbed completely interrupt the heating, turn off the pump, and disconnect the quartz tube from the ground glass joint (7). Place a large beaker under the absorption vessel (8), connect a small inflated rubber balloon to the spray trap (11), and force the absorbing liquid out of the tube under pressure. Rinse the whole absorption vessel with distilled water.

Titrate the sulphuric acid in the combined solutions in the presence of methyl orange. The values obtained by titration are always 0·7–1·2% lower than the true values because the sulphuric acid dissolves alkalies from the absorption vessel. It is therefore advisable to make the sulphuric acid solution slightly alkaline with ammonia, and to evaporate the solution on an electrically heated water bath. Dissolve the residue in 1 ml of 1 N hydrochloric acid and 50 ml of water, filter off silicic acid on a small filter paper, wash with a small volume of water and neutralize the filtrate with 0·5 N ammonia in the presence of methyl orange. Add 1 ml of 1 N hydrochloric acid and 1 g of ammonium chloride to the neutral solution, dilute with water to about 100 ml and add 10 ml of 5% barium chloride solution dropwise to the boiling solution. After precipitation is complete, boil the solution for a further 2 min, cover, and allow the mixture to stand overnight. Collect the precipitate on a G 4 glass or A 1 porcelain filter crucible or No. 4 glass texture filter-funnel, wash with 25 ml of cold and 25 ml of hot water, and dry at 130°C for 2 hr. Cool and weigh. Correct the weight of the precipitate obtained by multiplying by the factor 1·006 (L. W. Winkler). Stoichiometric factor: $S/BaSO_4 = 0{\cdot}13737$.

Notes. (1) The hydrogen peroxide used for the absorption must always be free of sulphate. If sulphate-free hydrogen peroxide is not available, 0·1% sodium chlorate solution can be used as absorbent according to F. Paulik.[1] The solution containing the sulphuric acid must then be evaporated several times on a water bath to decompose the chlorate ions.

(2) Only the roastable sulphur content of pyrites can be determined by this method. When the residual sulphur content of the pyrites ($CaSO_4$, $BaSO_4$, $PbSO_4$) must also be determined, the ignition must be made in a platinum vessel, and a 4–6 fold excess of anhydrous sodium metaphosphate must be added to the residue (L. Erdey and F. Paulik, 1954[1]). The ignition must then be repeated according to the above procedure. Sodium metaphosphate drives off sulphur trioxide from sulphates, and it can then be determined after absorption.

Sodium metaphosphate can be prepared from sodium dihydrogen phosphate by ignition above 630°C. The cooled solid residue must be powdered.

[1] L. Erdey and F. Paulik, *Acta Chim. Hung.* **4**, 37 (1954).

(3) It is advisable to place the platinum vessel inside a smaller quartz tube with fusions using sodium metaphosphate, in order to protect the ignition tube from spitting metaphosphate.

(4) Ignition with sodium metaphosphate can also be used for the direct determination of the sulphur content of all inorganic substances ($CaSO_4$, $BaSO_4$), (Erdey–Paulik, 1954).

54.3. DETERMINATION OF THE SULPHUR CONTENT OF NON-VOLATILE ORGANIC SUBSTANCES

(by the method of Grote-Krekeler)

W. Grote and H. Krekeler originally used the apparatus for the roasting of sulphides for the determination of the sulphur content of non-volatile organic substances. In these determinations, however, larger samples must be combusted, and therefore it is advisable to use the tube *B* shown in Fig. 54.3. for the ignition. Sintered quartz filter layers (14, 15) are fitted into the quartz combustion tube. Pure oxygen is introduced through side tube (13) in front of the first quartz filter (14). In the space between the quartz window (12) and the filter (14) the fumes of the organic substances are mixed thoroughly with oxygen, and the mixture is combusted at 1000°C in the space between the two quartz filters. The solid or liquid sample is weighed into a porcelain vessel, as in the analysis of pyrites, and the substance is distilled into the combustion zone in a slow current of air. If the substance explodes easily, a current of nitrogen must be used instead of air during the heating of the substance. The other details of the determination are similar to those described in the analysis of pyrites. The only difference is that the combustion must be carried out much more slowly, otherwise the gas current takes carbon over into the absorbent. At the end of the combustion it is sufficient to heat the tube once with a smaller burner. Uniform combustion can be facilitated by the insertion of a quartz wool stopper in front of the quartz window (12).

Note. The sulphuric acid collected in the absorber must be evaporated several times with hydrochloric acid on a water bath, because small amounts of nitric acid are always formed during the combustion and interfere in the sulphate determination.

54.4. DETERMINATION OF THE SULPHUR CONTENT OF VOLATILE ORGANIC SUBSTANCES (PETROL). LAMP SULPHUR

Volatile organic substances containing sulphur can also be combusted in the Grote–Krekeler apparatus if the sample is weighed into a small, sealed glass tube, and the capillary of the tube is broken just before the combustion is started. The glass container must be placed in a platinum vessel. On heating, fumes of the substance are mixed with oxygen and are combusted in the mixing chamber and on the quartz filters. There is a danger, however, particularly in the analysis of petrol, that the fumes may explode and losses occur. This difficulty can be overcome by combusting the substance in a small lamp, which can be weighed on an analytical

balance, and by absorbing the combustion products in the intensive washers or absorbers of the Grote–Krekeler device. In this lamp the substance is drawn up through a cotton thread. To avoid carbonization, in a modified apparatus secondary air can be fed to the burner to ensure uniform combustion. The glass apparatus is shown in Fig. 54.4.

The petrol to be determined must be weighed into the 50-ml flask (1). The cotton thread inserted into a glass tube (3) reaches the bottom of the flask. The glass tube is surrounded by a jacketing tube (2) through which air is drawn into the lower parts of the flame. The tube is connected by ground glass joints to the closed chimney (4). The air drawn in first cools down the combustion products, and later on the outer parts of the flame ensures complete combustion. The chimney can be connected to the absorber of the Grote–Krekeler apparatus, or to an absorber (5–6) which contains no sintered glass filter discs. Sulphate-free hydrogen peroxide–sodium carbonate solution can be used as the absorption liquid. A washing bottle filled with absorption liquid must be connected to the spray trap (7).[1]

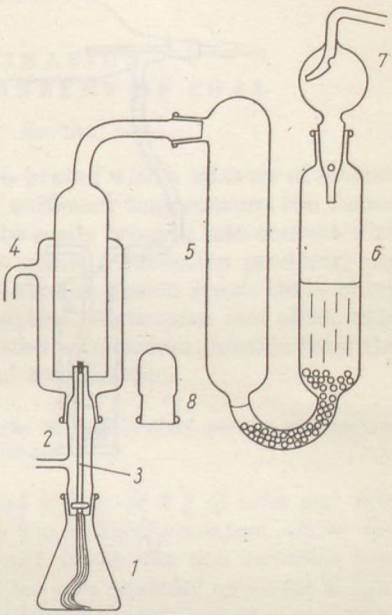


Fig. 54.4. Lamp apparatus for sulphur determination

Decompose excess hydrogen peroxide by boiling the absorbing solution. Acidify the solution with hydrochloric acid and evaporate to dryness. Dissolve the residue in water containing a small volume of hydrochloric acid, and precipitate sulphate ions by the usual method using barium chloride solution.

Note. By this method as little as 0·005% sulphur in hydrocarbons can be determined. The cotton thread must be covered with a cap (8) on weighing. In very accurate determinations it is advisable to wash the air with alkaline hydrogen peroxide solution before it reaches the apparatus. The air can be regulated by the taps fitted to the tubing at the inlets (2 and 4). Strongly carbonizing aromatic substances, or heavier refinement fractions can be diluted with sulphur-free petrol. A large amount of the sulphur-free solvent must then be combusted, after the sample has been combusted, in order to wash out the cotton thread. A chromatographic separation of the components of different boiling point may take place on the thread. The flame must not be lit with a match, because its sulphur content may cause errors.

[1] G 2 glass filter layers are fitted into the washing bottles. Through this layer the gas is dispersed into very fine bubbles and makes contact with the liquid over a large surface.

54.5. DETERMINATION OF THE TOTAL SULPHUR CONTENT OF GASES

(H. Drehschmidt, 1887; A. Roelen, W. Feisst, 1934)

The principle of the method is similar to the "lamp sulphur" determination. The gas is combusted in air, combustion products are absorbed in sodium carbonate or alkaline hydrogen peroxide solution, and the sulphate

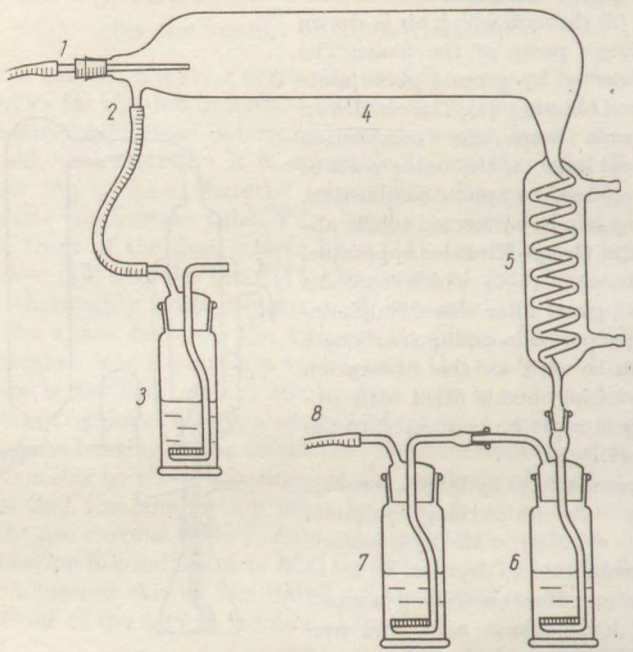


Fig. 54.5. Device for determination of total sulphur content of combustible gases

ions are precipitated with barium chloride. The apparatus is shown in Fig. 54.5. Gas flows in through the 2–3 mm wide end of the quartz tube (1), and is combusted. The flame can be stretched out to 10–12 cm by using a water pump connected to the rubber tube (8). Using this apparatus 100 litres of gas can be combusted per hour. The volume of gas can be measured with a dry gas counter.

Reagents required. (1) *Potassium ferricyanide solution :* Dissolve 150 g of crystalline $K_3[Fe(CN)_6]$ and 185 g of anhydrous sodium carbonate in 1 litre of water. Place 30 ml of this solution into the gas washing bottle (3) to wash the air. When large volumes of washing liquid are used it may foam over from the bottle into the combustion sphere. (2) *Absorption solution :* 0·1 N sodium carbonate solution, or alkaline hydrogen peroxide solution. The latter can be prepared from 100 ml of 0·1 N sodium hydroxide and 20 ml of 30% sulphate-free hydrogen peroxide. 50 ml of ab-

sorption solution must be poured into the gas washing flasks (6) and (7). When sodium carbonate solution is used a small amount of bromphenol blue indicator must be added to the washing flask (6). The colour change of the solution indicates that the solution is saturated.

After combustion, rinse the contents of the washing flasks (6) and (7) into a porcelain evaporating dish, add several millilitres of sulphate-free bromine water or 30% hydrogen peroxide, and evaporate to about 75 ml. Acidify the solution cautiously with hydrochloric acid and evaporate to dryness on a water bath. Dissolve the residue in a small volume of water, filter, and precipitate sulphate ions with barium chloride by the recommended procedure.

54.6. DETERMINATION OF THE SULPHUR CONTENT OF COAL

(according to A. Eschka)

When finely powdered mineral coal is heated with a mixture of magnesium oxide and sodium carbonate to a sufficient temperature the fusion mixture does not melt, therefore air can be easily brought into contact with the coal. The coal is combusted and the acidic combustion products, e.g. the oxides of sulphur, are retained by the alkaline fusion agent. On leaching the melt the accompanying metal hydroxides, carbonates and silicic acid remain behind. Sulphate can be precipitated with barium chloride from the filtrate after oxidation with bromine and acidification.

Eschka mixture. Thoroughly grind 2 parts of well-ignited porous magnesium oxide with 1 part of anhydrous sodium carbonate.

Procedure. Take 1 g of finely powdered carbon or 2 g of coke and mix in a small 5–10 ml platinum crucible with 3 g of Eschka mixture. Cover the crucible with a larger platinum crucible and invert the two crucibles (see Fig. 48.2.). Pour Eschka mixture between the two crucibles up to the height of the inside crucible. Place the outer crucible into a hole cut in an asbestos sheet and heat slowly with a gas flame, or preferably in an electric furnace, to a slight red glow. It is important that the sulphur-containing combustion products of the gas flame should not come into contact with the contents of the crucible.

After 30 min heat the crucible to a stronger red glow. When the coal is completely combusted (after about 1 hr) allow the crucible to cool, remove the internal crucible over a glossy paper, place both crucibles into a larger beaker and add about 150 ml of hot water. Heat on a water bath for 1 hour. Remove the crucibles using a bent glass rod, rinse, and filter the mixture by decantation on a filter paper. Rinse the residue with about 100 ml of hot water. Add 5–20 ml of saturated bromine water to the filtrate, neutralize cautiously with hydrochloric acid, and add 1 ml of concentrated hydrochloric acid in excess. Heat the solution to boiling and add 100 ml of hot 2·5% barium chloride solution rapidly. Allow the mixture to stand on a water bath for 1–2 hr, and filter after a further 2 hr, or next day. Wash the precipitate first with cold water and then with hot water. Dry (130 °C) or ignite (about 800 °C) and weigh as barium sulphate.

54.7. DIGESTION OF ORGANIC SUBSTANCES CONTAINING SULPHUR WITH RED FUMING NITRIC ACID IN A BOMB

(according to Carius)[1]

To the heat-resistant glass bomb add 1–3 ml of red fuming nitric acid and 1–2 drops of sulphate-free bromine water, and weigh into a small hard glass test tube 100–300 mg of the sample. Care must be taken that the substance does not become contaminated with nitric acid before sealing.

Seal the bomb and heat in a bomb furnace after slow initial heating at 250–300°C for 3–6 hr. See Chapter 48.1.1.for details of the procedure as used in the decomposition of organic halogen compounds.

When the decomposition is complete, rinse the liquid into a porcelain dish, remove the nitric acid by evaporation, and repeat the evaporation several times with concentrated hydrochloric acid. Dissolve the residue in water, filter, and precipitate sulphate ions in the form of barium sulphate. Weighing form: $BaSO_4$.

54.8. DETERMINATION OF THE SULPHUR CONTENT OF NON-VOLATILE ORGANIC SUBSTANCES BY COMBUSTION IN A BOMB (BOMB SULPHUR)

In the Berthelot-type bomb calorimeter the combustion of organic substances at 25–30 atm. oxygen pressure takes place in seconds. The sulphur content of organic substances is combusted partly to sulphur trioxide and partly to sulphur dioxide. When several millilitres of 3% hydrogen peroxide are added to the bomb before combustion, the sulphur fumes are dissolved quite rapidly in it and are oxidized to sulphuric acid. Sulphuric acid can then be determined in the solution by the usual method. Explosion in a bomb has several advantages. Thus, the combustion of the substance takes place instantaneously, a sulphuric acid solution which is free of foreign cations is obtained, and furthermore, because the combustion takes place in a closed space no loss occurs.

In the older types of bomb calorimeter with lead gaskets, there is a danger that the lead will react with the sulphuric acid, but the newer types of bombs, which have self-sealing rubber gaskets, do not present this danger. It is advisable, therefore, to use modern bomb calorimeters made of V2A acid-resistant steels, which are also constructed partly for this purpose. If the old type of bomb calorimeter is used, the lead gasket should be cleaned and finely coated with vaseline.

The section of a modern Berthelot–Mahler bomb calorimeter is shown in Fig. 54.6. The bomb head consists of two parts: On the standing part (1) the taps (7, and 9) and the insulated electrode (8) are mounted. The dutch mother screw (2) can be screwed on, and this presses the rubber packing gasket (4) to the metal ring (3). The rubber ring is pressed to the body of the

[1] L. Carius, *Ann. d. Chem.* **136**, 129 (1865). See Chapter 48.1.1.

bomb (5). When the bomb is assembled, the dutch mother (2) can only be fastened by hand.

Determination according to E. Schulek and O. Clauder (1937). Into the platinum vessel (6) of the bomb weigh a sample corresponding to 50–300 mg of barium sulphate. Add sufficient sulphur-free liquid paraffin to the sample to make the total weight of the substance in the platinum crucible 0·7–0·8 g. Connect the two electrodes in the bomb with a platinum or iron wire 0·1 mm in diameter. Connect a cotton thread 3–5 cm long to the middle of the wire, and immerse the end into the paraffin. Add 10 ml of sulphate-free 3% hydrogen peroxide solution to the bomb, and screw on the cover of the bomb. Flush out the bomb with oxygen through the open taps, close the tap (7) and increase the pressure of the oxygen in the bomb to 20–25 atm. Close the other tap (9), connect the electrode contacts (8, and 9) to the source of electricity, and place the bomb in a larger vessel. Add sufficient water to the vessel just to cover the bomb and leave the taps above the liquid level. The bomb can be fired with the mains current if a 150 W burner is connected in series with the firing circuit.

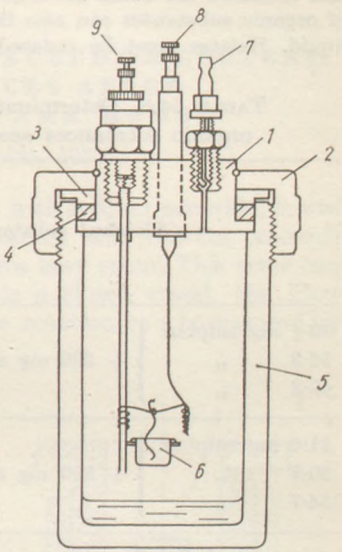


Fig. 54.6. Self-closing Berthelot-Mahler-type bomb calorimeter

Wait for 5–6 min after firing, remove the bomb from the water, dry it and mix its contents thoroughly. To ensure complete absorption allow the bomb to stand for 1 hr. Connect a gas washing bottle to tap (7) with a rubber tube. Add barium chloride solution containing hydrogen peroxide and 1–2 drops of hydrochloric acid to the washing bottle. Open tap (7) cautiously and allow the gas to bubble into the washer. If a precipitate is formed the absorption is not yet complete. Remove the head of the bomb, rinse the head and taps with water, combine this solution with the contents of the bomb, and filter through filter paper or cotton wool.

Neutralize the solution to methyl orange, add 1 ml of 1 N hydrochloric acid, 0·25 g of hydroxylamine hydrochloride and 1 g ammonium chloride, dilute to about 100 ml, and precipitate sulphate from the solution with barium chloride according to the procedure of L. W. Winkler (see Chapter 54.2.1.).

Notes. (1) When the solution to be determined contains other elements (nitrogen) as well as carbon, hydrogen, oxygen and sulphur, add to the solution 1 g of ammonium chloride and a small volume of hydrochloric acid, and evaporate the solution to dryness on a water bath using electrical heating. Repeat the evaporation after the addition of several millilitres of hydrochloric acid (1:1), dissolve the residue in water containing a small volume of hydrochloric acid, and, if necessary, filter again.

(2) If the air is not rinsed out from the bomb, or if the oxygen used for the combustion also contains nitrogen, nitric acid is also formed in the explosion. This must always be removed by evaporation as described above before precipitation.

(3) It is always advantageous to add hydroxylamine hydrochloride to the solution, because a small amount of iron is always dissolved from the bomb, and this must be reduced to the bivalent form.

(4) In the presence of halogens, the absorption of the gases takes place slowly, and therefore the bomb must be shaken for a longer period. The halogen content of organic substances can also be determined after combustion in the absorption liquid. Halates must be reduced with sulphurous acid before the precipitation.

TABLE 54.8. Determination of sulphur content of non-volatile organic substances according to E. Schulek and O. Clauder

Weighed substance	Weight of $BaSO_4$ precipitate mg	Sulphur content found	
		mg	%
10·4 mg sulphur + 300 mg mannitol	73·8	10·2	98·05
32·3 „ + 300 mg mannitol	234·9	32·4	100·50
49·8 „ + 300 mg mannitol	360·2	49·8	99·94
11·6 mg sulphur + 300 mg amidopirin	83·7	11·6	99·70
30·7 „ + 300 mg amidopirin	221·2	30·6	99·56
54·7 „ + 300 mg amidopirin	395·4	54·6	99·98
11·8 mg sulphur + 150 mg amidopirin and 150 mg diethyl bromoacetyl urea	70·8	11·8	100·23
31·0 „ + 150 mg amidopirin and 150 mg diethyl bromoacetyl urea	224·3	31·0	99·85
50·1 „ + 150 mg amidopirin and 150 mg diethyl bromoacetyl urea	359·9	49·7	99·76
9·7 mg sulphur + 150 mg amidopirin and iodine methoxy benzoic acid benzyl ester	70·8	9·8	100·08
30·9 „ + 150 mg amidopirin and iodine methoxy benzoic acid benzyl ester	223·3	30·9	99·85
50·5 „ + 150 mg amidopirin and iodine methoxy benzoic acid benzyl ester	363·6	50·3	99·76
10·2 mg sulphur + 150 mg amidopirin and 150 mg trichloro butyl salicylate	74·1	10·3	100·40
31·4 „ + 150 mg amidopirin and 150 mg trichloro butyl salicylate	225·9	31·2	99·41
52·4 „ + 150 mg amidopirin and 150 mg trichloro butyl salicylate	379·3	52·4	100·02
217·2 mg potassium guaiacol sulphonate	194·9	26·9	93·65
201·8 mg potassium guaiacol sulphonate	180·5	24·4	93·38 referred to the amount calculated from the formula

Note. The $BaSO_4$ values are not corrected. Sulphur values are calculated from $BaSO_4$ values corrected according to L. W. Winkler.

(5) The bomb sulphur method is also suitable for the determination of the sulphur content of coals. In this however (and also if the organic substance of (1) above leaves an insoluble ash on combustion) the ash must be fused with sodium carbonate, evaporated with hydrochloric acid, and the filtrate combined with the absorbing solution.

(6) The accuracy of the method can be judged from the data of Table 54.8., originating from E. Schulek and O. Clauder.

54.9. DETERMINATION OF THE SULPHUR CONTENT OF ORGANIC SUBSTANCES AFTER DECOMPOSITION IN A PARR BOMB

(according to B. Wurzschmidt, 1950)

In the description of the fusion of pyrites with sodium peroxide, it was mentioned that for easily combustible substances the reaction proceeds with explosive violence, and considerable losses may occur. This error can be overcome if the digestion is carried out in a closed vessel, the Parr bomb. The high temperature required for the reaction can be ensured by the addition of an easily combustible organic substance to sodium peroxide containing no sulphur or halogens. Thus, the reaction can be made to proceed rapidly without the need of heating the crucible externally, and a rubber ring can also be used as a packing gasket in the bomb. The sodium peroxide must not come into contact with the rubber. To avoid overheating of the rubber ring, a metal dutch mother screw (good heat-conductor) should be used.

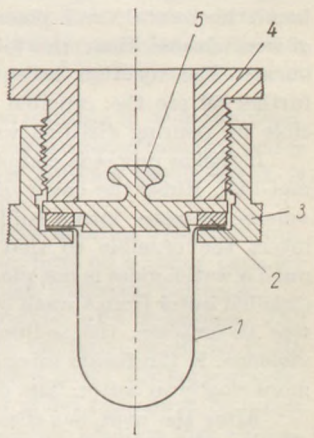


Fig. 54.7. Universal Parr-type bomb

A universal bomb of this type is shown in Fig. 54.7. The edged nickel or acid-resistant steel crucible (1)has a volume of 10–12 ml and a wall thickness of 2–4 mm. Between the cover (5) and the edge of the crucible a rubber ring (2), which can be closed fast by the dutch screws (3) and (4), can be placed. The cover (5) is partly inside the crucible and so prevents the sodium peroxide coming into contact with the rubber ring.

The bomb enables the complete destruction of organic substances (less than 500 mg) to be effected with sodium peroxide. The method is especially suitable for semimicro and micro determination.

Reagents required: (1) Sodium peroxide, analytical grade. (2) Analytically pure anhydrous sodium carbonate. (3) Analytically pure ethylene glycol. Ethylene glycol must be added from a suitable pipette or dropping tube so that the weight of 8 drops of ethylene glycol is about 160—170 mg.

Weighing. Solid organic substances can be weighed directly into the crucible of the bomb. Highly voluminous solid substances should be pressed into a pellet. Liquids can be weighed into a thin-walled spherical glass ampoule. The neck of the capillary must be sealed off short so that it does not protrude from the oxidation mixture. Pasty substances can be weighed into a thin-walled glass thimble.

Fusion. Fasten the crucible (1) vertically, and add 8 drops of ethylene glycol to it. Weigh the sample by difference, or place the glass ampoule or thimble containing the sample into it. The glass ampoule should not be in direct contact with the bottom of the crucible. Add small amounts of sodium peroxide to the sample to test that no reaction takes place in the cold. If no reaction occurs, for micro samples add 3–4 g, in other cases add sufficient sodium peroxide so that its surface is 2–3 mm lower than the edge of the crucible after tapping it down gently. Not more than 10 g should be used. If the substance reacts with sodium peroxide even in the cold, it must first be covered with a small amount of anhydrous sodium carbonate, and then with sodium peroxide.

From the start of the addition of sodium peroxide until the bomb is opened, protective glass and spectacles must be used.

After filling the bomb, place the cover and the rubber ring on the crucible, and press together by screwing the dutch mothers (3 and 4) by hand. Keep the bomb horizontal, and place it into the opening of a protective furnace made of iron sheets. Heat the lowest part of the crucible with the tip of a micro burner. The reaction takes place in the crucible in 10–20 sec, and after a further 60 sec the crucible can be removed from the furnace. Cool the crucible by pouring distilled water on to it. Open the bomb after drying it.

If fusion proceeds completely the contents of the crucible are more or less met-like. Rinse the cover of the bomb and the rubber packing with a small volume of water into a sufficiently large beaker or larger porcelain dish, then insert the crucible so that its contents do not come into contact with water, until a watch glass is not placed on the dish to cover the mixture. Add sufficient distilled water from a wash bottle to half fill the crucible with water. If the fusion was incomplete, the sodium peroxide may react with water with explosive violence. If the fusion mixture was melted, however, it dissolves considerably more slowly in water. The dissolution can be assisted by gentle heating.

After the melt has dissolved, remove the crucible from the beaker, and rinse it with distilled water. Acidify the cold solution cautiously with hydrochloric acid, and evaporate to dryness on a water bath. Repeat the evaporation several times with hydrochloric acid (1 : 1). Silicic acid which dissolves from the glass of the ampoule is dehydrated at the same time. Dissolve the residue in water containing a small volume of hydrochloric acid, and filter. Sometimes carbon particles remain behind after fusion, but usually the fusion is complete. If the alkaline solution is brown, however, the fusion was incomplete and must be repeated. Sulphate ions can be determined in the solution by the usual procedure.

Notes. (1) The halogen content of organic substances can also be determined by this method. The solution must then be acidified with nitric acid, and any halates formed must be reduced with sulphurous acid. Fusion with sodium peroxide can

also be used for the determination of the phosphorus and silicon content of organic substances. The method is especially advantageous for the determination of the silicon content of organic silicon compounds. In such cases the volatile substances must be weighed into silicon-free phosphate glasses.

(2) Organic sulphur and halogen compounds can also be fused with potassium metal in a Parr bomb, and the sulphide formed can be titrated oxidimetrically with sodium hypobromite using luminol as chemiluminescent indicator (L. Erdey and I. Buzás).[1]

54.10. DETERMINATION OF SULPHITE (SO_3^{2-}), DITHIONITE ($S_2O_4^{2-}$), THIOSULPHATE ($S_2O_3^{2-}$) AND PEROXYDISULPHATE ($S_2O_8^{2-}$) IONS

Sulphide, polysulphide, sulphite, thiosulphate, dithionite and sulphate ions, if present simultaneously, can be determined most easily by suitable titrimetric methods. Characteristic and complicated equilibria are set up in solutions of these ions. Gravimetric methods can be used only for the sulphide and total sulphur determination of such solutions.

Ions containing sulphur with a lower oxidation state than six can be oxidized to sulphate with suitable oxidizing ions, and can be weighed in the form of barium sulphate after the usual treatment. The following substances can be used as oxidizing agents: In acidic solution chlorine water, bromine water, or more suitably in alkaline solutions, sodium hypochlorite, sodium hypobromite, ammonia and bromine, or ammonia and hydrogen peroxide.

Procedure. (a) *Oxidation in acidic medium:* To the solution to be determined, add freshly prepared chlorine water, or sulphate-free saturated bromine water in large excess, wait for 10–20 min, or until the sulphur precipitated is dissolved, and remove the excess halogens by boiling.

(b) *Oxidation in alkaline solution:* Make the solution alkaline with ammonia, add 2–5 ml of sulphate-free 30% hydrogen peroxide, heat on a water bath for 30 min, and heat the solution to boiling to decompose hydrogen peroxide.

Alkali hypochlorite or hypobromite slowly reacts with ammonia, and therefore when these oxidizing agents are used the oxidation must be made in the presence of sodium hydroxide and then takes place instantaneously. Under these conditions, however, the interference of alkali salts must be taken into account. It is therefore advisable to make the solution alkaline with ammonia, add large amounts of bromine water rapidly to this solution, and to decompose the excess bromine by boiling. On boiling, excess ammonia is also removed.

From the solution, after acidification, remove any bromine formed by boiling, and determine the sulphate by the usual method.

Stoichiometric factors: $H_2SO_3/BaSO_4 = 0{\cdot}35167$; $SO_2/BaSO_4 = 0{\cdot}27446$; $Na_2SO_3/BaSO_4 = 0{\cdot}53999$; $Na_2SO_3 \cdot 7\,H_2O/BaSO_4 = 1{\cdot}0803$; $NaHSO_3/BaSO_4 = 0{\cdot}44582$; $Na_2S_2O_3/2\,BaSO_4 = 33868$.

Note. Peroxydisulphates, if boiled with water for a long period, can be completely converted to sulphates. Non-decomposed persulphate ions do not form a precipitate with barium ions.

[1] L. Erdey and I. Buzás, *Acta Chim. Hung.* **6**, 93 (1955).

54.11. SEPARATION OF SULPHITE (SO_3^{2-}) AND THIOSULPHATE ($S_2O_3^{2-}$)

The separation can be effected on the basis of the different solubilities of the strontium salts of these ions. Strontium sulphite is almost completely insoluble in water, while strontium thiosulphate is quite soluble in water.

Procedure. Oxidize sulphur compounds to sulphate in an aliquot of the solution of the alkali salts by the addition of a large volume of bromine water in ammoniacal medium (see above). Decompose the excess bromine by boiling and remove the ammonia at the same time. Acidify the solution with hydrochloric acid and precipitate the sulphate with barium chloride. Thus the total sulphur content, present in the form of sulphite and thiosulphate, can be determined.

Add a slight excess of strontium chloride solution to a second aliquot of the sample, dilute to the mark in a volumetric flask, shake well and allow it to stand overnight. Filter the clear part of the solution into a dry flask through a dry filter paper, taking care that the precipitate is not transferred to the filter. From an aliquot of the filtrate oxidize thiosulphate to sulphate with bromine, and precipitate the sulphate as barium sulphate. From the two results, the sulphite and thiosulphate content of the sample can be calculated.

Note. In practice it is advisable to carry out the determination by iodometric titration, as then any calcium and sulphate ions present do not interfere. To an aliquot of the original sample add a known excess of 0·1 N iodine solution and titrate the excess iodine with 0·1 N sodium thiosulphate solution. Precipitate strontium sulphite from a second aliquot with strontium chloride, and in an aliquot of the sample determine thiosulphate by titration with iodine. From the two results the sulphite and thiosulphate content of the sample can be determined.

54.12. SIMULTANEOUS DETERMINATION OF SULPHIDE (S^{2-}), SULPHITE (SO_3^{2-}) AND THIOSULPHATE ($S_2O_3^{2-}$)

To an aliquot of the original sample, add an excess of acidic 0·1 N iodine solution, and back-titrate the excess iodine with 0·1 N sodium thiosulphate solution.

Neutralize or make slightly alkaline a second aliquot of the solution, and add excess zinc chloride solution. Dilute the solution containing the zinc sulphide precipitate in a volumetric flask to a known volume, and filter the supernatant solution through a dry filter paper into a dry flask. In one aliquot part of the filtrate determine iodometrically the amount of 0·1 N iodine required to oxidize the sulphite and thiosulphate ions. By subtracting this volume from the result of the first titration, the amount of iodine equivalent to the sulphide content of the sample can be obtained. In a second aliquot of the sample precipitate strontium sulphite with strontium chloride solution according to the procedure described above, and titrate the thiosulphate ions in the filtrate with 0·1 N iodine solution.

The method is useful mainly in the determination of sodium or calcium sulphide used as an auxiliary material in the leather industry.

Procedure. Weigh 10–20 g of the solid sulphide into a 1-litre volumetric flask, dissolve and dilute to the mark. Filter the stock solution through a dry filter paper into a dry flask. Iron(II) sulphide remains behind on the filter.

Into a 1-litre flask place 300 ml of water, 1 ml of 25% hydrochloric acid and 50 ml of 0·1 N iodine solution, mix well and add 25 ml of the filtered stock solution from a pipette. Titrate the excess iodine with standard 0·1 N sodium thiosulphate solution.

To 100 ml of the filtered stock solution in a 200-ml volumetric flask, add 50 ml of 10% zinc chloride solution with stirring, and dilute the solution to the mark. Shake, allow the solution to stand for 2 hr, and filter the solution through a dry paper into a dry flask. Take 50·00 ml of the filtrate and add it to an acidified solution of 25·00 ml of 0·1 N iodine, prepared in a similar manner to the above solution, and back-titrate the excess iodine.

Take 100 ml of the solution filtered from the zinc sulphide, transfer it to a 200-ml volumetric flask, add 20 ml of 5% strontium chloride solution, and dilute the solution to the mark. Filter the clear part of the solution next day, and in 100 ml of the filtrate titrate thiosulphate with 0·1 N iodine solution in the presence of starch indicator. 1 ml of 0·1 N iodine solution is equivalent to 2·9022 mg Na_2S, 6·3022 mg Na_2SO_3 and 15·8114 mg $Na_2S_2O_3$.

54.13. DETERMINATION OF ELEMENTARY SULPHUR (S_x)

Elementary sulphur occurs in a number of industrial products, pesticides, and drugs. The practical value of these substances is determined by the physical state of the sulphur present in them. Thus, flowers of sulphur obtained by distillation of sulphur often contains no more than 30% of amorphous sulphur. There is an essential difference, therefore, between flowers of sulphur and powdered crystalline sulphur, which is indicated by their different solubility in carbon disulphide. Crystalline sulphur dissolves very easily in carbon disulphide, but the solubility of amorphous sulphur is low. As most inorganic substances accompanying crystalline sulphur are insoluble in carbon disulphide, in practice an extraction with carbon disulphide is made in many cases before the determination of sulphur.

The extraction of crystalline sulphur is usually carried out in a Soxhlet apparatus(see Fig. 54.8.).

Into the paper extraction thimble weigh an amount of substance to be determined which contains about 0·1–0·2 g of extractable sulphur. After extraction

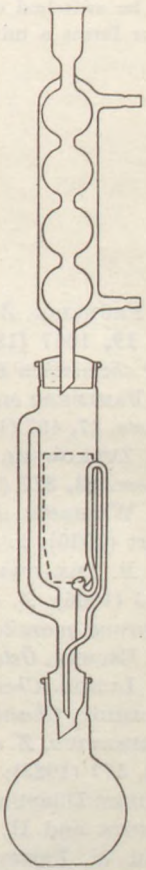


Fig. 54.8. Extraction apparatus according to Soxhlet

for about 12 hr, distil the excess carbon disulphide on a warm water bath, and dry the residue at about 90°C. Pour 30 ml of water and 2 ml of sulphuric acid-free bromine on to the residue, and dissolve the sulphur in bromine by cautious shaking of the flask. After 15–30 min pour on 5 ml of ether, and after a further 10 min add 15 ml of concentrated nitric acid. Evaporate the mixture almost to dryness on a water bath, and repeat the evaporation with 10 ml of concentrated hydrochloric acid until the nitric acid is completely decomposed. Dissolve the residue in water, neutralize with ammonia in the presence of methyl orange and determine sulphate by the usual method. Stoichiometric factor: $S/BaSO_4 = 0{\cdot}13737$.

Notes. (1) If the oxidation is made without extraction in the original sample, the total (amorphous + crystalline) sulphur content can be determined.

(2) During the extraction and evaporation utilizing carbon disulphide, all gas flames must be extinguished in the room, all uncovered electrical heating plates must be switched off, and smoking must be avoided, because carbon disulphide vapour forms a mixture with air which explodes at relatively low temperatures.

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to Table 54.1.

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CHAPTER 55

NITROGEN — N — 14·007

ELECTRICAL discharges in the atmosphere during storms produce traces of nitric acid and nitrous acid. In the soil, nitrates and nitrites are also formed by the action of nitrifying bacteria and by the oxidation of organic nitrogen compounds. Sodium nitrate, $NaNO_3$ (Chile saltpetre), occurs in nature in large amounts. Potassium nitrate (KNO_3) and calcium nitrate [$Ca(NO_3)_2$] also occur naturally. Nitric acid and other nitrates are produced in large amounts in industry as propellants, chemical fertilizers and materials for chemical industry. Nitrites are used in the dye industry and organic chemical industry. Considerable amounts of nitric acid, nitrates and nitrites are used for the surface treatment of metals.

Dissolution of the sample. The normal nitrates of all the common metals are soluble in water. Some basic metal nitrates and organic nitrates are insoluble in water. Some insoluble complex nitrites are known, e.g. $K_2CuPb(NO_2)_6$, $K_3Co(NO_2)_6$, $K_2CaNi(NO_2)_6$ etc. These can usually be decomposed, however, by boiling with sodium carbonate.

Forms of determination. Nitrite ions are usually determined by titrimetric or colorimetric methods. The most accurate determination of

TABLE 55.1. Forms of determination of nitrogen
(for References see p. 121)

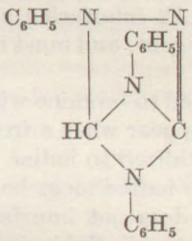
Ref. number	Forms of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	nitron nitrate $C_{20}H_{16}N_4 \cdot HNO_3$	nitron $C_{20}H_{16}N_4$	sulphuric or acetic acid	$C_{20}H_{16}N_4 \cdot HNO_3$	375·40	110
2.	dry nitrate + + quartz	quartz	dry, anhydrous, neutral	N_2O_5 weight decrease	108·016	> 970
3.	dry nitrate + + Na-tungstate	Na-tungstate	„	„	108·016	> 950
4.	dry nitrate + + $K_2Cr_2O_7$	$K_2Cr_2O_7$	„	„	108·016	> 815

nitrates can be achieved by titrimetric methods. The nitrates are usually reduced to ammonia and determined titrimetrically.[1] The gravimetric methods used for the determination of nitrate are shown in Table 55.1. Of these the nitron nitrate method, which can be regarded as a selective direct gravimetric method, is usually used. When dry nitrates are heated with heat-resistant acids (quartz, sodium tungstate, potassium pyrochromate) nitrogen pentoxide is liberated. The amount of nitrate present can be calculated from the loss in weight. These methods, however, can be used only for nitrates which leave a metal oxide of constant weight and do not contain other easily decomposed substances.

55.1. DETERMINATION IN THE FORM OF NITRON NITRATE

(M. Busch, 1905, L. W. Winkler, 1929)

1,4-diphenyl-3,5-endanilotriazoline (4, 5), or nitron, is a strong organic base which forms stable salts with the relatively weaker carbonic acids. It has the structure:



The free base is insoluble in water, slightly soluble in alcohol and ether, and soluble in chloroform. Nitron acetate and sulphate are quite soluble in water; Busch and Gutbier obtained the following data for the solubilities of the less soluble salts:

100 ml of slightly acidic water dissolves 9·9 mg of nitron nitrate, 610 mg of nitron bromide, 17 mg of nitron iodide, 190 mg of nitron nitrite, 60 mg of nitron chromate, 120 mg of nitron chlorate, 8 mg of nitron perchlorate and 40 mg of nitron thiocyanate.

According to Winkler the solubility of nitron nitrate is greater than the value mentioned. According to his experiments, at 20 °C 100 ml of water dissolves 37·1 mg, and at 0 °C 21·1 mg of nitron nitrate. When the water was saturated with nitron nitrate while hot, cooled, and allowed to stand until attainment of the solubility equilibrium (24 hr), at 20 °C, 53·1 mg, and at 0 °C, 33·7 mg of nitron nitrate was dissolved. In the presence of excess of nitron acetate

[1] L. Erdey, *Bevezetés a kémiai anlízisbe II. Térfogatos analízis.* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest (1965), p. 84. I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis II.* 2 Ed. Interscience, New York, London (1947), p. 172. L. Erdey, L. Pólos and Z. Gregorowicz, *Talanta* **2**, 384 (1959).

the solubility is essentially lower. He found that in 100 ml of solution, which contained 10 ml of 10% nitron acetate precipitant, only 2·0 mg of nitron nitrate was dissolved at 17·5°C. From the solubility of the precipitate it can be expected that considerable relative errors occur in the nitrate determination. This solubility error is compensated for, however, by coprecipitation of the nitron acetate.

According to the measurements of C. Duval (1952)[1], nitron nitrate when heated takes up small amounts of oxygen from the air, but releases it on cooling. The amount of oxygen taken up from the air is as much as 2% of the weight of the precipitate at 240°C. Above this temperature the precipitate decomposes with explosive violence, and at 470°C even the decomposition residues are volatilized. The precipitate can be dried at any temperature less than 240°C.

Interfering ions. Acetate, sulphate and iodate ions do not interfere. In the presence of chloride ions, the results are somewhat higher than the expected results (see corrections of L. W. Winkler later). Bromide, iodide, nitrite, chromate, chlorate, perchlorate and perrhenate ions interfere, as do the less frequently encountered anions: thiocyanate, ferrocyanide, ferricyanide, picrate and oxalate. All interfering anions form slightly soluble precipitates with the nitron reagent, and must therefore be removed before the precipitation of nitrate.

Bromide ions can be oxidized to bromine with chlorine water and boiled until a yellow colour does not appear when a fresh portion of chlorine water is added. Iodide ions can be oxidized to iodine in acetic acid medium with excess of potassium iodate; the iodine must be removed from the solution by boiling. The excess iodate does not interfere during the precipitation of nitrate, because nitron iodate is soluble in water. Nitrite ions can be decomposed by preparing a concentrated solution from the substance to be analysed (200 mg in 5–6 ml water), and adding this to 0·3 g of finely powdered hydrazine sulphate. Chromate ions can also be reduced with hydrazine sulphate in this manner.

Preparation of the precipitant. Dissolve 10·0 g of nitron in 100 ml of 5% acetic acid. Filter the red solution on a fine glass filter to remove resinous contamination. The solution is stable for a long period when stored in a dark glass bottle.

Procedure according to M. Busch. Dilute the solution, containing about 0·1 g of nitric acid or the equivalent amount of nitrate, to 80–100 ml, acidify with 10 drops of diluted sulphuric acid and heat the solution to boiling. Add 10–12 ml of nitron acetate precipitant rapidly to the solution. Cool the mixture in ice-water; silky needles of nitron nitrate crystallize. Allow to stand for 1 ½–2 hours, and filter the slightly yellow supernatant liquid on a G 4 glass, A 1 porcelain filter-crucible or No. 4 glass texture filter-funnel. With a small portion of the clear filtrate transfer the precipitate completely to the filter, and thoroughly remove the mother liquor at the pump. Wash the precipitate with 10–12 ml of ice-water used in small portions. Remove each portion of

[1] C. Duval and N. Xuong, *Anal. Chim. Acta* **6**, 245 (1952).

washing solution separately at the pump. Dry the precipitate at 110 °C to constant weight (about 1 hour), cool and weigh. Stoichiometric factors: $HNO_3/C_{20}H_{16}N_4 \cdot HNO_3 = 0{\cdot}16787$, $NO_3/C_{20}H_{16}N_4 \cdot HNO_3 = 0{\cdot}16518$.

Notes. (1) Perchlorate (see notes of Chapter 48.3.) and perrhenate ions can be determined in the same manner.

(2) According to the investigations of Winkler, 2–3 hours is not sufficient for the complete precipitation of nitron nitrate; the precipitation is complete, however, even at room temperature when the precipitate is left to stand for 24 hours. In his opinion the recommended amount of washing solution is also insufficient, and he prefers the use of a saturated nitron nitrate solution for washing. He recommends acetic acid instead of sulphuric acid for acidification.

Procedure according to L. W. Winkler. To 100 ml of the neutral solution, containing at least 10 mg but not more than 50 mg of nitrate, add 1 ml of glacial acetic acid, heat to 60–70 °C, and add 10 ml of nitron acetate precipitant. Allow the mixture to stand for 24 hours in a dark place at 15–20 °C, and stir from time to time. Collect the precipitate on a filter-crucible and wash with 50 ml of saturated nitron acetate solution. Remove the last traces of the washing solution at the pump. Dry the precipitate at 100 °C for 2–3 hours. Correct the weight of the precipitate by application of the corresponding correction.

Note. In the presence of chloride ions the results are somewhat higher than true values. The error, however, is constant, and the corrections of Table 55.2. can be used to advantage.

TABLE 55.2. Corrections to the nitron nitrate precipitate weights

Precipitate weight	100 ml solution contains g chloride			
	0·0	0·1	0·3	0·5
0·30 g	+0·4 mg	−2·0 mg	−4·4 mg	−6·8 mg
0·20 „	+0·8 „	−1·2 „	−3·0 „	−4·8 „
0·10 „	+1·2 „	−0·2 „	−1·5 „	−3·8 „
0·05 „	+1·4 „	+0·2 „	−0·8 „	−2·8 „

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to Table 55.1.

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CHAPTER 56

PHOSPHORUS – P – 30·974

P_x, H_3P, H_3PO_2, H_3PO_3, $H_4P_2O_6$, H_3PO_4, $(HPO_3)_x$, $H_4P_2O_7$

THE MOST important use of elementary phosphorus is in match production, for which red phosphorus is used. Yellow phosphorus is used for the manufacture of pyrotechnics because of its low ignition temperature. Large amounts of elementary phosphorus are now used for the preparation of phosphoric acid. Phosphorus occurs naturally mainly in the form of phosphates. Natural phosphates are found in small amounts in all better types of soil, and their presence is very important for plant growth. Phosphate fertilizers are partly natural mineral phosphates, e.g. phosphorite [$Ca_3(PO_4)_2$], apatite [$3\ Ca_3(PO_4)_2\ Ca(Cl, F, OH)_2$], coprolyte and osteolite, and partly bone phosphates (bone ash). Superphosphate, obtained by fusion of these materials with sulphuric acid, and Thomas slag are excellent fertilizers. Phosphorus is important for living organisms, and is found in all cells in the form of complicated compounds. Nerve cells and bones and teeth are particularly rich in phosphorus. Phosphorus pentoxide is used in the laboratory as a strong desiccant. Pure phosphoric acid and its normal and acidic alkali salts are used as chemicals. Tertiary sodium phosphate is used as a detergent and for softening water. Pure phosphoric acid and acidic sodium pyrophosphate is used in the food industry; various polymetaphosphates are used by the textile industry. Phosphorus can be found in most technically processed metals and alloys, as well as in calcium carbide in the form of phosphide. Industrial acetylene contains considerable amounts of hydrogen phosphide.

Forms of determination. In analytical samples phosphorus is found in the elementary form (P_x), as both yellow and red phosphorus, with the oxidation number +5 in the form of orthophosphoric acid H_3PO_4, pyrophosphoric acid $H_4P_2O_7$, and metaphosphoric acid $(HPO_3)_x$, and as their salts; with the oxidation number +4 in hypophosphoric acid, $H_4P_2O_6$, and its salts; with the oxidation number +3 in the form of orthophosphorous acid, H_3PO_3, pyrophosphorous acid, $H_4P_2O_5$, metaphosphorous acid HPO_2, and their salts; with the oxidation number +1 in hypophosphorous acid, H_3PO_2, and its salts; with the oxidation number −3 in phosphides and hydrogen phosphide, PH_3, as well as in the form of organic phosphorus compounds.

For the gravimetric determination of phosphorus compounds only the few forms shown in Table 56.1. are suitable, but some other forms can be

TABLE 56.1. Forms of determination of phosphorus and its compounds (for References see p. 164)

Ion to be determined	Ref. Number	Forms of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
PO_4^{3-}	1.	$(NH_4)_3P(Mo_3O_{10})_4$	$(NH_4)_2MoO_4$	nitric acid	$(NH_4)_3P(Mo_3O_{10})_4$	1876·50	180–410
	2.	„	„		$P_2O_5 \cdot 24\ MoO_3$	3596·8	800–850
	3.	„	„		$MgNH_4PO_4 \cdot 6\ H_2O$	245·44	room temperature
					$Mg_2P_2O_7$	222·59	560–850
	4.	$MgNH_4PO_4 \cdot 6\ H_2O$	magnesia mixture	ammoniacal	$MgNH_4PO_4 \cdot 6\ H_2O$	245·44	room temperature
					$Mg_2P_2O_7$	222·59	560–850

Seldom used forms of determination: 5. strychnine molybdophosphate, 6. trioxine molybdophosphate (oxinium-24-molybdo-2-phosphate) $[6\ C_9H_7ON \cdot P_2O_5 \cdot 24\ MoO_3 \cdot 11\ H_2O]$, 7. nitrato-pentammine cobalt(III) molybdophosphate $\{[CoNO_3(NH_3)_5]H_3PMo_{12}O_{41}\}$, 8. disilver thallium(I) phosphate $[Ag_2TlPO_4]$, 9. bismuth phosphate $[BiPO_4]$, 10. zirconium pyrophosphate $[(ZrO)_2P_2O_7]$.

$P_2O_7^{2-}$	11.	$Mg_2P_2O_7$	magnesia mixture	pH 4·5	$Mg_2P_2O_7$	222·59	900
	12.	$Zn_2P_2O_7$	$Zn(CH_3COO)_2$	pH 3·8	$Zn_2P_2O_7$	304·71	> 610
PO_3^{3-}	13.	Hg_2Cl_2	$HgCl_2$	acidic	Hg_2Cl_2	472·13	< 310

used for separation titrimetric methods. In practice phosphorus compounds are always converted to orthophosphates, and are then precipitated from nitric acid solution with ammonium molybdate (methods 1–3) or from ammoniacal solution with magnesia mixture (method 4).

The most important methods for the *preparation* of phosphorus compounds for analysis are as follows: (1) Dissolution, fusion or decomposition, (2) separation from interfering ions, (3) oxidation or acidic hydrolysis for conversion to orthophosphates. These operations can often be made in one operation.

Dissolution of the sample. Water-soluble analytical samples are only seldom encountered in practice. They include phosphoric acid, alkali and

ammonium phosphates and some polymetaphosphates. Hydrochloric acid or sulphuric acid should not be used for the dissolution of the sample; these acids can only be used when phosphate ions can be precipitated without previous separation in the form of magnesium ammonium phosphate. The solution should not be evaporated to sulphuric acid fumes even under these conditions, because above 200°C considerable amounts of phosphorus pentoxide evaporate and part of the residue is converted to pyrophosphoric acid. For the same reason fusion with alkali pyrosulphates should if possible also be carried out at low temperatures using covered crucibles. Pyrophosphates and metaphosphates can be converted to orthophosphates by boiling with diluted nitric acid (1 : 1) for 1–2 hr. The only acid solvents which can be generally used are nitric acid and *aqua regia*, although if the latter is used the solution obtained must be evaporated several times with nitric acid to remove chloride from the solution.

The fusion of *crude phosphate*, *bone ash* and *iron ores* can be effected for the determination of phosphorus by the following method:

Weigh 5–10 g of the finely powdered sample into a large beaker, add 50 ml of concentrated nitric acid, cover with a watch glass, and heat on a water bath for 1–2 hr. Dilute the solution with an equal volume of water and filter on an ash-free filter paper. Transfer the insoluble residue to the filter with diluted nitric acid (1 : 1), and wash until the nitric acid washings are not yellow owing to dissolved iron. Combust the filter paper, and fuse the residue with a six-fold excess of sodium carbonate. Dissolve the cold melt in diluted nitric acid, and add this solution to the former solution. Evaporate the combined filtrates to dryness and dehydrate the silicic acid at 120°C for 1 hr. Dissolve the residue in a small volume of nitric acid, filter, and wash the silicic acid. Dilute the filtrate to 500–1000 ml, and take an aliquot for the determination.

For *iron*, *steel* and *bronze* samples take 5–10 g and dissolve it in 50–100 ml diluted nitric acid (1 : 1); the phosphorus content of phosphides is then partly converted into phosphoric acid and partly to phosphorous acid. The latter can be oxidized to phosphate by boiling with excess potassium permanganate. The excess potassium permanganate and the precipitate of hydrated manganese dioxide formed on oxidation can be reduced with sodium nitrite or sodium sulphite. Aliquot parts of the solution must be taken for analysis. Small amounts of silicic acid present in the solution do not interfere in the precipitation in the form of ammonium phosphomolybdate.

When *tin-containing* alloys and compounds are dissolved in nitric acid, metastannic acid is formed which occludes the phosphate completely. The residue must therefore be evaporated to dryness, and must be fused with a mixture of sodium sulphide and sulphur (Chapter 2.5.8.) or by the Freiberg fusion (Chapter 2.5.7.). The sulphides of the cations of groups I and III can be filtered after aqueous extraction from the solution, and tin sulphide can be precipitated from the filtrate by acidification of the solution with sulphuric acid. Phosphate ions remain dissolved and can be determined after filtration.

Acid-insoluble *alloyed steels*, *ferrosilicon* and *iron sulphide* can be fused with a 10–15 fold excess of anhydrous sodium carbonate + magnesium oxide (2 : 1) mixture. The melt must be leached with nitric acid and the solution

evaporated to precipitate silicic acid. The residue must then be dissolved in nitric acid. The silicic acid must be filtered, and after combustion of the filter paper it must be evaporated with hydrogen fluoride and sulphuric acid. The residue must be fused with a small amount of sodium carbonate and dissolved in nitric acid. The acidic solutions must be evaporated to dryness to remove the silicic acid completely.

Titanium metal and titanium *alloys* and *compounds* can be fused in similar manner with sodium carbonate + magnesium oxide (2 : 1) mixture. The melt must be leached with water and the residue fused with sodium carbonate again. Phosphate can be determined in the aqueous extract of the melt after acidification.

Samples containing *tungsten* must be dissolved in nitric acid and evaporated to dryness. The evaporation with nitric acid must be repeated several times. The residue must be extracted with dilute nitric acid and washed with ammonium nitrate solution. Tungstic acid and silicic acid remain behind, and iron and phosphoric acid dissolve.

From samples containing *zirconium*, *titanium*, *iron* and *chromium(III)*, metal hydroxides can be precipitated with sodium hydroxide. Heat the mixture, which has been neutralized with nitric acid and is free of ammonium salts, to boiling, and rinse it into 100 ml of hot freshly prepared 10% sodium hydroxide solution. Filter the mixture and wash the precipitate with 5% sodium hydroxide. Rinse the precipitate into a beaker, boil with nitric acid, and repeat the precipitation with sodium hydroxide. The same result can be obtained by fusing the solid sample with solid sodium hydroxide, sodium carbonate or sodium peroxide.

Organic phosphorus compounds can be decomposed according to the method described in Chapter 2.6.4. with nitric acid and hydrogen peroxide. Organic phosphorus compounds can be decomposed rapidly in a Parr bomb with sodium peroxide, as described in Chapter 48.1.3.

The phosphorus content of *industrial gases* (acetylene) can be separated by drawing the measured gas sample through a sodium hypochlorite solution in a wash bottle. Sodium hypochlorite oxidizes hydrogen phosphide to phosphate, which can then be determined in the solution by colorimetric,[1] titrimetric[2] or gravimetric methods.

Red phosphorus can be oxidized with nitric acid saturated with bromine. Weigh 0·25 g of red phosphorus into a 100-ml beaker and add sufficient water to cover the sample by 2–3 cm. Cover the beaker with a watch glass and add nitric acid saturated with bromine in small portions. Heat on a water bath. Take care that the reaction proceeds slowly and phosphoric acid fumes are not formed in the beaker. After 20–30 min evaporate the solution in a porcelain dish, and repeat the evaporation twice with 5 ml of bromine–nitric acid. Dissolve the residue in a small volume of water and filter.

[1] L. Erdey, E. Bodor and W. Fleps, *Acta Chim. Hung.* **5**, 65 (1954).

[2] L. Erdey, *Bevezetés a kémiai analízisbe II. Térfogatos analízis* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest (1965) pp. 71–73; I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis* II. 2 Ed. Interscience, New York, London (1947), p. 139.

Yellow phosphorus can be oxidied with iodine and the excess of iodine can be back-titrated with sodium thiosulphate. The solution can be evaporated several times with bromine–nitric acid, and the phosphoric acid precipitated and weighed gravimetrically to check the titrimetric result.

Interfering ions. The precipitation of phosphates with ammonium molybdate in nitric acid medium is highly selective, and there is very little interference from foreign cations. Phosphoric acid, however, must always be present as orthophosphate, otherwise the precipitation is incomplete. Phosphorus compounds in which the phosphorus is in a lower oxidation state must be oxidized *(aqua regia,* bromine–nitric acid, hypochlorite, etc.), and condensed phosphate (pyro-, meta-, etc.) must be converted to orthophosphate by boiling with 20% nitric acid for 1–6 hr. Silicic acid, arsenic acid and tetravalent heavy metal cations interfere. Silicic acid and tungstic acid can be removed by repeated evaporation with nitric acid and filtration. The precipitation of tungstic acid is never complete under these conditions, however, and phosphate must be precipitated with magnesia mixture from an ice-cold solution containing tartrate. Arsenic acid can be reduced with hydrazine sulphate and sodium bromide and evaporated with hydrochloric acid; arsenic(III) chloride and bromide volatilize. Germanium can also be removed from phosphoric acid by this procedure. The separation of titanium(IV), zirconium and tin(IV) can be effected by the methods mentioned for the dissolution of the sample. Zirconium phosphate is insoluble in acid; this can be used for the separation of phosphate from large amounts of interfering ions:

To the solution of the phosphate sample, acidified with hydrochloric acid, add excess zirconium chloride solution and evaporate to dryness. Evaporate the residue with 30 ml of diluted hydrochloric acid (1 : 1) and diluted hydrogen bromide (1 : 1) to volatilize any arsenic contamination. Dissolve the residue in 20 ml of diluted hydrochloric acid (1 : 1), and dilute with 500 ml of hot water. Heat the mixture for 1 hr at 50 °C, filter, combust the filter paper, and fuse the zirconium phosphate with sodium carbonate or sodium hydroxide. Leach the melt with water and filter.

Small amounts of phosphate can also be precipitated in the presence of large amounts of iron(II), nickel, alkaline earth salts and chromates in the form of iron(III) phosphate (see Chapter 40.14.). The accompanying ions can be precipitated from the filtrate. Phosphate can be separated from molybdenum in ammoniacal medium by repeated precipitation with magnesia mixture.

56.1. DETERMINATION OF PHOSPHATE IONS (PO_4^{3-})

The most common acid in which phosphorus has an oxidation number +5 is orthophosphoric acid, H_3PO_4. From this, and especially from its acidic salts, a series of condensed phosphates can be prepared by dehydration and heat treatment. These condensed phosphates or polyphosphates are quite stable in aqueous solution and their hydrolysis takes place quite slowly, according to the pH of the solution. All condensed phosphates,

however, can be converted to orthophosphate by boiling the solution for a long time with nitric acid. The structures of most common condensed phosphates which can be derived from phosphoric acid are shown in Table 56.2. All condensed phosphates from the third member shown were initially regarded as derivatives of metaphosphoric acid. Polyphosphates containing more than four phosphorus atoms were called hexametaphosphates. Graham salt and Kurrol-salt are also members of these types. The separation of various simple and condensed phosphates from each other can be effected only incompletely with precipitate-forming reactions, owing to copre-

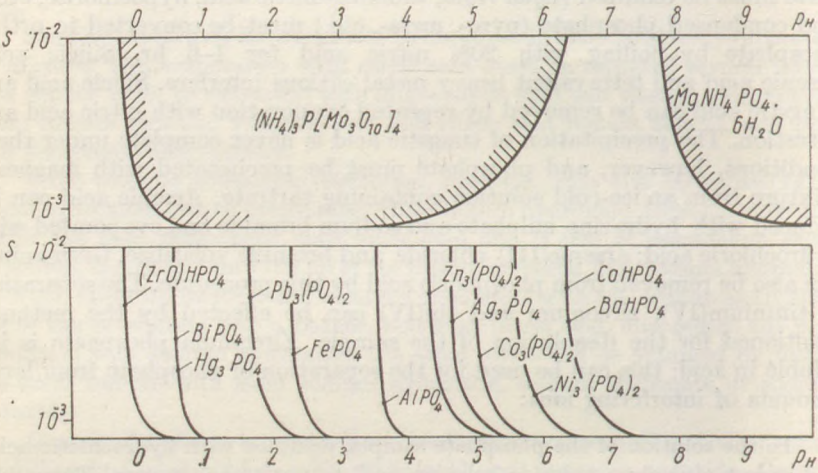


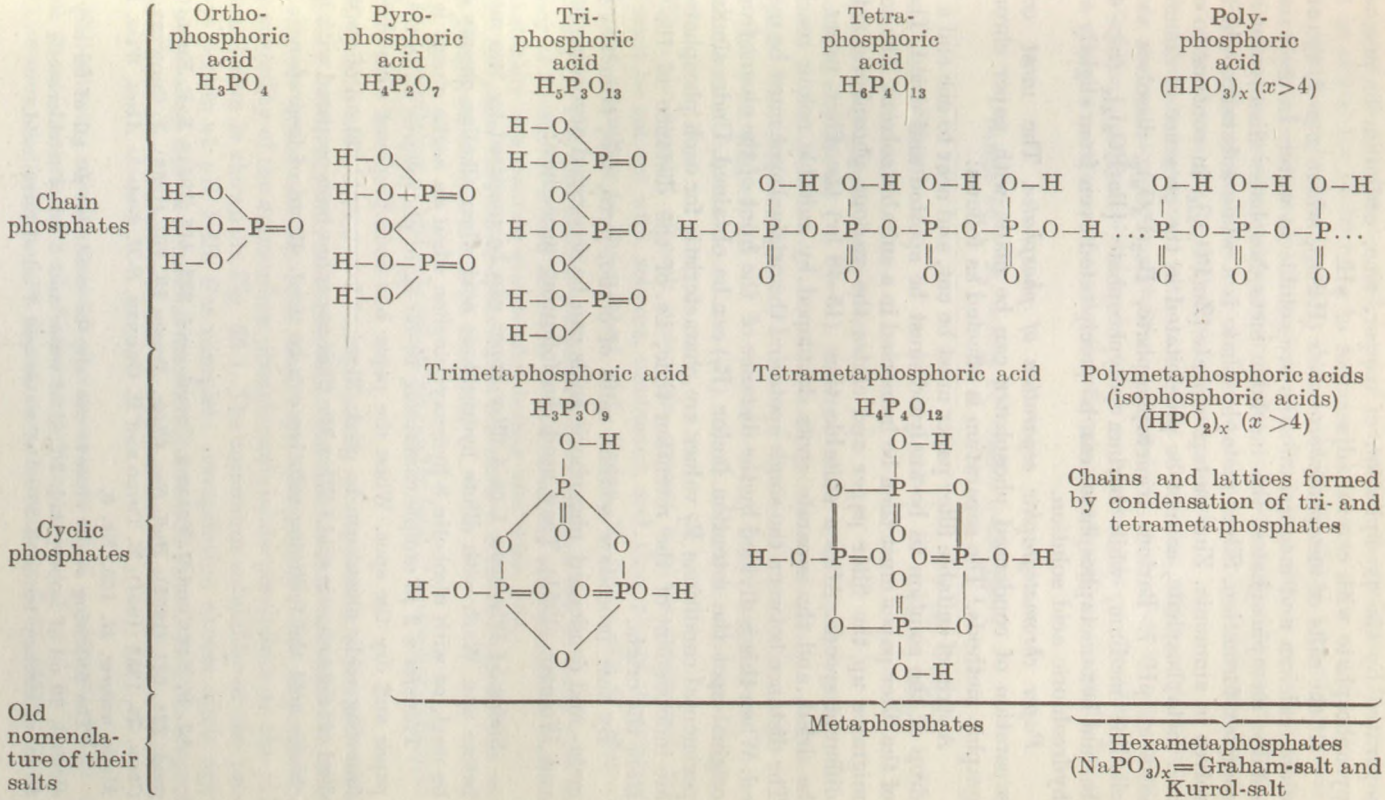
Fig. 56.1. Precipitation pH regions of some orthophosphates

cipitation and hydrolysis. Some separations are possible utilizing the fact that the pH region of precipitation of some heavy metal phosphates is different from that of the corresponding condensed phosphates.

The precipitation pH regions of some *orthophosphates* are shown in Fig. 56.1. As shown, the most important precipitate for gravimetric analysis, ammonium phosphomolybdate $(NH_4)_3P(Mo_3O_{10})_4$, can also be obtained from strongly acidic medium, and thus the interference of most heavy metal ions can be eliminated. Most heavy metal ions interfere in the precipitation of magnesium ammonium phosphate, $MgNH_4PO_4$.

Pyrophosphates can be converted to orthophosphates in hot nitric acid solution. Alkali and ammonium pyrophosphates are soluble in water. White silver pyrophosphate, $Ag_4P_2O_7$, is insoluble in acetic acid (difference from orthophosphate ions). Barium pyrophosphate, $Ba_2P_2O_7$, can be precipitated in neutral medium, and magnesium pyrophosphate, $Mg_2P_2O_7$, can be precipitated at pH 5, but the precipitates dissolve in the excess of pyrophosphoric acid. Copper, zinc and cadmium pyrophosphates, $Cu_2P_2O_7$, $Zn_2P_2O_7$, $Cd_2P_2O_7$, can be precipitated completely even at pH 3·8, in contrast to ortho- and metaphosphates. Ortho- and pyrophosphates can thus be

TABLE 56.2. Structural formulas of condensed phosphates (and polyphosphates)



separated by the precipitation of copper, zinc, cadmium or magnesium pyrophosphate with careful adjustment of pH.

Of the salts of *metaphosphoric acids* $(HPO_3)_x$ where $x > 2$, the ammonium, calcium and magnesium salts are soluble in water. In the excess of soluble metaphosphates, the insoluble metaphosphates dissolve owing to complex formation. Silver metaphosphate is a white substance which dissolves in ammonia. Zinc metaphosphate $[Zn(PO_3)_2]_x$, in contrast to ortho- and metaphosphate, cannot be precipitated in the presence of ammonium salts at pH 7. Barium trimetaphosphate, $Ba_3(P_3O_9)_2$, dissolves even in alkaline medium, while barium polyphosphate $[Ba(PO_3)_2]_x$ $(x > 4)$ (or barium hexametaphosphate) can be precipitated even from slightly acidic, hydrochloric acid solution.

Paper chromatographic separation of phosphates. The most certain separation of condensed phosphates can be made with paper chromatographic methods.[1] The separation is effected as follows:

A strip of suitable filter paper must be cut, and near to one end a small drop of the solution to be analysed must be spotted and dried. The end of the filter paper must then be immersed in a suitable solvent. The solvent migrates up the filter paper and elutes the various phosphoric acids at different speeds. After a suitable time (15–48 hr) the filter paper must be dried, and the separate spots developed by suitable colour reactions. The distance between the single spots and the original spot must be measured. When this is divided by the distance of the front of the eluent from the original spot the retention factor (R_f) can be obtained. Under similar experimental conditions R_f values are characteristic for each phosphate, and are independent of the retention time, i.e. of the distance of the front from the origin.

By this procedure sodium salts of ortho, pyro, tri-, trimeta-, tetrameta- and condensed phosphoric acids can be separated according to Ebel and Wolmar (1951). They used the following procedure:

Strips of Whatman 1 or 4 filter paper can be prepared by two methods before use: Wash with dilute hydrochloric acid when alkaline eluents are to be used, or with alcoholic 8-hydroxyquinoline when an acidic eluent is used.

Transfer a 2 μl sample containing 10–50 μg of phosphorus on to the dried paper and dry the spot. When the paper has been prepared with oxine the following acidic eluent can be used: 70 ml of isopropanol, 30 ml of water and 5 ml of trichloracetic acid.[2] When the filter paper has been prepared with hydrochloric acid the following solution can be used: 40 ml of isopropanol, 20 ml

[1] J. P. Ebel and V. Volmar, *Compt. rend.* **233**, 415 (1951); J. P. Ebel, *Compt. rend.* **234**, 621 (1952); *Bull. Soc. Chim. France* **10**, 991 (1953). J. Crowter, *Anal. Chem.* **26**, 1383 (1954); E. Thilo and H. Grunze, *S-B. deutsche Akad. Wiss. Berlin, Math. naturw. kl.* 155. Nr. 5.

[2] The following *acidic* eluents can also be used: (a) 40 ml of tertiary butyl alcohol, 30 ml of isopropanol, 30 ml of water and 5 ml of trichloracetic acid. (b) 80 ml of tertiary butanol, 20 ml of water and 4 ml of picric acid.

of isobutanol, 39 ml of water and 1 ml of concentrated ammonia.[1] The paper should be eluted for 15–30 hr.

The spots can be developed by two methods: (1) Spray a perchloric acid solution of ammonium molybdate on to the dry paper, dry in a drying oven at 80 °C, place in an atmosphere of hydrogen sulphide, and view under ultraviolet light. The phosphates are visible as blue spots (molybdenum blue). 5 μg of phosphorus can be detected by this method.

(2) After drying spray with a solution containing nitric acid, quinine sulphate and ammonium molybdate, dry at 80 °C, and view in ultraviolet light. Quinine phosphomolybdate is visible as black spots on the bluish-fluorescent paper. R_f values characteristic of each phosphate are shown in Table 56.3.

TABLE 56.3. R_f values of various phosphates

Solvent	ortho	pyro	tri	tri-meta	tetra-meta	poly
Isopropanol (70) + water (30) + trichloroacetic acid (5) ml	0·76	0·56	0·44	0·34	0·22	0·00
Isopropanol (40) + isobutanol (20) + water (39) + cc. NH_3 (1) ml	0·43	0·33	0·30	0·54	0·48	0·00

When the amount of each phosphate present is to be determined, the spots must be cut out with scissors, combusted, and their phosphate content determined according to the method of L. Erdey, E. Bodor and W. Fleps.[2]

Notes. (1) The quantitative colorimetric determination can be made with an accuracy of 2—5%. It is also advisable to determine the total phosphate content gravimetrically in a separate sample after boiling with nitric acid.

(2) The paper chromatographic separation method is recommended when unknown phosphate samples are to be analysed.

56.1.1. *Precipitation of orthophosphate ions in the form of ammonium phosphomolybdate,* $(NH_4)_3[P(Mo_3O_{10})_4]$

Molybdic acid forms a heteropolyacid, phosphomolybdic acid with phosphoric acid in nitric acid medium. The ammonium salt and its salts with organic bases are insoluble and crystallize easily. The dependence of the solubility of the ammonium phosphomolybdate precipitate on the pH of the solution is shown in Fig. 56.1. The minimum solubility of the precipitate occurs at pH 1·45. For complete precipitation excess nitric acid must be present, but in solutions more concentrated than 2 N with respect to nitric acid the solubility of the precipitate increases. When a suitable

[1] The following *alkaline* eluent is also suitable: 30 ml of n- propanol, 30 ml of ethanol, 39 ml of water and 1 ml of concentrated ammonia.

[2] L. ERDEY, E. BODOR and W. FLEPS, *Acta Chim. Hung.* **5**, 65 (1954).

excess of ammonium molybdate is added, the precipitate can be obtained quantitatively even from more concentrated nitric acid solutions. The precipitate is quite soluble in ammonia and dissolves very easily in alkalies. The dependence of the solubility of the precipitate on the nitric acid, ammonium molybdate and ammonium nitrate concentration can be explained by the solubility equilibrium and simultaneous equilibria maintained in the solution. From the expression for the solubility product

$$L = [NH_4^+]^3 \cdot [P(Mo_3O_{10})_4^{3-}]$$

it can be seen that increase in the ammonium ion concentration decreases the solubility of the precipitate to a considerable extent. Before the precipitation, therefore, 5–15% of ammonium nitrate must be added to the solution. In more concentrated ammonium nitrate solutions, however, the solubility of the precipitate increases owing to the foreign salt effect. The concentration of phosphomolybdate ions is regulated by the following equilibria:

$$3\,MoO_4^{2-} + 4\,H^+ \rightleftharpoons Mo_3O_{10}^{2-} + 2\,H_2O \qquad (1)$$

$$H_3PO_4 \rightleftharpoons 3\,H^+ + PO_4^{3-} \qquad (2)$$

$$PO_4^{3-} + 4\,Mo_3O_{10}^{2-} + 8\,H^+ \rightleftharpoons P(Mo_3O_{10})_4^{3-} + 4\,H_2O \qquad (3)$$

According to equations (1) and (3), an increase in the acid concentration causes an increase in the phosphomolybdate ion concentration. In strongly acidic solutions, however, the phosphate ion concentration decreases according to equation (2) owing to the formation of free phosphoric acid, and thus the solubility of the precipitate increases. The solubility increase effect of the nitric acid, however, can be compensated for with ammonium molybdate, partly because the hydrogen ion concentration decreases according to equation (1) and the trimolybdate ion concentration increases, and partly because increase in the ammonium ion concentration decreases the solubility. The concentrations of ammonium molybdate, ammonium nitrate and nitric acid for the precipitation must be chosen carefully so that the solubility of the precipitate is at the minimum (see the procedure of Woy). The precipitate is washed with dilute nitric acid containing ammonium nitrate; the precipitate is practically insoluble in this solution.

Chloride, sulphate and fluoride ions, organic substances and vanadium(IV) and (V) compounds increase the solubility and decrease the rate of precipitation. The phosphates of titanium(IV), zirconium, thorium and tin(IV) are insoluble in nitric acid, and these ions must be separated from phosphate before precipitation. For technical analyses the precipitation can be carried out in the presence of 3% of chloride or 10% of sulphate ions, but under these conditions the mixture must be left to stand for a longer period before filtration, as the precipitation then proceeds more slowly. Fluoride ions can be removed in the form of H_2F_2 by evaporation of the acidic solution, or boric acid can be added to the solution to complex the fluoride and eliminate its interference. Organic substances must be decom-

posed before the determination (see Chapter 2.6.4.). For the interference of arsenic and silicic acid and their removal see the chapters detailing these separations.

If ammonium phosphomolybdate is precipitated in a dilute nitric acid solution at 50°C, it contains nitric acid and water in agreement with the following formula: $(NH_4)_3[P(Mo_3O_{10})_4] \cdot 2\,HNO_3 \cdot H_2O$. The nitric acid may cause errors in the acidimetric titration of the precipitate. At 180°C, however, nitric acid and water is removed completely from the precipitate, but the precipitate remains rather hygroscopic (I. Sarudi, 1948).[1] When the wet precipitate is washed with sodium nitrate or potassium nitrate solution, considerable amounts of ammonium ions are exchanged for the sodium or potassium ions. This may cause an appreciable error in the gravimetric determination of the precipitate.

Ammonium phosphomolybdate can be precipitated more rapidly from a hot solution, and the precipitate obtained is easily filtered. When the solution is heated above 50°C, however, the precipitate will contain more than the stoichiometric amount of molybdenum trioxide. From hot solution, when substances which retard the precipitation are absent, the precipitation is complete within 2–3 hr after stirring, but it is advisable to allow the precipitate to stand at room temperature overnight. When the precipitation is carried out at room temperature the precipitation is complete only after 10 hr. When the precipitate is obtained in the presence of foreign ions (Fe, Al, Ca) it always contains occluded foreign cations. If the precipitation is effected from hot solution the danger of occlusion is smaller. In the presence of 0·1–0·4 g of citric acid or tartaric acid, the precipitation is slower, but the precipitate is less contaminated.

The thermal behaviour of the ammonium phosphomolybdate precipitate is shown in the thermoanalytical curves of Fig. 56.2. (measurements of G. Liptay). The precipitate loses water and nitric acid up to 210°C. Between 210 and 410°C the composition of the precipitate corresponds to the formula $(NH_4)_3P[Mo_3O_{10}]_4$. In this temperature range the precipitate has constant weight. In practice, however, the precipitate sometimes turns green owing to partial reduction. When this happens small amounts of solid ammonium nitrate and ammonium carbonate should be added to the precipitate, and the ignition repeated. The precipitate becomes yellow again. On heating between 410 and 560°C the precipitate loses ammonia and water. The bluish-black compound which has constant weight between 560 and 700°C corresponds to the formula: $P_2O_5 \cdot 24\,MoO_3$. This form is also suitable for weighing. On the thermogravimetric curve there is a minimum at 550°C, which is caused by the intermediate reduction of molybdenum trioxide by ammonia. When heated in air the precipitate is reoxidized. At 700°C molybdenum trioxide begins to sublime.

When suitable drying ovens or furnaces equipped with good regulators and thermometers are used, both weighing forms can be easily prepared. In practice these weighing forms are rarely used, however; usually only

[1] I. Sarudi, *Szervetlen mennyiségi analizis (Inorganic quantitative analysis)* II. (1948), p. 235.

when small amounts of precipitate are formed. This is partly because the composition of the precipitate is uncertain, and the errors caused by coprecipitation of accompanying ions may be considerable. Furthermore, only filter-crucibles can be used for the filtration, for filter paper reduces the precipitate. The ignition temperature must be accurately controlled. It is therefore preferable to dissolve the precipitate in ammonia and precipitate its phosphate content in the form of magnesium ammonium phosphate.

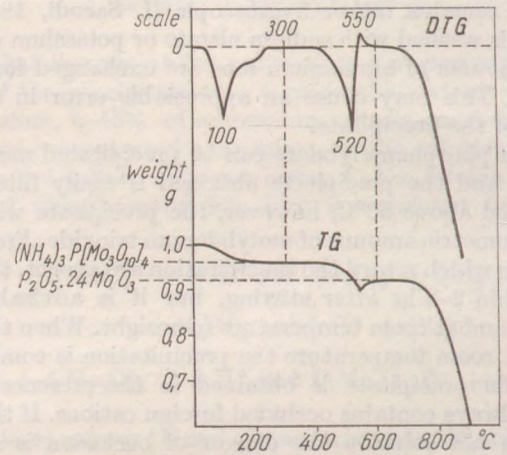


Fig. 56.2. Thermoanalytical curves of ammonium phosphomolybdate precipitate

The precipitate obtained then has a reliable composition, the filtration can be carried out on filter paper, and the precipitate can be rapidly converted to magnesium pyrophosphate by ignition.

Of the weighing forms of the ammonium phosphomolybdate precipitate, the form $P_2O_5 \cdot 24\,MoO_3$ yields better results than $(NH_4)_3P[Mo_3O_{10}]_4$. This is because some of the ammonium ions in the latter precipitate can be replaced by hydrogen ions when an unsuitable washing solution is used, and because the precipitate is hygroscopic. These errors can be eliminated if the precipitate is ignited between 560 and 700°C. The ignited bluish-black precipitate should not turn grey, however, because this indicates that the precipitate has been heated at too high a temperature and loss of molybdenum trioxide has occurred.

When the precipitation is carried out above 50°C the precipitate may be contaminated with molybdic acid. This may cause errors if the precipitate is dried, ignited and weighed. The molybdic acid content of the precipitate causes no error, however, when the precipitate is dissolved in ammonia and the phosphate is precipitated with magnesia mixture.

Procedure according to R. Woy (1897). Reagents: (1) 3% ammonium molybdate solution: Dissolve 30 g of powdered commercial ammonium molyb-

date, $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$, in 500 ml of water containing 2–5 ml of 10% ammonia on a water bath. Filter the cold solution and dilute to 1 litre. (2) 35% ammonium nitrate solution. (3) 25% nitric acid. (4) Washing solution: Dissolve 200 g of ammonium nitrate and 160 ml of concentrated nitric acid to 4 litres in water.

The following volumes of these solutions must be used, depending on the phosphorus content (L. W. Winkler and I. Sarudi):

g P_2O_5 in 50 ml solution	3% ammonium molybdate solution ml	35% ammonium nitrate solution ml	25% nitric acid solution ml
0·12	200	50	20
0·06	100	40	15
0·03	50	30	10
0·01	25	20	10
0·001	10	15	5

Dilute the solution, containing not more than 0·12 g of phosphorus pentoxide, to about 50 ml. If the original solution contains more than 0·12 g of phosphorus pentoxide, an aliquot must be taken and diluted to 50 ml.

Precipitation. To the neutral or slightly acidic nitric acid solution of phosphate in a 400-ml beaker, add first the 35% ammonium nitrate solution according to the Table and then 25% nitric acid and heat to boiling. Place the required amount (see Table) of 3% ammonium molybdate solution into a separate beaker, and heat the solution to boiling. Add the ammonium molybdate solution to the hot phosphate solution in a fine jet with constant stirring, and allow to stand for at least 3 hr. The precipitation becomes complete within this time. Filter the precipitate through a medium grade filter paper and wash with 50 ml of hot washing solution by decantation. Dissolve the traces of precipitate from the filter paper with 15 ml of hot 10% ammonia into beaker, and wash the filter with 30 ml of hot water.

(1) When the phosphate is to be precipitated by the method of Winkler in the form of magnesium ammonium phosphate, wash the filter with a further 70 ml of water. The procedure of L. W. Winkler must then be used (Chapter 56.1.2.2.).

(2) When the precipitate is to be weighed in the form of phosphomolybdate according to Woy, wash the filter with a further 20 ml of 35% ammonium nitrate solution, and, after the dissolution of the precipitate, add 1 ml of 3% ammonium molybdate solution to the filtrate. Heat the solution to 40–50 °C and add 20 ml of warm 25% nitric acid (40–50 °C) in a fine jet with constant stirring. Allow the mixture to stand overnight at room temperature. Collect the precipitate on a porcelain filter-crucible which has been ignited in a protecting crucible and weighed, and wash with an ammonium nitrate-nitric acid washing solution until the washings fail to give a brown colour with potassium ferrocyanide.

(a) Dry the precipitate at 200°C to constant weight, cool in a desiccator and weigh in a closed glass vessel. Stoichiometric factors: $P/(NH_4)_3P[(Mo_3O_{10})_4] = 0.016507$. Practical factor (according to Sarudi): 0·01639; $P_2O_5/2\,(NH_4)_3P(Mo_3O_{10})_4 = 0.037823$.

(b) Place the filter-crucible containing the precipitate into a protecting crucible in a cold electric furnace and heat the furnace cautiously to 600–800°C. Heat the precipitate at this temperature to constant weight. Cool and weigh. Stoichiometric factors: $2\,P/P_2O_5 \cdot 24\,MoO_3 = 0.017224$; $P_2O_5/P_2O_5 \cdot 24\,MoO_3 = 0.039466$.

Notes. (1) Ca, Sr, Mg, Zn, Mn, Cd, Al, Cr(III), Cu, Co, Ni and alkali metals do not interfere, or only slightly interfere. In the presence of iron(III) ions the precipitate contains traces of iron(III) even after the second precipitation. According to L. W. Winkler, therefore, in the presence of iron (III) ions the second precipitation must be carried out by the following method:

Redissolve the precipitate from the filter with 10 ml of 10% ammonia into the beaker, and wash with 50 ml of water. Add 10 ml of 3% ammonium molybdate solution to the solution and heat the solution to boiling without the addition of ammonium nitrate. To the clear solution add 20 ml of 25% nitric acid in a fine jet; the precipitate is then free of iron.

(2) Table 56.4. gives some data on the accuracy of the method and completeness of separation from iron(III) ions (measurements of Z. Rády).

TABLE 56.4. Separation of phosphate ions from iron(III) ions

PO_4^{3-} ions are precipitated, dried at 200°C and weighed as $(NH_4)_3P[Mo_3O_{10}]_4 \cdot Fe(III)$ ions are precipitated from the filtrate with ammonia and weighed as Fe_2O_3

	Sample	Number of measurements	Mean mg	Deviation from true value Δ%	Standard deviation %
1.	99·8 mg PO_4^{3-}	6	99·25	−0·55	±0·3
	20·2 mg Fe^{3+}	6	20·15	−0·25	±0·25
2.	49·9 mg PO_4^{3-}	5	49·85	−0·1	±0·2
	30·5 mg Fe^{3+}	3	50·43	−0·1	±0·1
3.	19·96 mg PO_4^{3-}	5	19·95	−0·05	±0·2
	101·0 mg Fe^{3+}	3	100·9	−0·1	±0·1

(3) In the presence of vanadium(V), the precipitation must be carried out in cold solution and vanadium must first be reduced to the tetravalent form. Cool the solution to 10–20°C and add sufficient iron(II) sulphate solution so that the solution becomes clear blue. Add several drops of sulphurous acid in excess. If the original solution did not contain iron, add 1 g of iron in the form of iron(III) nitrate after the reduction of vanadium. This prevents the reduction of molybdenum(VI) during the remaining procedure. The precipitation must be carried out according to the former procedure in cold solution with cold precipitant.

56.1.2. *Precipitation in the form of magnesium ammonium phosphate* ($MgNH_4PO_4 \cdot 6\,H_2O$)

The determination is the reverse of the method described for the determination of magnesium (see Chapter 42.1.). When excess magnesium chloride solution is added to a phosphate solution made alkaline with ammonia and containing ammonium chloride, magnesium ammonium phosphate is precipitated in crystalline form:

$$PO_4^{3-} + Mg^{2+} + NH_4^+ + 6\,H_2O = MgNH_4PO_4 \cdot 6\,H_2O.$$

The solubility and composition of the crystalline precipitate has already been described in its utilization for the determination of magnesium ions. The precipitation conditions for the determination of phosphate, however, are quite different because phosphate is always in excess at the precipitation. When a magnesium solution is slowly added dropwise to an ammoniacal solution of phosphate ions, the precipitate becomes contaminated with ammonium phosphate and its weight is lower than the theoretical value. On the other hand, when magnesium precipitant is added in one portion to the solution, the precipitate becomes contaminated with tertiary magnesium phosphate and its weight is somewhat higher than the true value, or will be identical owing to the compensation of errors. Similar errors occur when excess magnesium chloride is added to the acidic phosphate solution and the solution is neutralized with ammonia. Under both sets of conditions the error is caused by the great excess of magnesium ions. Errors resulting from the uncertain composition of the precipitate can be eliminated by the application of corrections (L. W. Winkler). An alternative method is to dissolve the precipitate of uncertain composition and reprecipitate it in the presence of the minimum excess of magnesium. The errors caused by the solubility of the precipitate, in spite of the repeated precipitation, are negligible.

The thermal behaviour of magnesium ammonium phosphate and problems connected with the weighing forms have already been discussed in the description of the magnesium determination (Chapter 42.1.).

Influence of foreign ions ; separation from interfering ions. When the precipitate is obtained in the presence of sulphate ions, it will contain sulphate and considerable losses may occur on ignition. This error can be eliminated effectively by repeated precipitation. Magnesium ammonium phosphate can only be precipitated when no other cations than the alkali metal cations are present. Sodium, and particularly potassium ions, however, are coprecipitated in considerable amounts. This error can also be eliminated by repeated precipitation. Ammonium molybdate does not interfere. This fact enables the selective precipitation of phosphate in the presence of the cations of groups I–IV to be effected with ammonium molybdate. Phosphate can then be determined in the ammoniacal solution of the precipitate as magnesium ammonium phosphate. Ammonium citrate slightly retards the precipitation of magnesium ammonium phosphate, but the precipitate is obtained in pure form, because ammonium citrate prevents the coprecipitation of magnesium oxide.

The interference of large amounts of iron(III) and aluminium, and smaller amounts of calcium, titanium, zirconium, vanadium and tin(IV), can be eliminated by precipitation in the presence of 3–5 g of citric acid using a large excess of magnesium chloride. The precipitate must be left to stand for 12–24 hr, especially if vanadium is present, then filtered and dissolved in hydrochloric acid. The second precipitation must be effected in the presence of 0·2–0·5 g of citric acid with 1–3 ml of magnesium chloride precipitant (citrate method). In the presence of large amounts of titanium, zirconium or tin(IV) ions, citric acid does not prevent the precipitation of the phosphates of these ions. Under these conditions the phosphate must be fused with sodium carbonate (see Chapter 2.5.1.).

The ammonium citrate method can be used for the direct determination of crude phosphates and superphosphates, without previous separation in the form of ammonium phosphomolybdate. In these substances the principal interferences are caused by calcium and iron(III) ions. Citric acid eliminates the interference of large amounts of iron(III) ions, but large amounts of calcium interfere. If the crude phosphates are fused with a mixture of concentrated sulphuric acid and nitric acid, most of the calcium is precipitated in the form of gypsum, and the small amount of calcium which remains in the solution does not interfere. The calcium salt of citric acid dissolves in the cold in the excess citric acid. Calcium citrate, however, is precipitated from hot solutions. The precipitation of magnesium ammonium phosphate, therefore, must be made in cold solution in the presence of calcium citrate. The precipitation can be made complete in cold solution by thorough stirring for 30–45 min. Although under these conditions the errors caused by the solubility are not negligible, they are just compensated for by coprecipitation. In the analysis of natural phosphates and superphosphates, therefore, the citrate method yields rapid and accurate results with a single precipitation.

In the presence of disodium ethylenediaminetetraacetate (Na_2EDTA), magnesium ammonium phosphate can be precipitated even in the presence of a large excess of calcium, and also Ba, Sr, Fe(III), Al, Cr(III), Ti, Be, Mn, Co, Ni, Zn, Cd, Cu and Pb (F. Huditz, H. Flaschka, I. Petzold 1952). When sufficient 5% tiron (pyrocatechol disulphonic acid) is added to the solution to be analysed, the interference from Bi, U(VI), Ti, Sn and Sb ions can also be eliminated. Chromium must always be oxidized before the precipitation. The precipitation of phosphate ions in the presence of Na_2EDTA and tiron can be carried out as follows:

To the slightly acidic solution to be analysed, add sufficient 1 M Na_2EDTA or 5% tiron solution (excess tiron does not interfere, excess Na_2EDTA, however, complexes part of the magnesium from the precipitant !). Dilute the solution to 200 ml, neutralize with 2·5% ammonia in the presence of phenolphthalein, and add 10–20 ml of saturated ammonium chloride solution. To the hot solution add 35 ml of magnesia mixture precipitant (see the end of the chapter for the preparation of the precipitant). Filter the precipitate next day. When only Na_2EDTA is added to the solution the precipitation must be made in the cold. Fe, Al and Ti can be masked with citric acid, and beryllium can be complexed

with thiosalicylic acid. Dissolve the washed precipitate with hydrochloric acid, add 0·2–0·5 g of citric acid and 3–4 ml of magnesia mixture, dilute to 100 ml, and repeat the precipitation with ammonia in hot solution.

Accompanying ions can be precipitated in the presence of phosphate by the following methods: Cations of groups I and II can be precipitated in acidic medium with hydrogen sulphide. In the presence of tin, the metastannic acid obtained by evaporation with nitric acid must be fused by the Freiberg fusion or with sulphur and crystalline sodium sulphide. When the solution is acidified tin(IV) sulphide is precipitated and phosphoric acid remains in solution. Iron(III), Co, Ni, Zn and Mn ions can be precipitated by saturating the acidic solution with hydrogen sulphide and cautiously making the solution alkaline with ammonia. Phosphate can be precipitated in the filtrate in the presence of ammonium sulphide.

When a solid sample is to be analysed it is advisable to use a fusion with sodium carbonate; sodium phosphate can then be dissolved from the carbonates and oxides of the metals present. Phosphate can be separated from aluminium ions in the form of ammonium phosphomolybdate. When the aluminium content of the solution is to be determined in the filtrate, aluminium phosphate must be precipitated with ammonium phosphate, ignited and weighed. Chromium(III) ions must be oxidized to chromate in ammoniacal medium with hydrogen peroxide, and phosphate ions can then be determined in the form of magnesium ammonium phosphate. Chromate ions can be determined in the filtrate in the form of lead chromate. Alkaline earth ions must be precipitated with sulphuric acid in slightly acidic hydrochloric acid solution, and a double volume of methanol must be added to the solution. In the filtrate, after the removal of alcohol by boiling, phosphate ions can be determined by the citrate method. Phosphate ions can be precipitated in the presence of magnesium with iron(III) chloride. Phosphoric acid can be precipitated in the presence of alkali metal ions with lead acetate from a neutral solution. Lead ions can be removed from the filtrate with hydrogen sulphide.

Reagent. Magnesia mixture : Dissolve 80 g of magnesium chloride, $MgCl_2 \cdot 6\,H_2O$ and 100 g of ammonium chloride in 500 ml of water, make alkaline with a small volume of ammonia and allow to stand overnight. If a precipitate is formed, the solution must be filtered. Acidify the filtrate with a small volume of hydrochloric acid and dilute to 1 litre with water.

56.1.2.1. *Procedure according to G. E. F. Lundell and J. I. Hoffman.* Original solution: (a) Phosphoric acid, or a slightly acidic solution of alkali phosphate, containing the equivalent of not more than 0·12 g of phosphorus pentoxide. (b) Ammoniacal solution of ammonium phosphomolybdate precipitate (see Chapter 56.1.1.), to which 0·5 g citric acid has been added.

Precipitation. Dilute solution (a) or (b) to 100 ml, acidify slightly with hydrochloric acid, add 10 ml of magnesia mixture and a further 0·1 ml for each milligram of phosphorus pentoxide present. Thus, a total of 22 ml of magnesia mixture must be added when 0·12 g of phosphorus pentoxide is present. Add diluted ammonia (1 : 1) to the cold solution, with constant stirring, until precipitation bes.gin Continue stirring after the addition of ammonia until

the precipitate becomes crystalline. Then continue the addition of ammonia. Make the solution slightly alkaline to phenolphthalein, add 10 ml of diluted ammonia (1 : 1) in excess, and allow the solution to stand for at least 4 hours, or overnight for more accurate determinations. Filter the mixture through an ash-free filter paper by decantation, and wash with 1% ammonia until chloride can no longer be detected in the washings. Take care that most of the precipitate remains in the beaker.

Dissolve the precipitate from the filter with 25 ml of hot diluted hydrochloric acid (1 : 1) and wash the filter with about 50 ml of diluted hydrochloric acid (1 : 20). Add 1–2 ml of magnesia mixture precipitant to the 75–100 ml solution and repeat precipitation with diluted ammonia (1 : 1) with constant stirring. Finally add 10 ml of ammonia in excess. Allow the mixture to stand overnight and filter through a medium-grade filter paper. Wash the precipitate on the filter paper with 1% ammonia until chloride can no longer be detected in the washings, dry in a drying oven, and add the main part of the precipitate to a weighed porcelain crucible. Combust the filter paper over the crucible so that the ash falls without loss into the crucible, and then ignite the precipitate at 900–1050°C to constant weight (about 30 min). Cool and weigh the magnesium pyrophosphate. Stoichiometric factors: $2\,P/Mg_2P_2O_7 = 0{\cdot}27831$, $2\,PO_4/Mg_2P_2O_7 = 0{\cdot}85336$, $P_2O_5/Mg_2P_2O_7 = 0{\cdot}63772$.

TABLE 56.5. Determination of phosphate ions in the form of magnesium pyrophosphate

Number of measurements	Mean of precipitate weights mg	True value mg	Deviation from true value Δ%	Standard deviation	
				mg	%
6	118·0	118·2	−0·1	±0·3	±0·3
6	236·4	236·4	±0·0	±0·4	±0·2
6	590·6	591·0	−0·07	±0·2	±0·03

Notes (1) The accuracy of the method is fairly good according to the data of Table 56.5. (measurements of Z. Rády).

(2) In the presence of foreign ions (Fe) the errors after the separation with ammonium molybdate may be as high as ±0·3%. If the precipitate is grey owing to traces of carbon, it must be evaporated with nitric acid after ignition, the evaporation repeated with 1 ml of concentrated ammonia, and the residue ignited again. If the evaporation is not repeated with ammonia after treatment with nitric acid, considerable losses may occur at ignition.

(3) In the presence of small amounts of Fe(III), Al, V, Zn, Sn, Ti or Zr add 3–5 g of citric acid and 25–50 ml of magnesia mixture to 100 ml of the solution before the first precipitation, and allow the solution to stand for 12–24 hr after precipitation. At the second precipitation add 0·2–0·5 g of citric acid and 3–4 ml of magnesia mixture to the solution.

56.1.2.2. *Procedure according to L. W. Winkler.* To 100 ml of the neutral solution in a 200-ml beaker, containing phosphate equivalent to about 0·1 g of phosphorus pentoxide, add 2·5 g of ammonium chloride and heat to 80–90°C. Add 10 ml of 10% ammonia and mix the solution. Add 0·5 ml of magnesium salt solution from a measuring pipette (10·0 g $MgCl_2 \cdot 6\ H_2O$ or $MgSO_4 \cdot 7\ H_2O$ + + 5 g NH_4Cl dissolved in water to 100 ml). A white flocculent precipitate is formed. Stir frequently and wait until the precipitate becomes crystalline and the initial opalescent solution becomes clear. The recrystallization takes place within several minutes. Continue the addition of the magnesium salt solution until a total of 10 ml has been added. Allow to stand overnight, collect the precipitate on a G 4 glass, A 2 porcelain filter-crucible or No. 4 glass texture filter-funnel, and wash with 50 ml of 1% ammonia and then with 12–15 ml of alcohol. Dry the edge of the filter and the funnel of the filtration apparatus with a linen cloth, and draw air filtered through cotton wool over the precipitate for about 40 min (see Chapter 42.1.2.). Weigh the crucible. Correct the weight of precipitate by the following corrections:

Weight of $MgNH_4PO_4 \cdot 6\ H_2O$ precipitate g:	0·50	0·10	0·05	0·01
Correction mg:	−1·4	−1·3	−1·1	−0·6

Stoichiometric factor: $P_2O_5/2\ MgNH_4PO_4 \cdot 6\ H_2O = 0{\cdot}28919$.

Notes. (1) When the original solution only contains several centigrams of phosphorus pentoxide per 100 ml, 1—2 ml of magnesium salt solution must be added to the hot ammoniacal mixture, otherwise precipitation does not occur. When the solution contains only several mg of phosphorus pentoxide, however, 10 ml of magnesium salt solution must be added at once. The precipitation then begins only after cooling the solution.

(2) When the precipitate is dried in a current of air, according to the above procedure, accurate results can be obtained even in the presence of 10 g of potassium or sodium chloride. Under these conditions ignition of the precipitate yields very inaccurate results.

56.1.2.3. *Procedure after precipitation of ammonium phosphomolybdate according to L. W. Winkler.* Precipitate phosphate ions by the method of Woy–Winkler in the form of ammonium phosphomolybdate, collect on a filter paper and wash (see Chapter 56.1.1.).

Dissolve the washed precipitate from the filter with 15 ml of hot 10% ammonia, and rinse the filter with 100 ml of 2·5% ammonium chloride solution. Precipitate magnesium ammonium phosphate from the hot ammoniacal solution with 10 ml of magnesium salt solution according to the above procedure.

In the presence of ammonium molybdate the weight of the dried precipitate is somewhat higher than the true value and the following corrections must be applied:

Weight of precipitate g:	0·50	0·30	0·20	0·10	0·05	0·01
Correction mg:	−2·5	−2·3	−2·2	−2·1	−1·5	−0·7

Notes. (1) By the method mentioned the determination can be carried out even in the presence of 10 g of potassium chloride, and thus large amounts of chloride do not affect the solubility of the ammonium phosphomolybdate precipitate.

(2) The accuracy of the method is only slightly affected by Ca, Mg, Zn, Mn and Al ions, if phosphate ions are first precipitated in the form of ammonium phosphomolybdate.

(3) In the presence of iron(III) ions, the ammonium phosphomolybdate precipitate contains considerable amounts of iron, from which it can be separated by repeated precipitation:

Dissolve the ammonium phosphomolybdate, after filtration and washing, in 10 ml of 10% ammonia and wash the filter paper with 50 ml of water. Add 10 ml of 3% ammonium molybdate solution[2] to the solution, heat to boiling, and add 20 ml of 25% nitric acid dropwise to the hot clear solution. The precipitate is obtained in quite pure form. Ammonium nitrate must not be added to the solution, because it is formed in sufficient amounts on reaction of the ammonia and nitric acid.

56.1.3. *Analysis of crude materials and products of the phosphate fertilizer industry*

The agricultural value of phosphate fertilizers depends on the total phosphorus content and on the water- and weak acid-soluble (citric acid) phosphate content, which can be used by plants. The technical analysis of phosphate fertilizers, therefore, includes the determination of the total phosphate, water-soluble phosphate and citric acid-soluble phosphate content. The results are presented in terms of P_2O_5. The chemical valuation of crude phosphates is made on the basis of the total phosphorus content.

In sampling, care must be taken that the laboratory sample, of at least 500 g, should have the same composition as the bulk phosphate. The whole laboratory sample must be mixed well and then sieved through a 2 mm sieve. For wet samples, superphosphates, it is sufficient to grind the whole sample in a porcelain mortar, and break up the coarser parts. When harder samples, e.g. Thomas slags, are to be analysed, the part which remains on the sieve must be broken in a mortar until the whole sample passes through the sieve. It is not advisable to sieve Thomas slags through a finer sieve and take out the iron particles with a magnet, because the average composition of the sample will then be changed.

The main fraction of crude phosphates consists of tertiary calcium phosphate, $Ca_3(PO_4)_2$, the P_2O_5 content of which is 45·8% when completely pure. Thomas slag contains more calcium oxide than that corresponding to this formula. Crude phosphates used for the production of phosphate fertilizers usually contain 25–40% of P_2O_5. Thomas slags contain 12–23% of P_2O_5, superphosphate fertilizers 14–18% P_2O_5, and double superphosphate contains a total of 40–45% P_2O_5.

In Thomas slags and superphosphate-type fertilizers it is important to distinguish between the total phosphate content and the soluble phosphate content, because the agricultural value of these fertilizers is determined mainly by the soluble phosphate content. In Thomas slags the phosphates must be dissolved with citric acid, and in superphosphates water or ammonium citrate solution should be used. Before the determination of the total phosphate content, the sample must be fused with concentrated sulphuric

[1] *Preparation of 3% ammonium molybdate solution :* Dissolve 3 g of finely powdered commercial ammonium molybdate in 30 ml of water and 2–5 ml of 10% ammonia, if necessary with heating, and dilute the solution to 100 ml.

acid, concentrated nitric acid or with the mixture of these acids. The hydrochloric acid must be removed by evaporation with nitric acid, and organic substances must be destroyed.

In the solution of the sample, aluminium, iron(III) and calcium ions are present as well as phosphoric acid. These ions interfere in the precipitation in the form of magnesium ammonium phosphate as they form precipitates in ammoniacal solution. The determination of phosphate, therefore, is usually made in technical practice by three methods:

(1) Ammonium phosphomolybdate is precipitated with ammonium molybdate from a solution containing sulphuric and nitric acids. The precipitate is then washed with acetone and dried in a vacuum desiccator. The precipitate can then be weighed (method of v. Lorenz).

(2) The ammonium phosphomolybdate can be dissolved in ammonia, and phosphate can be precipitated in the form of magnesium ammonium phosphate (method of Woy and Winkler).

(3) In the presence of small amounts of calcium (after fusion with sulphuric acid, or in the aqueous solution of superphosphates) trivalent ions can be complexed with ammonium citrate, and phosphate can be precipitated in the form of magnesium ammonium phosphate (citrate method).

Citric acid thus plays a double role in the analysis of phosphate fertilizers: as a complexing agent it complexes iron and aluminium and prevents the precipitation of the hydroxides of these metals (citrate method), and as a solvent for phosphate it is used for the determination of the citric acid-soluble or citrate-soluble phosphate content.

Of the technical analytical methods for phosphate fertilizers, the determination in the form of magnesium ammonium phosphate involves error compensation, while the errors of the ammonium phosphomolybdate methods are eliminated by the application of practical factors. Both methods require the close control of prescribed experimental conditions. The phosphate fertilizer industry therefore attempts to operate with internationally accepted standards. The most important of these methods are treated on special examples in the following text. Of these methods the most widely accepted is the phosphate determination according to v. Lorenz, which is less dependent on the composition of the sample and can be used after various methods of dissolution or fusion. Table 56.6. shows the methods of determination of phosphate which are recommended by international agreement for these crude materials and products.[1] In the following text first the standardized methods of dissolution or fusion are described:

Fusion before the determination of the total phosphate content. (1) *Fusion with sulphuric acid:* Weigh 5 g of finely powdered crude phosphate or phosphate fertilizer by difference into a 500-ml flask made of good quality glass. Add 15 ml of water and 30 ml of concentrated sulphuric acid with frequent stirring, and heat until completely dissolved (about 20 minutes). Dilute the hot solution with water until any hard pieces disintegrate. Cool, dilute the solution to 500 ml

[1] L. Schmitt, *Methodenbuch II. Die Untersuchung von Düngemitteln.* 2nd Ed. Neumann Verl. Radebeul u. Berlin (1954), p. 20.

TABLE 56.6. Analysis of the most important phosphate fertilizers

Name of phosphate	To be determined	Fusion or leaching reagent	Method of phosphate determination
1. Raw phosphate, Kolaphosphate, Hyperphosphate	total P_2O_5	$HNO_3 + H_2SO_4$ (3)	(a) citrate method (b) v. Lorenz method
2. Bone powder, fish powder, meat powder, animal faeces, guano	total P_2O_5	$HNO_3 + H_2SO_4$ (4)	v. Lorenz method
3. Superphosphate	total P_2O_5	H_2SO_4 (1)	citrate or v. Lorenz method
	water-soluble P_2O_5	water	citrate method
	citrate-soluble P_2O_5	Petermann solution of NH_4-citrate	v. Lorenz method
	free phosphoric acid	water + alcohol	by titration
4. Thomas slag	total P_2O_5	H_2SO_4 (1)	(a) citrate method (b) v. Lorenz method
	citric acid-soluble P_2O_5	2% citric acid	(a) citrate method (b) v. Lorenz method (c) iron(III) citrate method
5. Dicalcium phosphate (precipitatum) Kampka	total P_2O_5	H_2SO_4 (1)	(a) citrate method (b) v. Lorenz method
	citric acid-soluble P_2O_5	2% citric acid	v. Lorenz method
	citrate-soluble P_2O_5	Petermann solution of NH_4-citrate	v. Lorenz method

TABLE 56.6. *(contd.)*

Name of phosphate	To be determined	Fusion or leaching reagent	Method of phosphate determination
6. Röchling phosphate	total P_2O_5	$HNO_3 + H_2SO_4$ (4)	v. Lorenz method
	citric acid-soluble P_2O_5	2% citric acid	v. Lorenz method
	citrate-soluble P_2O_5	Petermann solution of NH_4-citrate	v. Lorenz method
7. Rhenania phosphate	total P_2O_5	H_2SO_4 (1)	(a) citrate method (b) v. Lorenz method
	citrate-soluble P_2O_5	Petermann solution of NH_4-citrate	v. Lorenz method
8. Camaphos	total P_2O_5	H_2SO_4 (1)	(a) citrate method (b) v. Lorenz method
	citric acid-soluble P_2O_5	2% citric acid	v. Lorenz method
9. Am-Sup Am-Sup-Ka	citric acid-soluble P_2O_5	2% citric acid	(a) citrate method (b) v. Lorenz method
10. Nitrophosphate "Höchst" Volldünger Ruhr-Volldünger V	total P_2O_5	HNO_3 (2)	v. Lorenz method
	water-soluble P_2O_5	water	v. Lorenz method
	citrate- soluble P_2O_5	Petermann solution of NH_4- citrate	v. Lorenz method

in a volumetric flask, and shake well. Filter the mixture through a dry folded filter paper into a dry flask, and reject the first portion of the filtrate. Take aliquots of the rest of the filtrate for analysis.

Note. The solution must be stirred and diluted rapidly, otherwise gypsum, which is precipitated later, causes difficulties in the dilution. Fusion with sulphuric acid is used in the determination of the total phosphorus content of dicalcium phosphate, calcium ammonium phosphate, superphosphate, Thomas slag and Rhenania-

phosphate. Phosphate can be determined in the filtered solution by the citrate method (Chapter 56.1.3.2.), or according to the method of v. Lorenz (Chapter 56.1.3.4.).

(2) *Fusion with nitric acid:* Weigh 5 g of finely powdered sample into a 500-ml flask and mix with 200 ml of water. Add 50 ml of concentrated nitric acid and boil for 10 minutes. Cool, dilute the mixture to volume in a 500-ml volumetric flask, and take 10 ml (0·1 g sample) for analysis. Phosphate can be determined by the method of v. Lorenz (Chapter 56.1.3.4.).

Note. By this method only those phosphate fertilizers which contain only a small amount of calcium can be analysed. Most triple phosphates, e.g. Nitrophoska, Kampka, are of this type.

(3) *Fusion with nitric acid and sulphuric acid:* Weigh 5 g of finely powdered sample into a 500-ml flask, add 25 ml of water, 60 ml of concentrated nitric acid and 35 ml of concentrated sulphuric acid, mix well, and heat on a water bath for 3 hr. Boil for 15 min, cool thoroughly, and dilute to the mark in a 500-ml volumetric flask. Filter the mixed solution through a dry folded filter paper into a dry flask. Discard the first part of the filtrate and transfer a 15-ml aliquot (0·15 g sample) of the rest of the filtrate to a 250-ml beaker. Add 35 ml of nitric acid (sp. gr. 1·2) to the solution, and without adding a mixture of nitric acid and sulphuric acid, determine the phosphate according to the method of v. Lorenz (see Chapter 56.1.3.4.).

(4) *Fusion of phosphate samples containing organic substances:* Weigh 5 g of finely divided sample into a 500-ml flask, add 15 ml of water, a few (0·5 g) copper(II) sulphate crystals, and 20 ml of concentrated nitric acid. Add 30–40 ml of concentrated sulphuric acid to the flask with constant stirring. When the initial vigorous reaction has subsided, boil the contents of the flask until the solution becomes clear. If the solution becomes brown add further nitric acid, and finally evaporate until sulphuric acid fumes appear. Cool, dilute the contents of the flask cautiously with 200 ml of cold water, and after complete cooling dilute to the mark in a 500-ml volumetric flask. Mix, filter the solution through a dry folded filter into a dry flask, discard the first part of the filtrate, and take a 15-ml aliquot (0·15 g sample) from the remaining filtrate for analysis.

Notes. (1) Phosphate can be determined in an aliquot of the sample by the method of v. Lorenz (Chapter 56.1.3.4.). If the original substance contains a large amount of organic material, it must be allowed to stand overnight before heating. This method can be used for the preparation of crude phosphates, bone ash, fish and meat powder, guano, hyperphosphate, and stable and humus fertilizers.

(2) See Chapter 56.1.3.2. for the dissolution of *citric acid-soluble phosphate*, and Chapter 56.1.3.1. for the dissolution of *water-soluble phosphate*.

Dissolution of ammonium citrate–soluble phosphates. Preparation of ammonium citrate solution according to Petermann: Mix 173 g of lead-free citric acid with that volume of concentrated ammonia which contains 42·0 g of nitrogen in the form of ammonia. Cool the solution to 15°C and dilute to 1 litre. The specific gravity of the prepared solution is 1·082–1·083 at 15°C.

To avoid loss of ammonia, the citric acid solution must be added to the weighed amount of ammonia through a dropping funnel fitted into a rubber

stopper with constant cooling. Air displaced from the flask first bubbles through the citric acid and so cannot remove ammonia. It is advisable to control the ammonia content of the prepared solution by dilution of 25 ml to 250 with water, and by liberating ammonia from 25 ml of this sample with sodium hydroxide. The ammonia must be distilled into a known amount of hydrochloric acid, and excess acid must be titrated acidimetrically. The nitrogen content of the prepared solution is 0·1050 g.

Procedure. Weigh 2·5 g of phosphate sample, finely powdered to less than 1 mm grains, into a 250-ml Stohmann flask[1] and dilute to the mark with ammonium citrate. Close the flask with a rubber stopper and attach it to a shaking apparatus. Shake the flask 30–40 times a minute for 2 hr. The temperature must be about 20°C. After this time filter the solution immediately. Determine phosphate in 1 ml of the solution (0·1 g sample) by the method of v. Lorenz (see Chapter 56.1.3.4.).

56.1.3.1. *Determination of the total phosphate content of crude phosphate and bone ash.* The finely powdered mineral phosphate or bone ash must be dissolved in *aqua regia*, and the chlorides must be removed by repeated evaporation with nitric acid. The precipitated silicic acid must be removed by filtration. Phosphate can be determined in the filtrate after separation in the form of ammonium phosphomolybdate and redissolution in the form of magnesium ammonium phosphate according to the method of Woy–Winkler.

In practice, however, the application of the citrate method enables the previous separation with ammonium molybdate to be avoided.

Reagents. (1) *Ammoniacal ammonium citrate solution:* Diossolve 50 g of crystalline citric acid in 250 ml of water, and add 175 ml of concentrated (25%) ammonia slowly while cooling. Dilute the solution to 500 ml.

(2) *Magnesium salt solution:* Dissolve 11·0 g of pure, crystalline magnesium chloride and 14·0 g of ammonium chloride in 130 ml of water, add 70 ml of 8% ammonia and remove any precipitate which is formed after standing overnight.

Procedure. Weigh 5·0 g of the finely divided mineral phosphate, or 10 g of bone phosphate, into a 500-ml volumetric flask, add 20 ml of concentrated nitric acid and 50 ml of concentrated sulphuric acid, and heat for 30 min. Cool, dilute cautiously with water, mix, cool thoroughly and dilute the solution to the mark. Filter the solution through a dry filter paper into a dry flask. Discard the first part of the filtrate, take an aliquot of the remaining filtrate. If the sample contains more than 20% of phosphorus pentoxide take a 25-ml aliquot, or take 50 ml when it contains less than 20% P_2O_5, into a 400-ml beaker. Add 100 ml of ammoniacal citrate solution and 25 ml of magnesium salt solution, and stir vigorously for 30 min. Stir with an electrically-driven bent glass rod. Collect the precipitate without delay on an ash-free filter paper wash with 2% ammonia until chloride can no longer be detected in the washings

[1] A cylindrical volumetric flask with a diameter of at least 2 cm, in which at least 8 ml of air space must remain after dilution to the mark.

combust in a platinum or porcelain crucible in the wet state, ignite and weigh. Weighing form: $Mg_2P_2O_7$.

56.1.3.2. *Determination of the water-soluble phosphate content of superphosphate fertilizers.* Tertiary calcium phosphate, $Ca_3(PO_4)_2$, present in phosphate raw materials is insoluble in water and dilute organic acids, and therefore plants only assimilate it slowly. In the processing of chemical fertilizers this water-insoluble raw phosphate is converted to water-soluble calcium dihydrogen phosphate by fusion with sulphuric acid. The superphosphate consists mainly of $Ca(H_2PO_4)_2 \cdot H_2O + 2\,CaSO_4 \cdot 2\,H_2O$, with which variable amounts of iron(III) sulphate, aluminium sulphate, silicic acid and other contaminanst are mixed. In superphosphates containing iron the water-soluble phosphate content decreases during storage, because water-insoluble iron(III) phosphate is formed:

$$Fe_2(SO_4)_3 + Ca(H_2PO_4)_2 = 2\,FePO_4 + CaSO_4 + 2\,H_2SO_4.$$

Thus, if the raw material contains more than 2% of iron it is not suitable for the production of superphosphate. The commercial value of superphosphate is therefore determined by the water-soluble phosphate content. This can be determined most conveniently by the citrate method.

Procedure. Weigh 10·0 g of the superphosphate sample into a thick-walled 500-ml volumetric flask, add 400 ml of water, close the flask with a rubber stopper, and shake vigorously for 30 min in a suitable apparatus or by hand. Dilute the solution to the mark, shake its contents, and filter through a dry filter paper into a dry beaker. To 50 ml of the filtrate, add 50 ml of ammoniacal citrate solution and 25 ml of magnesium salt solution, stir vigorously for 30 min, and follow the procedure described above.

Note. Double superphosphates usually also contain small amounts of pyrophosphoric acid. This must be converted to orthophosphoric acid before precipitation. Take 25 ml of the aqueous extract and boil with 10 ml of concentrated nitric acid for 10—20 min, neutralize with concentrated ammonia, and follow the procedure of the citrate method described above.

56.1.3.3. *Determination of citric acid-soluble phosphate content of Thomas slags.* The phosphorus pentoxide content of Thomas slags cannot be extracted with water, but it is soluble in 2% citric acid. Plants can therefore use the phosphate content of Thomas slags because the dissolving power of organic acids produced by the plants is similar to the diluted citric acid solution. From the point of view of the analysis of Thomas slags, therefore, the determination of the citric acid-soluble phosphate content is the most important.

Procedure according to Wagner. Weigh 5 g of finely powdered Thomas slag into a dry 500-ml volumetric flask. The neck of the flask should be at least 2 cm in diameter and at least 8 cm air space must remain above the graduation mark (Stohmann flask). Dilute to volume with 2% citric acid solution at 17·5 °C, close with a rubber stopper, and shake in a shaking apparatus for 30 min.

A constant temperature can be maintained in the flask by wrapping it in an insulating material, e.g. felt. After shaking, filter the contents of the flask through a dry folded filter paper, add 7·5 ml of concentrated hydrochloric acid to 100 ml of the filtrate, and evaporate on a water bath until the solution becomes syrupy, to remove silicic acid. The evaporation must be continued only until hydrochloric acid fumes are evolved, and the residue should not become dry. Add 2 ml of concentrated hydrochloric acid to the residue, wash into a 200-ml volumetric flask, and dilute to volume with water. Shake, filter the solution through a dry filter into a dry flask, and determine the phosphate content of 100 ml of the filtrate by the citrate method or by the method of v. Lorenz.

56.1.3.4. *Determination of the phosphorus pentoxide content of phosphate fertilizers according to v. Lorenz.*[1] Because the composition of the ammonium phosphomolybdate precipitate varies with the experimental conditions, it can only be used for accurate analyses under carefully controlled conditions. N. v. Lorenz, however, found that when the precipitate is produced with a large excess of ammonium molybdate reagent containing sulphate, the phosphorus content of the precipitate is fairly constant. Under his recommended experimental conditions, the presence of Ca, Al, Fe(III) and silicic acid do not affect the composition of the precipitate. Thus, although the precipitate does not have a stoichiometric composition, it is quite suitable for the accurate determination of the phosphate content of fertilizers, if carefully determined practical factors are applied in the calculations. When the precipitate is rinsed with acetone after washing, it can be dried very rapidly to constant weight in a vacuum desiccator. The precipitate, after washing with acetone, contains a well-defined amount of acetone, similar to water of crystallization, according to W. Spengler, and therefore the drying must be effected at 15–20 mm Hg in a vacuum desiccator containing not more than three crucibles for 1 hr. Under these conditions the composition of the precipitate corresponds to the formula:

$$8\,[(NH_4)_3PO_4 \cdot 12\,MoO_3] \cdot 5\,NH_4HMoO_4 \cdot 4\,H_2MoO_4 \cdot 24\,H_2O \cdot 5\,CH_3COCH_3.$$

When the precipitate is dried at higher or lower pressure, its acetone content is changed. The required vacuum can be produced easily with an efficient water pump, but the pump must be in operation during the whole drying process to remove the acetone fumes from the desiccator.

The accuracy of the method, when the amount of P_2O_5 present is less than 50 mg, is independent of the sample size. Relatively large amounts of ammonium molybdate must be used for the precipitation. The regeneration of the spent reagent is economical.

[1] N. v. Lorenz, *Landwirtschaftliche Versuchstationen* **51**, 183 (1901); *Z. anal. Chem.* **46**, 193 (1907); *Österreich. Chemiker Z.* [2] **14**, 1 (1911); Chem. Zentr. **82**, I. 686 (1911); H. Neubauer and F. Lücker, *Z. anal. Chem.* **51**, 161 (1912); W. Spengler, *Z. anal. Chem.* **110**, 321, 124 (1937); (1942) 241; L. Schmitt, *Methodenbuch II. Die Untersuchung von Düngemitteln.* 2 Ed. Neumann, Radebeul-Berlin (1954), p. 28.

The following procedure is accepted by international analytical methods commissions.

Reagents. (1) *Sulphate-molybdate reagent :* In a 10-litre bottle mark the volume corresponding to 10 litres. Weigh 500 g of ammonium sulphate into the bottle and dissolve it in 4500 ml of concentrated nitric acid (sp. gr. 1·4). Dissolve 1500 g of powdered ammonium molybdate reagent in 4 litres of hot water in a large porcelain vessel with stirring. Add the cold solution in a thin stream to the ammonium sulphate-nitric acid solution with constant stirring, cool the solution, dilute to 10 litres, shake thoroughly, and filter into a brown bottle. Store the solution in a cold place, and, if necessary, filter after 2 days. Specific gravity of the solution: 1·320. The solution can be used for 2–3 weeks. If necessary it can be filtered before use.

(2) *Nitric acid (sp. gr. 1·20)*: Dilute 500 ml of concentrated nitric acid (sp. gr. 1·4) with 700 ml water.

(3) *Sulphuric acid-nitric acid :* Add 30 ml of concentrated sulphuric acid (sp. gr. 1·84) to 1 litre of diluted (sp. gr. 1·20) nitric acid.

(4) *Washing solution :* Dissolve 20 g of chemically pure ammonium nitrate in 1 litre of water, and acidify with 5 ml of 20% nitric acid.

(5) *Acetone :* Store chemically pure commercial acetone in a brown bottle. When the acetone is diluted with an equal volume of water the solution should remain clear and show a neutral reaction to litmus. The acetone should not contain substances with boiling points above 60°C. The acetone must be tested for water, ammonia and aldehyde by the following methods:

Test for water content : Add anhydrous copper(II) sulphate to the acetone sample and shake. Only a faint blue colour should form. If the acetone contains water it must be shaken with anhydrous potassium carbonate and the acetone filtered off and distilled cautiously.

Test for ammonia : Place a moist red litmus paper into the vapour above the acetone. It should not become blue even after several hours. If the acetone contains ammonia, it must be shaken with powdered oxalic acid and distilled cautiously on a water bath.

Test for aldehyde : Boil 10 ml of acetone with 5 ml of ammoniacal silver nitrate on a water bath under reflux. The solution should not turn brown.

Procedure. Transfer a sample of the prepared pure phosphate solution containing the equivalent of not more than 50 mg of P_2O_5 to a thick-walled 250–300 ml Erlenmeyer flask with a pipette; 1 ml of the solution should contain at least 1 mg of P_2O_5. The optimum volume of the solution is 10 ml. The solution must be pipetted carefully in a calibrated pipette. Add 40 ml of sulphuric acid-nitric acid mixture (reagent 3) to the solution, mix, heat to boiling, remove the source of heat and mix by rotating the flask again. After 1–5 min add 50 ml of sulphate-molybdate reagent (1) rapidly in a fine jet to the hot solution, and take care that the reagent does not flow down the wall of the vessel. The addition of the reagent can be made most conveniently from a 50-ml pipette which has a 2–2·5 second flow-time, but not more than 5 sec, and the end of the pipette must be broken for this purpose. The tip of the pipette must be held within 1–2 cm of the surface of the solution.

After the addition of the reagent mix the solution by rotating the flask several times. Allow most of the precipitate to settle (usually this takes 5 min), rotate the flask for 20–30 sec, and mix well. For pure alkali phosphates wait for 30 or 60 min, and for phosphate fertilizers for 3–4 hr, and

filter the mixture through a G 4 glass filter-crucible or a Neubauer filter-crucible. When less than 3 mg of P_2O_5 is present, the filtration must be carried out after 12–18 hr. The supernatant solution must be added to the filter first and the precipitate which remains behind must be washed 2–3 times with the washing solution (4) by decantation.

Shake thoroughly and wait for 1–2 min before pouring the solution on to the filter. Finally transfer the precipitate to the filter. Traces of precipitate which adhere to the walls of the flask can be loosened with a small rubber tube fitted on a glass rod. Thoroughly mix the precipitate in the crucible twice with the washing solution using a small glass rod. Remove the solution at the pump so that its vapour cannot be detected in the filter flask. Dry the walls of the crucible and the edge of the rubber tubing with a linen cloth. Fit the crucible in the filter flask again, fill it almost completely with acetone, and stir the contents of the crucible thoroughly with a small glass rod. Remove the acetone at the pump, taking care that the precipitate does not cake together. Repeat the washing twice using half a crucible volume each time. With the last portion of acetone transfer the traces of the precipitate which adhere to the glass rod into the crucible. If the acetone is to be recovered, the filter flask must be changed for an empty flask before washing. Finally remove the acetone rinsing solution thoroughly. The precipitate should have only a slight odour of acetone.

Dry the outside of the crucible, place it immediately in a vacuum desiccator, and dry it for 1 hr at 15–20 mm Hg pressure. No more than three crucibles should be placed in the vacuum desiccator at the same time. The vacuum should be controlled by a mercury manometer, and the desiccator should be connected to the water pump during the drying period. The precipitate should not smell of acetone before weighing, otherwise the drying must be continued.

When the drying is finished, place the crucible immediately on a balance and weigh, or place it in a desiccator which contains 1 volume of water and 1 volume of concentrated sulphuric acid. The following practical factor (v. Lorenz) is accepted by international standards: P_2O_5/ammonium phosphomolybdate: 0·03295.

Notes. (1) According to the accurate measurements of Spengler, taking account of the new atomic weights, more accurate results can be obtained if the P_2O_5 content of the sample is calculated using the factor 0·032866. For crude phosphates the practical factor is 0·032648; for Renania phosphates the factor 0·032702 gives more accurate results.

(2) The solution prepared for precipitation must contain 0·8—1·5 ml of free concentrated sulphuric acid (sp. gr. 1·84) and 10—20 ml of free concentrated nitric acid. Not more than 0·5 g of hydrochloric acid, 1 g of citric acid, 1 g of ammonium salt or 0·5 g of sodium salt, potassium chloride, iron(III) oxide, aluminium oxide, magnesium oxide, manganese salt and calcium salt, or 5 g of potassium nitrate, or 1 g of potassium sulphate may be present. In the presence of large amounts of sulphate the results are somewhat low. If the fertilizer solution has been prepared by the usual method, 10—20 ml of the solution contains less accompanying material than this. Hydrochloric acid or chlorides can be removed by evaporation with nitric acid, and sulphuric acid by cautious fuming.

TABLE 56.7. Determination of phosphate according to v. Lorenz

	Number of measurements	Weight of precipitate mg	Weight of P_2O_5 calculated from the weight of precipitate mg ($f = 0.03295$)	P_2O_5 content mean mg	True value P_2O_5 mg	Deviation from true value Δ%	Maximum deviation	
							mg	%
With freshly prepared precipitant	4	1000·8	32·98	33·00	32·95	+0·15	−0·02	−0·06
		1001·6	33·00					
		1002·0	33·01				+0·03	+0·10
		1002·5	33·03					
							Standard deviation	
							mg	%
With 1 month old precipitant	6	993·8	32·74	32·76	32·95	−0·57	±0·15	±0·4
		992·2	32·70					
		997·1	32·85					
		1000·0	32·95					
		994·5	32·77					
		990·6	32·64					

(3) The method yields very precise results (see Table 56.7., measurements of G. Rády and J. Takács). The difference between the true value and determined values may approach 0·25% when unknown samples are analysed. The difference can be reduced to 0·1%, if the accompanying substances, and thus the valid practical factor, are determined by test analyses.

(4) It is advisable to regenerate ammonium molybdate from the filtrate and collected precipitate.[1]

Test analysis. Dry potassium dihydrogen phosphate, KH_2PO_4, or ammonium dihydrogen phosphate, $NH_4H_2PO_4$, to constant weight at 100°C. Dissolve 6·3153 g of dry KH_2PO_4 or 5·3385 g of dry $NH_4H_2PO_4$ in water and dilute to 200 ml in a volumetric flask. Store the solution in a well-stoppered glass bottle. Dilute 20 ml of this solution to 200 ml and carry out the test analysis on 10 or 20 ml of this solution. 20 ml of the diluted solution contains 0·03295 g of P_2O_5, and thus the weight of the precipitate will be exactly 1·000 g, if the factor of v. Lorenz is accurate in the given example. The test analysis can be made accurate by the addition of the accompanying substances present in the solution to be analysed (e.g. citric acid) to the test solution, before dilution with nitric acid–sulphuric acid.

Table 56.7. shows some results of test analyses (measurements of G. Rády and J. Takács). In our experience the accuracy of the results depend on the careful preparation and storage of the sulphate–molybdate reagent. From the results of Table 56.7. it is evident that if the sulphate–molybdate reagent is stored for about 1 month, the deviations from the true values are higher (about −0·5%).

[1] H. NEUBAUER and E. WOLFERTS, *Z. anal. Chem.* **58**, 445 (1919).

56.2. DETERMINATION OF PYROPHOSPHATE IONS ($P_2O_7^{4-}$)

If other phosphates are not present, pyrophosphate can be converted to orthophosphate by boiling with nitric acid, and can be precipitated either in the form of ammonium phosphomolybdate or magnesium ammonium phosphate, depending on the other ions present. Hydrolysis can be made by the following method.

To about 25 ml of the solution containing not more than 0·12 g of phosphorus pentoxide present as pyrophosphate, add 10 ml of concentrated nitric acid and boil gently for 1–2 hr.

The separation of pyrophosphate from orthophosphate is based on the different solubility of the corresponding magnesium and zinc salts.

56.2.1. *Separation of pyrophosphate ($P_2O_7^{4-}$) from orthophosphate (PO_4^{3-})* (M. Berthelot, G. André, 1896 and R. Dworzak, W. Reich-Rohrwig 1929)

Magnesium pyrophosphate can be quantitatively precipitated from acetate-buffered solution at about pH 4·5; under the same conditions magnesium ammonium phosphate remains in solution. The method yields a good separation when the amounts of ortho- and pyrophosphate in the solution are about the same, or if the pyrophosphate is present in excess. When orthophosphate is present in large excess, magnesium pyrophosphate can only be precipitated after evaporation of the solution, but the separation is not very accurate under these conditions.

Magnesia mixture. Dissolve 55 g of crystalline magnesium chloride, $MgCl_2 \cdot 6H_2O$ and 105 g of ammonium chloride in water to 1 litre, and make the solution slightly acid in the presence of methyl red with hydrochloric acid.

Procedure. To 50 ml of the nearly neutral solution containing not more than 0·2 g of phosphorus, add 100 ml of magnesia mixture, 20 ml of cold saturated ammonium chloride solution and 20 ml of cold saturated ammonium acetate solution. Acidify the mixture with 40 ml of 2 N acetic acid, and heat on a water bath for 4–5 hr. Cool, collect the magnesium pyrophosphate, $Mg_2P_2O_7$, precipitate on a filter paper, and wash with water containing 1% of ammonium acetate, acetic acid and ammonium chloride. Evaporate the filtrate to about 100 ml on a water bath; a small amount of dissolved magnesium pyrophosphate (0·5–3%) precipitates. Collect this precipitate on a second filter paper, and wash with the same washing solution. When the filtrate is evaporated again, no further precipitate is usually formed.

Dissolve the precipitates from the filters with 30 ml and 10 ml of hot 2 N nitric acid respectively, combine the solutions and boil for 1–2 hr; pyrophosphate is hydrolysed to orthophosphate. Neutralize the excess nitric acid with ammonia, add 2 ml of magnesia mixture to the solution, dilute to 100 ml, and precipitate magnesium ammonium phosphate with ammonia. Collect the precipitate next day on a filter paper, wash with 1% ammonia, and ignite

between 900–1050°C to magnesium pyrophosphate. Cool and weigh. Stoichiometric factors: $2\ P/Mg_2P_2O_7 = 0{\cdot}27831$; $P_2O_5/Mg_2P_2O_7 = 0{\cdot}63772$.

Notes. (1) R. Dworzak and W. Reich-Rohrwig found in a solution containing about equal amounts of orthophosphate and pyrophosphate 98·56 mg of phosphorus as pyrophosphate, instead of 98·71 mg.

(2) When the amount of orthophosphate present is about ten times that of the pyrophosphate, the procedure must be modified as follows: After the addition of the recommended amounts of magnesia mixture, ammonium chloride and ammonium acetate, only 1—5 ml of 2 N acetic acid must be added. The solution must be evaporated to small volume (about 50 ml) and the precipitate filtered. By this method, the above authors found 18·68 mg of phosphorus as pyrophosphate instead of 19·74 mg, in the presence of a ten-fold excess of orthophosphate.

56.2.2. *Separation of pyrophosphate ($P_2O_7^{4-}$) from orthophosphate (PO_4^{3-}) and metaphosphate (PO_3^-)*

Zinc pyrophosphate is appreciably soluble in acetic acid at pH values less than 3·7; above this pH it can be precipitated quantitatively. The precipitation of zinc orthophosphate, however, only becomes complete above pH 4·7, and thus in the pH range 3·7–4·7 zinc pyrophosphate can be selectively precipitated from solutions containing orthophosphate. When the solution also contains large amounts of ammonium salts, zinc metaphosphate remains in solution. From the filtrate, on accurate neutralization (pH 7), orthophosphate is precipitated in the form of zinc ammonium phosphate, $ZnNH_4PO_4$. When the filtrate from this precipitate is acidified with nitric acid and boiled for 6–8 hr, metaphosphate is converted to orthophosphate, and on accurate neutralization (pH 7) they can also be precipitated in the form of zinc ammonium phosphate.

The zinc pyrophosphate precipitate can be ignited to constant weight above 610°C, and can be weighed after cooling (Duval, 1953).[1]

Procedure. (a) *Precipitation with zinc sulphate:* To 100 ml of the neutral solution containing not more than 0·4 g of phosphorus pentoxide from the various alkali phosphates, add 5–10 g of ammonium chloride.

Add a slight excess of zinc sulphate solution (12·5 g of $ZnSO_4 \cdot 7\ H_2O$ in 100 ml of water) to the sample solution, and adjust the pH of the solution to 4·0–4·5 with 0·1 N acetic acid. Control the pH with an indicator paper sensitive to at least 0·3 pH units or use a suitable pH meter. Zinc pyrophosphate, $Zn_2P_2O_7$, is precipitated when the solution is heated. Allow to precipitate and settle for 30–60 min, collect the precipitate on a filter paper, and wash with a 0·1 N acetate–acetic acid buffer (pH 4·5). Dissolve the precipitate from the filter with 15–20 ml of 2 N nitric acid, wash with 30 ml of water, and boil the filtrate for 1–2 hr; pyrophosphate hydrolyses and orthophosphate is formed. Cool the solution, add 25 ml of zinc sulphate solution, adjust the solution to pH 8 with ammonia, and filter and wash the zinc ammonium phosphate precipitate. Finally ignite the precipitate to pyrophosphate (see the determination of zinc, Chapter 24.2.). Weighing form: $Zn_2P_2O_7$.

[1] C. Duval, *Inorganic Thermogravimetric Analysis*. Elsevier, Amsterdam (1953). p. 128.

Notes. (1) The first filtrate contains ortho- and metaphosphate. If zinc sulphate is added to the solution, and the solution is neutralized with ammonia to pH 8, orthophosphate is also precipitated in the form of zinc ammonium phosphate and can be determined in the form of zinc pyrophosphate by the method described in Chapter 56.2.2.

(2) Metaphosphate in the filtrate can be hydrolysed to orthophosphate by the addition of 30—50 ml of concentrated nitric acid to the solution, and boiling for 6—8 hr. After neutralisation with ammonia (pH 8), precipitate orthophosphate in the form of zinc ammonium phosphate and weigh as zinc pyrophosphate.

Procedure. (b) *Precipitation with zinc acetate:* To about 100 ml of the neutral solution of the alkali phosphates, containing not more than 0·4 g of phosphorus pentoxide, add 5–10 g of ammonium chloride. Dissolve 8 g of crystalline zinc acetate and 25 ml of glacial acetic acid in 175 ml of water, and add 30–40 ml of this precipitant to the cold solution, mix, and allow the mixture to stand for 30–60 min. Collect the precipitate on a filter paper, wash with 0·1 N acetate–acetic acid buffer, and dissolve the precipitate from the filter with 20 ml of hot 2 N sodium hydroxide solution. Wash the filter paper with 80 ml of water, neutralize the filtrate with 2 N acetic acid and add 5 ml of zinc acetate precipitant. Collect the pure zinc pyrophosphate precipitate on an A 2 porcelain filter-crucible, wash with 0·1 N acetic acid–acetate buffer and then with water, and ignite at 700–900 °C to constant weight. Cool and weigh as zinc pyrophosphate, $Zn_2P_2O_7$.

Notes. (1) This method has the advantage over the first method in that it is not necessary to control the pH, because the composition of the precipitant ensures the correct pH. This can only be attained, of course, if the original solution is neutral.

(2) In the combined filtrate orthophosphate and metaphosphate can be determined as in the above method.

56.3. DETERMINATION OF PHOSPHITE IONS (PO_3^{3-})

Phosphorous acid, H_3PO_3, in which phosphorus has the oxidation number +3, is a moderately strong dibasic acid. Alkali metal and calcium phosphites are soluble in water, but the other metal phosphites are only slightly soluble or completely insoluble in water. Aqueous solutions of phosphorous acid and phosphites are practically constant in composition and can be stored without deterioration. Phosphite can be oxidized easily to orthophosphate with elementary halogens, nitric acid, or with hypochlorite in alkaline medium. Several volumetric methods for phosphite utilize its ease of oxidation.

For gravimetric determination the mercury(I) chloride and magnesium pyrophosphate methods are the most important.

56.3.1. *Determination of phosphite ions by weighing mercury(I) chloride*
(W. Manchot and F. Steinhäuser, 1924)

In acidic solution phosphite reduces mercury(II) chloride to mercury(I) chloride, which can be collected on a filter and weighed after washing and drying.

$$H_3PO_3 + 2\,HgCl_2 + H_2O = Hg_2Cl_2 \downarrow + H_3PO_4 + 2\,HCl.$$

The formula weight of mercury(I) chloride is equivalent to the formula weight of phosphorous acid or phosphite.

$$Hg_2Cl_2 \equiv H_3PO_3 \equiv HPO_3^{2-}$$

Procedure. Prepare 50 ml of 3% mercury(II) chloride solution in a 250-ml beaker. Add 20 ml of 10% sodium acetate and 5 ml of glacial acetic acid. To this solution add the phosphite sample solution dropwise with constant stirring; 30 ml of the solution should contain about 0·1 g of phosphite. Heat the mixture on a water bath at 50 °C for 2 hr, and allow to stand overnight. Collect the mercury(I) chloride precipitate on a G 4 glass, A 1 porcelain filter-crucible or No. 4 glass texture filter funnel, and wash with 6% hydrochloric acid and then with hot water until the filtrate does not become turbid in the presence of tin(II) chloride. Dry the filter and precipitate at 100–105°C to constant weight, cool and weigh. Stoichiometric factors: $H_3PO_4/Hg_2Cl_2 = 0{\cdot}17368$, $PO_3/Hg_2Cl_2 = 0{\cdot}16727$.

Note. The precipitation becomes complete only slowly, but it can be filtered after 2 hours when great accuracy is not required. The solution containing the precipitate should not be heated above 60°C, otherwise metallic mercury may be precipitated.

56.3.2. *Determination of phosphite in the form of orthophosphate after oxidation*

Phosphite ions can be oxidized to phosphate with concentrated nitric acid. The phosphate can then be precipitated, depending on the accompanying ions present, either as magnesium ammonium phosphate or ammonium phosphomolybdate.

Procedure. To 100 ml of the phosphite solution add 5 ml of concentrated nitric acid, and evaporate on a water bath to several millilitres. Add an equal volume of concentrated nitric acid to the residue and heat for 1–2 hr. Phosphate can be precipitated from the diluted solution with magnesia mixture (Chapter 56.1.2.) or with ammonium molybdate (Chapter 56.1.1.). Stoichiometric factors: $2\ H_3PO_3/Mg_2P_2O_7 = 0{\cdot}73677$, $2\ PO_3/Mg_2P_2O_7 = 0{\cdot}70960$.

Note. Phosphorous acid or phosphites can also be oxidized with bromine water without evaporation. When this method is used, however, the phosphomolybdate method can only be applied after several evaporations with nitric acid.

56.4. DETERMINATION OF HYPOPHOSPHITE IONS ($H_2PO_2^-$)

Hypophosphorous acid, H_3PO_2, in which phosphorus has the oxidation number +1, is easily soluble in water and is a monobasic acid. Metal hypophosphites, $Me^IH_2PO_2$, are soluble in water, and the alkali hypophosphites can also be dissolved in alcohol.

56.4.1. *Separation of hypophosphites from pyrophosphate, hypophosphate and phosphate ions*

The alkaline earth hypophosphites are soluble in water, and this can be utilized to effect the separation of hypophosphite from pyrophosphate $P_2O_7^{4-}$, hypophosphate $P_2O_6^{4-}$, and phosphate PO_4^{3-} ions.

Procedure. Dilute the nearly neutral solution of alkali hypophosphite, alkali pyrophosphate, alkali hypophosphate and alkali phosphate to about 100 ml with water, add 1 ml of 5% acetic acid and 25 ml of 20% sodium acetate, and add excess cold saturated barium nitrate solution dropwise. Filter the precipitate on a filter paper by decantation, wash three times with cold water, add mercury(II) chloride to the hypophosphite in the filtrate, and weigh the equivalent amount of calomel after filtration and drying at 100–105 °C.

Notes. (1) Hypophosphite can be determined in the same way as phosphite using the mercury(I) chloride weighing form, or after conversion to orthophosphate. The determination can be carried out exactly as in the procedure described for phosphite ions. Mercury(II) chloride, however, reacts with hypophosphorous acid as in the following equation:

$$4\ HgCl_2 + H_3PO_2 + 2\ H_2O = 2\ Hg_2Cl_2 \downarrow + H_3PO_4 + 4\ HCl.$$

Thus one formula weight of hypophosphorous acid is equivalent to two formula weights of mercury (I) chloride:

$$H_3PO_2 \equiv 2\ Hg_2Cl_2.$$

(2) Several titrimetric methods are available for the determination of hypophosphite.

56.4.2. *Determination of phosphite and hypophosphite ions in the presence of each other*

(a) *Determination by extraction with alcohol:* The alkali metal salts of hypophosphorous acid are quite soluble in 96% alcohol, but the alkali metal phosphites are insoluble.

Procedure. Evaporate the mixture of the salts of the two phosphorous acids almost to dryness in a porcelain dish, add a slight excess of alcoholic potassium hydroxide solution, and evaporate to dryness. Extract the residue 6–8 times with 96% alcohol; potassium hypophosphite dissolves. Filter the alcoholic solution through a dry filter and rinse with 96% alcohol. Evaporate the alcohol and titrate the residue iodometrically, or boil with concentrated nitric acid and determine the phosphate formed gravimetrically.

Take a second sample of the original material and determine the total phosphorus content after oxidation with nitric acid. From the two results the H_3PO_2 and H_3PO_3 content of the sample can be calculated.

(b) *Indirect determination:* Oxidize part of the sample by evaporation several times with concentrated nitric acid. Weigh the orthophosphate in the form of $Mg_2P_2O_7$ (see Chapter 56.1.2.).

In a second part of the sample reduce an excess of mercury(II) chloride, according to the procedure described for the determination of phosphite, and weigh the calomel formed (see Chapter 56.3.1.). The results can be calculated as in the following example:

Weight of $Mg_2P_2O_7$ precipitate: p
Weight of Hg_2Cl_2 precipitate: q
$H_3PO_2 = q \cdot 0{\cdot}1339 - p \cdot 0{\cdot}5933$
$H_3PO_3 = p \cdot 1{\cdot}4738 - q \cdot 0{\cdot}1738$

56.5. DETERMINATION OF HYPOPHOSPHATE IONS ($P_2O_6^{4-}$)

When an aqueous solution of hypophosphoric acid or an acidic solution of hypophosphate is boiled, phosphoric and phosphorous acids are formed owing to hydrolysis:

$$H_4P_2O_6 + H_2O = H_3PO_4 + H_3PO_3.$$

The decomposition takes place even in crystalline hypophosphoric acid owing to its crystalline water content. Each hydrogen atom of the tetrabasic hypophosphoric acid can be replaced by metals, and therefore it forms salts of various compositions. Except for the alkali metal hypophosphates, all of its salts are difficult to dissolve in water. The salts decompose when heated. Hypophosphoric acid is a weak reducing agent.

When no other anions containing phosphorus are present apart from hypophosphate, it is advisable to boil the solution with concentrated nitric acid and oxidize hypophosphate ions to orthophosphate ions, which can then be weighed as magnesium pyrophosphate. When other cations apart from alkali metal or ammonium ions are also present, orthophosphate ions must first be precipitated in the form of ammonium phosphomolybdate.

The most characteristic gravimetric method for the determination of hypophosphate is based on the insolubility of silver hypophosphate. Silver hypophosphate, however, decomposes easily on drying and is not suitable as a weighing form. After washing, therefore, the precipitate must be dissolved in ammonia and the silver precipitated in the form of silver chloride and weighed.

Procedure according to J. Probst (1929).[1] To 100–150 ml of the neutral solution, or a solution which has been neutralized with sodium bicarbonate, and contains about 0·5 g $Na_2H_2P_2O_6 \cdot 6\,H_2O$, add excess 0·1 N silver nitrate solution with constant stirring. Allow the mixture to stand for 4–12 hours in the dark, and filter on a filter paper. Wash the precipitate by decantation with hot water until the washings fail to give a precipitate with hydrochloric acid. Ensure that only a small amount of the precipitate is transferred to the filter. Dissolve the precipitate from the filter with hot 15% ammonia into the original beaker. Dilute the solution with water, add sufficient nitric acid just to redissolve the precipitate which is formed intermediately, and add a slight excess of diluted hydrochloric acid with constant stirring. Collect the silver chloride precipitate on a weighed filter, wash with diluted acetic acid, dry at 130°C, cool and weigh (see Chapter 5.1.). Stoichiometric factor: $P_2O_6/4\,AgCl = 0{\cdot}27549$.

Notes. (1) Phosphites interfere because they slowly reduce silver ions to the metal.

(2) Silver hypophosphate, $Ag_4P_2O_6$, can also be precipitated from slightly acidic, sulphuric acid solution (pH 2); under these conditions orthophosphate does not form a precipitate with silver ions. This effects the separation of *hypophosphate* and *orthophosphate* ions.

[1] J. Probst, *Z. anorg. Chem.* **179**, 155 (1929).

56.5.1. *Separation of hypophosphate ($P_2O_6^{4-}$) and orthophosphate (PO_4^{3-}) ions*

Dilute the solution of the alkali metal salts of the two phosphoric acids to about 100 ml, and add sufficient sodium bisulphate to make the pH of the solution 2. To the cold solution add excess 0·1 N silver nitrate solution dropwise with constant stirring. Filter the precipitate through a fine filter. Wash the precipitate 4–5 times with 1% sodium bisulphate solution, and then dissolve it in a small volume of hot 15% ammonia. The remaining procedure is then as in the above method. $4\,AgCl \rightarrow P_2O_6^{4-}$.

Acidify the filtrate with nitric acid and precipitate the excess silver with sodium chloride solution. Remove the precipitate by filtration, and determine orthophosphate in the filtrate as magnesium pyrophosphate (see Chapter 56.1.2.).

Separation of phosphorus compounds

Excluding the separations mentioned in Chapter 56.1.2. in connection with the precipitation of phosphate in the form of magnesium ammonium phosphate, the following important separations must be mentioned.

56.6. PO_4^{3-} — Cu, Cd, Al, Fe(III), Cr(III), Ni, Co, Mn, Zn, Ca, Sr, Ba, Mg and alkali metal ions

Separation by precipitation in the form of ammonium phosphomolybdate (see Chapter 56.1.1.). The possibility of the interference of ammonium molybdate in the filtrate on further procedures must be taken into consideration.

56.7. PO_4^{3-} — As

The separation can be carried out (a) by distillation of arsenic(III) chloride by the method described in Chapter 11.6; (b) by extraction of arsenic(III) chloride with carbon tetrachloride by the method of F. Fischer and W. Harre (see procedures of Chapter 11.8.), or (c) by precipitation of arsenic(V) sulphide with hydrogen sulphide from 6 N hydrochloric acid solution according to F. Neher (see Chapter 11.2.).

Remove excess hydrochloric acid from the residue or filtrate by evaporation, and precipitate $MgNH_4PO_4 \cdot 6\,H_2O$ with magnesia mixture in ammoniacal medium. Purify the precipitate by repeated precipitation after dissolution in hydrochloric acid. Weighing form: $Mg_2P_2O_7$.

56.8. PO_4^{3-} — from heavy metal cations with 8-hydroxyquinoline (R. Berg, 1925 and S. Ishimaru, 1935)[1]

The single heavy metal ions can be precipitated with 8-hydroxyquinoline after suitable adjustment of pH in the form of their oxinates, even in the presence of phosphate ions. The separation can be carried out in acetic

[1] R. Berg, *Das o-Oxychinolin, "Oxin"*. Enke, Stuttgart (1925), p. 42; S. Ishimaru, *J. Chem. Soc. Japan* **56**, 62 (1935).

acid solution for the following metal ions: Cu (Chapter 8.7.), Cd (Chapter 10.7.), Ni (Chapter 22.5.), Co (Chapter 23.7.), Zn (Chapter 24.5.) and Mn (Chapter 24.26.b.).

Determination of PO_4^{3-} in the filtrate from the oxine precipitation. (a) Small amounts of phosphate less than 10 mg of P_2O_5 can also be precipitated in the form of oxinium-24-molybdo-2-phosphate, according to the procedure of Chapter 19.46.6. Weighing form: $Ox_3 \cdot H_7[P(Mo_2O_7)_6] \cdot 2\,H_2O$.

(b) When the strongly ammoniacal solution is evaporated, the excess 8-hydroxyquinoline is usually volatilized without residue. It is advisable, however, to repeat the evaporation with concentrated ammonia.

(c) In neutral or acidic solution the excess 8-hydroxyquinoline can be destroyed by boiling with a mixture of concentrated nitric acid and hydrogen peroxide, and by evaporation. The addition of nitric acid and hydrogen peroxide, as well as the evaporation, must be carried out several times.

In (b) and (c) the phosphate content of the oxine-free residue can be determined in the form of magnesium ammonium phosphate or ammonium phosphomolybdate.

56.9. PO_4^{3-} — from cations of groups I and II with hydrogen sulphide

Procedure. The solution of the cations must be 1–2 N in hydrochloric or 2 N in sulphuric acid. Pass gaseous hydrogen sulphide into the hot solution until it is cool. Dilute the solution to 2–3 times its volume, and repeat the saturation with hydrogen sulphide. Collect the precipitate on a filter paper, and wash with hot, diluted sulphuric acid saturated with hydrogen sulphide. Remove hydrogen sulphide from the filtrate by boiling, and precipitate $MgNH_4PO_4 \cdot 6\,H_2O$ with magnesia mixture (see Chapter 56.1.2.). Dissolve the precipitate in hydrochloric acid and repeat the precipitation. Ignite the precipitate to $Mg_2P_2O_7$.

Note. In the presence of insoluble tin(IV) salts this separation cannot be carried out. Similar difficulties arise in the analysis of phosphorbronzes and phosphorus tin alloys. For these materials the finely divided or cut sample must be fused by the Freiberg method (Chapter 2.5.7.).

Leach the fusion melt with water, and remove the insoluble sulphides (CuS, PbS, FeS) by filtration. Add potassium cyanide solution until the solution is decolourized; polysulphides are decomposed. Acidify the solution in a well-ventilated fume-cupboard with sulphuric acid; tin(IV) sulphide is precipitated and phosphoric acid remains in solution.

56.10. PO_4^{3-} — from Fe, Co, Ni, Zn and Mn ions with ammonium sulphide

Procedure. Saturate the strongly acidic solution with gaseous hydrogen sulphide; iron(III) ions are reduced and sulphur is formed. Make the solution alkaline with ammonia and saturate again with hydrogen sulphide. Precipitate $MgNH_4PO_4 \cdot 6\,H_2O$ from the filtrate from the sulphides without destroying ammonium sulphide. Dissolve the precipitate in hydrochloric acid, repeat the precipitation with ammonia in the presence of a small amount of magnesia mixture. Weighing form: $Mg_2P_2O_7$.

56.11. PO_4^{3-} — Al

(a) Separation by precipitation in the form of ammonium phosphomolybdate according to Woy. See Chapters 19.46. and 56.1.1. (b) Separation by precipitation of aluminium oxinate from ammoniacal ammonium tartrate solution according to Berg (1927). See Chapter 19.2.2. (c) Separation by precipitation of aluminium oxinate from slightly alkaline sodium hydroxide solution according to G. Balanescu and M. D. Motzoc (1932)[1] (see Chapter 19.2.). (d) Separation on ion exchange resin according to Samuelson (see Chapter 20.26.).

56.12. PO_4^{3-} — Fe(III)

(a) Separation according to Woy by repeated precipitation of ammonium phosphomolybdate using the procedure of Chapter 20.25. (b) Separation by precipitation of oxinium-24-molybdo-2-phosphate according to Chapter 20.25.b. (c) Separation by precipitation of iron(III) oxinate as described in Chapters 20.25.b. and c. (d) Separation on ion exchange resin as in Chapter 20.26.

56.13. PO_4^{3-} — Cr(III)

(a) Separation by precipitation of ammonium phosphomolybdate according to Woy. See Chapters 21.14. and 56.1.1. (b) Separation by ion exchange as in Chapter 21.15. (c) Separation by the precipitation of magnesium ammonium phosphate in the presence of disodium ethylenediaminetetraacetate according to the procedure in Chapter 56.1.2. (d) Oxidize Cr(III) ions to chromate in ammoniacal medium with hydrogen peroxide, and precipitate phosphate as magnesium ammonium phosphate (Chapter 56.1.2.).

56.14. PO_4^{3-} — Zn

(a) Separation by precipitation of zinc sulphide in acidic medium as described in Chapter 24.1.2. (b) Separation by precipitation of ammonium phosphomolybdate according to Woy (Chapter 56.1.1.). (c) Separation by precipitation of zinc quinaldinate according to Chapter 24.7. (d) Separation with 8-hydroxyquinoline according to Berg in acetic acid solution, as described in Chapter 24.5.

56.15. PO_4^{3-} — Ti(IV)

See the separation of Ti(IV)–PO_4^{3-}, Chapter 26.13.

56.16. PO_4^{3-} — Zr

Separation by fusion with sodium carbonate or sodium hydroxide as described in Chapters 27.6. and 27.7. Samples containing silicic acid must first be evaporated with sulphuric acid and hydrogen fluoride, and the residue fused with sodium carbonate. The fusion with sodium carbonate must be repeated at least twice.

[1] G. Balanescu and M. D. Motzoc, *Z. anal. Chem.* **91**, 188 (1932).

In the determination of zirconium with cupferron or phenylarsonic acid small amounts of phosphoric acid do not interfere when the precipitation is effected in the presence of 10% by volume of sulphuric acid.

56.17. PO_4^{3-} — Mo(VI) Separation with 8-hydroxyquinoline

(according to G. Balanescu, 1931)

Precipitation of Mo(VI). To 150 ml of the nearly neutral solution, containing not more than 100 mg of molybdenum trioxide and 100 mg of phosphorus pentoxide, add 5 g of ammonium acetate and 20 ml of glacial acetic acid. Heat to boiling. Add a slight excess of a solution of 3% oxine acetate to the solution, with constant stirring after removing the source of heat. *(Oxine acetate precipitant:* 3 g of 8-hydroxyquinoline dissolved in 100 ml of 4 N acetic acid.) Boil and stir the mixture for 2–3 min., allow to settle, and filter on a G 4 glass filter-crucible. Wash with hot water. Dry the precipitate at 130–140 °C to constant weight, cool and weigh. Weighing form: $MoO_2(C_9H_6ON)_2$. Stoichiometric factor: $Mo/MoO_2(Ox)_2 = 0{\cdot}23050$.

Determination of phosphate in the filtrate. Destroy the organic material in the filtrate (concentrated HNO_3 + concentrated H_2O_2), and precipitate phosphate in ammoniacal medium with magnesia mixture (Chapter 56.1.2.). Weighing form: $Mg_2P_2O_7$.

56.18. PO_4^{3-} — W(VI)

(a) Separation by precipitation of magnesium ammonium phosphate in ammoniacal solution. See Chapters 32.8. and 56.1.2. (b) Separation by precipitation of tungsten oxinate, according to the procedure of Chapter 32.4.

56.19. PO_4^{3-} — V(V)

(a) Separation with cupferron according to the procedure of Chapter 33.3. (b) Separation with 8-hydroxyquinoline by precipitation of vanadium oxinate according to Chapter 33.4.

56.20. PO_4^{3-} — U(VI)

(a) Separation by precipitation of the uranium(IV) cupferronate according to the prescriptions of Chapter 34.6. (b) Separation with 8-hydroxyquinoline according to R. Berg:

Dissolve the uranyl phosphate precipitate with ammonium carbonate, dilute to 200 ml, and acidify with 6 N acetic acid to the methyl red colour change. Heat the solution to boiling, and precipitate uranyl oxinate with 4% oxine acetate reagent. The procedure is then as described in Chapter 37.4.

The separation can also be carried out in the form of uranyl oxinate in the presence of disodium ethylenediaminetetraacetate, as described in Chapter 34.8.

56.21. PO_4^{3-} — Th and rare earths

See the separation of Th, RE–PO_4^{3-}, Chapter 28.21.

56.22. PO_4^{3-} — Ca

See the separation of Ca–PO_4^{3-}, Chapter 39.14. See also procedures of Chapters 39.1.8. and 56.1.1.

56.23. PO_4^{3-} — Sr

See the separation of Sr–PO_4^{3-}, in Chapters 40.14. and 56.1.1.

56.24. PO_4^{3-} — Ba

See the separation of Ba–PO_4^{3-} in Chapters 41.13. and 56.1.1.

56.25. PO_4^{3-} — Mg

See the separation of Mg–PO_4^{3-} in Chapters 42.14. and 56.1.1.

56.26. PO_4^{3-} — F^-

(a) Separation according to H. Rose and A. Koch (1904). From the accurately neutralized solution phosphate can be precipitated in the form of silver phosphate, and the solution can be filtered. Fluoride ions are present in the filtrate. The detailed procedure is described in Chapter 51.0.2.

(b) *Procedure.* Make 100–150 ml of the slightly acidic solution of phosphate and fluoride alkaline with sodium hydroxide in the presence of phenolphthalein, and add about 1 g of freshly precipitated cadmium hydroxide. Boil the mixture for 30 minutes. Phosphate is adsorbed on the precipitate together with any silicate present. Collect the precipitate on filter paper and wash 4–5 times with hot water. Dissolve the cadmium hydroxide-cadmium phosphate precipitate from the filter with 10–15 ml of hot 2 N nitric acid, and wash the filter paper with water containing nitric acid. Precipitate phosphate from the solution in the form of ammonium phosphomolybdate according to the method of Woy (Chapter 56.1.1.).

Notes. (1) Fluoride ions can be determined in the filtrate in the form of calcium fluoride (Chapter 51.1.) or lead chlorofluoride (Chapter 51.2.).

(2) Silicic acid can be dehydrated from the cadmium hydroxide precipitate by several evaporations with hydrochloric acid, and can then be removed by filtration.

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to Table 56.1.

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CHAPTER 57

CARBON — C — 12·011

C, CO, CO_2, H_2CO_3

ELEMENTARY carbon occurs naturally in crystalline form as graphite and diamond, and in amorphous form (more precisely mesomorphous) in coal. Graphite is also made artificially and is used for the manufacture of crucibles, electrodes, arc-lamp carbons and pencils. Considerable amounts of suspended graphite are now used for the lubrication of crucibles at high pressures. Pure graphite is also used in atomic reactors. High grade diamond is polished and used in jewellery, while the low quality material is used in the production of industrial boring and cutting instruments (glass cutters).

Mineral coal is used as fuel or for gas production. The product of the dry distillation of coal, coke, is a very useful metallurgical reducing agent. Mineral coals and their distillation products are important raw materials in the chemical industry.

Carbon monoxide, formed on incomplete combustion of carbon and carbon compounds, is found in almost all fuel gases. Owing to its high heat of combustion and its reducing properties, large amounts of carbon monoxide are produced industrially, usually mixed with other gases. Thus in generator gases it is mixed with nitrogen, and in synthesis gas and water gas it is mixed with hydrogen.

Carbon dioxide is formed on complete combustion of coal and substances containing carbon. Carbon dioxide is a component of the atmosphere (0·35–0·40%). In closed rooms and working places the carbon dioxide content of air may increase considerably owing to expiration. Aspiration becomes difficult in air which contains 3–4% of carbon dioxide. The carbon dioxide content of the air in mines and metallurgical plants often attains this concentration; mine lamps are extinguished and matches cannot be ignited. Large amounts of carbon dioxide are also found in the gases from some gas and oil wells. The carbon dioxide content of soil air and soil waters is also considerable. At 0°C, 1 volume of water dissolves about 1·80 volumes of carbon dioxide. Part of the dissolved carbon dioxide is converted to carbonic acid (H_2CO_3). Its salts, the carbonates, occur widely in nature. Calcite or limestone ($CaCO_3$), and dolomite [$CaMg(CO_3)_2$] are abundant in rock-formation. Some rocks also contain large amounts of magnesite ($MgCO_3$). Calcium and magnesium bicarbonates are always present in natural waters. The water loses part of its carbon dioxide on heating, and calcium and

magnesium carbonates are precipitated (boiler stone). Calcium and magnesium bicarbonate account for the so-called "temporary hardness" of water.

Carbon is the most important element in organic substances and living organisms. Mineral oil, all natural organic substances, tissues of living organisms and their products consist of widely different carbon compounds. The synthetic carbon compounds, produced by the organic chemical industry, are also very important.

Carbon dioxide can be removed quite easily from analytical samples containing carbonate by heating or by treatment with strong acids, and can be determined easily by gravimetric or other analytical methods. Other carbon compounds, or coals, can be combusted completely by heating in air or a current of oxygen with chromic acid; the carbon dioxide formed during the process can be determined by similar methods. Most methods for the determination of carbon in coals and carbon compounds are based on the determination of carbon dioxide. Carbon dioxide can be determined gravimetrically after absorption of the dry gas in a suitable vessel filled with potassium hydroxide solution, or with a solid porous substance containing sodium hydroxide (soda lime, soda asbestos). The strongly alkaline substance present absorbs carbon dioxide, and therefore from the weight increase of the vessel the carbon dioxide content of the gas passed through it can be calculated.

The water vapour present in the gas interferes in the determination of carbon dioxide by this method because the absorbents are very hygroscopic. The gas must therefore be dried before absorption in a hygroscopic substance [$CaCl_2$, $Mg(ClO_4)_2$, P_2O_5], and should be passed through a tube filled with the drying agent. All acidic gases also interfere in the determination of carbon dioxide by absorption.

Hydrochloric acid and hydrogen sulphide can be removed with anhydrous copper(II) sulphate. When carbonates are decomposed with hydrochloric acid, the removal of hydrogen chloride can be avoided by fitting the decomposition vessel with a reflux condenser. Water which collects in the condenser dissolves the gaseous hydrogen chloride. The evolution of hydrogen sulphide can be avoided by the use of acids which also contain chromic acid for the decomposition, or by the addition of mercury(II) chloride to the solution. The hydrogen sulphide is oxidized to sulphuric acid when chromic acid is present, or is retained as acid-insoluble mercury(II) sulphide when mercury(II) chloride is added.

Sulphur dioxide can be retained using a mixture containing chromic acid and concentrated sulphuric acid. Sulphur dioxide present in the gas bubbling through this solution is oxidized to sulphate by the chromic acid, and remains behind in the vessel. When the carbonate contains reducing contaminants, the formation of sulphur dioxide during the decomposition can be avoided by the addition of chromic acid to the acidic solution.

57.1. DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC SUBSTANCES BY COMBUSTION

(according to Liebig)

It is often necessary to determine the carbon and hydrogen content of organic substances. The combustion must be carried out in a heat-resistant (Supremax) tube 80 cm in length and 12–16 mm in diameter which can be heated to 800°C. The tube must be filled with material which will effect the complete combustion of the carbon content of the organic substance to carbon dioxide, and the combustion of hydrogen to water. A granular copper(II) oxide filling is quite suitable, and can be produced by the oxidation of copper wire 0·5 mm in diameter. When organic compounds con-

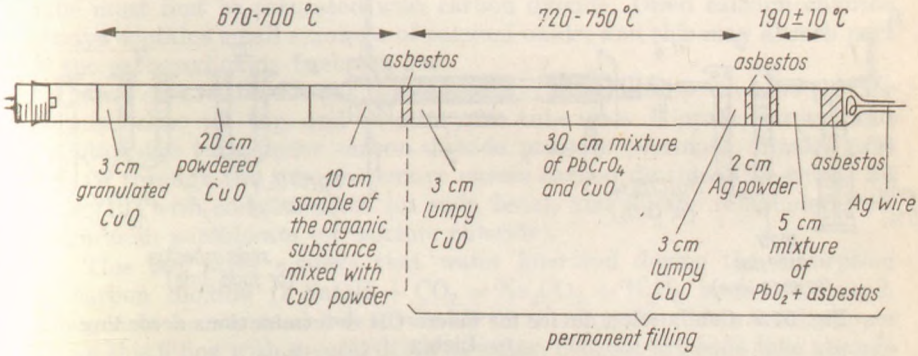


Fig. 57.1. Universal tube filling for macro CH determinations according to Liebig in compounds containing halogen, sulphur and nitrogen

taining nitrogen, halogens and sulphur are combusted, however, nitrogen oxides, elementary halogens and sulphur dioxide are also formed using this filling. Under these conditions, therefore, a universal filling which prevents the formation of acidic gases must be used. The composition of a universal tube filling is shown in Fig. 57.1.

A silver wire mounted into the drawn end of the tube ensures, by its good conductivity, that no traces of water condense in this part of the tube. A lead dioxide filling, which must be kept at about 190°C during the determination by heating a copper or aluminium block surrounding this part of the tube, absorbs nitrogen oxides. If great accuracy is not required this filling may be omitted. The lead chromate ensures the complete combustion of organic vapours, and at the same time absorbs halogens and sulphur. The lead chromate layer is held between two thin copper oxide layers, and the whole filling is held at each end by thin layers of asbestos.

The organic substance to be determined must be weighed by difference into a spherical flask, mixed with sufficient ignited and cooled copper oxide powder to fill a 10-cm length of the tube, and packed into the tube through

a smooth-surface copper funnel. The mixing flask must be rinsed with several portions of powdered copper oxide until a 30-cm layer of copper oxide is packed into the tube. Finally the layer must be held secure with a 3-cm layer of coarse copper oxide.

After the preparation of the tube filling, the combustion apparatus must be assembled (see Fig. 57.2.). Oxygen must be used for the combustion, and air to rinse through the combustion products. Both can be stored in 5–10 litre reservoirs. The two-way stop-cock (1) is used to pass oxygen or air into the apparatus. The sweep gases are washed by a 50% potassium hydroxide solution in the washing bottle (2) to remove any carbon dioxide present. The left side of the large U-tube (3) is filled with

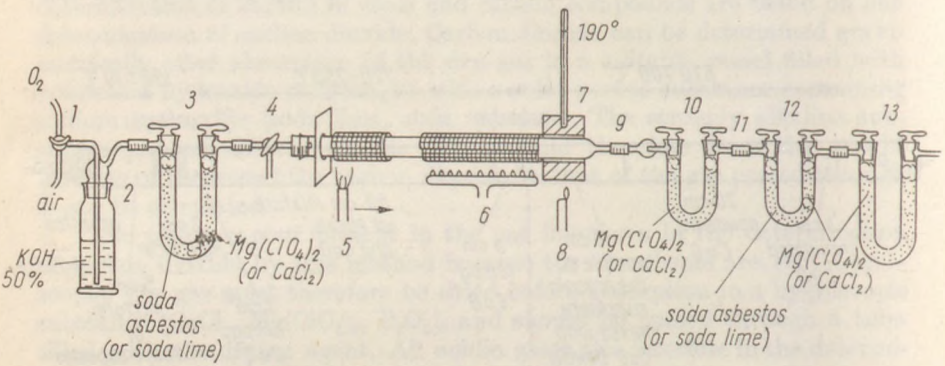


Fig. 57.2. Combustion device for macro CH determinations according to Liebig

soda asbestos (or soda lime), while the right side should be filled with magnesium perchlorate (or anhydrous $CaCl_2$). This tube absorbs the last traces of any carbon dioxide, and thoroughly dries the gas. The filling of this tube must be changed at the same time as the fillings of tubes (10) and (12).

The copper or aluminium block (7), mounted on the end of the combustion tube, must be heated to 190 $\pm$ 10°C with an easily controlled microburner, and care must be taken to ensure that the temperature remains within these limits during the combustion. The permanent filling must be heated to 720–750°C by a series of burners (6), or better by a regulated electric furnace. The substance to be determined must be distilled into the permanent filling by the moving burner (5) or electric furnace. The part of the tube containing the sample must be heated slowly and the burner moved gradually towards the permanent filling. The combustion tube is connected by a vacuum rubber tube (9) to the absorption tube (10) which absorbs the water. The rubber connections (9) and (11) are the most sensitive parts of the apparatus. Carbon dioxide diffuses through the rubber very easily and losses may occur. This error can be overcome by connecting the

combustion tube and the absorption tubes (10, 12) so that the glass of each is in contact within the rubber.

For the connection of the tubes thick-walled rubber vacuum tubing prepared in paraffin or vaseline melted on a water bath must be used. It is advisable to carry out the preparation in a spherical flask and maintain a vacuum above the paraffin with a water pump. After about 30 min air is completely removed from the rubber, bubbling ceases, and when the vacuum is cut off, paraffin passes into the pores of the rubber. After cooling, the paraffin must be cleaned from the rubber.

The absorption tube (10) is filled with dried magnesium perchlorate or calcium chloride and serves to absorb the water. The weight increase of this tube is equal to the water formed on combustion of the hydrogen in the organic compound. The tube must always be filled with the same drying substance as in the second half of the U-tube (3). Drying tube (3) then does not give up water to absorption tube (10). If calcium chloride is used the tube must first be saturated with carbon dioxide. Dried calcium chloride always contains small amounts of calcium oxide, and this may absorb part of the carbon dioxide from the gas.

Pass carbon dioxide gas through the prepared absorption tube (10) for 10 min, close its tap, and connect the tube to a Kipps apparatus and maintain the tube under carbon dioxide pressure overnight. Finally pass dry air through the tube to remove excess carbon dioxide. Two-thirds fill tube (12) with soda asbestos (or soda lime), and fill the remainder with magnesium perchlorate (or calcium chloride).

This last layer ensures that water liberated during the absorption of carbon dioxide ($2\,NaOH + CO_2 = Na_2CO_3 + H_2O$) is not removed. When soda lime is used it is advisable to moisten the cotton wool stopper above this filling with several drops of water, because dry soda lime absorbs carbon dioxide very slowly. The drying tube (13) prevents the take- up of moisture into the absorption tubes from the air.

Combustion. Assemble the apparatus. Open the tap of the oxygen reservoir and adjust the rate of flow of gas so that 2 bubbles/sec pass into the bubbler. Heat the permanent filling to about 700 °C in 20 min. The metal block surrounding the lead dioxide filling must be heated to 190 °C at the same time. Then heat the left side of the tube with a moving burner or furnace towards the permanent filling. During this time the combustion of the organic substance begins, and is combined with expansion. This can be observed by the fact that the number of bubbles in bubbler (2) decreases temporarily. The furnace must be moved further towards the sample when the number of bubbles again attains the original value. The combustion of the substance becomes complete in about 40–60 min. Heat from the left side of the tube with the moving furnace again for 30 min, and then pass air through the tube for 30 min to flush the combustion products into the absorption vessel. Remove the absorption tubes slowly from the apparatus, and place them in the balance case for 30 min. Open the taps for a moment after the temperatures have been equalized, and weigh the tubes. During this time stop the heating of the ignition tube and allow the filling to cool in an air stream.

The percentage of carbon and hydrogen in the sample can be calculated as follows:

$$\%\,C = \frac{g\ CO_2}{g\ \text{sample weight}} \cdot \frac{1200}{44}$$

$$\%\,H = \frac{g\ H_2O}{g\ \text{sample weight}} \cdot \frac{201{\cdot}6}{18{\cdot}016}.$$

Notes. (1) During the handling and weighing of the absorption tubes the precautions described in Chapter 57.2. should be observed.

(2) The part of the tube filled with the lead chromate should not be heated to too high a temperature as lead chromate melts at 844°C. It is advisable, instead of pure lead chromate, to use granular copper(II) oxide which has been heated on an iron plate to red heat and has had lead chromate thrown on it. Molten lead chromate coats the copper oxide surface. After cooling, grind the material in a mortar, and sieve the powder.

(3) When the substance to be determined does not contain large amounts of halogens, sulphur and nitrogen, coarse ground copper oxide held between asbestos layers can be used as the permanent filling.

When the substance to be determined contains only halogens, carbon and hydrogen, a silver gauze can be placed at the end of the above copper oxide filling. The silver gauze should be rolled into an 8-cm cylinder. Neither a lead dioxide nor a lead chromate filling is then required.

(4) Liebig's combustion method gives good results when the combustion is carried out slowly. The determination therefore takes a long time. The C and H determination can be carried out much more rapidly by the microanalytical method of Pregl. By this method, which requires good technique and a sensitive microbalance, one determination with 3–4 mg samples can be completed in 35–50 min.

References for the determination of carbon in organic compounds:

J. Liebig, *Anleitung zur Analyse organischer Köper.* 2 Ed. (1853), p. 55; Reisehauer, *Z. anal. Chem.* **2**, 197 (1863); E. Erlenmeyer, *Z. anal. Chem.* **6**, 110 (1867); J. Löwe, *Z. anal. Chem.* **9**, 216 (1871); C. R. Fresenius, *Anleitung zur quantitativen chemischen Analyse.* II. 6 Ed. Vieweg, Braunschweig, (1901), p. 10; F. Pregl and H. Roth, *Quantitative organische Mikroanalyse.* 6 Ed. Springer, Wien (1949), p. 16.

57.2. DETERMINATION OF CARBONATES

The carbon dioxide liberated from carbonates by heating or treatment with acids can be measured by two methods: (1) *By direct weighing.* Carbon dioxide must be expelled with a rinsing gas (air, H_2, N_2, O_2) into an alkaline absorbing solution, and the weight increase of the absorption vessel determined. The increase in weight is equal to the weight of the carbon dioxide. (2) *By measurement of weight loss.* Carbonate is decomposed in a suitable vessel, weighed before decomposition, and after the removal of carbon dioxide the weight of the apparatus again determined. The weight loss is equal to the amount of carbon dioxide removed. Both methods yield quite accurate results. The first method, however, is somewhat slow and yields good results usually when the amount of carbonate in the sample is low. The second method is best applied to carbonate-rich samples.

Determination of carbonates by direct weighing. For the decomposition of carbonates, hydrochloric acid less concentrated than 20%, diluted perchloric acid or syrupy (about 80%) phosphoric acid can be used. In the presence of chlorides, or if hydrochloric acid is used, a decomposition flask fitted with a reflux condenser must be used. In the presence of sulphides and sulphites, phosphoric acid which contains 3–4 g of chromic acid (CrO_3) must be used to decompose the carbonate. The use of concentrated phos-

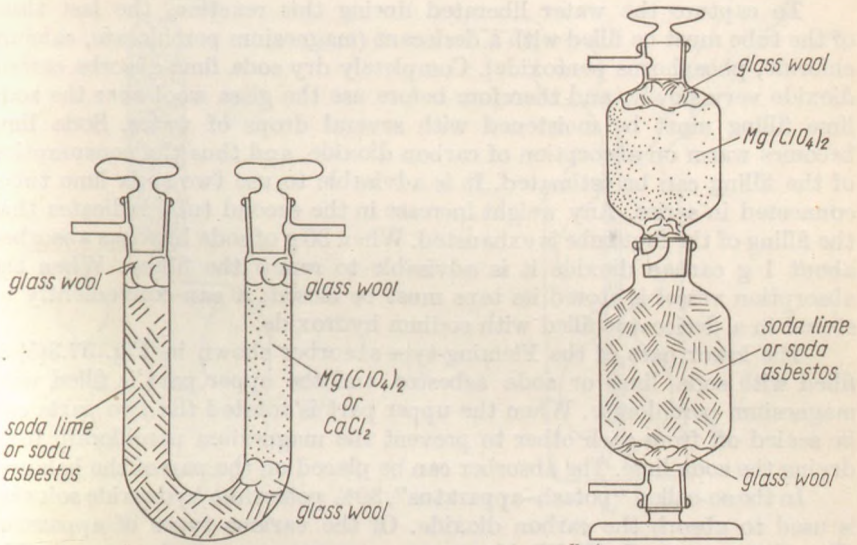


Fig. 57.3. (a) Absorption U-shaped tube for determination of carbon dioxide, (b) carbon dioxide absorber according to Fleming

phoric acid is also advantageous because it does not contain volatile componentts, and no volatile component is formed during the decomposition.

Absorption tubes and apparatus. Part of the absorbents serve for the absorption of the hydrogen chloride or hydrogen sulphide content of the gas, and to absorb moisture. These absorbents therefore serve for the purification of the gas. The other absorbents serve for the absorption of carbon dioxide. For both purposes both solid and liquid absorbents can be used, and according to this the absorption vessels can have various shapes and structures. For solid absorbents U-shaped tubes with taps can be most conveniently used.

Absorbents for carbon dioxide. Figures 57.3(a) and (b) show the absorption apparatus used for the absorption of carbon dioxide. The size of the U-shaped tube shown in Fig. 57.3(a) must be such that the tube can be suspended on a balance with a wire. The weight of the filled tube should not exceed 70 g, i.e. it should not approach the loading limit of the balance. The grain size of the absorbent should be between 1–3 mm to ensure that it has a high active surface. Powdered material, however, must be removed by sieving

as it may easily block the tube and the gas may carry away some of the powder. Soda lime (CaO moistened with NaOH solution), soda asbestos (Askarite) or soda lime asbestos (Carbosorb) can be used to absorb the carbon dioxide. The active part of each absorbent is sodium hydroxide, which reacts with carbon dioxide according to the following equation:

$$CO_2 + 2\,NaOH = Na_2CO_3 + H_2O.$$

To capture the water liberated during this reaction, the last third of the tube must be filled with a desiccant (magnesium perchlorate, calcium chloride, phosphorus pentoxide). Completely dry soda lime absorbs carbon dioxide very slowly, and therefore before use the glass wool over the soda lime filling must be moistened with several drops of water. Soda lime becomes warm on absorption of carbon dioxide, and thus the consumption of the filling can be estimated. It is advisable to use two soda lime tubes connected in series. Any weight increase in the second tube indicates that the filling of the first tube is exhausted. When 30 g of soda lime has absorbed about 1 g carbon dioxide it is advisable to renew the filling. When the absorption vessel is stored its taps must be closed; it can conveniently be stored in a desiccator filled with sodium hydroxide.

The lower part of the Fleming-type absorber shown in Fig. 57.3(*b*) is filled with soda lime or soda asbestos and the upper part is filled with magnesium perchlorate. When the upper part is rotated the two parts can be sealed off from each other to prevent the magnesium perchlorate from drying the soda lime. The absorber can be placed on the pan of the balance.

In the so-called "potash–apparatus", 30% potassium hydroxide solution is used to absorb the carbon dioxide. Of the various types of apparatus (Fig. 57.4.(a–c) the L. W. Winkler type apparatus proves to be very good in practice (Fig. 57.4.(a.). The lower vessel of the apparatus has a volume of about 30 ml, and the drying tube is about 10 cm high and has an internal diameter of 15–18 mm. The complete weight of the apparatus when full should not be more than 70 g, and therefore the vessel must be made from thin glass. The lower vessel of the apparatus is filled with 30% sodium hydroxide, and sodium hydroxide pellets must be placed in the upper drying tube. Potassium hydroxide is suitable for the absorption of carbon dioxide, because the potassium carbonate formed is quite soluble in alkalies, while sodium carbonate is not soluble. For drying, however, solid sodium hydroxide is very suitable. The apparatus can be weighed by placing it on the pan of a balance.

Before the weighing of the soda lime tube or the potash apparatus the surface of the vessel must be dried by rubbing it with a moist flannel-cloth or deerskin, and before weighing the vessels must be allowed to stand in the box of the balance for at least half an hour to allow the moisture on the surface to equilibrate with that of the atmosphere (see handling of $CaCl_2$ tubes in water determinations, Chapter 4.6.). Before weighing the taps must be opened for an instant to equalize the pressures.

The purpose of the drying absorbents is to absorb the moisture from gases containing carbon dioxide. These absorbents must not be weighed

in the carbon dioxide determination of carbonates. Any of the drying substances used for the direct moisture determination can be used (see Chapter 4.6.). The cheapest drying agent is anhydrous calcium chloride. This must be dried before use in a large porcelain dish at 180°C, and the melt cooled and broken in a mortar to 1–3 mm grain size. The powdered material must

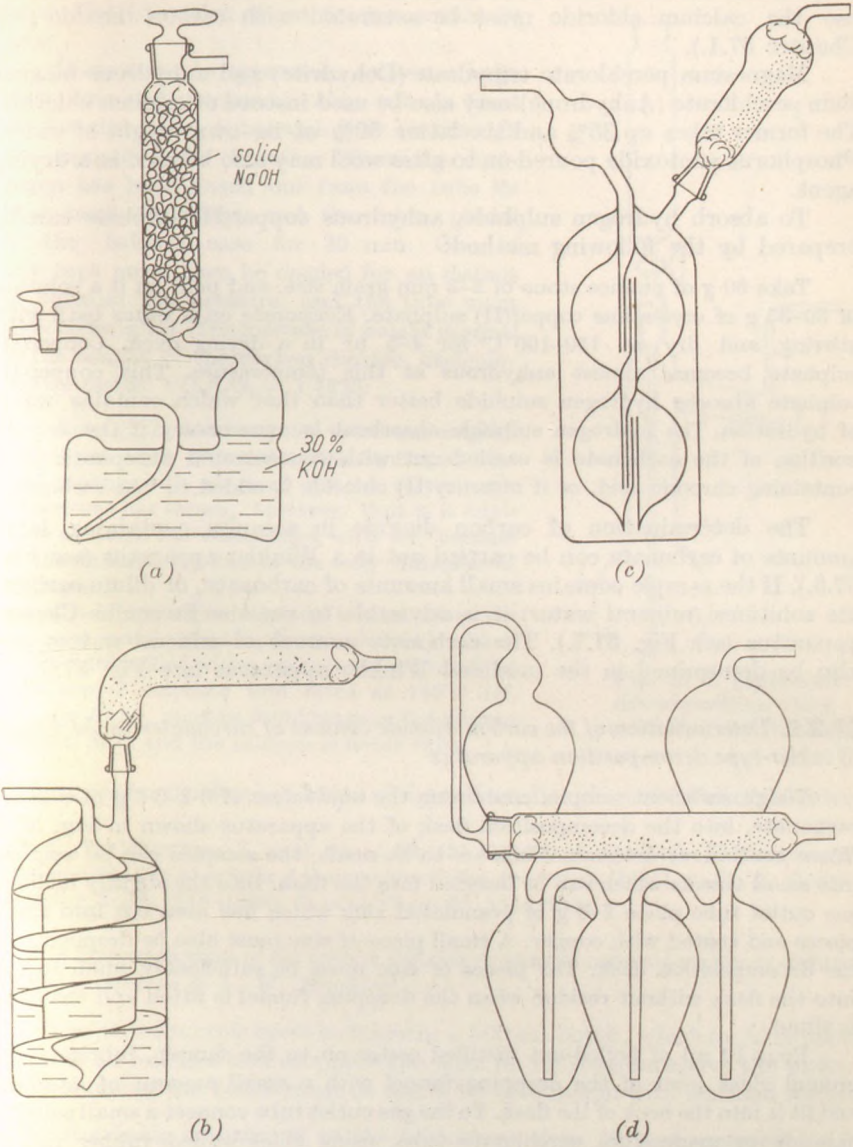


Fig. 57.4. (a) Potassium hydroxide apparatus according to Winkler, (b) and (c) other potassium hydroxide apparatus, (d) potassium apparatus according to Geissler

then be sieved out. It is advisable to store the dry calcium chloride in vessels coated with paraffin. The dry calcium chloride must be filled into a large U-tube, a compact cotton-wool layer must be placed on its surface, and it must then be connected in front of the soda lime tube. The calcium chloride must be renewed at the same time as the soda lime, and the same preparation must be used in the last third of the soda lime tube. Before use the calcium chloride must be saturated with carbon dioxide (see Chapter 57.1.).

Magnesium perchlorate trihydrate (Dehydrite) and anhydrous magnesium perchlorate (Anhydrone) may also be used instead of calcium chloride. The former takes up 35% and the latter 50% of its own weight of water. Phosphorus pentoxide poured on to glass wool may also be used as a drying agent.

To absorb hydrogen sulphide, anhydrous copper(II) sulphate can be prepared by the following method:

Take 60 g of pumice stone of 2–3 mm grain size, and pour on it a solution of 30–35 g of crystalline copper(II) sulphate. Evaporate on a water bath with stirring, and dry at 150–160°C for 4–5 hr in a drying oven. Copper(II) sulphate becomes almost anhydrous at this temperature. This copper(II) sulphate absorbs hydrogen sulphide better than that which contains water of hydration. The hydrogen sulphide absorbent is unnecessary if the decomposition of the carbonate is carried out with concentrated phosphoric acid containing chromic acid, or if mercury(II) chloride is added to the carbonate.

The determination of carbon dioxide in samples containing large amounts of carbonate can be carried out in a Winkler apparatus (see Fig. 57.5.). If the sample contains small amounts of carbonate, or dilute carbonate solutions (mineral water) it is advisable to use the Fresenius–Classen apparatus (see Fig. 57.7.). The carbonate content of mineral waters can also be determined in the modified Winkler apparatus (see Fig. 57.6.).

57.2.1. *Determination of the carbon dioxide content of carbonates in the simple Winkler-type decomposition apparatus*

Weigh sufficient sample, containing the equivalent of 0·2–0·5 g of calcium carbonate, into the decomposition flask of the apparatus shown in Fig. 57.5. When continuous determinations are to be made, the samples can be weighed into small vessels which can be inserted into the flask. Into the slightly inclined gas outlet tube place 2–3 g of granulated zinc which has been cut into small pieces and coated with copper. A small piece of zinc must also be dropped into the decomposition flask. The pieces of zinc must be sufficiently small to fall into the flask without residue when the dropping funnel is fitted and the flask is tilted.

Pour 10 ml of boiled-out distilled water on to the sample, lubricate the ground glass joint of the dropping funnel with a small amount of vaseline, and fit it into the neck of the flask. To the gas outlet tube connect a small calcium chloride or magnesium perchlorate tube, using thick-walled rubber tubing coated with vaseline or paraffin wax (see Chapter 57.1.). A soda lime or potash apparatus can be connected to this tube using similar rubber tubing. Connect

a wash-bottle filled with 30% potassium hydroxide to the carbon dioxide absorber. Add 20 ml of boiled out 10% hydrochloric acid to the flask from the funnel; a vigorous evolution of gas occurs. When the gas current subsides, transfer the zinc from the side tube to the flask and add a further 20 ml of hydrochloric acid. The 1·5 litres of hydrogen evolved rinses the carbon dioxide quantitatively into the soda lime absorption tube. The liberation of gas finishes within 20 min.

Disconnect the apparatus, connect a large soda lime and calcium chloride tube in front of the absorption tube, and draw air through the apparatus for 5 min. When the hydrogen has been rinsed out from the tube its taps must be closed, and the tube placed in the balance case for 30 min. One of the taps must then be opened for an instant to equalise the pressure, and the tube must then be weighed. The increase in weight is equal to the weight of the carbon dioxide. Stoichiometric factor: $CO_3/CO_2 = 1{\cdot}3635$.

Notes. (1) If the absorption vessel was weighed before use after saturation with hydrogen, the final rinsing with air need not be carried out. Experience has shown, however, that it is advisable to weigh the vessel filled with air, because of the uncertainty due to the easy diffusion of hydrogen.

(2) If hydrogen sulphide is also liberated from the sample when hydrochloric acid is added, another tube filled with pumice stone impregnated with copper sulphate and dried at 180°C (cf. Chapter 57.2.), must be fitted between the decomposition flask and the calcium chloride tube.

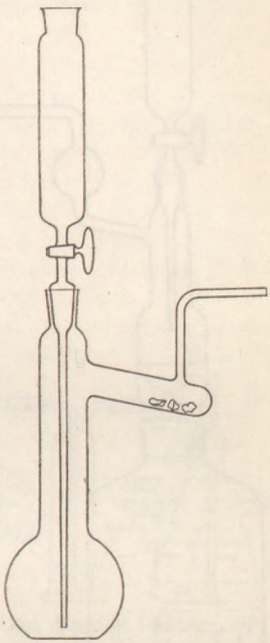


Fig. 57.5. Carbonate decomposition flask according to Winkler

References for the determination of the carbon dioxide content of carbonates:

L. W. Winkler, *Z. anal. Chem.* **52**, 421 (1913); *Ausgewählte Untersuchungsverfahren für das chemische Laboratorium.* Enke, Stuttgart (1931), p. 81; L. Ecker, *Chemiker Z.* **29**, 1316 (1905); *Z. anal. Chem.* **52**, 436 (1913).

57.2.2 *Determination of the carbon dioxide content of mineral waters or natural waters according to L. W. Winkler*

The water sample must be taken in a 500-ml bottle, which suold be filled without air bubbles and stoppered so that no air remains above the water. The volume of the bottle must be found by calibration with distilled water.

After being transferred to the laboratory, drop 20 g of granulated zinc and a small piece of copper sulphate into the water; this displaces about 2·5 ml of the water sample from the bottle. Thus the volume of sample taken for analysis

is less by this amount. The bottle must be stoppered rapidly with a stopper which consists of a dropping funnel and a gas outlet tube (see Fig. 57.6.) and has a volume of about 50 ml. Connect the gas outlet tube to a large calcium chloride (or magnesium perchlorate) tube, through a U-tube filled with cotton wool, and a weighed soda lime tube (or potash apparatus) and washing bottle filled with 30% potassium hydroxide. Over a period of 2 hr add a total of 25 ml of 18% hydrochloric acid to the water sample through the dropping funnel.

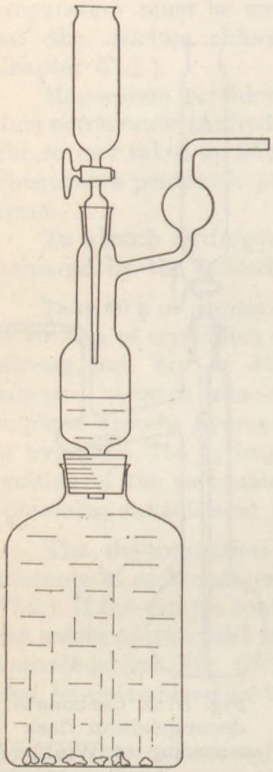


Fig. 57.6. Winkler apparatus for determination of the carbon dioxide content of mineral or natural waters

Because of its greater specific gravity the hydrochloric acid solution sinks to the bottom of the bottle and comes into contact with zinc. Hydrogen is liberated. Its volume is so large that it removes the carbon dioxide liberated by the acid quantitatively without heating. The carbon dioxide content of the sample can be determined from the increase in weight of the soda lime tube.

Note. The tube filled with cotton wool removes any droplets of acid from the gas.

References for the determination of carbon dioxide in natural waters and mineral waters:

L. W. Winkler, *Z. anal. Chem.* **40,** 523 (1901); **42,** 735 (1903); **52,** 421, 431 (1913); *Ausgewählte Untersuchungsverfahren für das chemische Laboratorium.* Enke, Stuttgart (1936), p. 129; I. Sarudi, *Szervetlen mennyiségi analízis. (Quantitative inorganic analysis).* II. Szeged (1947), p. 439.

57.2.3. *Determination of carbon dioxide in carbonates according to Fresenius–Classen*

Carbon dioxide can be liberated with a strong acid in the decomposition flask, fitted with a reflux condenser, and can be boiled out of the flask and flushed into an absorption tube with carbon dioxide-free air through a drying apparatus.

The apparatus is shown in Fig. 57.7. The decomposition of the carbonate sample can be effected in the 250–400 ml flask (4). The gas outlet tube of the flask is fitted with a condenser (5). The acid, which decomposes the carbonate, can be added through tap (3) of the dropping funnel (2). A 15- cm long soda lime tube (1) is fitted to the top of the funnel with a rubber stopper. The soda lime filling is supported by layers of cotton wool 2 cm wide at both ends. The tap and ground glass cone of the dropping funnel are lubricated with vaseline. The tube of the dropping funnel reaches the bottom of the flask and is bent in a spiral. The gas outlet tube is connected

through a bent glass tube to the tube (6) filled with pumice stone coated with anhydrous copper(II) sulphate. This tube filling absorbs any hydrogen sulphide and hydrogen chloride evolved from the decomposition flask. The drying tube (7) is filled with anhydrous calcium chloride (or magnesium perchlorate). The U-tube, fitted with taps (8), is connected to the drying

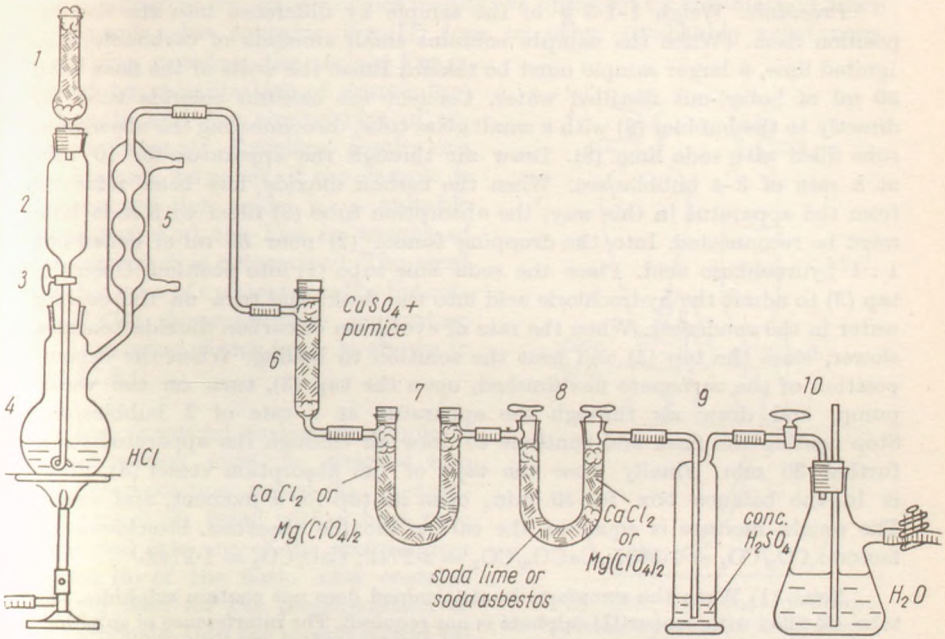


Fig. 57.7. Apparatus for determination of the carbon dioxide content of carbonates

tube and absorbs the carbon dioxide. The filling of this tube consists of two-thirds soda lime (or sodium asbestos), and one-third anhydrous calcium chloride (or magnesium perchlorate). Concentrated sulphuric acid must be added to the bubbling flask (9). The flow rate can be regulated by adjusting the height of the guard tube connected to the latter and immersed in a large bottle.

The efficiency of sealing of the apparatus must be checked before the determination. The open end of the soda lime tube (1) must be closed tightly with a rubber stopper. Pour 20 ml of water into the decomposition flask and close the tap (10). Begin suction and open tap (10) cautiously; a slow stream of bubbles appears in the bubbler. If the apparatus is sufficiently air-tight, the stream of bubbles ceases after a time. If the bubbles do not stop, the tap (3) and then the taps of the soda lime tube (8) must be closed; any leak can then be detected in each part of the apparatus.

If the apparatus is efficiently sealed the rubber stopper must be removed from the soda lime tube (1), and air must be drawn through the apparatus at a slow rate (2 bubbles/sec, which corresponds to 2 litres

of air per hour). Then close the taps of the soda lime tube (8). Dry the tube with a moist flannel cloth and then rub with a leather cloth, and place it in the balance box. The weight of the tube should not exceed 70 g. If the weight of the tube after repeating the flushing with air is constant to within $\pm 0{\cdot}5$ mg the determination can be started.

Procedure. Weigh 1–1·5 g of the sample by difference into the decomposition flask. (When the sample contains small amounts of carbonate, e.g. ignited lime, a larger sample must be taken.) Rinse the walls of the flask with 50 ml of boiled-out distilled water. Connect the calcium chloride tube (7) directly to the bubbler (9) with a small glass tube, disconnecting the absorption tube filled with soda lime (8). Draw air through the apparatus for 10 min at a rate of 3–4 bubbles/sec. When the carbon dioxide has been removed from the apparatus in this way, the absorption tube (8) filled with soda lime must be reconnected. Into the dropping funnel (2) pour 50 ml of boiled-out 1 : 1 hydrochloric acid. Place the soda lime tube (1) into position. Open the tap (3) to admit the hydrochloric acid into the flask, and turn on the cooling water in the condenser. When the rate of evolution of carbon dioxide becomes slower, close the tap (3) and heat the solution to boiling. When the decomposition of the carbonate has finished, open the tap (3), turn on the water pump, and draw air through the apparatus at a rate of 2 bubbles/sec. Stop heating the flask and continue to draw air through the apparatus for a further 30 min. Finally close the taps of the absorption vessel (8), place it in the balance box for 30 min, open its tap for a moment, and weigh. The weight increase is equal to the carbon dioxide absorbed. Stoichiometric factors: $CO_3/CO_2 = 1{\cdot}3635$; $CaCO_3/CO_2 = 2{\cdot}2742$; $CaO/CO_2 = 1{\cdot}2742$.

Notes. (1) When the sample to be determined does not contain sulphides, the tube (6) filled with copper(II) sulphate is not required. The interference of sulphides and sulphites can also be avoided by dissolving 3–4 g of chromic acid in the 50 ml of syrupy phosphoric acid (sp. gr. 1·75) used for the decomposition.

(2) The standard deviation of the results obtained by this method is not greater than $\pm$ 0·3%.

(3) For syderites ($FeCO_3$) weigh 0·5 g, for cements 5 g and for ignited lime 5–10 g. With cement samples hydrogen sulphide evolution must also be expected.

(4) The apparatus can also be used for the determination of the carbon dioxide content of natural waters if a larger decomposition flask is used. Care must be taken, however, that carbon dioxide losses do not occur during the filling of the flask.

References for the determination of carbon dioxide by the Fresenius-Classen method.

R. C. Fresenius, *Z. anal. Chem.* **14**, 174 (1875); A. Classen, *Z. anal. Chem.* **15**, 288 (1876); J. Volhard, *Liebigs Ann.* **176**, 142 (1875); W. Reich-Rohrwig, *Z. anal. Chem.* **95**, 315 (1933); F. P. Treadwell, *Lehrbuch der analytischen Chemie.* II. Ed. 11. Deuticke, Wien (1949), p. 326. I. Sarudi, *Szervetlen mennyiségi analizis (Quantitative inorganic analysis)* I. Szeged (1947), p. 220.

57.2.4. *Determination of the carbon dioxide content of carbonates by measurement of the weight loss.*

This method can be used if the sample to be determined consists mainly of carbonate. Thus, good results can be obtained for the analysis of alkali

and ammonium carbonates, limestone, magnesite, dolomite, baking powders, etc. The determination of the carbon dioxide content of calcium or magnesium carbonate can also be carried out by determination of the loss on ignition of the sample. On ignition, however, the moisture in the sample is also removed, and therefore the determination of the loss on ignition gives only qualitative results. Incorrect results are obtained by this method when the sample also contains iron(II) ions or other oxidizable substances. In baking powders the weight loss is caused by volatilization of ammonium carbonate and the combustion of organic substances. Excellent results can be obtained, however, if the sample is decomposed by acids in a suitable apparatus, and the loss in weight of the apparatus is determined. The most suitable type of apparatus is the Schrötter (1871) decomposition apparatus; an apparatus of this type is shown in Fig. 57.8.

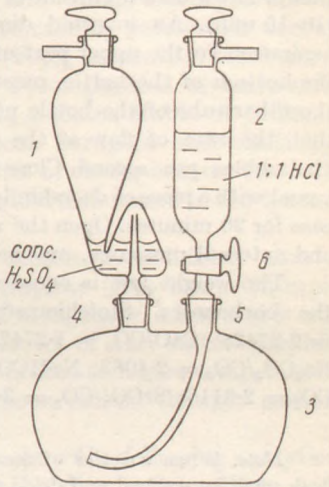


Fig. 57.8. Carbonatedecomposition apparatus according to Schrötter

The powdered carbonate sample to be determined must be weighed into the decomposition vessel (3). A dropping funnel (2) fitted with a bent tube is inserted into one of the ground glass sockets (5) of the flask. This contains the acid used for the decomposition of the carbonate. Into the second socket (4) a drying tube filled with concentrated sulphuric acid should be fitted to dry the gas. The size of the apparatus is such that when filled with hydrochloric and sulphuric acid it weighs less than 75 g, and can be placed on the pan of an analytical balance.

Clean the drying (1) and dropping funnel (2) parts of the apparatus separately and dry them by rubbing with a slightly moist deerskin. Lubricate the tap and joint with vaseline. Pour into the drying apparatus (1) 2–3 ml of concentrated sulphuric acid, and to the dropping funnel (2) add about 10–15 ml of 15% hydrochloric acid. Place both vessels into one beaker and allow to stand near the balance. Degrease the decomposition flask (3) and its ground glass sockets (4 and 5), rinse the vessel outside and inside with distilled water, dry in a drying oven. Cool, rub its outer surface with a slightly moist deerskin, and place it in the balance case for 30 min. Weigh the vessel (3).

Through the wider ground joint (4) add 0·2–0·5 g of powdered carbonate sample to the vessel, and weigh the vessel again to obtain the accurate weight of the sample. Moisten the sample with a small volume of water (not if the sample is baking powder). Fit the lubricated drying tube (1) and dropping funnel (2) in place and check that the apparatus seals perfectly at the joints (4 and 5). Place the assembled apparatus into the balance case and after 15 min open the

two upper taps for a moment and weigh the whole apparatus. Then open the upper taps of both parts, and allow the hydrochloric acid to flow into the decomposition flask (3). Close the tap (6) and the upper tap of the dropping funnel.

When the liberation of gas becomes slow, place the apparatus on a closed water bath and heat the lower parts of it to 80 °C. Connect a soda lime tube and a wash bottle filled with concentrated sulphuric acid to the upper tap of the dropping funnel, and connect the upper tap of the drying tube to a water pump. Draw a slow current of air through the apparatus until completely cool (10–15 min). An inverted distilled water washing bottle can be used as an aspirator. To the upper part of the drying tube (1) the jet tube, which reaches the bottom of the bottle, must be connected through a small rubber tube. On the other tube of the bottle place a small rubber tube and fit it with a tap so that the rate of flow of the water can be regulated to produce a flow of 2–3 air bubbles per second. Close the upper tap of the apparatus. Dry the lower vessel with a piece of deerskin leather again, and place the apparatus in a balance case for 30 minutes. Open the upper taps for a moment to equalize the internal and external pressures, and weigh the apparatus.

The weight loss is equal to the weight of carbon dioxide liberated from the carbonates. Stoichiometric factors: $CO_3/CO_2 = 1{\cdot}3635$; $CaCO_3/CO_2 = 2{\cdot}2742$; $CaO/CO_2 = 1{\cdot}2742$; $MgCO_3/CO_2 = 1{\cdot}9161$; $MgO/CO_2 = 0{\cdot}91613$; $Na_2CO_3/CO_2 = 2{\cdot}4083$; $NaHCO_3/CO_2 = 1{\cdot}9088$; $KHCO_3/CO_2 = 2{\cdot}2749$; $MnCO_3/CO_2 = 2{\cdot}6118$; $SrCO_3/CO_2 = 3{\cdot}3546$.

Note. When a series of measurements is made only the lower decomposition flask must be washed and dried out; the washing device (1) and dropping funnel (2) can be allowed to stand in a tall beaker. The accuracy of the method can be judged from the data of J. V. Mellor (1936) in Table 57.1.

TABLE 57.1. Determination of the carbon dioxide content of calcium carbonate by weight-loss method

Weighed $CaCO_3$, mg	215·3	201·1	200·4	200·6	202·0	201·8
Calculated $CaCO_3$ from the weight loss, mg	214·9	201·0	199·9	200·3	201·7	201·7
Deviation, mg	−0·4	−0·1	−0·5	−0·3	−0·3	−0·1

References for the determination of carbon dioxide in carbonates by measurement of the weight loss:

A. R. SCHRÖTTER, *Ber. Wien Acad.* **63**, 471 (1871); C. H. CRIBB, *Analyst* **21**, 62 (1896); J. L. KREIDER, *Am. J. Sci.* **19**, 188 (1905); *Z. anorg. Chem.* **44**, 154 (1905); J. W. MELLOR and H. Y. THOMPSON, *A Treatise on Quantitative Inorganic Analysis* 2 Ed. Griffin, London (1938), p. 625.

57.3. DETERMINATION OF THE CARBON CONTENT OF IRON AND STEEL

Molten iron takes up considerable amounts of carbon. According to the carbon content and heat-treatment, on cooling iron assumes various textures and mechanical properties. Steel and cast iron containing less carbon than 1·8% and 0·5% respectively, after freezing at high temperature contain the carbon in solid solution (martensite). At the temperature of ignition, steel can be formed easily by casting and rolling. During slow cooling at low temperatures, the solid solution containing martensite decomposes and pure iron (ferrite) and iron carbide (Fe_3C, cementite) are formed. On rapid cooling (hardening), however, the decomposition of martensite is very slow, therefore the solid solution also remains stable at ordinary temperatures and the material exhibits great hardness and elasticity. The hardness of cast iron is much less than that of steels, because the solid solution is very dilute. Thus there are only gradual differences in the texture of cast iron and steel.

When melts containing more than 2% carbon are solidified slowly, part of the carbon separates in the form of graphite (grey iron). On rapid cooling, or in the presence of large amounts of manganese, a less stable iron carbide (cementite) structure is formed instead of the stable graphite structure (white iron). When the white iron is heated to higher temperatures however, cementite decomposes and amorphous carbon (temper carbon) is formed.

The carbon formations of irons and steels show the following analytical properties. Steels containing martensite can be dissolved in dilute acids and hydrocarbons are formed. Combined carbon is insoluble in dilute acids, but can easily be dissolved in concentrated mineral acids with the formation of hydrocarbons. Graphite and temper carbon are insoluble in acids, and therefore remain behind after the dissolution of the iron.

In alloyed steels carbides formed with alloying elements (Cr, W, Mo) have a large influence on the properties of the steel. Thus if the carbon content is changed by as little as 0·1% the mechanical properties of the steel may be considerably affected. The total carbon content of alloyed steels may be as high as 3%. In analytical measurements it is usually enough to determine the total carbon content of steels; separate determinations of the graphite and temper carbon content are rarely required. The carbide carbon content in this case can be determined from the difference between the total carbon and graphite (temper carbon) content.

The most accurate determination of the carbon content can be made by combustion in an oxygen atmosphere. The carbon dioxide formed can be measured by gravimetric, volumetric or gas-volumetric methods. The latter method is used in industrial analysis because of the rapidity of the determination. In important analyses the gravimetric method must always be used. Only the gravimetric method is treated in detail here.

The experimental conditions for the combustion must be such that the carbon is completely combusted to carbon dioxide, and no carbon monoxide is formed. Carbon monoxide may be formed in carbon-rich irons, hard

alloys and difficultly combustible steels and alloys. If the combustion is carried out as in the Liebig carbon–hydrogen determination in a tube filled with copper oxide, a combustion temperature of 750°C usually effects complete combustion. In furnaces without a tube filling, however, much higher temperatures must be maintained, and a large excess of oxygen must be present. When slag-forming substances, or substances which transfer oxygen, are mixed with the iron or steel sample complete combustion is attained. The most commonly used additive is pure iron (Armco iron), 2–3 g of which must be added to the sample to be determined. The carbon content of the substances added must be determined in a separate sample and corrected for. A convenient additive consists of a mixture of 2 parts

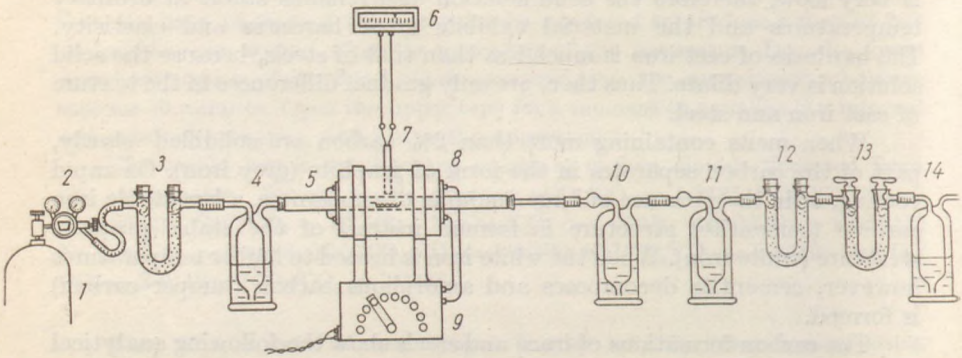


Fig. 57.9. Apparatus for determination of carbon content of iron and steel

of lead dioxide and 1 part of cobalt oxide. For carbon steel samples, lead dioxide, copper(II) oxide or metallic copper can also be used to advantage. Other additives are zinc oxide, lead oxide and bismuth oxide.

The rate of combustion becomes faster as the combustion temperature is raised. In gravimetric determinations, if the combustion proceeds too rapidly, complete absorption of the carbon dioxide may not be obtained. It is thus advisable to combust at a lower temperature for a longer period. For repeated measurements a temperature of 1050–1100°C is the most suitable.

Sulphur dioxide formed on combustion can be removed most easily by using a washing bottle filled with chromic acid [$2\,CrO_3 + 3\,SO_2 = Cr_2(SO_4)_3$].

An apparatus suitable for the determination of carbon in iron and steel samples is shown in Fig. 57.9. The oxygen supply for combustion is obtained from the steel cylinder (1) fitted with a regulator tap (2), a phosphorus pentoxide–magnesium perchlorate drying tube (3), and a bubbler (4) filled with concentrated sulphuric acid. The gas is then passed to the combustion tube (5). The tube is made of unglazed porcelain, alundum or quartz, and is 50–60 cm long and 2–2·5 cm in diameter. A Marsh furnace

with two silite rods can be used for heating the tube. A furnace equipped with platinum resistance wire, which can be heated to 1200°C, can be also used. When a resistance is connected in the furnace circuit, the temperature can be regulated to 1050–1100°C. The thermocouple (7), connected to the milliammeter (6), touches the surface of the combustion tube above the combustion vessel.

The combustion products and the excess oxygen are passed through the washing bottles filled with chromic acid (10 and 11) to absorb any sulphur dioxide present in the gas. The drying tube (12) is filled with phosphorus pentoxide (or magnesium perchlorate) on glass wool. The carbon dioxide absorption tube (13) is two-thirds filled with soda lime (or soda asbestos), and the rest of the tube contains phosphorus pentoxide (or magnesium perchlorate) poured on glass wool. The final layer ensures that water liberated on the absorption of carbon dioxide is not removed from the tube in the gas stream. The bubbler (14), filled with concentrated sulphuric acid, serves to control the rate of flow of the gas. The large diameter internal tubes of washing bottles (4, 10, 11 and 14) ensure that sulphuric acid should not pass into the absorption tubes when a change in pressure occurs.

The drying and absorption tubes must be filled in the same manner as described for the determination of carbonate (Chapter 57.2.3.). The washing bottles contain concentrated sulphuric acid, in 100 ml of which 4–6 g of chromium(VI) oxide, CrO_3, are dissolved. The contents of the washing bottle (10) must be changed after every 50 determinations. This can be carried out by replacing it with washing bottle (11) and using the fresh solution in the second bubbler.

An unglazed porcelain or alundum vessel can be used as the combustion vessel. Iron oxide formed in the combustions adheres so strongly to the tube that usually only one combustion can be carried out in each tube. The vessel must be ignited strongly before use. The vessel can be used several times, however, if alumina powder (Al_2O_3) is poured on the bottom of it.

Combustion. Heat the furnace to 1050°C and pass a slow stream of oxygen through the assembled apparatus (2 bubbles/sec.). After 15 min disconnect the soda asbestos tube, close its taps, place it near to the balance for 30 min, and weigh. During this time weigh the sample to be determined into a porcelain vessel. The sample should weigh 1·5 g if the carbon content of the steel is less than 1·3%, 3 g if the carbon content is smaller, and 0·5–1 g if coarse iron or alloyed steels are to be analysed.

Pour the sample in a thin layer, and add 2–3 g of Armco iron or 1·5 g of other additive material. Reconnect the weighed soda lime tube, open its taps, remove the first rubber stopper of the combustion tube, and with a steel rod position the vessel at the hottest part of the tube. Close the tube immediately with its rubber stopper, and increase the temperature of the furnace to 1150–1200°C by altering the rheostat in the circuit. At the beginning of the ignition the number of bubbles increases in wash bottle (4), and decreases in wash bottle (14). Adjust the oxygen regulator so that the rate of flow of gas increases in bubbler (14) to its original value (2 bubbles/sec), and then close the tap slowly, until the original flow rate is attained in bubbler (4).

Decrease the temperature of the furnace to about 900 °C, and pass oxygen through the furnace for 10 min. During this time carbon dioxide is quantitatively transferred to the soda lime tube. Close the taps of the tube, place it in the balance box for 30 min, and weigh.

The blank value of the additive must be determined in the same way and the value subtracted from the increase in weight of the soda lime tube. Stoichiometric factor: $C/CO_2 = 0{\cdot}27291$.

Notes. (1) For series analyses it is advisable to carry out control combustions each day with a standard steel sample of known carbon content to check the efficiency of the apparatus. 30 g of soda lime can absorb about 1 g of carbon dioxide, and when the increase in weight reaches this value the soda lime filling must be changed. The cotton wool stopper of the new soda lime tube must be moistened with 1–2 drops of water.

(2) For the determination of *graphite* and *temper carbon* dissolve 2 g of the coarse iron sample in 50 ml of diluted nitric acid (1 : 1), heat for 1–2 hr at about 90°C, add several drops of hydrofluoric acid, and heat to boiling. Dilute the solution with 100 ml of hot water, and oxidize by boiling with 10 ml of 1·5% potassium permanganate solution. Excess potassium permanganate must be reduced with iron(II) sulphate or sulphurous acid. Collect the carbon which remains behind on a small asbestos filter. Wash the filter with hot water, dry at 110°C, and place the precipitate and asbestos in a small porcelain combustion vessel. Remove graphite from the walls of the funnel with a small pad of asbestos, and place the pad in the combustion vessel also. Cover the sample with copper oxide powder. Carry out the ignition according to the method described above. Blank tests should be conducted on the asbestos and copper oxide used.

References for the determination of the carbon content of iron and steel:

E. Hintz and H. Weber, *Z. anal. Chem.* **33**, 725 (1894); **34**, 191 (1895); H. Weber, *Z. anal. Chem.* **55**, 537 (1916); B. Neumann, *Stahl u. Eisen* **28**, 128 (1908); G. Marsh, *Stahl u. Eisen* **29**, 1155 (1909); Lunge-Berl, *Chemisch-Technische Untersuchungsmethoden II.* Ed. 2. Springer (Berlin), 1922, p. 183; R. Weihrich, *Die chemische Analyse in der Stahlindustrie.* 2 Ed. Enke, Stuttgart (1939), p. 11.

CHAPTER 58

SILICON — Si — 28·09

Si, SiO_2, H_2SiO_3

ELEMENTARY silicon does not occur naturally, but is found in small amounts as a contamination or alloying element in almost all metals and metal alloys produced by metallurgical processes. Technical silicon, containing about 97% Si, is used for the deoxidation of copper alloys. Iron–silicon alloys, containing 25–75% silicon (ferro-silicon) are used for the deoxidation of molten steel and as a previous alloy. From iron-based alloys containing 15–20% silicon (termisilicide), acid-resistant casts are made for the chemical industry.

Silicon compounds are found in large amounts in nature. In the outer shell of the earth, silicon is the second most abundant element after oxygen (27·6% by weight). Various forms of silicon dioxide (SiO_2) e.g. sand, quartz, mountain crystal, as well as many kinds of silicates, are found in almost all rocks except carbonate ones. The glass, ceramic, cement and building material industries process large amounts of various artificial silicates. Glass and quartz apparatus is widely used in laboratories and chemical engineering. Metallurgical plants use many auxiliary materials containing quartz and also produce large amounts of slag. Silicic acid and some silicates are also found in living organisms, especially in some grasses. Thus the presence of silicic acid or silicates is expected in most analytical samples.

Forms of determination. Elementary silicon can be oxidized to silicic acid with nitric acid and can be weighed in this form. In the presence of silicic acid or silicon dioxide, elementary silicon can be determined selectively by dissolution of the sample in alkali and by measurement of the hydrogen formed by a gas volumetric method:

$$Si + 2\,NaOH + H_2O = Na_2SiO_3 + 2\,H_2 \uparrow .$$

The amount of silicon can be calculated from the volume of hydrogen evolved. An alternative method is to ignite the sample in a current of chlorine gas; volatile silicon tetrachloride is formed from the elementary silicon, and silicic acid and silicates remain behind unchanged (Chapter 2.5.10.). Silicon tetrachloride can be absorbed in water, and the silicic acid formed by hydrolysis can be determined gravimetrically:

$$Si + 2\,Cl_2 = SiCl_4 \uparrow$$

$$SiCl_4 + 3\,H_2O = H_2SiO_3 \downarrow + 4\,HCl.$$

The most important forms of determination of silicic acid are shown in Table 58.1. For samples containing less than 5 mg silicic acid, or in micro determinations, silicic acid can be precipitated in the form of the salts of silicomolybdic acid formed with nitrogen-containing bases, and can be weighed after drying. The molecular weights of these salts are high, and therefore very small amounts of silicic acid can be determined accurately in this form.

TABLE 58.1. Forms of determination of silicic acid

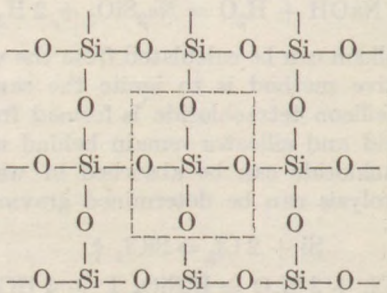
(for References see p. 203)

Ref. Number	Forms of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	$SiO_2 \cdot n\,H_2O$	(a) HCl (b) H_2SO_4 (c) $HClO_4$ (d) gelatine (e) HCl + $AlCl_3$	acidic	SiO_2	60·09	approx. 1000
2.	$(C_9H_7N)_4 \cdot SiO_2 \cdot 12\,MoO_3 \cdot 2\,H_2O$	quinoline + + $(NH_4)_2MoO_4$ + + HCl	acidic	$(C_9H_7N)_4SiO_2 \cdot 12\,MoO_3 \cdot 2\,H_2O$	2339·7	approx. 150

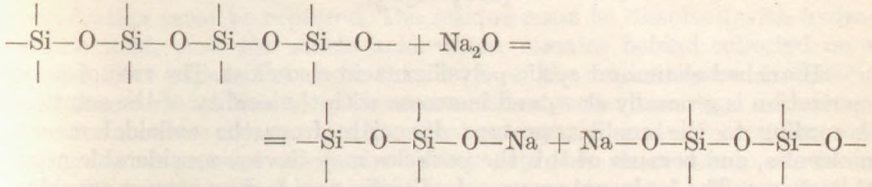
Seldom used forms of determination: 3. potassium fluorosilicate [K_2SiF_6], 4. oxinium-12-molybdosilicate [$4\,C_9H_6ON \cdot SiO_2 \cdot 12\,MoO_3 \cdot 2\,H_2O$], 5. hexammine-12-molybdosilicate [$4\,C_6H_{12}N_4 \cdot SiO_2 \cdot 12\,MoO_3 \cdot 4\,H_2O$], 6. piramidone–12–molybdosilicate [$3\,C_{13}H_{17}ON_3 \cdot SiO_2 \cdot 12\,MoO_3 \cdot 4\,H_2O$], 7. pyridine-12-molybdosilicate [$SiO_2 \cdot 12\,MoO_3 \cdot 4\,Py \cdot 6\,H_2O$].

In practice silicic acid is usually precipitated with strong acids after fusion with sodium carbonate, and is weighed as SiO_2 after ignition.

Analytical properties of silicic acid, silicon dioxide and silicates. Silicon dioxide has a macromolecular structure with a cubic lattice in which the Si—O main valence bonds bind the whole substance together:



The great hardness of silicon dioxide and its water- and acid-insolubility can also be explained by this fact. The SiO_4^{4-} tetrahedrons can be replaced by slightly basic or acidic oxides (Fe_2O_3, Al_2O_3, TiO_2, P_2O_5 etc.) but the macromolecular character and insolubility of the substance is not changed appreciably. In silicates containing strongly basic oxides (Na_2O, CaO, MgO), however, depolymerization occurs, and the melting point decreases because oxygen ions break up the main valence chains:

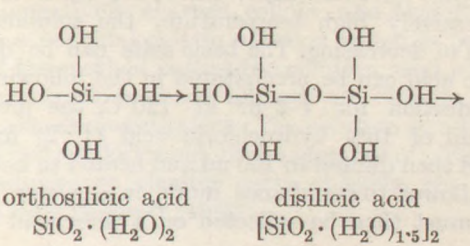


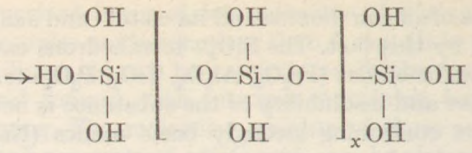
In the presence of sufficient sodium oxide the depolymerisation may be so great that the alkali silicate becomes water-soluble (water-glass). If the weight ratio of sodium oxide to silicon dioxide becomes 1 : 3, the water-glass formed can be dissolved in water at 140–160°C in autoclaves. When silicon dioxide is melted with increasing amounts of calcium oxide the degree of polymerization also decreases, but the calcium silicates formed are insoluble in water. If the amount of calcium oxide present attains that required for the formation of orthosilicate (Ca_2SiO_4), e.g. a ratio of 2 CaO : : SiO_2, the silicic acid is depolymerized to monomeric form and by the effect of the strong acid the silicate decomposes:

$$Ca_2SiO_4 + 4\,HCl = 2\,CaCl_2 + H_4SiO_4 \downarrow$$

58.1. PRECIPITATION AND DEHYDRATION OF SILICIC ACID

Freshly precipitated silicic acid, in the same way as silicon dioxide, tends to polymerize and slowly becomes insoluble in water. The degree of polymerization increases with increase in the acidity of the solution. On heating with strong alkalies, silicic acid becomes depolymerized and dissolves. In aqueous solutions silicic acid behaves as a very weak, dibasic acid ($K_1 = 10^{-9}$, $K_2 = 10^{-13}$), and thus even carbon dioxide displaces it from its soluble salts. When alkali silicates are acidified with hydrochloric acid they decompose, first by formation of orthosilicic acid (H_4SiO_4), and then on losing water the single silicic acid molecules form longer chains:





polysilicic acid
$[SiO_2 \cdot H_2O]_n$

Branched-chain and cyclic polysilicic acid also exist. The rate of polymerization is generally slow, and increases with the acidity of the solution. According to the acidity, protons dissociate from the colloidal macromolecules, and because of this the particles may have a considerable negative charge. The hydroxyl groups of polysilicic acids may attract considerable numbers of water molecules; a colloid of hydrophilic character is then produced. The silicic acid is thus prone to colloidal dissolution. The isoelectric point of the colloid occurs at about pH 3–5, and it can thus be coagulated most easily from solutions in this pH range. From strongly acidified solution silicic acid is precipitated as a gel, usually only after the evaporation of water. Thus silicic acid cannot be precipitated quantitatively by simple acidification and boiling.

When the solution is evaporated to dryness, however, and the precipitated silicic acid is dehydrated at 110–150°C for a longer period, the tendency of silicic acid towards peptization and water retention decreases considerably. Silicic acid gel sometimes contains 90% or more water, but when dehydrated at 100°C the water content of silicic acid decreases to less than 20%. The structural water present in dried silicic acid can only be completely removed at higher temperatures. It is not advisable however to carry out dehydration at too high temperatures. Iron(III) chloride or aluminium chloride, which accompany silicic acid, form basic salts when heated at more than 120°C, and cannot be dissolved from the silicic acid with hydrochloric acid. When the original substance has been fused with sodium carbonate, or when magnesium oxide is also present in the sample, sodium or magnesium chloride is formed on evaporation. These chlorides react with silicic acid at temperatures higher than 120°C:

$$H_2SiO_3 + 2\,NaCl \rightleftharpoons Na_2SiO_3 + 2\,HCl \downarrow .$$

In the presence of these salts, therefore, when the dehydration is effected at excessively high temperature, the solubility of silicic acid increases instead of decreasing. The basic salts can be dissolved and the redissolved silicic acid can be precipitated in the following manner:

After dehydration for 1–2 hr at 120°C, the precipitate must be heated with 20 ml of 10% hydrochloric acid (1 : 2) for 10–30 min on a water bath, and then diluted to 100 ml and heated to boiling. The solution must finally be allowed to stand once more on a water bath for 30 min. The precipitate must then be collected on a filter and washed with hot

water. In the mother liquor, even if the dehydration has been carried out with the greatest care, silicic acid is peptized. The filtrate contains 1–5% of the original amount of dissolved silicic acid in colloidal form. The amount of colloidally dissolved silicic acid depends on the method of dehydration, the quality and quantity of the accompanying ions, and also on the absolute amount of silicic acid present. From large amounts of silicic acid the percentage of redissolved material is higher than that from small amounts. The filtrate, therefore, must be evaporated to dryness again, and the dehydration must be repeated. The residue must be dissolved with hydrochloric acid, and the silicic acid which remains behind collected on a second filter paper. Not more than 0·3% of the original amount of silicic acid then remains behind in the second filtrate after washing.

For accurate measurements a third evaporation and dehydration must be made; the amount of dissolved silicic acid then decreases to one-tenth of its former value. It is not advisable, however, to carry out even further evaporations, because the amount of silicic acid dissolved from the vessels may cause large errors.

Dehydration with other acids. Dehydration can be effected with sulphuric and perchloric acids as well as with hydrochloric acid. When sulphuric acid and perchloric acid are used, azeotropic mixtures of these acids are formed, the boiling points of which are higher than 120°C. Thus when solutions acidified with sulphuric acid or perchloric acid are evaporated until fumes appear, dehydration takes place. Sulphuric acid has the disadvantage that when the solution is evaporated to sulphuric acid fumes, any iron(III) and aluminium sulphate present is precipitated in anhydrous form, and can be redissolved only after dilution with water and prolonged boiling. A second disadvantage is that the sulphates of calcium, strontium, barium and lead remain behind with the silicic acid.

When perchloric acid is used for evaporation, these disadvantages do not occur. With the exception of potassium, all metal perchlorates are soluble in water and dilute perchloric acid. Perchloric acid can also be used in the presence of silver salts. Perchloric acid, when heated to perchloric acid fumes, also dehydrates the silicic acid. The precipitate obtained is purer than that obtained with hydrochloric acid. Although the amount of peptized silicic acid in the mother liquor is lower than when hydrochloric acid is used, the filtrate must be evaporated again. Potassium perchlorate can be dissolved from the silicic acid with a large volume of hot water.

Silicic acid can also be dehydrated, according to W. Tongeren (1937), with a mixture of ammonium nitrate and concentrated nitric acid.

Precipitation of silicic acid with gelatin. Silicic acid liberated with hydrochloric acid is a negatively charged colloid, and therefore can easily be precipitated with a colloidal gelatin solution which is positively charged. The advantage of the method is that the solution need not be evaporated, and when the concentrations of acid and salt are suitable, the precipitation of silicic acid is almost quantitative. The solution must contain at least 20% by weight of hydrochloric acid. In the presence of considerable amounts of iron(III), aluminium or alkaline earth chloride, the concentration of hydrochloric acid may be lower (10%).

Gelatin solution can be prepared by dissolving 1·5 g of gelatin in 100 ml of hot water (90°C). When the solution is more concentrated a gel may be formed on cooling. The solution can be used for up to 8 days; after this time a fresh solution should be prepared. For the precipitation of 1 g of silicic acid, 0·1 g of gelatin (about 8 ml of 1·5% solution) is required. Sometimes gelatin is added in solid form to a solution which contains hydrochloric acid and has been heated to 60°C. After dissolution it can be then added to the solution. Leather glue can also be used, instead of gelatin.

Procedure. Boil the solution of silicic acid, containing 20% by weight of hydrochloric acid, for 10 min, cool to 60°C, add 2–5 ml of concentrated hydrochloric acid, and then add the gelatin solution dropwise with constant stirring. After stirring for 1–2 min allow the solution to stand, and test whether the layer of solution below the surface becomes clear in 30 sec. If not, add further gelatin, mix well, and dilute to double volume with water after 5 min. The precipitate can be filtered easily and may be washed with hot water.

Notes. (1) NaCl, KCl and $FeCl_3$ can be washed from the precipitate easily. In the presence of large amounts of titanium, the precipitate must first be washed with 4% hydrochloric acid solution and then with water. Zirconium phosphate, titanium phosphate, tungstic acid, tantalic and niobic acid, and also molybdic acid, may contaminate the precipitate. If the filtrate is boiled longer with nitric acid, the gelatin is decomposed and further determinations can be made in the filtrate.

(2) Gelatin precipitates silicic acid even from solutions which are 35% by weight in sulphuric acid or 45% in nitric acid.

Ignition and volatilization of silicic acid. Dehydrated and washed silicic acid must be placed with the filter paper in the wet state into a weighed platinum crucible, and dried on a small flame. The paper must be combusted and the residue converted to silicon dioxide, SiO_2, by ignition. During these operations care must be taken that air does not circulate in the crucible otherwise mechanical losses may occur. Ignited silicic acid is a light, fine powder, a part of which may be carried away by the air circulation. The thermal behaviour of dehydrated silicic acid is shown in the thermoanalytical curves of Fig. 58.1. (measurements of F. Paulik and G. Liptay). The maximum shown at about 100°C on the derivative thermogravimetric curve (DTG), as well as the corresponding step on the thermogravimetric curve, indicates the loss of about 4% of water. Even at 200°C, however, considerable amounts of water remain behind in the precipitate. On further heating of the precipitate this structural water is removed also. The slight

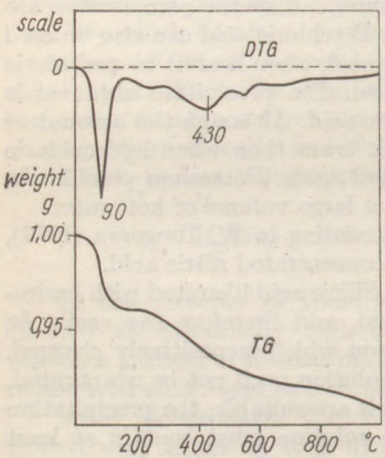


Fig. 58.1. Thermoanalytical curves of dehydrated silicic acid

maxima of the DTG curve at 400 and 550°C indicate that part of the water is bound with strong, well-defined bonds.

When the precipitate is ignited for 1 hr at 900°C as much as 0·9% water remains behind; this amount is reduced to 0·5% at 1000°C, 0·2% to 1100°C and 0·1% at 1200°C. The last traces of water can thus only be removed at high temperatures and very slowly. When the precipitate is heated at less than 1000°C for short times it becomes hygroscopic on cooling and can only be weighed in a stoppered vessel. If the precipitate is heated above 1000°C it loses its hygroscopic nature slowly. At the same time its active surface decreases. This can be proved also by the fact that while the hygroscopic precipitate adsorbs basic dyes, after strong ignition this adsorption ability of the precipitate decreases considerably. Silicic acid, therefore, must be ignited above 1000°C for at least 1 hr. At temperatures above 1100°C platinum, and especially platinum crucibles containing iridium, are volatilized to such an extent that the losses may attain milligram proportions. For accurate determinations, therefore, it is advisable to determine the volatilization loss of platinum crucibles by a blank test, igniting an empty crucible under similar conditions.

The silicic acid obtained when the precipitate is ignited cannot be regarded as pure silicon dioxide, as it may contain considerable amounts of accompanying salts either adsorbed or chemically bound. Tri- and tetravalent metal oxides and acidic oxides are inclined to coprecipitate with the silicic acid even in strongly acidic solutions. The most frequently encountered contaminations of crude silicic acid are therefore the following: Fe_2O_3, Al_2O_3, Cr_2O_3, SnO_2, Sb_2O_3, TiO_2, WO_3, P_2O_5, ZrO_2, ZrP_2O_7, $Ti_2P_2O_9$, $Ta(Nb)_2O_5$, $BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$.

In the absence of sulphate ions, alkali and alkaline earth ions do not contaminate the precipitate in appreciable amounts, because their salts do not usually hydrolyse to form acid-insoluble basic salts, and thus they can be washed out more easily from the precipitate. Aluminium oxide and titanium dioxide are more difficultly soluble in acids than iron(III) oxide, and therefore may contaminate the precipitate to a greater extent. In the presence of phosphate ions the degree of contamination is especially high, as titanium dioxide is then precipitated almost quantitatively with the silicic acid in the form of pyrophosphate. The contamination is greater when the dehydration is carried out with sulphuric acid than when the silicic acid is precipitated with gelatin or perchloric acid.

The silicon dioxide content of contaminated crude silicic acid can easily be determined by evaporation with hydrogen fluoride. Silicon dioxide forms gaseous silicon tetrafluoride (SiF_4) with hydrogen fluoride, and therefore the loss in weight of the residue is equivalent to the silicon dioxide content of the sample:

$$SiO_2 + 4\,HF \rightleftharpoons SiF_4 \uparrow + 2\,H_2O.$$

The reaction is only complete in the presence of dehydrating agents (concentrated sulphuric acid, perchloric acid). The decrease in weight after evaporation with sulphuric acid and hydrogen fluoride accurately corre-

sponds to the silicon dioxide content only if the composition of the accompanying substances is the same before and after the evaporation, and if the residue does not contain other material which is volatilized with hydrogen fluoride. The first requirement is more easily fulfilled with sulphuric acid than with perchloric acid.

On evaporation with sulphuric acid the metal oxides which usually contaminate crude silicic acid are converted into the sulphates:

$$2\,AlF_3 + 3\,H_2SO_4 = Al_2(SO_4)_3 + 6\,HF.$$

On ignition the sulphates are decomposed to the oxide and sulphur trioxide:

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3\,SO_3\uparrow.$$

Of the metal sulphates, $ZnSO_4$ has constant weight up to 830°C, $CdSO_4$ up to 820°C, and $PbSO_4$ up to 900°C. The following metal sulphates decompose at less than 800°C: $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Cr_2(SO_4)_3$, $CuSO_4$, $Bi_2(SO_4)_3$, $CoSO_4$, $NiSO_4$, $Zr(SO_4)_2$, $Th(SO_4)_2$ and $Ti(SO_4)_2$. Alkali metal sulphates are volatilized considerably above 900°C, but the alkaline earth metal sulphates are decomposed only above 1100°C. The decomposition of $MgSO_4$ begins at above 900°C. AlF_3, TiF_4, SbF_3, and to a lesser extent MnF_2, FeF_3 and CrF_3, are volatile in the presence of sulphuric acid, and losses may occur even on evaporation with sulphuric acid. This loss can be avoided by the use of excess sulphuric acid. The amount of sulphuric acid used must be determined primarily according to the degree of oxide contamination, and also according to the amounts of silicic acid present.

Of the less common contaminations, the effect of calcium sulphate and alkali metal chlorides must be mentioned separately. When calcium sulphate is heated alone it decomposes only at about 1200°C, but in the presence of silicic acid the decomposition takes place at much lower temperatures. This phenomenon makes the determination of silicic acid inaccurate when the precipitate contains large amounts of calcium. When alkali metal chlorides are incompletely washed out from the precipitate, especially after fusion with sodium carbonate, crude silicic acid may also be contaminated by these ions. Part of the alkali metal chloride is volatilized on ignition, while the part which remains behind is weighed with SiO_2 in the form of chloride. On evaporation with sulphuric acid the chlorides are converted to sulphates, and thus after the evaporation of silicon tetrafluoride the weight of the residue is greater than it should be. This error can be partly compensated for by moistening the precipitate with a few drops of sulphuric acid before ignition, but the silicic acid formed on heating partly decomposes the alkali metal sulphates with the formation of alkali metal silicate. Alkali metal sulphates, therefore, have an effect similar to calcium sulphate on the weight of the silicon dioxide. If the crude silicic acid is contaminated by phosphates, the evaporation of sulphuric acid must be made at low temperatures if possible, to avoid losses owing to the volatility of phosphoric acid.

The purer the crude silicic acid, therefore, the less the error incurred on evaporation with hydrogen fluoride and sulphuric acid.

Procedure. Ignite the crude silicic acid in a platinum crucible at 1100 °C for about 1 hr, place it in a desiccator, allow to cool for 30 min, then weigh. If the precipitate is contaminated with alkali metals or calcium, it must be moistened with several drops of diluted sulphuric acid (1 : 4), ignited at 800 °C for 15 min, and weighed after cooling. Add 0·5 ml of diluted sulphuric acid (1 : 4), and about 10 ml of hydrogen fluoride solution (approx 45%) to the residue. Evaporate on a water bath for 30 min, then heat on an air bath until no more sulphuric acid fumes are liberated. Add 3–4 drops of concentrated sulphuric acid and 5 ml of hydrogen fluoride to the residue, heat on an air bath until the liberation of sulphuric acid fumes ceases, then ignite at 800 °C for 15 min. In this manner the residue obtained consists of the same sulphate–oxide mixture present in the first weighing.

The weight difference is equal to the SiO_2 content of the crude silicic acid. Stoichiometric factor: $Si/SiO_2 = 0{\cdot}46747$.

58.2. DETERMINATION OF THE SILICIC ACID CONTENT OF SILICATES

From the chemical properties of silicic acid and silicates, it is evident that the possibility of acid decomposition of a silicate depends on its composition with respect to strongly alkaline alkali metal and alkaline earth metal oxides (and zinc oxide, lead oxide), silicic acid, and structural water. Strongly basic ($CaO : SiO_2 \geq 2$) and strongly hydrated silicates are usually easily decomposed by strong acids, while acidic silicates can be made acid-soluble by fusion with strongly basic agents (sodium carbonate, sodium hydroxide). Silicates can therefore be divided into two groups for analytical purposes:

(1) *Silicates which are decomposed by acids.* Into this group fall Portland cement (60–67·1% CaO, 18–23·7% SiO_2, 4·5–8·1% Al_2O_3, 2·1–4·7% Fe_2O_3, $MgO < 5\%$, $SO_3 < 2{\cdot}5\%$), blast furnace slag, natural and artificial zeolites (alkali metal or calcium alkali metal-silicate containing water), water-glass (Na_2SiO_3, K_2SiO_3) with the exception of silicic acid-rich water-glasses; allanite [(OH)(Ca, Ce, Th)$_2$(Al, Fe)$_3$Si$_3$O$_{12}$], allophane ($Al_2SiO_5 \cdot nH_2O$), analcime ($NaAlSi_2O_6 \cdot H_2O$), botriolite ($HCaBSiO_5$), brewsterite [(Sr, Ba, Ca)$Al_2Si_6O_{16} \cdot 5\ H_2O$], calamine ($H_2Zn_2SiO_5$), chabazite ($CaAl_2Si_4O_{12} \cdot 6\ H_2O$), cronstedtite ($H_8Fe^{II}_4Fe^{III}_4Si_3O_{20}$), datolite ($HCaBSiO_5$), dioptase ($H_2CuSiO_4$), eulitine ($Bi_4Si_3O_{12}$), gadolinite ($Be_2FeY_2Si_2O_{10}$), helvine [3(Mn, Fe)$BeSiO_4 \cdot MnS$], ilvaite [$CaF_2(FeOH)(SiO_4)_2$] or lievrite, laumonite ($CaAl_2Si_4O_{12} \cdot 4\ H_2O$), montmorillonite ($H_2O \cdot Al_2O_3 \cdot 4\ SiO_2$), nathrolite ($Na_2Al_2Si_3O_{10} \cdot 2\ H_2O$), okenite ($CaSi_2O_5 \cdot 2\ H_2O$), olivine [(Mg, Fe)$_2SiO_4$], pectolyte [$HNaCa_2(SiO_3)_3$], prehnite [$H_2Ca_2Al_2(SiO_4)_3$], tefroite ($Mn_2SiO_4$), wernerite, which is a turbid form of mejonite ($CaCO_3 \cdot 3\ CaAl_2Si_2O_8$ or $Ca_4Al_6Si_6O_{24} \cdot CO_3$) because of imbeddings, wollastonite ($CaSiO_3$), willemite (Zn_2SiO_4). Silicates which contain large amounts of water usually fall in this group.

(2) *Silicates which are not decomposed by acids.* Glasses, ceramic materials, porcelain, chamotte, quartz (SiO_2), albite ($NaAlSi_3O_8$), andaluzite (Al_2SiO_5), augite (Fe_2O_3 and Al_2O_3 containing silicates), beryl ($Be_3Al_2Si_6O_{18}$),

axinite [$HCa_2(Fe, Mg, Mn)Al_2BSi_4O_{16}$], carfolite ($H_4MnAl_2Si_2O_{10}$), cianite ($Al_2SiO_5$), mica (potassium and aluminium silicates), diallage (Fe–Al-silicate, containing Ca, Mg), epidote [$(OH)Ca_2(Al, Fe)_3Si_3O_{12}$], euclas ($HBeAlSiO_5$), felspar (alkali and calcium aluminium silicate), garnierite [$(Mg, Ni)SiO_3$ + aq; 24–38% NiO], labradorite (a principal constituent of basic eruptive rocks), orthoclase ($KAlSi_3O_8$), petalite ($LiAlSi_4O_{10}$), pinite, which is the pseudomorph form of muscovite ($H_2KAlSi_3O_{12}$), procolite (aluminium silicate containing magnesium), serpentine ($H_4Mg_3Si_2O_9$), sillimanite (Al_2SiO_5), talc [$Mg_6(Si_8O_{20})(OH)_4$ or $H_2Mg_3Si_4O_{12}$], topaz [$Al_2(SiO_4)(F, OH)_2$], turmaline (boron- and fluorine-containing alkali aluminium silicate), vesuvian [$Ca_{10}Al_4(Mg, Fe)_2(OH)_4Si_9O_{34}$] and many other silicate rocks not mentioned here. Granite, olivine, staurolithe and sillimanite are very difficult to fuse, and their fusion can only be effected with sodium carbonate at about 1000°C. Clays and kaolin can only be partly dissolved with acids, but kaolin is more easily decomposed by acids after pre-heating at 500–600°C.

58.2.1. *Determination of the silicon dioxide content of silicates which are decomposed by acids*

It is very important that both acid-decomposable and non-decomposable silicates should be thoroughly powdered before analysis. A thin layer of silicic acid gel may form on the surface of the acid-decomposable silicate particles, and this retards the diffusion of acids towards the inside of the particle. When acid-resistant silicates are subjected to alkaline fusion the highly viscous glass formed on the surface of the grain may retard diffusion towards the inside of the melt. In both cases the heterogenous reaction can be accelerated by increasing the surface of the solid sample, i. e. by powdering. The methods of powdering and errors which occasionally occur during this operation are described in Chapter 2.5.1.

(a) *Hydrochloric acid method.* Powder the silicate in a diamond mortar, and then in an agate mortar to a flour-like powder, and sieve it through a fine silk or bronze sieve (3600 knots/cm^2). Grind the residue remaining on the sieve in a agate mortar again until the sample all passes through the sieve. Weigh 0·7–1·0 g of the flour-like powder by difference into a 150-ml porcelain or platinum dish, or into a chemically-resistant glass beaker, add 50 ml of water and mix well to avoid hardening of cements or hydraulic silicates. Cover the dish or beaker with a watch glass, boil the liquid for 1–2 min to ensure that the silicate powder is distributed uniformly, and then cool for a short time. Add 25 ml of concentrated hydrochloric acid in one portion to the solution with constant stirring. Place the mixture on a water bath, and mix several times with a glass rod.

After some minutes the silicate dissolves without coagulation of the silicic acid. The precipitation of silicic acid gel usually begins on standing. Rinse the glass rod and watch glass, and evaporate the mixture completely to dryness. Repeat the evaporation and drying twice with 3 ml of diluted hydrochloric acid (1 : 1); finally heat the dry residue on a water bath until the smell of hydrochloric acid disappears. Place the vessel containing the dry residue into a drying oven, and heat at 110–120°C for at least one

hour. Cool, add 20 ml of 10% (1 : 2) hydrochloric acid to the dehydrated residue, and heat on a water bath for 10–30 min. After the basic salts have dissolved dilute the solution to 100 ml with hot water, and heat on a water bath for a further 30 min. Loosen the residue adhering to the bottom of the vessel using a glass rod. Collect the silicic acid on a 9-cm medium grade filter paper, wash 6–10 times with dilute hydrochloric acid (1 : 100), and then continue washing with hot water until the washings become free of acid. Fold the wet filter paper containing the precipitate, and store it until the second silicic acid portion is precipitated from the filtrate.

The filtrate contains a considerable amount of silicon dioxide (1–5%) dissolved in colloidal form, and must therefore be evaporated again. The filtrate must be collected with the first two portions of the washing solution. The remaining washing solutions contain only negligible amounts of silicic acid and may be rejected. When possible the evaporation must be made in porcelain or platinum dishes. The dry residue must be dehydrated, after the disappearance of the hydrochloric acid smell, in a drying oven at 110–120°C for 1–2 hr.

Add 20 ml of 10% hydrochloric acid to the residue and heat on a water bath for 10–30 min. Add 100 ml of hot water and heat for a further 30 minutes on the water bath. Collect the silicic acid precipitated on a 7-cm filter paper. Collect the adhering silicic acid from the dish using small filter paper strips, and add these to the main part of the precipitate. Wash the precipitate with hot, dilute hydrochloric acid (1 : 100) and then with hot water, until the last part of washing solution shows no acidic reaction. Combine the filtrate with the washing solution of the first precipitate, and use it for the determination of metals in the silicate after evaporation.

Combust the two filter papers in the wet state in a platinum crucible, and ignite the residue at 1000–1100°C for 1 hr, using a blow-flame and covering the crucible with a lid. Allow the crucible to cool in a desiccator and weigh. Ignite again for 15 min and test for constant weight.

Add to the weighed crude silicic acid, 0·5 ml of diluted sulphuric acid (1 : 4) and about 10 ml of about 45% hydrogen fluoride. Evaporate the solution in a well ventilated fume-cupboard for about 30 minutes, and then heat on an air bath until no more sulphuric acid fumes are liberated. Add 3–4 drops of concentrated sulphuric acid and about 5 ml of hydrogen fluoride, heat on an air bath until no more sulphuric acid fumes appear, and then ignite on a blow flame for 15 min. Cool and weigh. The difference in weight between the crude silicic acid and the residue is equal to the silicon dioxide content. Stoichiometric factor: $Si/SiO_2 = 0{\cdot}46747$.

Notes. (1) When the crude silicic acid contains alkali and alkaline earth metal salts, the ignition and evaporation must be carried out according to the procedure of Chapter 58.1.

(2) When the precipitate contains so much iron(III) oxide that the crude silicic acid is somewhat red, the temperature at which the dehydration was conducted was too high. Under these circumstances the determination must be repeated with a new sample.

(b) *Perchloric acid method.* When perchloric acid is used for dehydration the above procedure is modified as follows:

Mix the sample with 10 ml of water, and add 2 ml of concentrated hydrochloric acid and 15 ml of 60–70% perchloric acid. Evaporate the solution cautiously on an air bath until the perchloric acid begins to fume. Cover the beaker with a watch glass and continue heating for 15 min. Care must be taken that *organic material* does not come into contact with the perchloric acid, otherwise *dangerous explosions* may occur. Cool the solution slightly, and add 70 ml of dilute hydrochloric acid (1 : 9). After heating to boiling, follow the procedure described above for hydrochloric acid.

The filtrate must also be evaporated again in this perchloric acid method. The filter paper with the precipitate should not be dried in a drying oven, because perchloric acid which remains behind may cause an explosion. For the same reason the perchloric acid must be washed out carefully from the precipitate.

58.2.2. *Determination of silicic acid in the presence of fluorides. Determination of silicofluoride ions (SiF_6^{2-}) (W. T. Schrenk, W. H. Ode, 1929)*

Silicates containing fluoride are decomposed when acidified; volatile silicon tetrafluoride is formed and silicic acid losses occur. If the solution also contains boron, however, boron trifluoride gas is formed and the silicic acid remains behind without loss. The method is suitable primarily for the determination of the silicic acid content of fluorites (CaF_2).

Procedure. Mix 0·5 g of the finely powdered sample, in a chemically resistant glass beaker, with 15 ml of 20% perchloric acid which has been saturated with boric acid at 50 °C. Evaporate the solution to perchloric acid fumes, and then heat for a further 4–5 min. Add a few millilitres of water to the residue and repeat the evaporation. Dissolve the residue in 75 ml of water, heat the solution to boiling, and collect the silicic acid and insoluble silicates on a filter paper. Wash the precipitate with hot 1% perchloric acid solution, and then with hot water until the washings no longer give a calcium reaction with ammonium oxalate in ammoniacal solution.

Combust the precipitate and filter paper in a platinum crucible and ignite the residue at 1000–1100 °C. Add 2 drops of concentrated sulphuric acid to the residue, evaporate the sulphuric acid on a water bath, and ignite the residue at 800 °C to constant weight. Add 0·5 ml of diluted sulphuric acid (1 : 4) and about 10 ml of hydrogen fluoride to the crude weighed silicic acid, evaporate the liquid, and finally remove the excess sulphuric acid. Repeat the evaporation with 3–4 drops of concentrated sulphuric acid and 5 ml of hydrogen fluoride, and then ignite the residue at 800 °C to constant weight. The difference in weight between the crude silicic acid and the residue is equal to the silicon dioxide content of the sample.

Note. The method can also be used for silicates which are not decomposed by acids, if they are first fused with a 5–6 fold excess of sodium carbonate. 20% perchloric acid solution saturated with boric acid should be added to neutralize the aqueous extract. A further 15 ml of perchloric acid must be added and the above procedure followed. The method is rapid and yields fairly accurate results.

The old classical Berzelius method is described in the determination of fluoride (Chapter 51.0.1.).

58.2.3. *Fusion of silicates which are not decomposed by acids*

Most natural and artificial silicates cannot be decomposed by simple acidic evaporation and thus they must first be fused. The fusion can be effected with alkaline substances (Na_2CO_3, NaOH). During the fusion the amount of basic oxides present increases in relation to silicic acid, and thus polysilicic acid is depolymerized and the silicate becomes soluble in acids. Sodium carbonate (Na_2CO_3) is usually used for the fusion. Pure sodium carbonate is preferred rather than potassium carbonate or a mixture of potassium and sodium carbonates, because potassium carbonate is hygroscopic and its melting point is lower and the fusion proceeds more slowly. Potassium ions may also cause interference during the determination of other metal oxides present. On fusion, part of the sodium carbonate reacts with the silicic acid and an equivalent amount of carbon dioxide is formed.

Thermogravimetric measurements have shown that when silicic acid is fused with sodium carbonate only 70% of the carbon dioxide, equivalent to sodium orthosilicate (Na_2SiO_4), is removed from the melt (measurements of F. Paulik). This indicates that the reaction does not proceed until complete depolymerization, and only polysilicates with low molecular weights (di-, tri-, tetrasilicates) are formed. At least a four-fold excess of sodium carbonate must be used for the fusion, otherwise an equilibrium is established. Thermogravimetric measurements have also shown that the amount of carbon dioxide liberated on fusion with potassium carbonate is less (about 50%), and thus the depolymerization ability of potassium carbonate is lower than that of sodium carbonate. The lower fusion efficiency of potassium carbonate is also explained by this fact. Silicate samples must be powdered very carefully and sieved before fusion to ensure that no large particles are present in the sample (see Chapters 2.5. and 58.2.1.). The details of the fusion with sodium carbonate are described in Chapter 2.5.1.

Sodium hydroxide can be used instead of sodium carbonate for the fusion of silicates. Fusion with sodium hydroxide is more effective than with sodium carbonate. One advantage is that the silicate need not be powdered very finely, and also the reaction proceeds smoothly at a temperature corresponding to a red glow (500°C), and the melt can be leached more easily from the crucible. A silver or nickel crucible can be used for the fusion; a platinum crucible cannot be used. When the dissolved melt is acidified carbon dioxide is not evolved. The sodium hydroxide melt only attacks a pure nickel crucible at temperatures greater than 550°C, and the fusion must therefore be effected below 500°C, i. e. the bottom of the crucible should not be heated to a visible red glow. Under these conditions the traces of nickel which are dissolved can be neglected. See Chapter 2.5.4. for details of the method.

For silicates which contain fluoride it is advisable to use a 8–10 fold excess of a mixture of crystalline borax and anhydrous sodium carbonate (231 : 336). When the melt is leached and the solution acidified with perchloric acid, volatile boron trifluoride is formed and silicic acid remains behind quantitatively. After fusion with sodium carbonate–borax mixture the melt is transparent, and this property can be used to check for complete fusion. In the presence of boric acid it is not advisable to carry out the

dehydration with hydrochloric acid, because silicic acid losses may occur. If a dehydration with hydrochloric acid is required, however, several millilitres of methyl alcohol must be added to the mixture, and the methyl borate must be removed by distillation. The evaporation with methyl alcohol must be repeated 3–4 times. When the dehydration is carried out with perchloric acid, losses do not occur. Methyl alcohol or other organic substances should not be added to the solution containing perchloric acid because dangerous explosions may occur.

58.3. DETERMINATION OF OXIDES ACCOMPANYING SILICIC ACID

The analysis of silicates always requires an initial fusion or acidic decomposition, and precipitation of silicic acid. The determination of the other substances can be carried out in the filtrates obtained, after double evaporation of the residue with acid. The methods used depend on the substances present in the solution. The residue obtained after the evaporation of silicic acid must be combined with the filtrate after dissolution or fusion.

For silicates which are not decomposed by acids the determination of the alkali metals (K, Na) cannot of course be effected after fusion with sodium carbonate or sodium hydroxide. The alkali metal ions, therefore, must be determined in a separate sample by the method of J. L. Smith by fusing with ammonium chloride and calcium carbonate (see Chapter 2.5.2.). When ions which form precipitates with sulphate ions are absent (Ca, Sr, Ba, Pb), evaporation with sulphuric acid and hydrogen fluoride according to Berzelius can be also used (see Chapter 2.5.3.). For the rapid analysis of glasses the evaporation with hydrogen fluoride can be accomplished also by nitric acid, and all the accompanying oxides can be determined in the aqueous solution of the evaporated residue.

Some silicates (feldspar) and quartz are very resistant to hydrogen fluoride. The method of Körner utilizes this property in the determination of the quartz (sand) and feldspar content of clays. The clay sample must be evaporated with sulphuric acid. The silicic acid gel present in the form of kaolin is precipitated and the quartz and feldspar remain behind unchanged. The insoluble residue must then be boiled for a short time with 0·5% hydrogen fluoride; only the silicic acid gel reacts to form SiF_4, quartz and feldspar remain behind and can be weighed. G. Keppler and H. Ippach[1] developed a method which did not require the use of platinum utensils.

The boric acid in special glasses and glazes can be separated in the form of methyl borate by distillation with methyl alcohol and sulphuric acid[2]. The distillate must be collected in sodium hydroxide and the boric acid determined volumetrically after neutralization and the addition of mannitol.

[1] G. Keppler and H. Ippach, *Sprechsaal* **56**, 356 (1924).

[2] L. Erdey, *Bevezetés a kémiai analízisbe II. Térfogatos analízis.* (Introduction to Chemical Analysis. II. Volumetric Analysis). 8 Ed. Tankönyvkiadó, Budapest (1965), p. 64; I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis.* Interscience, New York, London (1947). p. 114.

The determination of iron(II) oxide in silicates is very important, because without this data the amounts of FeO and Fe_2O_3 in the sample cannot be calculated. Without this value the results of the complete analysis cannot be checked to find whether the sum of the results is 100%. The sample must be dissolved in an atmosphere free of air with a mixture of hydrogen fluoride and sulphuric acid, and the iron(II) sulphate content of the residue must be determined by permanganometric titration.

Procedure. Weigh 0·5–1·5 g of the not too finely powdered sample into a platinum crucible, add 2 ml of concentrated sulphuric acid, and place the crucible in the middle of a sand bath. Cover the crucible with a large funnel, and pass carbon dioxide into the crucible through the stem of the funnel. The excess carbon dioxide escapes through the sand bath. Lift the funnel and add 10 ml of concentrated hydrogen fluoride solution to the crucible, cover immediately with the funnel, start the carbon dioxide current, and heat the sand bath gently. Dissolution is complete in 30–40 min. Cool and rinse the solution from the crucible into a 600-ml beaker containing 5–10 g of finely powdered or precipitated silicic acid, 20 g of potassium sulphate, 2 ml of concentrated sulphuric acid and 100 ml of water. Rinse the residue from the crucible with boiled-out distilled water, and titrate the iron(II) in the solution with potassium permanganate.

Notes. (1) The reagents in the beaker absorb hydrogen fluoride and thus the end-point is easily detected. If the residue is dissolved in water alone, the hydrogen fluoride may consume permanganate owing to the catalytic effect of manganese(II) ions.

(2) If the sample is powdered too finely, part of the iron(II) is oxidized to iron(III). Sulphides, organic substances (humus soils) cause positive errors, and manganese(IV) oxide causes negative errors.

58.4. DETERMINATION OF SILICIC ACID IN THE FORM OF THE QUINOLINE SALT OF SILICOMOLYBDIC ACID, $(C_9H_7N)_4H_4SiO_4 \cdot 12\,MoO_3 \cdot 2\,H_2O$

(H. N. Wilson, 1949; M. Armand and J. Berthoux, 1953)

In the presence of ammonium molybdate in a strongly acidic hydrochloric acid medium, silicomolybdic acid is formed, and can be precipitated by the hydrochloric acid salt of quinoline, in the form of an insoluble precipitate which has a high molecular weight (M.W. = 2339·7). This precipitate can be dried at 150°C and weighed.

In the above determination of silicic acid the aim was to precipitate the silicic acid as completely as possible and in its most insoluble form. In this determination care must be taken that the orthosilicic acid formed on acidification should not be polymerized, and should not precipitate before the addition of the molybdic acid. It is therefore advisable to dissolve the sample by fusion with sodium hydroxide. When the alkaline melt is acidified with hydrochloric acid, orthosilicic acid, H_4SiO_4, is formed. This forms yellow silicomolybdic acid in a rapid reaction when ammonium molybdate is added:

$$H_4SiO_4 + 12\,(NH_4)_2MoO_4 + 24\,HCl = H_4[Si(Mo_3O_{10})_4] + 24\,NH_4Cl + 12\,H_2O\,.$$

The reaction can be regarded as complete when a small excess of ammonium molybdate is present. The pH of the solution, however, affects the structure of the complex and the ease of filtration. When the pH of the solution is about 3·5 when the silicomolybdic acid is formed, α-isomeric silicomolybdic acid is produced and its quinoline salt is difficult to filter. When the solution is strongly acidic on the addition of ammonium molybdate (pH 1·0–1·5), however, a β-isomeric silicomolybdic acid is formed and yields a crystalline easily filtered precipitate with the hydrochloric acid salt of quinoline. The silicomolybdic acid, therefore, is sensitive to the acidity of the solution, and the hydrogen ion concentration of the solution also affects its rate of formation.

When the complex formation is complete and before the addition of the quinoline reagent, the solution must be strongly acidified, otherwise quinoline molybdate is precipitated with quinoline silicomolybdate. Quinoline molybdate dissolves only in strongly acidic, hydrochloric acid solution, and is precipitated often during filtration when the washing solution dilutes the strongly acidic filtrate. If the precipitate is obtained from a strongly acidic solution it has stoichiometric composition:

$$4\ C_9H_7N \cdot HCl + H_4[Si(Mo_3O_{10})_4] = (C_9H_7N)_4H_4\,[Si(Mo_3O_{10})_4] + 4\ HCl.$$

The solubility of the precipitate in 1 N hydrochloric acid is not negligible at 25°C, 100 ml of 1 N hydrochloric acid dissolves 35 mg, and at 90°C, 200 mg of the precipitate. When even a slight excess (0·02%) of quinoline is added however, the solubility becomes negligible at 25°C and is not greater than 25 mg at 90°C. When the solution contains a 0·20% excess of quinoline hydrochloride the precipitate is practically insoluble even at 90°C. In contrast to the decrease in solubility produced by the presence of excess quinoline, this effect for excess ammonium molybdate is not observed. This can be explained easily from the expression for the solubility product:

$$[C_9H_7NH^+]^4 \cdot [Si(Mo_3O_{10})_4^{4-}] = L.$$

The precipitate does not dissociate directly to molybdate ions, and therefore the presence of excess molybdate does not decrease the solubility.

The thermogravimetric curves shown in Fig. 58.2. indicate (measurements of S. Gál) that the precipitate can be dried below 210°C without danger of decomposition. In the temperature range 210–420°C quinoline and structural water is removed from the precipitate, while in the range 420–600°C, the precipitate attains constant weight again. In this temperature range the composition of the precipitate corresponds to the formula $SiO_2 \cdot 12\,MoO_3$. Between 600 and 950°C, MoO_3 sublimes from the precipitate, and on prolonged heating at about 1000°C pure SiO_2 is finally obtained. In practice the precipitate is usually dried at 150°C and weighed in this form. This procedure then takes advantage of the high molecular weight of the precipitate. The precipitate attains constant weight within 1 hr at this temperature.

The method can be used advantageously for the determination of silicic acid in sodium carbonate, sodium hydroxide, limestone, ignited lime, gypsum, galenite and in metallic aluminium and its alloys. For silicates, quartz and samples rich in silicic acid only a few milligrams of sample must be used. In the presence of boric acid, fluoride ions do not interfere. Phosphate and arsenate ions naturally cannot be present in the sample.

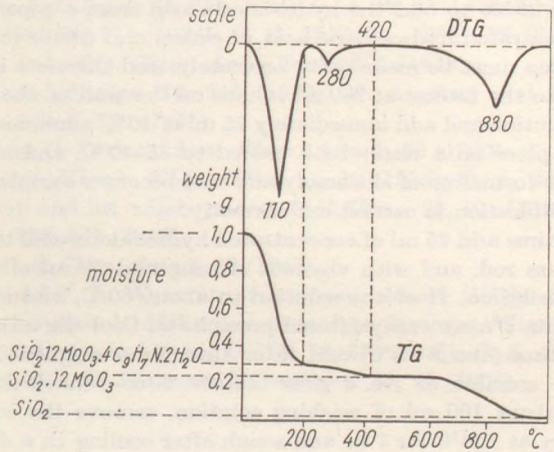


Fig. 58.2. Thermoanalytical curves of quinoline silicomolybdate

The precipitate can be titrated acidimetrically after dissolution in excess (30 ml) of 0·5 N sodium hydroxide solution. The excess sodium hydroxide is titrated with 0·5 N hydrochloric acid in the presence of cresol red—thymol blue indicator until the colour changes from pink to yellow:

$$(C_9H_7N)_4 \cdot H_4[Si(Mo_3O_{10})_4] + 24\,NaOH = 4\,C_9H_7N + SiO_2 + 12\,H_2O + \\ + 12\,Na_2MoO_4.$$

Under these conditions quinoline and silicic acid do not consume titrant.

Reagents. (1) 10% *ammonium molybdate solution.* Dissolve 50·0 g of analytically pure ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$, in 500 ml of water, allow to stand for 24 hr and filter. The solution slowly dissolves silicic acid from the glass bottle, and therefore should not be stored for longer than one week.

(2) 2% *quinoline hydrochloride solution.* Purify the technically pure quinoline by distillation (boiling point 237·7°C). For the preparation of the reagent use the fraction which distils between 230–240°C. Slowly add 20·0 ml of purified quinoline to 800 ml of hot water, allow to cool slightly and acidify with 25 ml of concentrated hydrochloric acid with constant stirring. Shake the old solution with filter paper pulp, filter on a glass filter, and remove moisture thoroughly at the pump. Dilute the filtrate to 1 litre with water.

(3) *Washing solution.* Dilute 25 ml of 2% quinoline hydrochloride solution with water to 1 litre.

Procedure. Fuse the finely powdered sample, containing not more than 15 mg of silicon dioxide, in a nickel or silver crucible with 10–20 g of solid sodium hydroxide at not more than 500 °C. Leach the melt with about 100 ml of water, and neutralize with concentrated hydrochloric acid in a 600-ml beaker in the presence of 8 drops of methyl orange. Near the end of the neutralization it is advisable to add the hydrochloric acid from a pipette. Then add 3·0 ml of concentrated hydrochloric acid in excess and dilute to 250 ml after cooling. (Dilution must be made quite accurately, and therefore it is advisable first to calibrate the beaker at 250 ml volume on the wall of the beaker.) Mix the acidified solution and add immediately 25 ml of 10% ammonium molybdate solution, mix, place on a water bath heated to 35–40 °C, and allow to stand for 15 min. The formation of silicomolybdic acid becomes complete during this time if the acidification is carried out correctly.

After this time add 25 ml of concentrated hydrochloric acid to the solution, mix with a glass rod, and with vigorous stirring add 20 ml of 2% quinoline hydrochloride solution. Heat the solution to about 80 °C, and mix from time to time to obtain a more easily filtered precipitate. Cool the mixture to below room temperature (about 15 °C) and filter through a weighed G 4 glass, A 2 porcelain filter- crucible or No. 4 glass texture filter- funnel. Rinse the precipitate with about 100 ml of washing solution, remove the solution at the pump, then dry at 150 °C for 1 hr and weigh after cooling in a desiccator.

$$\text{Stoichiometric ratio: } \frac{(C_9H_7N)_4 \cdot H_4Si(Mo_3O_{10})_4}{SiO_2} = 38{\cdot}81$$

$$\text{Stoichiometric factor: } \frac{1}{38{\cdot}81} = 0{\cdot}025678.$$

Notes. (1) Although the expected amount of precipitate usually becomes dry during the time mentioned, it is advisable to check for constant weight after a second drying and weighing. The dry precipitate very slowly absorbs water, but the weight increase produced in normal air is not greater than 0·5% even after several hours.

(2) Blank tests must be made on the reagents used, and the weights of the precipitates obtained must be corrected for the blank. If a precipitate of more than 5 mg is obtained in the blank, one of the reagents contains large amounts of silicic acid and therefore cannot be used.

(3) To determine the silicic acid content of sodium hydroxide, 20-g samples as solid or in solution should be weighed and dissolved in water. Aluminium metal samples must be dissolved in a nickel dish with 12–35 ml of 10 N sodium hydroxide, if necessary in the presence of a few drops of concentrated hydrogen peroxide.

(4) If the silicomolybdic acid containing hydrochloric acid turns blue owing to the presence of reducing substances, a few drops of 0·1 N potassium permanganate solution must be added to the solution.

(5) For 10-mg samples of silicon dioxide the true value differed from the mean of 12 determinations by +0·2%, and the standard deviation was ±0·48% (H. N. Wilson).

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to Table 58.1.

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CHAPTER 59

BORON — B — 10·81

ELEMENTARY boron does not occur naturally. Artificially manufactured boron has no significant practical importance. The most important alloys of boron (ferroboron, calcium boron) are used in the processing of steel, cast iron, iron alloys, copper and copper alloys as deoxidants. Boron steels can be hardened to glass-like hardness, and boron carbide is also used in practice because of its great hardness. Boron compounds occur naturally in large amounts in some places. Boric acid is found in small amounts (0·2 g/ml) in the waters of hot wells and in sea water. The most important boron compounds found in the form of minerals are the following: boric acid (H_3BO_3, sassoline), borax ($Na_2B_4O_7 \cdot 10\,H_2O$, tinkal), boronatrocalcite ($NaCaB_5O_9 \cdot 8\,H_2O$), boracite ($Mg_6Cl_2B_{14}O_{26}$), colemanite ($Ca_2B_6O_{11} \cdot 5\,H_2O$). Some borosilicates of complicated composition also exist (axinite, turmaline, datholite). Some industrial products, e.g. some types of glass and enamels contain boron compounds. Boron halides are used as catalysts in the industrial synthesis of organic compounds.

Dissolution of the sample. Crystalline elementary boron is only slightly attacked by acids and bases, but amorphous boron dissolves in concentrated nitric acid and sulphuric acid. Both forms can be fused by the following method:

Mix 0·5 g of the powdered sample with 2 g of potassium sodium carbonate and 4·5 g of solid sodium hydroxide in a nickel crucible (about 70 ml capacity), and melt cautiously in the covered crucible. When the melt solidifies add 3 g of sodium peroxide, melt the mixture again, and heat at 500°C for about 10–15 min. Cool, dissolve the melt in water, and filter the solution. Reject any unchanged residue.

During the dissolution and fusion of boric acid and borates when the neutral or acidic solution is boiled boric acid losses may occur, because boric acid is volatile with water vapour. Thus a reflux condenser must be used when neutral or acidic solutions of boric acid are boiled. A similar danger exists when solid boric acid is heated. At 100–200°C structural water is lost and considerable amounts of boric acid may be volatilized. At the temperature of red heat pure boron trioxide is also somewhat volatile. When anhydrous borax is ignited slight loss of boron may also occur. When an alkaline solution is boiled, or when the alkaline melt is ignited, there is no danger of loss of boron.

Ferroboron and *calcium boron* can be decomposed most easily using a mixture of hydrogen peroxide and nitric acid:

To 0·1–0·3 g of the sample add 30 ml of water and 30 ml of 30% hydrogen peroxide, fit the flask with an efficient reflux condenser, and then add 5–10 drops of diluted nitric acid (1 : 1) to the flask through the condenser. After the evolution of gas has subsided boil the solution until the hydrogen peroxide is decomposed. Collect the undissolved material, which consists of boron, borides and boron nitride, on a filter paper, and transfer the paper to a platinum crucible. Moisten the paper with 5% potassium hydroxide and dry. Moisten the residue with 10% sodium nitrate solution, dry, and finally fuse with a small amount of solid potassium sodium carbonate. Cool, add a small piece of potassium nitrate to the melt, and heat in a covered crucible at the temperature corresponding to red heat for 10 min. Dissolve the cold melt in water and combine the solution with the filtrate obtained after the dissolution in peroxide. When the aluminium and iron(III) hydroxide have dissolved evaporate the alkaline solution to small volume.

Dissolve *iron* and *steel* samples (1 g) containing boron in 20 ml of dilute hydrochloric acid (1 : 1) using a reflux condenser. Add 10 ml of 3% hydrogen peroxide solution to the solution and boil until the liberation of gas ceases. Cool, transfer the solution to a 500-ml volumetric flask, add 25 ml of 20% sodium hydroxide, dilute to volume and mix thoroughly. Filter the mixture containing the iron(II, III) oxide precipitate through a dry filter paper into a dry flask, and take 300 ml of the filtrate (0·6 g sample) and determine the boric acid content.

Silicates, *glasses* and *enamels* containing boron can be fused with a 6–8 fold excess of sodium carbonate. To the aqueous extract of the melt add not less than that weight of ammonium chloride equivalent to the amount of sodium carbonate used for the fusion. Boil the solution until most of the ammonia has evaporated. Precipitate the silicic acid which remains in the solution with ammoniacal zinc oxide (see Chapter 51.0.1.), heat the solution to boiling, and boil until the smell of ammonia can no longer be detected. Filter and wash the precipitate. The filtrate contains the boric acid from the sample.

A similar procedure must be adopted for silicates containing *fluoride*. Make the filtrate obtained after the precipitation of silicic acid with zinc oxide slightly alkaline with sodium carbonate, and add excess of calcium chloride to precipitate the fluoride. Make the filtrate alkaline with sodium hydroxide and evaporate to remove the ammonia. Ignite the precipitate consisting of CaF_2, $Ba(BO_2)_2$ and $CaCO_3$, cool, add dilute acetic acid, evaporate to dryness and leach with water containing a small amount of acetic acid. $CaCO_3$ and $Ca(BO_2)_2$ dissolve and CaF_2 remains behind undissolved.

Boric acid is more soluble in water and in alcohol than in mineral acids. Tartaric acid dissolves boric acid very easily. Minerals containing boron can usually be dissolved easily by boiling with hydrochloric acid under reflux. Boron minerals which are insoluble in hydrochloric acid must be fused with sodium carbonate. Mineral waters containing boron must be made alkaline

and then evaporated. The dry residue must be acidified with concentrated hydrochloric acid and extracted in a stoppered flask with 96% alcohol for 15–20 hours. The contents of the flask must be shaken periodically. The extraction must be repeated with a second portion of alcohol. After the second alcoholic extraction the residue is usually free of boric acid. The alcoholic extract is made alkaline and the alcohol is distilled off. Determine boric acid in the residue.

Forms of determination. The most important method for the determination of boric acid is based on the titration of a complex boric acid (mannitol, glycerine) with alkali. Boron can be separated most easily from accompanying interfering ions by distillation in the form of methyl borate (1). This method of separation and determination can usually be applied; the gravimetric method for the determination of boric acid in the form of CaB_2O_4 (2) is only seldom used, usually only when the samples are free of silicic acid, aluminium and iron(III). Boric acid can also be extracted with ether and weighed gravimetrically after evaporation of the solvent (3).

59.1. SEPARATION OF BORIC ACID BY DISTILLATION. GRAVIMETRIC DETERMINATION IN THE FORM OF CALCIUM BORATE

(According to F. A. Gooch, 1887).

The heavy metal salts of boric acid are insoluble in water, but can only be obtained as contaminated precipitates which are difficult to filter. They are therefore not suitable for gravimetric determination. In practice boric acid is usually distilled with methyl alcohol (B.P. 64·7°C) in the form of methyl borate (B.P. 65°C). The ester in the distillate can be decomposed by the addition of a known excess of basic oxide (CaO).

$$H_3BO_3 + 3\,CH_3OH \rightleftharpoons (CH_3O)_3B + 3\,H_2O$$

$$CaO + 3\,H_2O + 2\,(CH_3O)_3B = Ca(BO_2)_2 + 6\,CH_3OH.$$

After the evaporation of water and methyl alcohol, the residue must be ignited. The increase in weight of the basic oxide is equal to the weight of boron trioxide: $Ca(BO_2)_2 \rightarrow CaO \cdot B_2O_3$.

Sodium tungstate, which is not hygroscopic, can be used instead of calcium oxide to decompose the distillate.

In the distillation of methyl borate, in contrast to the distillation used before the acidimetric titration of boric acid, neither free hydrochloric nor sulphuric acid may be present in the solution. Hydrochloric and sulphuric acid may distil with the boric acid, and the calcium oxide then reacts with it to form calcium chloride and sulphate, and a weight increase is produced. Acetic acid must therefore be used for the acidification. Calcium acetate formed in the collector flask can be decomposed easily by ignition:

$$(CH_3COO)_2Ca = CaO + CO_2 + (CH_3)_2CO$$

Owing to the displacement of sulphuric acid by acetic acid the ester formation is incomplete, and therefore the distillation with methyl alcohol must be repeated several times.

The calcium oxide used to collect the boric acid must first be ignited to constant weight at 900–1000°C ($\frac{1}{2}$ hr). After the evaporation of methyl alcohol and water, any boric acid which remains together with the calcium oxide decomposes in the same way as free boric acid on heating. The thermal behaviour of the latter is shown in Fig. 59.1. (measurements of F. Paulik and S. Gál). The thermogravimetric (TG) curve reveals the loss of structural water in the range 100–300°C. The corresponding derivative thermogravimetric curve (DTG) shows two maxima (150 and 190°C), i.e. the loss takes place in two steps. It is probable that $H_2B_4O_7$ is formed intermediately and

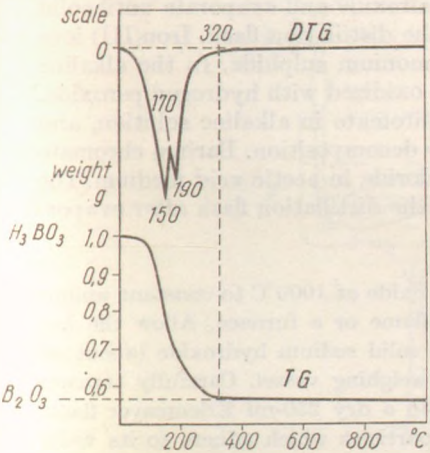

Fig. 59.1. Thermoanalytical curves of boric acid

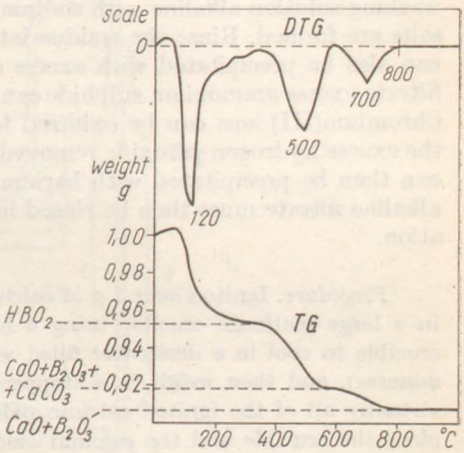

Fig. 59.2. Thermoanalytical curves of boric acid in the presence of calcium oxide

is decomposed rapidly to B_2O_3 and water. The B_2O_3 which remains behind loses only a few tenths per cent of its weight when ignited at 1000°C.

When the ignition is made in the presence of calcium oxide, however, the weight loss is even less. The thermogravimetric curves of Fig. 59.2. (measurements of I. Markovits) show the decomposition of boric acid in the presence of a five-fold molar amount of calcium oxide. When compared to the curves for pure boric acid, it is seen that the loss of water of metaboric acid in the presence of calcium oxide takes place at a higher temperature (about 500°C) in a separate step. The maximum at 700°C on the DTG curve denotes the decomposition of calcium carbonate. Above 800°C the residue has constant weight: $CaO + B_2O_3$.

Removal of interfering ions. Aluminium, chromium(III) and iron(III) salts interfere in the determination. In the presence of these ions 10–30% of the boric acid remains behind in the distillation flask. The hydroxides formed during the distillation therefore retain considerable amounts of boric acid. A similar error can be experienced in the presence of silicic acid, and the distillation must then be carried out in the presence of large amounts

of methyl alcohol from a sulphuric acid solution. Under these conditions it is advisable to collect the boric acid in sodium hydroxide solution and complete the determination by a titrimetric method. Aluminium and iron(III) ions can be precipitated as their phosphates from slightly acidic medium. Buffer the solution with sodium acetate and acetic acid, and add disodium hydrogen phosphate solution dropwise with constant stirring until the precipitate coagulates and the supernatant liquid does not become turbid when more reagent is added. Filter the mixture, and wash with water until phosphate can no longer be detected in the washings. During this time the precipitate also becomes free of boric acid. Make the combined filtrate and washing solution alkaline with sodium hydroxide and evaporate until solid salts are formed. Rinse the residue into the distillation flask. Iron(III) ions can also be precipitated with excess ammonium sulphide. In the alkaline filtrate excess ammonium sulphide can be oxidized with hydrogen peroxide. Chromium(III) ions can be oxidized to chromate in alkaline solution, and the excess hydrogen peroxide removed by decomposition. Barium chromate can then be precipitated with barium chloride in acetic acid medium. The alkaline filtrate must then be rinsed into the distillation flask after evaporation.

Procedure. Ignite about 1 g of calcium oxide at 1000°C to constant weight in a large platinum crucible using a hot flame or a furnace. Allow the hot crucible to cool in a desiccator filled with solid sodium hydroxide (about 40 minutes), and then weigh in a stoppered weighing vessel. Carefully transfer virtually all of the ignited calcium oxide to a dry 250-ml Erlenmeyer flask, place the crucible and the calcium oxide particles which adhere to its walls in the desiccator, and store during the distillation. Add 10 ml of hot water cautiously to the calcium oxide in the Erlenmeyer flask, and cool.

Make the 30–50 ml of borate solution, which contains not more than 0·2 g of boron trioxide, just acid with hydrochloric acid in the presence of litmus, and then neutralize accurately with 1 N sodium hydroxide solution. Make the solution just alkaline with one drop of 1 N sodium hydroxide solution, and then make the solution just acid with a few drops of 1 N acetic acid. The acidification must be made very cautiously, because if the solution remains alkaline, boric acid does not distil with the methyl alcohol, but if hydrochloric acid remains in excess it also distils and causes an increase in weight.

Add the prepared solution to the 200-ml distillation flask. The apparatus should be fitted with a dropping funnel. Rinse the vessel three times with 2–3 ml of water.

Figure 59.3. shows a distillation apparatus which can be easily prepared from a 200-ml pipette. The advantage of this apparatus is that there are no ground glass joints. The diameter of the tubing must be at least 0·7 cm. An efficient cork stopper must be used to connect the vapour tube to the condenser. The collector flask (8), containing the calcium oxide and water, must also be connected with a cork stopper (7) to the condenser. A second hole or a slot must be made in this stopper to avoid pressure differences. The borate solution must be added to distillation vessel (3) through the funnel (1), which must then be rinsed with a small volume of water. Tap (2) must then be closed.

Immerse the distillation flask (3) in a bath containing molten paraffin, and heat to 130–140 °C. Water which distils during this time is collected in the collector flask (8) containing calcium oxide. When the liquid has completely distilled, lower the paraffin bath and cool the distillation flask (3) somewhat, and then add 10 ml of absolute, acetone-free methyl alcohol to the vessel (3) through the funnel (1). Close the tap (2) and distil the methyl alcohol. Repeat distillation three times with 10-ml portions of methyl alcohol. During this

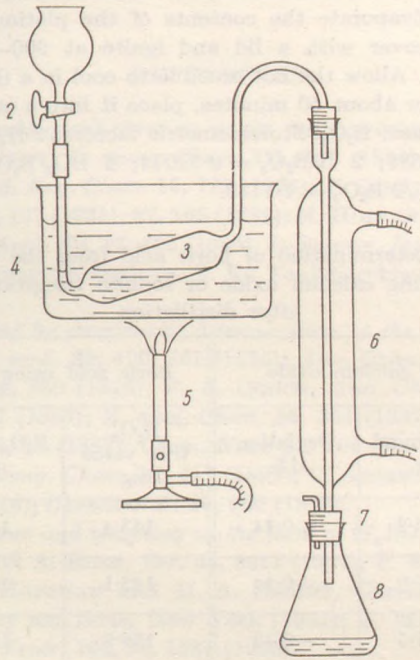

Fig. 59.3. Distillation apparatus for boric acid

process the contents of the distillation flask become slightly alkaline, and the litmus turns blue because the acetic acid also distils with the methyl alcohol. After the third distillation add 2–3 ml of water and a few drops of acetic acid to the vessel (3); the litmus then shows an acidic reaction again. Then add 10 ml of methyl alcohol, distil again, and repeat the distillation twice with 10-ml portions of methyl alcohol. When a total of 60 ml of methyl alcohol has distilled boric acid has been quantitatively collected in the collector flask.

At the end of the distillation the distillation flask must be removed from the bath, otherwise solidifying paraffin may break the vessel. Stopper the collector flask, shake its contents thoroughly, and allow it to stand for 1–2 hr. During this time methyl borate is quantitatively saponified. Evaporate the contents of the flask to dryness in small portions in a large platinum dish (e.g. in the crucible used for the ignition of the calcium oxide) at a low temperature if possible (less than 65 °C). The methyl alcohol should not be allowed

to boil during this process. Dissolve the calcium oxide which adheres to the wall of collector flask (8) with a few drops of acetic acid or nitric acid, and rinse the solution into the dish. Rinse the flask with water.

After the evaporation of the alcohol place the dish on a vapour bath and evaporate its contents to dryness. Then heat the dish with a small flame to decompose the calcium acetate. Cool, add a small volume of water to the residue, and transfer it without loss to the platinum crucible. Dissolve any adhering material from the dish with nitric acid or acetic acid, and rinse the solution into the crucible. Evaporate the contents of the platinum dish to dryness on a water bath, cover with a lid and ignite at 900–1000°C to constant weight (30 minutes). Allow the hot crucible to cool in a desiccator filled with sodium hydroxide for about 40 minutes, place it into a stoppered vessel, and weigh. Weight increase: B_2O_3. Stoichiometric factors: 2 $H_3BO_3/B_2O_3 = 1{\cdot}7760$; 2 $HBO_2/B_2O_3 = 1{\cdot}2588$; 2 $B/B_2O_3 = 0{\cdot}31074$; 2 $BO_2/B_2O_3 = 1{\cdot}2298$; 2 $BO_3/B_2O_3 = 1{\cdot}6893$; $B_4O_7/2\ B_2O_3 = 1{\cdot}1149$.

TABLE 59.1. Determination of boric acid from the collector flask, using calcium oxide or sodium tungstate, after distillation

Boric acid using calcium oxide			Boric acid using sodium tungstate		
B_2O_3 true value mg	B_2O_3 found mg	Deviation Δ%	B_2O_3 true value mg	B_2O_3 found mg	Deviation Δ%
206·5	206·2	−0·14	143·4	141·8	−1·1
206·7	207·0	+0·14	143·1	143·3	+0·1
207·7	207·5	−0·10	158·9	158·7	−0·1
179·1	179·5	+0·20	143·3	142·2	−0·8

Notes. (1) Sodium tungstate can be used instead of calcium oxide to decompose the methyl borate. Weigh 4–7 g of sodium tungstate and 0·5 g of tungsten trioxide into the platinum dish, and melt the mixture to remove any carbon dioxide. Cool and weigh the crucible and its contents.

(2) Methyl borate can also be collected in diluted ammonium carbonate solution instead of in calcium oxide. Under these conditions the solution collected in the flask must be mixed imme diately with calcium oxide and water in a platinum crucible and evaporated to dryness. The residue, however, contains a considerable amount of calcium carbonate and therefore the ignition must be made very carefully.

(3) The accuracy of the method can be judged from the data presented in Table 59.1. (measurements of F. A. Gooch and L. C. Jones).

From this data it can be seen that when sodium tungstate is used to collect the boric acid the results are sometimes considerably lower than the true values.

(4) The results obtained after separation of aluminium, iron(III) and chromium(III) ions are 0·3–1·2% lower than the true value.

(5) *Continuous distillation.* Interruption and repetition of the distillation can be avoided if the distillation is carried out while methyl acohol vapour is introduced. The methyl alcohol must be boiled in a flask, and the vapours introduced in a slow current of air or nitrogen into the distillation flask heated to 130–140°C; the distillation can then be finished within 30–50 min. The collection flask must be cooled in ice water.

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CHAPTER 60

APPENDIX

60.1. CLEANING OF VESSELS USED IN ANALYSIS

The most widely used pieces of apparatus in gravimetric analysis are beakers, funnels, glass rods, porcelain dishes and crucibles.

The cleaning of apparatus is an important laboratory task. It is advisable to wash apparatus immediately after use. Before washing apparatus, solutions and precipitates must be removed mechanically, and then the vessels must be rinsed with tap water. These operations must be carried out immediately after the apparatus has been used, and the beakers and flasks must be stored filled with tap water until they are cleaned. Dishes must be rinsed with lukewarm tap water. It is not advisable to rinse several vessels in the same water. Solid contamination can be removed from the walls of vessels with a brush, and the vessel should be completely filled with water to avoid smearing the impurities. Care must be taken that the whole internal surface of the beaker should be brushed, pressing the brush firmly against the glass.

The beaker then must be rinsed several times with tap water, and it must be noted whether the water adheres to the wall as a film or forms drops on the surface. When drops are formed the surface is contaminated with grease. Precipitates adhere strongly to greasy surfaces and are difficult to remove. The grease is most easily removed by soap. With the soapy brush a foam must be produced inside the vessel using a small volume of tap water. The foam must then be removed with distilled water. Persistent grease particles can be removed with chromic acid (15 g of $K_2Cr_2O_7$ dissolved in 500 ml of concentrated sulphuric acid), which must be left to stand in the vessel overnight and then poured back into its container. The vessels must then be rinsed in a current of tap water, and the tap water must be rinsed out with 2-3 portions of distilled water. The beaker must then be dried by rubbing it with a linen cloth which leaves no fibres. A clean beaker should be transparent, and water should not collect into drops on its internal surfaces when wet.

Sometimes completely dry beakers are required, and they can be dried inverted in a drying shelf or in a drying oven. Clean, dry beakers must be stored inverted in a dust-free cupboard. Funnels, watch-glasses, porcelain dishes and glass rods must be cleaned with similar care. Porcelain crucibles after cleaning must be ignited at the required temperature.

Cleanliness and care are essential in quantitative analytical work. The vessels must remain completely dry outside, and the laboratory benches must also be kept completely dry, otherwise spray losses cannot be detected. Although the loss of 1 drop from 100 ml of solution causes less than 0·1% error, the error produced on the loss of 2–3 drops is not negligible. These errors can be avoided quite easily. In semimicro analysis all perceptible losses and dust grains cause considerable errors. The care taken in semimicro analysis should be extended to all analytical work.

60.2. CHEMICALS USED IN ANALYSIS

The chemicals used in chemical analysis contain varying amounts of impurities. The nature and concentration of these impurities depend on the particular substance and its method of manufacture. Commercial chemicals are distinguished by the following names according to their purity: technical (crude), pure (pure), chemically pure (purissimum), analytical pure (for analysis). It is not necessary to use chemically pure reagents in all analytical work, so long as no other constituents are present which may affect the result of the analysis. Often interfering substances (silicates, alkalies) are dissolved from the bottles in which the reagents are stored. Gases and solid reagents can usually be stored for long periods without danger of decomposition, but solutions may be decompozed or oxidized, or may absorb carbon dioxide or be decomposed by bacteria, or they may dissolve so much contamination from the glass vessel that they become unsuitable for analytical work. Chemicals for quantitative analysis should therefore be stored in solid form if possible, and only sufficient reagent should be prepared from them to carry out the analysis. Solutions must be filtered through a dry filter before use, even when no visible solid impurities are present in them.

Chemicals of unknown purity must be checked for interfering impurities by suitable methods before use.[1]

60.2.1. *Distilled water*

Distilled water must be tested several times for dissolved material; 500 ml of the water should be evaporated in small portions in a weighed platinum or glass dish on a water bath, and the weight of residue determined. Special tests must be carried out for volatile substances (CO_2, NH_3, nitrogen oxides). In very important analyses double distilled water must be used. The second distillation must be carried out if possible in an all glass distillation apparatus. The condenser must be made of high quality glass or quartz. A small amount of potassium permanganate must be added to the water before distillation and the first part of the distillate, which contains the volatile substances, must be rejected. Distilled water which has been stored in wash bottles may contain a considerable amount of dissolved carbon dioxide and perhaps organic substances. The purity of distilled water can also be checked by measurement of its conductivity. The conductivity of

[1] The purity of analytical reagents can be checked by the procedures described in the book: E. MERCK, *Prüfung der chemischen Reagentien auf Reinheit.* Ed 5. Darmstadt, Verlag Chemie GmbH. Berlin W 35 (1939).

water, in an open vessel made of high quality glass, is about $1–2 \cdot 10^{-6}$ ohm^{-1}. Water which has been deionized on ion exchange columns sometimes contains organic substances.

60.2.2. *Ammonium hydroxide solution*

Ammonium hydroxide (NH_4OH, containing about 25% NH_3, specific gravity about 0·91) absorbs carbon dioxide from the air. Ammonia which contains carbonate cannot be used in the separation of the metal ions of groups III and IV. Considerable amounts of silicic acid may also be present in ammonia which has been stored in glass. Moderately concentrated, diluted ammonia solutions particularly dissolve considerable amounts of silicic acid, but also when concentrated ammonia solutions are stored in a new bottle they may contain large amounts of silicon dioxide. Ammonia must therefore be tested by the following method before use: 100 ml of the solution must be evaporated to dryness and dried at 105°C. For analytical purposes concentrated ammonia should not produce more than 2·3 mg of dry residue.

Carbon dioxide and silicic acid can be removed from ammonia by the following method:

Mix 500 ml of concentrated ammonia in a 1-litre flask with 10 g of freshly prepared hydrated lime, and allow the flask to stand stoppered with a cork. Boil 400 ml of distilled water for 15 min to remove carbon dioxide, cool it rapidly, and distil the ammonia from the first flask into the water through a condenser.

It is advisable to store pure ammonia in a polyethylene bottle. Pure ammonia solution can be prepared quite simply from pure gaseous ammonia by absorbing it in boiled distilled water while cooling in ice.

Ammonia obtained from water-gas may also contain tar products (pyridine bases). When the ammonia is neutralized with nitric aid it then smells of pyridine and may develop a pink colour from the oxidation products of the tars. These impurities may cause difficulties, especially in colorimetric determinations, as they form complexes with metals which have different colours from the ammonia complexes.

60.2.3. *Sodium hydroxide*

Sodium hydroxide (NaOH) may contain even larger amounts of carbonate and silicate than ammonia. Even solid sodium hydroxide may contain a considerable amount of carbonate. This impurity, however, does not interfere in most gravimetric determinations, and it is usually sufficient to dissolve the carbonate from the surface of the solid sodium hydroxide by rinsing with water, and then to dissolve the residual solid substance in boiled and cooled distilled water which is free of carbon dioxide. Sodium hydroxide must be dissolved in apparatus made of high quality glass, porcelain, nickel, silver or platinum. When the solid is dissolved in ordinary glassware, a considerable amount of silicic acid may pass into solution. Freshly prepared sodium hydroxide must always be used in gravimetric determinations. Unreliable preparations may also contain aluminates or ferrates.

60.2.4. *Hydrochloric acid*

Hydrochloric acid (HCl, about 37% HCl, sp. gr. *ca.* 1·19) is usually produced from gaseous hydrogen and chlorine, and is therefore fairly pure. Sometimes it contains free chlorine, sulphate and traces of iron.

The presence of free chlorine can be detected by diluting 10 ml of concentrated hydrochloric acid with an equal volume of water, and adding a small amount of solid potassium iodide and 0·5 ml of starch solution. When the mixture is shaken it should not become blue after 10 minutes when stored in the dark. When free chlorine is present it usually interferes in iodometric titrations.

200 g (178 ml) analytically pure hydrochloric acid, when evaporated to dryness and ignited gently in a weighed platinum crucible, should not leave more than 1 mg of residue.

Hydrochloric acid can be freed from non-volatile residues by distillation in an all-glass apparatus (see Fig. 49.1.). The collector, a flask, must be cooled in water and should contain a volume of distilled water equal to one-third of the volume of the hydrochloric acid to be distilled. The end of the condenser tube should stand 1 mm above the surface of the water. About two-thirds of the hydrochloric acid should be distilled.

60.2.5. *Sulphuric acid*

Sulphuric acid (H_2SO_4, approximately 95–97%, sp. gr. *ca.* 1·84) must first be tested for complete volatility. 200 g (109 ml) of analytically pure sulphuric acid, when evaporated in an ignited and weighed porcelain crucible in a well ventilated fume-cupboard, should leave less than 1 mg of residue after gentle ignition. The purity of sulphuric acid used for the determination of nitrogen or ammonia by the Kjeldahl method or for the detection of arsenic, must be checked by blank determinations. The sulphuric acid used for redox titrations should not contain oxidizible substances (nitrosyl-sulphuric acid, sulphurous acid etc.). To 39 ml of water, 11 ml (20 g) of concentrated sulphuric acid and 0·05 ml of 0·1 N potassium permanganate must be added. The pink colour should not disappear within 5 min.

60.2.6. *Nitric acid*

Nitric acid (HNO_3, approximately 65% HNO_3, sp. gr. *ca.* 1·40), is almost always prepared by oxidation of ammonia and is therefore usually pure. It is usually sufficient to check its ignition residue and for the presence of hydrochloric acid: 200 (143 ml) of chemically pure concentrated nitric acid (sp. gr. 1·4), when evaporated in a weighed platinum dish and gently ignited, should not leave more than 1 mg of residue. 15 ml (21 g) of concentrated nitric acid, diluted with 40 ml of water, should not become turbid when 1 ml of 0·1 N silver nitrate is added. Nitric acid used for forensic purposes to destroy substances containing arsenic must be free of arsenic, and therefore a blank test must be conducted on the recommended volume of nitric acid.

60.2.7. *Hydrogen peroxide*

Hydrogen peroxide (H_2O_2) contains traces of sulphuric acid and usually preserving agents also (phosphates, tartaric acid). The 30% reagent is available commercially in paraffin bottles; 100 g of this reagent (89·5 ml) when decomposed in the cold in a platinum dish and then evaporated to dryness on a water bath and dried to constant weight at 105°C, should not leave more than 1 mg of residue. Even specially pure reagents contain small amounts of free sulphuric acid. When hydrogen peroxide is used for acid-base titrations, therefore, the amount of alkali consumed by the hydrogen peroxide must be determined in a blank determination. The weighed amount of hydrogen peroxide must be diluted ten times with water, a small piece of manganese dioxide or platinum sponge must be added, and the solution must be heated. When the liberation of oxygen ceases, the solution must be filtered and titrated with 0·1 N sodium hydroxide solution from a micro burette in the presence of phenolphthalein (or other indicator as used in the main titration).

60.2.8. *Sodium peroxide*

Sodium peroxide (Na_2O_2) is usually packed in tinplated iron boxes, and thus the grains near the walls of the container usually contain traces of iron and tin. The sample must therefore be taken from the middle of the box, using a porcelain, nickel or stainless steel spoon.

60.2.9. *Sodium carbonate*

Sodium carbonate (Na_2CO_3) often contains traces of sulphate and chloride which make it unsuitable for the determination of sulphur and halogens. Anhydrous sodium carbonate must be used as the reagent.

60.2.10. *Sulphur*

The purity of elementary sulphur is only rarely good enough for analytical purposes. It usually contains traces of calcium sulphate and therefore cannot be sublimed without residue on heating. It is therefore advisable to recrystallise the sulphur from carbon dioxide.

Add an equal weight of carbon disulphide (CS_2) to the weighed sulphur sample in an Erlenmeyer flask, and heat the flask in a large water bath to 60°C until the sulphur dissolves completely. Filter the solution rapidly through a funnel which has been heated in a drying oven and has a short stem. The excess sulphur separates from the solution on cooling, and must be filtered off and air dried.

Carbon disulphide must not be handled near naked flames, because carbon disulphide and air form a dangerously explosive mixture. The water bath used must not be heated with a flame.

To check its purity, 10 g of the sulphur must be combusted in an ignited and weighed porcelain crucible over a small flame. The flame should be just high enough to boil the sulphur vigorously. The non-combustible residue must then be ignited and weighed after cooling. Pure sulphur should not leave any weighable residue.

60.2.11. *Sodium sulphide*

Crystalline sodium sulphide ($Na_2S \cdot 9\,H_2O$) often contains traces of iron, and the presence of iron must be taken into account if it is used for fusion.

60.2.12. *Ammonium carbonate and ammonium nitrate*

These reagents [$(NH_4)_2CO_3$ and NH_4NO_3] must be tested for their volatility. They should volatilize without leaving a weighable residue.

60.2.13. *Bromine*

Elementary bromine often contains traces of sulphuric acid. It must therefore be distilled from an all-glass apparatus. The presence of sulphuric acid causes errors in the determination of pyrites and sulphur.

60.2.14. *Hydrogen fluoride*

High purity hydrogen fluoride (HF; 38–40%) is commercially available in paraffin, hard rubber or polythene bottles. When it is used for silicate analysis two tests must be made: (a) for volatility and (b) for consumption of potassium permanganate.

(a) Evaporate 20 g of hydrogen fluoride to dryness in a platinum dish on a water bath. Add 1 ml of concentrated sulphuric acid and evaporate on an air bath. Ignite gently. Analytically pure hydrogen fluoride leaves less than 1 mg of residue.

(b) Dilute 10 g of hydrogen fluoride to 50 ml with water in a platinum dish. Add 0·05 ml of 0·1 N potassium permanganate. The pink colour should not disappear completely within 10 min.

60.2.15. *Acetic acid*

Acetic acid (CH_3COOH, *ca.* 90%) and glacial acetic acid (CH_3COOH, *ca.* 99–100%) may contain traces of chloride, sulphate and also sulphurous acid and formic acid. The latter can be detected by adding 5–6 drops of bromine water to a sample diluted to twice its volume with water. If the acetic acid is pure the yellow colour of the solution should not fade within 1 hr.

60.3. GASES USED FOR ANALYSIS

Gases used for analysis should if possible be handled in glass apparatus. Rubber tubing connections should be avoided, and even if used the ends of the glass tubes should be in contact inside the rubber sleeve to avoid contact of the gas with the rubber surface. The same rubber tube should always be used for the same gas. Chlorine attacks rubber, and it should therefore only be used when absolutely necessary. Flexible polyvinyl chloride or polyethylene tubes can be used to advantage for handling gaseous chlorine. When rubber tubing is used it must be coated in molten paraffin or vaseline. Rubber tubing permits the diffusion of carbon dioxide and hydrogen to a slight extent, and therefore these gases should also be

handled in glass tubing if possible. Apparatus filled with carbon dioxide or hydrogen, when assembled with rubber tubing, must be taken apart immediately after use because a pressure drop occurs inside the apparatus. Organic solvents and alkalies partly dissolve rubber. New rubber tubing also contains talc and this must be removed by washing. Rubber may also contain sulphur, and red rubber may contain antimony (Sb_2S_5), and this may cause interference in analysis.

The most important gases can be prepared in the laboratory by the following methods:

60.3.1. *Oxygen (O_2)*

Place lumps of potassium dichromate in the middle sphere of a Kipp apparatus, and in the upper sphere place acidified hydrogen peroxide solution. For 100 ml of 3% hydrogen peroxide add 15 ml of concentrated sulphuric acid. Instead of a rubber plate, place pieces of broken glass or porcelain between the middle and lower sphere.

To obtain oxygen, and most other gases, the Winkler-type gas generator (see Fig. 60.1.) can be used to advantage. Its greatest advantage is that it can be used for gases of higher pressures, and the spent acid can be removed without taking the apparatus apart.

Concentrated sulphuric acid or phosphorus pentoxide can be used to dry oxygen.

60.3.2. *Hydrogen (H_2)*

Hydrogen can be generated from granulated zinc and 20% sulphuric acid or diluted hydrochloric acid (1 : 1) in a Kipp or Winkler apparatus. If the zinc is contaminated with arsenic, the gas also contains hydrogen arsenide. This can be removed from the gas by washing it with alkaline saturated potassium permanganate solution. The gas must be dried by passing it through sulphuric acid.

60.3.3. *Chlorine (Cl_2)*

Solid potassium permanganate must be placed in the flask of the simple gas generator shown in Fig. 60.2. The flask must be cooled, and concentrated hydrochloric acid added dropwise from a dropping funnel. 11·2 g of chlorine can be obtained from 10 g of potassium permanganate and 60–65 ml of concentrated hydrochloric acid. The gas must be passed through saturated potassium permanganate solution and dried with concentrated sulphuric acid.

Chlorine can also be produced easily in a Kipp apparatus (see Chapter 2.5.10.).

60.3.4. *Carbon dioxide (CO_2)*

Carbon dioxide can be produced from marble ($CaCO_3$) and diluted hydrochloric acid (1 : 1) in a Kipp apparatus. Air-free gas can only be produced if the water used for dilution of the hydrochloric acid is first boiled out, and if one piece of marble is added to the funnel of the apparatus through the upper sphere. The carbon dioxide formed here then prevents the hydrochloric acid from becoming saturated with air again.

Completely air-free carbon dioxide suitable for microanalytical purposes can be produced from solid carbon dioxide, by placing it into a Dewar vessel (thermos bottle) and allowing it to evaporate slowly. The mouth of the bottle must be stoppered with a two-hole rubber stopper. One hole of the stopper must be fitted with a safety tube filled with mercury, and the

Fig. 60.1. Gas generator apparatus according to Winkler

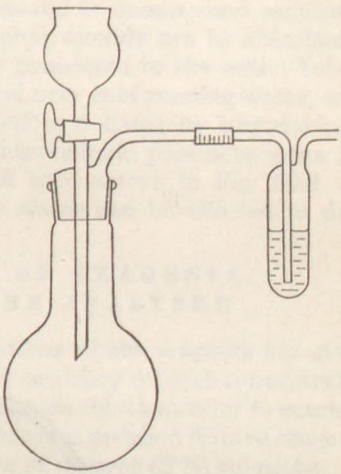

Fig. 60.2. Simple apparatus for gas production

gas delivery tube must be inserted into the second hole. After about 12 hr standing, the bottle produces a slow current of completely air-free carbon dioxide.

If the marble contains traces of sulphide, the carbon dioxide may be contaminated with hydrogen sulphide. The hydrogen sulphide, as well as any droplets of hydrochloric acid, can be removed from the gas by washing it with concentrated sodium bicarbonate solution. Concentrated sulphuric acid or phosphorus pentoxide can be used to dry the gas.

60.3.5. *Carbon monoxide (CO)*

This can be prepared as follows: Place sodium formate (HCOONa) into the flask of the apparatus shown in Fig. 60.2. Add concentrated sulphuric acid dropwise through the dropping funnel. Heat the mixture to about 70°C. Formic acid (HCOOH) can be used instead of sodium formate.

33% sodium hydroxide solution can be used to wash the gas, and concentrated sulphuric acid or dried calcium chloride can be used to dry it.

60.3.6. *Hydrogen chloride gas (HCl)*

The simple gas generator shown in Fig. 60.2. should contain concentrated hydrochloric acid. Concentrated sulphuric acid must then be added dropwise. Dry hydrogen chloride gas can be produced at an easily regulated rate in a Kipp apparatus from lumps of ammonium chloride and concentrated

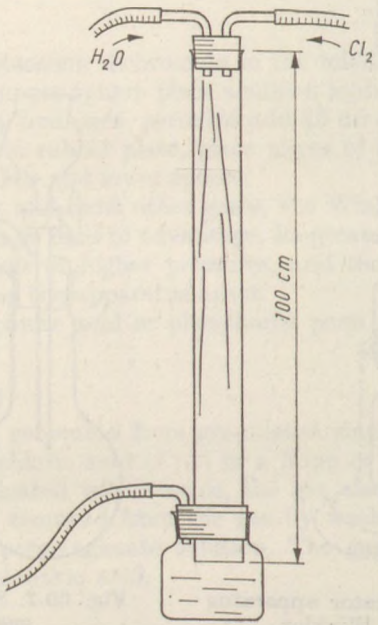

Fig. 60.3. Absorption of toxic water-soluble gases

sulphuric acid. In this case the device should not be fitted with a rubber stopper.

Concentrated sulphuric acid can be used to dry the gaseous hydrogen chloride.

60.3.7. *Hydrogen sulphide (H_2S)*

Hydrogen sulphide can be produced from iron(II) sulphide and diluted hydrochloric acid (1 : 1) in a Kipp apparatus. Distilled water can be used to wash the gas.

60.3.8. *Sulphur dioxide (SO_2)*

Sulphur dioxide can be produced from lumps of sodium hydrogen sulphite ($NaHSO_3$) or $Na_2S_2O_5$ and concentrated sulphuric acid in a simple gas

generator (see Fig. 60.2.). The gas can be washed with water and dried with concentrated sulphuric acid.

When suitable large pieces of sodium hydrogen sulphite are available, the gas can also be generated in a Kipp apparatus.

60.3.9 *Ammonia gas (NH_3)*

This can be produced from concentrated ammonium hydroxide by heating with sodium hydroxide solution. Calcium oxide (CaO), solid sodium hydroxide or soda lime can be used to dry the gas.

The gases mentioned, with the possible exception of hydrogen chloride, hydrogen sulphide and carbon monoxide, are also available commercially in cylinders, but their purity is not always satisfactory.

Excess and unused gases must be removed or decomposed cautiously. Thus chlorine, hydrogen sulphide and sulphur dioxide can be absorbed by sodium hydroxide solution in an absorber connected to the outlet tube of the apparatus. Excess ammonia must be led over cold running water, while excess carbon monoxide can be combusted in a flame by introducing it through the air inlet tube of a burner. Water-soluble poisonous gases (Cl_2, H_2S, SO_2, NH_3) can be introduced into a tube shown in Fig. 60.3. and absorbed in large amounts of water. The water can be allowed to drain away.

60.4. CONCENTRATION OF REAGENTS AND SOLUTIONS TO BE ANALYSED

In most cases the accurate concentrations of the reagents are given. Where no concentration data are given, the ordinary reagent concentration (2 N) is implied. Concentrated acid and ammonia solutions refer to commercial concentrated products. When the instructions mention diluted reagents, they must be made by twenty-fold dilution of reagent (2 N) solutions.

Acid and ammonia are often used as diluted solutions. The 1 + 3 and 1 : 3 diluted hydrochloric acid, for example, is prepared by mixing 1 volume of commercial concentrated hydrochloric acid and 3 volumes of water. The first number (x) of the expression for the mixing ratio ($x + y$ or $x : y$) always refers to the commercial concentrated acid or ammonia, while the second (y) refers to the volume of water.

In most procedures the weight limits of the sample to be determined are given. When it is not mentioned, sufficient sample should be taken to obtain about 100–300 mg of precipitate. The volume of the solution at precipitation is also given in most cases, but if not the precipitation should be made from 100–300 ml of solution.

60.5. NUMERICAL CALCULATION OF THE RESULT

From the data from the analytical determinations, the percentage of the substance determined in the sample must be calculated. In the calculations the numbers defined by 0·1% accuracy must be multiplied or divided, with sufficient accuracy so that the result also expresses the true accuracy of the method. Thus if the final result is calculated either to a greater or

smaller number of decimal places than is defined, a false impression may be gained (see Chapters 2.12 and 2.13.5.).

The arithmetic usually involves the multiplication of two numbers consisting of four figures, and the division of the product by a similar number. The result must also be obtained for four or five numbers. Psychological experiments have revealed that this arithmetic requires considerable mental concentration, especially for young people studying in their first years at universities. The probability of erroneous calculation is therefore very high. Psychologists use multiplication and division of this sort to test concentration ability. Erroneous results are only in a small number of cases caused by insufficient knowledge of arithmetic. From all this it follows that personal errors caused by inadequate concentration can occur in the calculations, as well as in analytical operations and observations. The elimination of errors in calculations can be effected on similar principles to those used for measurements. In all numerical calculations, therefore, care must be taken over the following points:

(a) Numbers should be written carefully, well separated from each other. Numbers may be copied incorrectly and must be checked. It is advisable, however, to avoid copying out the numbers several times, and where possible the calculation should be performed with the minimum of writing.

(b) Concentration is essential during the performance of the calculations.

(c) The calculations should be repeated and checked. The reliability of unchecked calculations is as low as that of single analytical measurements. When the calculation is repeated care must be taken not to repeat unwittingly any error in the first calculation.

(d) Arithmetical errors can be avoided most easily by checking each operation. Multiplication can be checked by division and division by multiplication.

(e) The magnitude of the result and its nearest value must be checked by mental arithmetic using round numbers.

(f) Even experienced people should check their calculations.

Calculation with machines. Calculation with calculating machines requires much less mental concentration. The addition and subtraction machines print the numbers on strips of paper, and their results can also be checked at later times. In multiplication-division type the results shown on the machine should be checked by re-reading. Errors very rarely occur owing to failure of the mechanism. Addition machines must be checked from time to time using a control. Multiplication and division machines can be checked with the number-pairs 14, 28, 57. When these pairs are multiplied by numbers which are non-divisible by 7, the same number-pairs result in different orders. If these number-pairs are multiplied by numbers greater than 7 the single pairs divide to their members. If seven or its multiples are used for multiplication, the numbers consist of 9 or its multiples.

Calculation with logarithms. The operation of addition or subtraction requires much less concentration than multiplication or division, and there-

fore can be carried out more surely even for many numbers. Thus in analytical practice, apart from calculation with machines, the calculations are usually performed with logarithms. The use of logarithms enables simple operations in calculation to replace more complicated operations, and in spite of the need to refer to tables of logarithms it ensures greater reliability. Calculations with logarithms, however, leads to limited accuracy and eliminates the use of too many figures in calculation. If a calculation method of limited accuracy is used, the error of the calculation should be negligible in comparison to the error of the measurements. In the following calculation it is shown how the error in a logarithm (y) depends on the error in the number (x).

$$y = {}^{10}\log x$$

Using natural logarithms (base e):

$$y = a \ln x, \quad \text{where} \quad a = 0{\cdot}4343$$

The difference quotient of the logarithm function:

$$\frac{\Delta x}{x} = 2{\cdot}303 \, \Delta y \, .$$

This expression shows that in the whole region of the logarithm function a given absolute error in the logarithm (Δy) yields the same relative error ($\Delta x/x$) in all numbers. It is also apparent that the smaller the error in the logarithm (Δy), i.e. using logarithms calculated to more places of decimals, the smaller is the error of the numbers ($\Delta x/x$).

Table 60.3. lists the errors incurred in the use of various logarithms and slide rules. When the most accurate methods are used with great care the errors can be reduced to $\pm 0{\cdot}01\%$ in analyses; not more than the same errors are allowed in the calculation. Logarithm tables of 7 or 5 figures fulfil these requirements, even if graphical interpolation is used. Seven figure logarithm tables are unnecessarily accurate for normal analytical work, and should only be used when atomic weights are to be determined with very great accuracy, or in astronomy. Five figure logarithm tables give sufficient accuracy even with graphical interpolation, and this is the table usually used in analytical work.[1] Four figure logarithms can be used with repeated interpolation for the calculation of analysis results accurate to within 0·1%. For technical analyses, therefore, four figure logarithms can generally be used. The accuracy of slide rules is insufficient for analytical calculations. They should only be used for approximate calculations.

The table of five figure logarithms of Briggs can be used for all analytical calculations. These tables, however, include too many numbers and cover about 20–26 pages. Reference to these tables thus requires considerable

[1] L. Erdey and L. Mázor, *Analitikai zsebkönyv* (Analytical Handbook), Műszaki Könyvkiadó, Budapest (1955).

TABLE 60.1. Accuracy of various logarithm tables and slide rules

	Absolute error of logarithm Δy	Relative error of the numbers in per cent $=\frac{\Delta x}{x} \cdot 100\%$
7 figure logarithm table with double interpolation	$\pm 0{\cdot}0000001$	$\pm 0{\cdot}000023$
5 figure logarithm table with double interpolation	$\pm 0{\cdot}00001$	$\pm 0{\cdot}0023$
5 figure logarithm table with graphic interpolation	$\pm 0{\cdot}00003$	$\pm 0{\cdot}0069$
4 figure logarithm table with double interpolation	$\pm 0{\cdot}0001$	$\pm 0{\cdot}023$
25 cm slide rule	$0{\cdot}0005 \sim 0{\cdot}001$	$0{\cdot}12 \sim 0{\cdot}25$
12·5 cm slide rule	$\pm 0{\cdot}002$	$\pm 0{\cdot}5$

time. K. Jordán observed that it is sufficient to present each tenth number of the ordinary Briggs table of logarithms; the intermediate logarithms can then be calculated by threefold linear interpolation. The logarithm of a six figure number differs from the number obtained by twofold linear interpolation of the Briggs table by not more than one unit in the fifth figure.

Table 60.4. contains five figure logarithms of this type, and the differences are also presented to assist the interpolation. The logarithm of the first three figures of the number can be obtained directly from the table. The logarithm of the next three figures can then be found by linear interpolation, and must be added to the first three figures obtained directly. The accurate logarithm is thus obtained. It is advisable to perform the interpolation with a shortened multiplication of limited accuracy.

Example of the multiplication of two six figure numbers: The calculation should be made without the use of the characteristics. The magnitude of the result can be obtained by mental arithmetic:

$x = 1{\cdot}83926 \cdot 2{\cdot}32918$

	log 1·83926	26245	1000 237
$\Delta = 237$	23·7 · 9·26	213·3	926 .... Δ_1
		2·7	
		1·4	$\Delta_1 = 23{\cdot}7 \cdot 9{\cdot}26$
		26462	
	log 2·32918	36549	1000 187
$\Delta = 187$	18·7 · 9·18	168·3	918 .... Δ_2
		1·9	
		1·5	$\Delta_2 = 18{\cdot}7 \cdot 918$
	x = Num. log	63183	
		144 428	1000 102
$\Delta = 102$		3900 : 102 ... 3	Δ_x 39
		840 8	
		240 2	$\Delta_x = \frac{39000}{102}$
		x = 4·28383	

Note. The linear interpolation can be performed more easily using the graphs in Figs. 60.4. and 60.5. or with a slide rule.

The shortened table of five figure logarithms can also be used instead of the four figure table. The last figure of the numbers may then be neglected after correction, and only a twoo-fold interpolation is then required. The four figure table of logarithms can also be used then for the logarithms of five figure numbers.

As the analysis results not only have a considerable effect on economies, but may also affect the fate of mankind, the results should be given only when it is certain that they are correct to within the stated accuracy, when responsibility is assured for the result. The reliability of the analyst is thus as important for good analyses as is a reliable balance.

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TABLE 60.1. Solubility products of the most important analytical precipitates at room temperature

Precipitate	Ionic product	L	p_L
$Ag[Ag(CN)_2]$	$[Ag^+] \cdot [Ag(CN)_2^-]$	$2 \cdot 10^{-12}$	11·7
Ag_3AsO_4	$[Ag^+]^3 \cdot [AsO_4^{3-}]$	$1 \cdot 10^{-22}$	22·0
AgBr	$[Ag^+] \cdot [Br^-]$	$4{\cdot}1 \cdot 10^{-13}$	12·3
$AgBrO_3$	$[Ag^+] \cdot [BrO_3^-]$	$5 \cdot 10^{-5}$	4·3
Ag_2CO_3	$[Ag^+]^2 \cdot [CO_3^{2-}]$	$6 \cdot 10^{-12}$	11·2
$Ag_2C_2O_4$ (oxalate)	$[Ag^+]^2 \cdot [C_2O_4^{2-}]$	$5 \cdot 10^{-12}$	11·3
$AgC_5H_9O_2$ (valerianate)	$[Ag^+] \cdot [C_5H_9O_2^-]$	$8 \cdot 10^{-5}$	4·1
$AgC_7H_5O_2$ (benzoate)	$[Ag^+] \cdot [C_7H_5O_2^-]$	$9{\cdot}3 \cdot 10^{-5}$	4·03
$AgC_7H_5O_3$ (salicylate)	$[Ag^+] \cdot [C_7H_5O_3^-]$	$1{\cdot}4 \cdot 10^{-5}$	4·85
AgCl	$[Ag^+] \cdot [Cl^-]$	$1{\cdot}1 \cdot 10^{-10}$	9·96
Ag_2CrO_4	$[Ag^+]^2 \cdot [CrO_4^{2-}]$	$2 \cdot 10^{-12}$	11·7
$Ag_2Cr_2O_7$	$[Ag^-]^2 \cdot [Cr_2O_7^{2-}]$	$2 \cdot 10^{-7}$	6·7
$Ag_4Fe(CN)_6$	$[Ag^+]^4 \cdot [Fe(CN)_6^{4-}]$	$1{\cdot}6 \cdot 10^{-41}$	40·8
AgI	$[Ag^+] \cdot [I^-]$	$1 \cdot 10^{-16}$	16
$AgIO_3$	$[Ag^+] \cdot [IO_3^-]$	$2 \cdot 10^{-8}$	7·7
Ag_2MoO_4	$[Ag^+]^2 \cdot [MoO_4^{2-}]$	$3{\cdot}2 \cdot 10^{-11}$	10·5
AgOH	$[Ag^+] \cdot [OH^-]$	$2 \cdot 10^{-8}$	7·7
Ag_2S	$[Ag^+]^2 \cdot [S^{2-}]$	$1{\cdot}6 \cdot 10^{-49}$	48·8
Ag_2SO_4	$[Ag^+]^2 \cdot [SO_4^{2-}]$	$6{\cdot}3 \cdot 10^{-5}$	4·2
AgSCN	$[Ag^+] \cdot [SCN^-]$	$4{\cdot}9 \cdot 10^{-11}$	10·3
$AgVO_3$	$[Ag^+] \cdot [VO_3^-]$	$1{\cdot}3 \cdot 10^{-10}$	9·9
Ag_2WO_4	$[Ag^+]^2 \cdot [WO_4^{2-}]$	$5 \cdot 10^{-10}$	9·3
$Al(C_9H_6ON)_3$ (oxinate)	$[Al^{3+}] \cdot [C_9H_6ON^-]^3$	$5 \cdot 10^{-33}$	32·3
$Al(OH)_3$	$[AlO_3H_2^-] \cdot [H^+]$	$1{\cdot}6 \cdot 10^{-14}$	13·8
$AlPO_4$	$[Al^{3+}] \cdot [PO_4^{3-}]$	$1 \cdot 10^{-6}$	6
As_2S_3	$[As^{3+}]^2 \cdot [S^{2-}]^3$	$4 \cdot 10^{-29}$	28·4
As_2S_5	$[As^{5+}]^2 \cdot [S^{2-}]^5$	$1 \cdot 10^{-30}$	30
$BaCO_3$	$[Ba^{2+}] \cdot [CO_3^{2-}]$	$7 \cdot 10^{-9}$	8·16
BaC_2O_4 (oxalate)	$[Ba^{2+}] \cdot [C_2O_4^{2-}]$	$1{\cdot}7 \cdot 10^{-7}$	6·77
$BaCrO_4$	$[Ba^{2+}] \cdot [CrO_4^{2-}]$	$2 \cdot 10^{-10}$	9·7
$Ba(IO_3)_2$	$[Ba^{2+}] \cdot [IO_3^-]^2$	$6 \cdot 10^{-10}$	9·22
$BaSO_4$	$[Ba^{2+}] \cdot [SO_4^{2-}]$	$1 \cdot 10^{-10}$	10
$Be(OH)_2$	$[Be^{2+}] \cdot [OH^-]^2$	$1 \cdot 10^{-20}$	20·0
$Bi(OH)_3$	$[Bi^{3+}]^2 \cdot [OH^-]^3$	$2 \cdot 10^{-16}$	15·7
BiOCl	$[BiO^+] \cdot [Cl^-]$	$2 \cdot 10^{-9}$	8·7
$BiPO_4$	$[Bi^{3+}] \cdot [PO_4^{3-}]$	$3{\cdot}2 \cdot 10^{-20}$	19·5
Bi_2S_3	$[Bi^{3+}]^2 \cdot [S^{2-}]^3$	$1{\cdot}6 \cdot 10^{-72}$	71·8
$CaCO_3$	$[Ca^{2+}] \cdot [CO_3^{2-}]$	$1{\cdot}2 \cdot 10^{-8}$	7·92
CaC_2O_4 (oxalate)	$[Ca^{2+}] \cdot [C_2O_4^{2-}]$	$2 \cdot 10^{-9}$	8·7
$CaC_4H_4O_6$ (tartrate)	$[Ca^{2+}] \cdot [C_4H_4O_6^{2-}]$	$7{\cdot}7 \cdot 10^{-7}$	6·11
CaF_2	$[Ca^{2+}] \cdot [F^-]^2$	$3{\cdot}4 \cdot 10^{-11}$	10·46

TABLE 60.1 *(contd.)*

Precipitate	Ionic product	L	p_L
$Ca(IO_3)_2$	$[Ca^{2+}] \cdot [IO_3^-]^2$	$6{\cdot}5 \cdot 10^{-7}$	6·19
$Ca_3(PO_4)_2$	$[Ca^{2+}]^3 \cdot [PO_4^{3-}]^2$	$1 \cdot 10^{-25}$	25
$CaSO_4$	$[Ca^{2+}] \cdot [SO_4^{2-}]$	$6{\cdot}1 \cdot 10^{-5}$	4·22
CdC_2O_4 (oxalate)	$[Cd^{2+}] \cdot [C_2O_4^{2-}]$	$1{\cdot}1 \cdot 10^{-8}$	7·96
CdS	$[Cd^{2+}] \cdot [S^{2-}]$	$4 \cdot 10^{-29}$	28·4
$Ce_2(C_2O_4)_3$ (oxalate)	$[Ce^{3+}]^2 \cdot [C_2O_4^{2-}]^3$	$2{\cdot}6 \cdot 10^{-29}$	28·39
$Ce_2(C_4H_4O_6)_3$ (tartrate)	$[Ce^{3+}]^2 \cdot [C_4H_4O_6^{2-}]^3$	$9{\cdot}7 \cdot 10^{-20}$	19·01
$Ce(IO_3)_3$	$[Ce^{3+}] \cdot [IO_3^-]^3$	$3{\cdot}5 \cdot 10^{-10}$	9·46
CuBr	$[Cu^+] \cdot [Br^-]$	$4{\cdot}1 \cdot 10^{-8}$	7·39
CuC_2O_4 (oxalate)	$[Cu^{2+}] \cdot [C_2O_4^{2-}]$	$2{\cdot}9 \cdot 10^{-8}$	7·54
CuCl	$[Cu^+] \cdot [Cl^-]$	$1 \cdot 10^{-6}$	6
CuI	$[Cu^+] \cdot [I^-]$	$5 \cdot 10^{-12}$	11·3
$Cu(IO_3)_2$	$[Cu^{2+}] \cdot [IO_3^-]^2$	$1{\cdot}4 \cdot 10^{-7}$	6·85
$Cu(OH)_2$	$[Cu^{2+}] \cdot [OH^-]^2$	$1{\cdot}4 \cdot 10^{-19}$	18·85
Cu_2S	$[Cu^+]^2 \cdot [S^{2-}]$	$2 \cdot 10^{-47}$	46·7
CuS	$[Cu^{2+}] \cdot [S^{2-}]$	$8{\cdot}5 \cdot 10^{-45}$	44·07
CuSCN	$[Cu^+] \cdot [SCN^-]$	$1{\cdot}6 \cdot 10^{-11}$	10·80
$Cr(OH)_3$	$[Cr^{3+}] \cdot [OH^-]^3$	$1 \cdot 10^{-30}$	30
$Fe(OH)_3$	$[Fe^{3+}] \cdot [OH^-]^3$	$1{\cdot}1 \cdot 10^{-36}$	35·96
$Ga(OH)_3$	$[Ga^{3+}] \cdot [OH^-]^3$	$1 \cdot 10^{-35}$	35
Hg_2Br_2	$[Hg_2^{2+}] \cdot [Br^-]^2$	$1{\cdot}3 \cdot 10^{-21}$	20·89
Hg_2Cl_2	$[Hg_2^{2+}] \cdot [Cl^-]^2$	$3{\cdot}1 \cdot 10^{-18}$	17·5
Hg_2CrO_4	$[Hg_2^{2+}] \cdot [CrO_4^{2-}]$	$2 \cdot 10^{-9}$	8·7
Hg_2I_2	$[Hg_2^{2+}] \cdot [I^-]^2$	$1{\cdot}2 \cdot 10^{-28}$	27·92
HgI_2	$[Hg^{2+}] \cdot [I^-]^2$	$3{\cdot}2 \cdot 10^{-29}$	28·5
HgO (+ H_2O)	$[Hg^{2+}] \cdot [OH^-]^2$	$1{\cdot}4 \cdot 10^{-26}$	25·9
HgS	$[Hg^{2+}] \cdot [S^{2-}]$	$4 \cdot 10^{-53}$	52·4
$In(OH)_3$	$[In^{3+}] \cdot [OH^-]^3$	$1 \cdot 10^{-33}$	33
$K[B(C_6H_5)_4]$	$[K^+] \cdot [B(C_6H_5)_4^-]$	$2{\cdot}25 \cdot 10^{-8}$	7·65
$KHC_4H_4O_6$ (bitartrate)	$[K^+] \cdot [HC_4H_4O_6^-]$	$3 \cdot 10^{-4}$	3·5
$K_2NaCo(NO_2)_6$	$[K^+]^2 \cdot [Na^+] \cdot [Co(NO_2)_6^{3-}]$	$2 \cdot 10^{-11}$	10·7
K_2PtCl_6	$[K^+]^2 \cdot [PtCl_6^{2-}]$	$1 \cdot 10^{-5}$	5
$La_2(C_2O_4)_3$ (oxalate)	$[La^{3+}]^2 \cdot [C_2O_4^{2-}]^3$	$2 \cdot 10^{-28}$	27·7
$La_2(C_4H_4O_6)_3$ (tartrate)	$[La^{3+}]^2 \cdot [C_4H_4O_6^{2-}]^3$	$2 \cdot 10^{-19}$	18·7
$La(IO_3)_3$	$[La^{3+}] \cdot [IO_3^-]^3$	$5{\cdot}9 \cdot 10^{-10}$	9·23
$MgCO_3$	$[Mg^{2+}] \cdot [CO_3^{2-}]$	$2 \cdot 10^{-4}$	3·7
MgC_2O_4 (oxalate)	$[Mg^{2+}] \cdot [C_2O_4^{2-}]$	$8{\cdot}6 \cdot 10^{-5}$	4·07
$Mg(C_9H_6ON)_2$ (oxinate)	$[Mg^{2+}] \cdot [C_9H_6ON)^-]^2$	$2{\cdot}5 \cdot 10^{-17}$	16·6
MgF_2	$[Mg^{2+}] \cdot [F^-]^2$	$7 \cdot 10^{-9}$	8·16
$MgNH_4PO_4$	$[Mg^{2+}] \cdot [NH^+] \cdot [PO_4^{3-}]$	$2{\cdot}5 \cdot 10^{-13}$	12·6
$Mg(OH)_2$	$[Mg^{2+}] \cdot [OH^-]^2$	$1{\cdot}2 \cdot 10^{-11}$	10·92
$Mn(OH)_4$	$[Mn^{4+}] \cdot [OH^-]^4$	$1 \cdot 10^{-56}$	56

TABLE 60.1 *(contd.)*

Precipitate	Ionic product	L	p_L
$PbCO_3$	$[Pb^{2+}] \cdot [CO_3^{2-}]$	$3{\cdot}3 \cdot 10^{-14}$	13·48
PbC_2O_4 (oxalate)	$[Pb^{2+}] \cdot [C_2O_4^{2-}]$	$3{\cdot}4 \cdot 10^{-11}$	10·47
$PbCl_2$	$[Pb^{2+}] \cdot [Cl^-]^2$	$2 \cdot 10^{-4}$	3·7
$PbCrO_4$	$[Pb^{2+}] \cdot [CrO_4^{2-}]$	$1{\cdot}8 \cdot 10^{-14}$	13·75
PbF_2	$[Pb^{2+}] \cdot [F^-]^2$	$7 \cdot 10^{-9}$	7·5
PbI_2	$[Pb^{2+}] \cdot [I^-]^2$	$1{\cdot}3 \cdot 10^{-8}$	7·5
$Pb(IO_3)_2$	$[Pb^{2+}] \cdot [IO_3^-]^2$	$1{\cdot}2 \cdot 10^{-13}$	12·92
PbS	$[Pb^{2+}] \cdot [S^{2-}]$	$1 \cdot 10^{-29}$	29
$PbSO_4$	$[Pb^{2+}] \cdot [SO_4^{2-}]$	$1 \cdot 10^{-8}$	8
Sb_2S_3	$[SbO^+]^2 \cdot [H_2S]^3$	$3 \cdot 10^{-27}$	26·5
$Sn(OH)_4$	$[SnO_3^{2-}] \cdot [H^+]^2 + H_2O$	$7{\cdot}8 \cdot 10^{-33}$	32·1
$SrCO_3$	$[Sr^{2+}] \cdot [CO_3^{2-}]$	$1{\cdot}6 \cdot 10^{-9}$	8·80
SrC_2O_4 (oxalate)	$[Sr^{2+}] \cdot [C_2O_4^{2-}]$	$5 \cdot 10^{-8}$	7·3
$Sr(IO_3)_2$	$[Sr^{2+}] \cdot [IO_3^-]^2$	$2{\cdot}5 \cdot 10^{-10}$	9·6
$SrSO_4$	$[Sr^{2+}] \cdot [SO_4^{2-}]$	$2{\cdot}8 \cdot 10^{-7}$	6·56
$TlBr$	$[Tl^+] \cdot [Br^-]$	$4 \cdot 10^{-6}$	5·7
$TlBrO_3$	$[Tl^+] \cdot [BrO_3^-]$	$8{\cdot}5 \cdot 10^{-5}$	4·07
$TlCl$	$[Tl^+] \cdot [Cl^-]$	$1{\cdot}5 \cdot 10^{-4}$	3·82
TlI	$[Tl^+] \cdot [I^-]$	$2{\cdot}8 \cdot 10^{-8}$	7·55
$TlIO_3$	$[Tl^+] \cdot [IO_3^-]$	$2{\cdot}2 \cdot 10^{-6}$	5·66
Tl_2S	$[Tl^+]^2 \cdot [S^{2-}]$	$4{\cdot}5 \cdot 10^{-23}$	22·35
TiO_3H_2	$[TiO^{2+}] \cdot [OH^-]^2$	$1 \cdot 10^{-30}$	30
$Ti(OH)_3$	$[Ti^{3+}] \cdot [OH^-]^3$	$1 \cdot 10^{-35}$	35
$Th(IO_3)_4$	$[Th^{4+}] \cdot [IO_3^-]^4$	$1{\cdot}24 \cdot 10^{-16}$	15·91
$ZnCO_3$	$[Zn^{2+}] \cdot [CO_3^{2-}]$	$2 \cdot 10^{-8}$	7·7
ZnS	$[Zn^{2+}] \cdot [S^{2-}]$	$1 \cdot 10^{-23}$	23

STOICHIOMETRIC FACTORS[1]

The factors of the following table are presented so that the weight of the element and some its simple compounds can be directly calculated from the measured weight of precipitate. In addition, stoichiometric factors for calculation of the most frequent compounds of the element are given for all elements in one or two weighing forms. Thus, by multiplying two suitable factors for any precipitate form the weight of the common compound required can be calculated.

Example. Aluminium has been determined in the form of aluminium oxinate from an alum solution. What weight of crystalline alum, $KAl(SO_4)_2 \cdot 12\ H_2O$, corresponds to the weight of the precipitate?

For the aluminium oxinate weighing form the stoichiometric factor for alum is not given. Factors for Al and Al_2O_3 are given, however. For Al_2O_3 as weighing form the factors of the most frequent compounds of aluminium are given, among them that of alum, $KAl(SO_4)_2 \cdot 12\ H_2O$. From the weight of aluminium oxinate the corresponding amount of alum can be calculated by multiplying the following two factors:

$$\frac{KAl(SO_4)_2 \cdot 12\ H_2O}{Al(C_9H_6ON)_3} = \frac{KAl(SO_4)_2 \cdot 12\ H_2O}{Al_2O_3} \cdot \frac{Al_2O_3}{Al(C_9H_6ON)_3} = 9.3056 \cdot 0.11096\,.$$

If calculations are made with logarithms, the sum of the logarithms of the two factors gives the logarithm of the required factor.

[1] The table was drawn up and checked by Éva Buzágh, Ilona Buzás, Tibor Kántor, Mária Pápay, László Pólos and Katalin Vigh.

TABLE 60.2. Stoichiometric factors

Required	Found	Factor	log
Ag_3AsO_4	Ag	1·4292	*15 510*
AgBr	,,	1·7408	*24 075*
AgCN	,,	1·2412	*09 384*
AgCl	,,	1·3287	*12 342*
Ag_2CrO_4	,,	1·5377	*18 687*
AgI	,,	2·1764	*33 774*
$AgNO_3$	,,	1·5748	*19 722*
Ag_2O	,,	1·0742	*03 107*
Ag_3PO_4	,,	1·2935	*11 175*
$Ag_4P_2O_7$	,,	1·4031	*14 709*
Ag_2S	,,	1·1486	*06 018*
AgSCN	,,	1·5384	*18 708*
Ag_2SO_4	,,	1·4452	*15 994*
$AgVO_3$	,,	1·9172	*28 267*
Ag_3VO_4	,,	1·3552	*13 200*
CN	,,	0·24118	*38 235*
KCN	,,	0·60362	*78 077*
Ag	AgBr	0·57445	*75 925*
AgCl	,,	0·76326	*88 267*
AgI	,,	1·2503	*09 699*
As	,,	0·13296	*12 373*
Br	,,	0·42555	*62 895*
BrO_3	,,	0·68114	*83 324*
HBr	,,	0·43091	*63 439*
KBr	,,	0·63375	*80 192*
$KBrO_3$	,,	0·88935	*94 907*
NH_4Br	,,	0·52161	*71 734*
NaBr	,,	0·54797	*73 876*
Ag	$Ag_2C_2O_4$ (oxalate)	0·71025	*85 141*
AgCl	,,	0·94368	*97 483*
Ag	$Ag(C_3H_2ONS_2)$ (rhodanine)	0·44937	*65 260*
AgCl	,,	0·59707	*77 602*
Ag	$Ag(C_6H_4N_3)$ (benzotriazole)	0·47734	*67 883*
AgCl	,,	0·63423	*80 225*
Ag	$Ag(C_6H_4NCS_2)$ (mercaptobenzthiazole)	0·39354	*59 499*
AgCl	,,	0·52288	*71 840*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Ag	$Ag(C_{12}H_{10}ONS)$ (thionalide)	0·33279	*52 217*
AgCl	,,	0·44217	*64 559*
Ag	AgCl	0·75263	*87 658*
Ag_3AsO_4	,,	1·0757	*03 168*
AgBr	,,	1·3102	*11 734*
AgCN	,,	0·93416	*97 042*
Ag_2CrO_4	,,	1·1573	*06 345*
AgI	,,	1·6380	*21 432*
$AgNO_3$	,,	1·1852	*07 380*
Ag_3PO_4	,,	0·97350	*98 834*
$Ag_4P_2O_7$	,,	1·0560	*02 367*
Ag_2S	,,	0·86449	*93 676*
AgSCN	,,	1·1579	*06 366*
Ag_2SO_4	,,	1·0877	*03 652*
As	,,	0·17420	*24 106*
$BaCl_2$	,,	0·72652	*86 125*
Cl	,,	0·24737	*39 334*
ClO_3	,,	0·58224	*76 510*
ClO_4	,,	0·69387	*84 128*
HCl	,,	0·25440	*40 552*
$HClO_4$	,,	0·70090	*84 566*
KCl	,,	0·52015	*71 613*
$KClO_3$	,,	0·85503	*93 198*
$KClO_4$	,,	0·96665	*98 527*
NH_4Cl	,,	0·37323	*57 197*
NaCl	,,	0·40777	*61 041*
$NaClO_3$	,,	0·74264	*87 078*
$NaClO_4$	,,	0·85427	*93 159*
P_2O_6	,,	0·27549	*44 010*
Ag	Ag_2CrO_4	0·65033	*81 313*
AgCl	,,	0·86407	*93 655*
CrO_4	,,	0·34967	*54 366*
Ag	AgI	0·45947	*66 226*
AgCl	,,	0·61049	*78 568*
AgBr	,,	0·79985	*90 301*
HI	,,	0·54482	*73 625*
I	,,	0·54053	*73 282*
KI	,,	0·70706	*84 945*
NH_4I	,,	0·61736	*79 054*
NaI	,,	0·63845	*80 512*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Ag	Ag_3PO_4	0·77312	*88 825*
PO_4	,,	0·22688	*35 579*
P_2O_5	,,	0·16955	*22 929*
Ag	Ag_2S	0·87061	*93 982*
AgCl	,,	1·1568	*06 324*
S	,,	0·12939	*11 190*
Ag	AgSCN	0·65002	*81 292*
AgCl	,,	0·86366	*93 634*
$BaSO_4$	,,	1·4065	*14 813*
KSCN	,,	0·58558	*76 758*
NH_4SCN	,,	0·45868	*66 151*
SCN	,,	0·34998	*54 405*
Ag	$AgVO_3$	0·52159	*71 733*
V	,,	0·24634	*39 153*
V_2O_5	,,	0·43973	*64 319*
Ag	Ag_3VO_4	0·73791	*86 800*
V	,,	0·11617	*06 509*
V_2O_5	,,	0·20737	*31 674*
Al	$Al(C_6H_5O_2N_2)_3$ (cupferronate)	0·061550	*78 922*
Al_2O_3	,,	0·11630	*06 558*
Al	$Al(C_9H_6ON)_3$ (oxinate)	0·058722	*76 880*
Al_2O_3	,,	0·11096	*04 516*
Al	$Al(C_9H_4ONBr_2)_3$ (dibromo oxinate)	0·028921	*46 121*
Al_2O_3	,,	0·054647	*73 757*
Al	Al_2O_3	0·52923	*72 364*
$AlCl_3$	,,	2·6157	*41 759*
$AlCl_3 \cdot 6\ H_2O$	,,	4·7362	*67 543*
AlF_3	,,	1·6473	*21 678*
$Al(NO_3)_3$	,,	4·1782	*62 099*
$Al(NO_3)_3 \cdot 9\ H_2O$	,,	7·3587	*86 680*
$Al_2O_3 \cdot H_2O$	,,	1·1767	*07 065*
$Al_2O_3 \cdot 2\ H_2O$	,,	1·3534	*13 142*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
$Al(OH)_3$	Al_2O_3	1·5301	*18 472*
$AlPO_4$	,,	2·3922	*37 880*
$Al_2(SO_4)_3$	,,	3·3558	*52 579*
$Al_2(SO_4)_3 \cdot 18\ H_2O$	,,	6·5363	*81 533*
$KAl(SO_4)_2 \cdot 12\ H_2O$	,,	9·3056	*96 874*
$(NH_4)Al(SO_4)_2 \cdot 12\ H_2O$	,,	8·8923	*94 901*
Al	$AlPO_4$	0·22123	*34 484*
$AlCl_3$	,,	1·0934	*03 879*
$Al(NO_3)_3$	,,	1·7466	*24 219*
Al_2O_3	,,	0·41802	*62 120*
$Al_2(SO_4)_3$	,,	1·4028	*14 699*
PO_4	,,	0·77881	*89 143*
P_2O_5	,,	0·58198	*76 491*
As	Ag_3AsO_4	0·16195	*20 938*
As_2O_3	,,	0·21384	*33 008*
As_2S_3	,,	0·26594	*42 478*
$Mg_2As_2O_7$	,,	0·33560	*52 582*
As	As_2O_5	0·65190	*81 418*
As	As_2S_3	0·60898	*78 460*
Ag_3AsO_4	,,	3·7603	*57 522*
$AsCl_3$	,,	1·4737	*16 841*
AsH_3	,,	0·63353	*80 177*
AsO_3	,,	0·99920	*99 965*
AsO_4	,,	1·1293	*05 280*
As_2O_3	,,	0·80409	*90 530*
As_2O_5	,,	0·93416	*97 042*
As_2O_7	,,	1·0642	*02 702*
As_2S_5	,,	1·2607	*10 060*
As_2Se_3	,,	1·5718	*19 641*
H_3AsO_4	,,	1·1539	*06 215*
$Mg_2As_2O_7$	,,	1·2619	*10 104*
$Mg(NH_4)AsO_4 \cdot 6\ H_2O$	,,	2·3524	*37 152*
As	As_2S_5	0·48306	*68 400*
AsO_3	,,	0·79258	*89 905*
As_2O_3	,,	0·63782	*80 470*
As_2O_5	,,	0·74100	*86 982*
As_2S_3	,,	0·79322	*89 940*
$Mg_2As_2O_7$	,,	1·0010	*00 043*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
As	$BiAsO_4$	0·21531	*33 307*
As_2O_3	,,	0·28430	*45 377*
As	$Mg_2As_2O_7$	0·48257	*68 356*
Ag_3AsO_4	,,	2·9798	*47 418*
$AsCl_3$	,,	1·1678	*06 737*
AsH_3	,,	0·50203	*70 073*
AsO_3	,,	0·79179	*89 861*
AsO_4	,,	0·89487	*95 176*
As_2O_3	,,	0·63718	*80 426*
As_2O_5	,,	0·74026	*86 938*
As_2O_7	,,	0·84333	*92 600*
As_2S_3	,,	0·79243	*89 896*
As_2S_5	,,	0·99900	*99 957*
As_2Se_3	,,	1·2456	*09 537*
H_3AsO_4	,,	0·91435	*96 111*
$Mg(NH_4)AsO_4 \cdot 6\ H_2O$	,,	1·8641	*27 048*
As	$Mg(NH_4)AsO_4 \cdot 6\ H_2O$	0·25887	*41 309*
As_2O_3	,,	0·34181	*53 379*
As_2S_3	,,	0·42509	*62 848*
$Mg_2As_2O_7$	,,	0·53644	*72 952*
$AuBr_3$	Au	2·2170	*34 576*
AuCl	,,	1·1800	*07 188*
AuCN	,,	1·1321	*05 388*
$AuCl_3$	,,	1·5399	*18 751*
$Au_2(SO_4)_3$	,,	1·7315	*23 842*
$Au_2(SO_4)_3 \cdot H_2O$	,,	1·7772	*24 973*
$HAuCl_4$	,,	1·7251	*23 681*
$KAu(CN)_4$	,,	1·7268	*23 724*
$KAu(CN)_4 \cdot H_2O$	,,	1·8182	*25 965*
B	B_2O_3	0·31074	*49 240*
BO_2	,,	1·2298	*08 982*
BO_3	,,	1·6893	*22 770*
B_4O_7	,,	1·1149	*04 723*
HBO_2	,,	1·2588	*09 994*
H_3BO_3	,,	1·7760	*24 944*
KBF_4	,,	3·6163	*55 827*
$Na_2B_4O_7$	,,	1·4450	*15 987*
$Na_2B_4O_7 \cdot 10\ H_2O$	,,	2·7386	*43 753*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Ba	$Ba[BeF_4]$	0·61770	*79 078*
BaO	,,	0·68966	*83 864*
$BaSO_4$	,,	1·0497	*02 106*
Ba	$BaCO_3$	0·69595	*84 258*
$BaCrO_4$	,,	1·2837	*10 847*
BaO	,,	0·77702	*89 043*
$BaSO_4$	,,	1·1827	*07 286*
Ba	BaC_2O_4 (oxalate)	0·60946	*78 494*
$BaC_2O_4 \cdot H_2O$ (oxalate)	,,	1·0800	*03 341*
$BaCrO_4$	,,	1·1242	*05 084*
$BaSO_4$	,,	1·0357	*01 522*
Ba	$BaC_2O_4 \cdot H_2O$ (oxalate)	0·56434	*75 154*
$BaCrO_4$	,,	1·0410	*01 743*
$BaSO_4$	,,	0·95900	*98 182*
Ba	$BaCrO_4$	0·54213	*73 411*
$Ba[BeF_4]$	,,	0·87765	*94 332*
$BaCO_3$	,,	0·77898	*89 153*
BaC_2O_4 (oxalate)	,,	0·88953	*94 916*
$BaC_2O_4 \cdot H_2O$	,,	0·96065	*98 257*
$BaCl_2$	,,	0·82200	*91 487*
$BaCl_2 \cdot 2\,H_2O$	,,	0·96424	*98 419*
$Ba(IO_3)_2$	,,	1·9228	*28 393*
$Ba(NO_3)_2$	,,	1·0316	*01 352*
BaO	,,	0·60528	*78 196*
$Ba(OH)_2$	,,	0·67640	*83 020*
$Ba(OH)_2 \cdot 8\,H_2O$	,,	1·2452	*09 574*
$BaSO_4$	,,	0·92126	*96 438*
Ba	$Ba(IO_3)_2$	0·28195	*45 017*
$BaCrO_4$	,,	0·52007	*71 607*
$BaSO_4$	,,	0·47912	*68 045*
Ba	$BaSO_4$	0·58847	*76 972*
$Ba[BeF_4]$	,,	0·95266	*97 894*
$BaCO_3$	,,	0·84556	*92 714*
BaC_2O_4 (oxalate)	,,	0·96556	*98 478*
$BaC_2O_4 \cdot H_2O$	,,	1·0428	*01 818*
$BaCl_2$	,,	0·89225	*95 049*
$BaCl_2 \cdot 2\,H_2O$	,,	1·0467	*01 980*
$BaCrO_4$	,,	1·0855	*03 562*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
$Ba(IO_3)_2$	$BaSO_4$	2·0871	*31 955*
$Ba(NO_3)_2$	,,	1·1198	*04 913*
BaO	,,	0·65701	*81 757*
$Ba(OH)_2$	,,	0·73421	*86 582*
$Ba(OH)_2 \cdot 8\ H_2O$	,,	1·3516	*13 086*
Ba	$BaS_2O_3 \cdot H_2O$	0·51350	*71 054*
$BaSO_4$	,,	0·87260	*94 081*
Be	BeO	0·36033	*55 670*
$BeCO_3$	,,	2·7595	*44 083*
$BeCO_3 \cdot 4\ H_2O$	,,	5·6406	*75 132*
$BeCl_2$	,,	3·1954	*50 453*
$BeCl_2 \cdot 4\ H_2O$	,,	6·0766	*78 366*
BeF_2	,,	1·8795	*27 405*
$Be(NH_4)PO_4$	,,	4·8788	*68 831*
$Be(NH_4)PO_4 \cdot 6\ H_2O$	,,	9·2004	*96 381*
$Be(NO_3)_2$	,,	5·3184	*72 578*
$Be(NO_3)_2 \cdot 4\ H_2O$	,,	8·1995	*91 379*
$Be_2P_2O_7$	,,	3·8375	*58 405*
$BeSO_4$	,,	4·2007	*62 333*
$BeSO_4 \cdot 4\ H_2O$	,,	7·0816	*85 013*
Be	$Be_2P_2O_7$	0·09897	*97 265*
$BeCO_3$	,,	0·71909	*85 678*
$BeCO_3 \cdot 4\ H_2O$	,,	1·4699	*16 729*
$BeCl_2$	,,	0·83268	*92 048*
$BeCl_2 \cdot 4\ H_2O$	,,	1·5829	*19 946*
BeF_2	,,	0·48978	*69 000*
$Be(NH_4)PO_4$	,,	1·2713	*10 426*
$Be(NH_4)PO_4 \cdot 6\ H_2O$	,,	2·3975	*37 975*
$Be(NO_3)_2$	,,	1·3859	*14 173*
$Be(NO_3)_2 \cdot 4\ H_2O$	,,	2·1367	*32 973*
BeO	,,	0·26058	*41 595*
$BeSO_4$	,,	1·0946	*03 927*
$BeSO_4 \cdot 4\ H_2O$	,,	1·8454	*26 608*
Bi_2O_3	Bi	1·1148	*04 721*
$BiPO_4$	,,	1·4544	*16 269*
As	$BiAsO_4$	0·21531	*33 307*
AsO_4	,,	0·39927	*60 127*
Bi	,,	0·60073	*77 868*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Bi_2O_3	$BiAsO_4$	0·66971	*82 589*
$BiPO_4$	,,	0·87372	*94 137*
Bi	$Bi(C_6H_3O_3)$ (pyrogallate)	0·62935	*79 889*
Bi_2O_3	,,	0·70162	*84 610*
$BiPO_4$	,,	0·91534	*96 158*
Bi	$Bi(C_9H_6ON)_3$ (oxinate)	0·32582	*51 297*
Bi_2O_3	,,	0·36323	*56 018*
$BiPO_4$	,,	0·47388	*67 566*
Bi	$Bi(C_9H_6ON)_3 \cdot H_2O$ (oxinate)	0·31692	*50 094*
Bi_2O_3	,,	0·35331	*54 815*
$BiPO_4$	,,	0·46093	*66 364*
Bi	$Bi(C_{12}H_{10}ONS)_3 \cdot H_2O$ (thionalide)	0·23862	*37 770*
Bi_2O_3	,,	0·26602	*42 491*
$BiPO_4$	,,	0·34705	*54 040*
Bi	$Bi[Cr(SCN)_6]$	0·34289	*53 516*
Bi_2O_3	,,	0·38227	*58 237*
$BiPO_4$	,,	0·49871	*69 785*
Bi	Bi_2O_3	0·89700	*95 279*
$BiAsO_4$	,,	1·4932	*17 411*
$BiCl_3$	,,	1·3535	*13 146*
BiF_3	,,	1·1416	*05 753*
$Bi(IO_3)_3$	,,	3·1491	*49 818*
$Bi(NO_3)_3$	,,	1·6954	*22 927*
$Bi(NO_3)_3 \cdot 5\ H_2O$	,,	2·0820	*31 848*
BiOBr	,,	1·3087	*11 683*
BiOCl	,,	1·1179	*04 839*
BiOI	,,	1·5103	*17 908*
$Bi(OH)_3$	,,	1·1160	*04 765*
$BiPO_4$	,,	1·3046	*11 548*
Bi_2S_3	,,	1·1034	*04 273*
$Bi_2(SeO_3)_3$	,,	1·7143	*23 410*
$KBiI_4$	,,	3·2435	*51 102*
Bi	BiOBr	0·68543	*83 596*
Bi_2O_3	,,	0·76413	*88 317*
$BiPO_4$	,,	0·99690	*99 865*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Bi	BiOCl	0·80243	*90 441*
Bi_2O_3	,,	0·89457	*95 161*
$BiPO_4$	,,	1·1671	*06 710*
Bi	BiOI	0·59390	*77 371*
Bi_2O_3	,,	0·66210	*82 092*
$BiPO_4$	,,	0·86379	*93 641*
Bi	$BiPO_4$	0·68756	*83 731*
$BiAsO_4$	,,	1·1445	*05 863*
$BiCl_3$	,,	1·0375	*01 598*
BiF_3	,,	0·87507	*94 204*
$Bi(IO_3)_3$	,,	2·4138	*38 270*
$Bi(NO_3)_3$	,,	1·2995	*11 379*
$Bi(NO_3)_3 \cdot 5\ H_2O$	,,	1·5959	*20 299*
Bi_2O_3	,,	0·76651	*88 452*
$Bi(OH)_3$	,,	0·85540	*93 217*
BiOBr	,,	1·0031	*00 135*
BiOCl	,,	0·85685	*93 290*
BiOI	,,	1·1577	*06 359*
Bi_2S_3	,,	0·84576	*92 725*
$Bi_2(SeO_3)_3$	,,	1·3141	*11 861*
$KBiI_4$	,,	2·4862	*39 553*
PO_4	,,	0·31244	*49 477*
P_2O_5	,,	0·23349	*36 827*
Bi	Bi_2S_3	0·81294	*91 006*
Bi_2O_3	,,	0·90630	*95 727*
$BiPO_4$	,,	1·1824	*07 275*
$BaCO_3$	CO_2	4·4846	*65 172*
BaO	,,	3·4846	*54 215*
C	,,	0·27291	*43 602*
CO_3	,,	1·3635	*13 467*
C_2O_4	,,	1·0000	*00 000*
$CaCO_3$	,,	2·2742	*35 683*
CaO	,,	1·2742	*10 525*
K_2CO_3	,,	3·1404	*49 698*
$KHCO_3$	,,	2·2749	*35 696*
K_2O	,,	2·1404	*33 049*
Li_2CO_3	,,	1·6789	*22 503*
Li_2O	,,	0·67892	*83 182*
$MgCO_3$	,,	1·9161	*28 243*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
MgO	CO_2	0·91613	*96 196*
$MnCO_3$	,,	2·6118	*41 695*
MnO	,,	1·6119	*20 733*
Na_2CO_3	,,	2·4083	*38 172*
$NaHCO_3$	,,	1·9088	*28 077*
Na_2O	,,	1·4083	*14 870*
$(NH_4)_2CO_3$	,,	2·1833	*33 912*
$SrCO_3$	,,	3·3546	*52 565*
As_2O_7	$Ca_2As_2O_7$	0·76560	*88 400*
Ca	,,	0·23440	*36 996*
$CaCO_3$	,,	0·58536	*76 742*
CaC_2O_4 (oxalate)	,,	0·74917	*87 458*
$CaC_2O_4 \cdot H_2O$	,,	0·85455	*93 174*
CaO	,,	0·32797	*51 584*
CO_2	$CaCO_3$	0·43971	*64 317*
Ca	,,	0·40044	*60 254*
$Ca_2As_2O_7$	,,	1·7084	*23 258*
CaC_2	,,	0·64044	*80 648*
CaC_2O_4 (oxalate)	,,	1·2798	*10 716*
$CaC_2O_4 \cdot H_2O$	,,	1·4599	*16 432*
$CaCN_2$	,,	0·80035	*90 328*
$CaCl_2$	,,	1·1089	*04 489*
$CaCl_2 \cdot 2\,H_2O$	,,	2·1889	*34 023*
CaF_2	,,	0·78010	*89 215*
$Ca(IO_3)_2$	,,	3·8955	*59 056*
$CaMoO_4$	,,	1·9985	*30 070*
$Ca(NO_3)_2$	,,	1·6395	*21 472*
$Ca(NO_3)_2 \cdot 4\,H_2O$	,,	0·23595	*37 282*
CaO	,,	0·56029	*74 841*
$Ca_3(PO_4)_2$	,,	1·0330	*01 412*
$Ca(H_2PO_4)_2$	,,	2·3385	*36 894*
$CaHPO_4 \cdot 2\,H_2O$	,,	1·7195	*23 539*
$CaSO_4$	$CaCO_3$	1·3603	*13 363*
$CaSO_4 \cdot 2\,H_2O$	,,	1·7203	*23 559*
$CaWO_4$	,,	2·8774	*45 900*
Ca	CaC_2O_4 (oxalate)	0·31288	*49 538*
$CaCO_3$	,,	0·78134	*89 284*
$CaC_2O_4 \cdot H_2O$	,,	1·1407	*05 716*
CaO	,,	0·43778	*64 126*
$CaSO_4$	,,	1·0628	*02 647*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
CO_2	$CaC_2O_4 \cdot H_2O$ (oxalate)	0·60240	*77 988*
C_2O_4	,,	0·60240	*77 988*
Ca	,,	0·27430	*43 822*
$Ca_2As_2O_7$	,,	1·1702	*06 826*
CaC_2	,,	0·43869	*64 216*
$CaCN_2$	,,	0·54823	*73 896*
$CaCO_3$	,,	0·68498	*83 568*
CaC_2O_4	,,	0·87668	*94 284*
$CaCl_2$	,,	0·75958	*88 057*
$CaCl_2 \cdot 6\ H_2O$	,,	1·4994	*17 591*
CaF_2	,,	0·53436	*72 783*
$Ca(IO_3)_2$	,,	2·6684	*42 624*
$CaMoO_4$	,,	1·3689	*13 639*
$Ca(NO_3)_2$	,,	1·1230	*05 040*
$Ca(NO_3)_2 \cdot 4\ H_2O$	,,	1·6162	*20 850*
CaO	$CaC_2O_4 \cdot H_2O$	0·38379	*58 410*
$Ca_3(PO_4)_2$	,,	0·70761	*84 980*
$Ca(H_2PO_4)_2$	,,	1·6018	*20 462*
$CaHPO_4$	,,	0·93117	*96 903*
$CaSO_4$	,,	0·93177	*96 931*
$CaSO_4 \cdot 2\ H_2O$	,,	1·1783	*07 127*
$CaWO_4$	,,	1·9710	*29 468*
Ca	$CaC_4H_4O_6 \cdot H_2O$ (tartrate)	0·19440	*28 870*
CaO	,,	0·27201	*43 458*
Ca	$Ca(C_9H_6ON)_2$ (oxinate)	0·12205	*08 654*
$CaCO_3$	,,	0·30479	*48 400*
$CaC_2O_4 \cdot H_2O$ (oxalate)	,,	0·44495	*64 832*
CaO	,,	0·17077	*23 242*
Ca	$Ca(C_{10}H_7O_5N_4)_2 \cdot 7\ H_2O$ (picrolonate)	0·057870	*76 245*
$CaCO_3$	,,	0·14452	*15 992*
$CaC_2O_4 \cdot H_2O$ (oxalate)	,,	0·21098	*32 423*
CaO	,,	0·080972	*90 833*
Ca	CaF_2	0·51332	*71 039*
$CaCO_3$	,,	1·2819	*10 785*
CaC_2O_4 (oxalate)	,,	1·6406	*21 501*
$CaC_2O_4 \cdot H_2O$	,,	1·8714	*27 217*
CaO	,,	0·71824	*85 627*
$CaSO_4$	,,	1·7437	*24 148*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Ca	$CaMoO_4$	0·20037	*30 183*
$CaCO_3$	,,	0·50037	*69 930*
CaC_2O_4 (oxalate)	,,	0·64040	*80 645*
$CaC_2O_4 \cdot H_2O$	,,	0·73049	*86 361*
CaO	,,	0·28036	*44 771*
MoO_3	,,	0·71964	*85 712*
CO_2	CaO	0·78479	*89 475*
Ca	,,	0·71469	*85 412*
$Ca_2As_2O_7$	,,	3·0490	*48 416*
CaC_2	,,	1·1430	*05 806*
$CaCN_2$	,,	1·4284	*15 486*
$CaCO_3$	,,	1·7848	*25 158*
CaC_2O_4 (oxalate)	,,	2·2842	*35 874*
$CaC_2O_4 \cdot H_2O$	,,	2·6056	*41 590*
$CaCl_2$	,,	1·9791	*29 648*
$CaCl_2 \cdot 6\ H_2O$	,,	3·9067	*59 181*
$Ca(IO_3)_2$	,,	6·9526	*84 215*
$CaMoO_4$	,,	3·5669	*55 229*
$Ca(NO_3)_2$	,,	2·9262	*46 630*
$Ca(NO_3)_2 \cdot 4\ H_2O$	,,	4·2111	*62 440*
$Ca(OH)_2$	,,	1·3213	*12 099*
$Ca_3(PO_4)_2$	,,	1·8437	*26 570*
$Ca(H_2PO_4)_2$	,,	4·1737	*62 052*
$CaHPO_4$	,,	2·4262	*38 493*
$CaSO_4$	,,	2·4278	*38 521*
$CaSO_4 \cdot 2\ H_2O$	,,	3·0703	*48 717*
$CaSiO_3$	,,	2·0715	*31 629*
$CaWO_4$	,,	5·1355	*71 058*
Ca	$CaSO_4$	0·29438	*46 891*
$CaCO_3$	,,	0·73515	*86 637*
CaC_2O_4 (oxalate)	,,	0·94087	*97 353*
$CaC_2O_4 \cdot H_2O$	,,	1·0732	*03 069*
CaO	,,	0·41190	*61 479*
Ca	$CaWO_4$	0·13917	*14 354*
$CaCO_3$	,,	0·34753	*54 100*
CaC_2O_4 (oxalate)	,,	0·44479	*64 816*
$CaC_2O_4 \cdot H_2O$	,,	0·50736	*70 532*
CaO	,,	0·19472	*28 942*
WO_3	,,	0·80507	*90 583*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Ca	$K_2Ca[Ni(NO_2)_6]$	0·088469	*94 679*
CaO	,,	0·12379	*09 267*
CdO	Cd	1·1423	*05 779*
$Cd_2P_2O_7$	,,	1·7737	*24 889*
CdS	,,	1·2852	*10 897*
$CdSO_4$	,,	1·8546	*26 824*
Cd	$Cd(C_5H_5N)_2(SCN)_2$ (pyridine thiocyanate)	0·29063	*46 333*
$Cd_2P_2O_7$	,,	0·51549	*71 222*
CdS	,,	0·37351	*57 231*
$CdSO_4$	,,	0·53898	*73 157*
Cd	$Cd(C_5H_5N)_4(SCN)_2$ (pyridine thiocyanate)	0·20626	*31 441*
$Cd_2P_2O_7$	,,	0·36585	*56 330*
CdS	,,	0·26509	*42 339*
$CdSO_4$	,,	0·38253	*58 267*
Cd	$Cd(C_9H_6ON)_2$ (oxinate)	0·28052	*44 796*
$Cd_2P_2O_7$	,,	0·49757	*69 685*
CdS	$Cd(C_9H_6ON)_2$	0·36053	*55 694*
$CdSO_4$	,,	0·52024	*71 620*
Cd	$Cd(C_9H_6ON)_2 \cdot 1\frac{1}{2}\ H_2O$ (oxinate)	0·26280	*41 962*
$Cd_2P_2O_7$	,,	0·46613	*66 851*
CdS	,,	0·33775	*52 859*
$CdSO_4$	,,	0·48737	*68 786*
Cd	$Cd(C_{10}H_6O_2N)_2$ (quinaldinate)	0·24611	*39 113*
$Cd_2P_2O_7$	,,	0·43654	*64 002*
CdS	,,	0·31631	*50 011*
$CdSO_4$	,,	0·45643	*65 937*
Cd	$Cd(NH_3)_2(C_7H_4NS_2)_2$ (mercaptobenzthiazole)	0·23469	*37 049*
$Cd_2P_2O_7$	,,	0·41627	*61 938*
CdS	,,	0·30163	*47 947*
$CdSO_4$	,,	0·43524	*63 873*
Cd	$Cd(NH_4)PO_4 \cdot H_2O$	0·46175	*66 441*
$Cd_2P_2O_7$	,,	0·81903	*91 330*
Cds	,,	0·59345	*77 338*
$CdSO_4$	,,	0·85635	*93 265*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Cd	$Cd(N_2H_4)_2I_2$ (hydrazine iodide)	0·26122	*41 701*
$Cd_2P_2O_7$	$Cd(N_2H_4)_2I_2$	0·46333	*66 590*
CdS	,,	0·33572	*52 598*
$CdSO_4$	,,	0·48445	*68 525*
Cd	CdO	0·87540	*94 221*
$Cd_2P_2O_7$	,,	1·5527	*19 109*
CdS	,,	1·1251	*05 118*
$CdSO_4$	,,	1·6235	*21 044*
Cd	$Cd_2P_2O_7$	0·56378	*75 111*
$Cd(C_2H_3O_2)_2$ (acetate)	,,	1·1561	*06 298*
$CdCl_2$	,,	0·91943	*96 352*
CdI_2	,,	1·8368	*26 406*
$Cd(NH_4)PO_4 \cdot H_2O$	,,	1·2210	*08 670*
$Cd(NO_3)_2$	,,	1·1858	*07 401*
$Cd(NO_3)_2 \cdot 4\,H_2O$	,,	1·5472	*18 955*
CdO	,,	0·64403	*80 891*
$Cd(OH)_2$	,,	0·73441	*86 594*
CdS	,,	0·72458	*86 009*
$CdSO_4$	,,	1·0456	*01 935*
$CdSO_4 \cdot {}^8/_3\,H_2O$	,,	1·2865	*10 942*
Cd	CdS	0·77809	*89 103*
Cd (empirical)	,,	0·7781	*89 104*
$Cd(C_2H_3O_2)_2$ (acetate)	,,	1·5955	*20 290*
$CdCl_2$	,,	1·2689	*10 343*
CdI_2	,,	2·5350	*40 398*
$Cd(NH_4)PO_4 \cdot H_2O$	,,	1·6851	*22 662*
$Cd(NO_3)_2$	,,	1·6365	*21 392*
$Cd(NO_3)_2 \cdot 4\,H_2O$	,,	2·1353	*32 946*
CdO	,,	0·88884	*94 882*
$Cd(OH)_2$	,,	1·0136	*00 585*
$Cd_2P_2O_7$	,,	1·3801	*13 991*
$CdSO_4$	,,	1·4430	*15 927*
$CdSO_4 \cdot {}^8/_3\,H_2O$	,,	1·7755	*24 933*
Cd	$CdSO_4$	0·53921	*73 176*
$Cd(C_2H_3O_2)_2$ (acetate)	,,	1·1057	*04 363*
$CdCl_2$	,,	0·87936	*94 417*
CdI_2	,,	1·7568	*24 471*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
$Cd(NH_4)PO_4 \cdot H_2O$	$CdSO_4$	1·1678	*06 735*
$Cd(NO_3)_2$	,,	1·1341	*05 466*
$Cd(NO_3)_2 \cdot 4\ H_2O$	,,	1·4798	*17 020*
CdO	,,	0·61596	*78 956*
$Cd(OH)_2$	,,	0·70240	*84 659*
$Cd_2P_2O_7$	,,	0·95642	*98 065*
CdS	,,	0·69300	*84 073*
$CdSO_4 \cdot {}^8/_3\ H_2O$	,,	1·2305	*09 007*
Ce	$Ce_2(C_2O_4)_3$ (oxalate)	0·51488	*71 171*
CeO_2	,,	0·63246	*80 104*
Ce	CeO_2	0·81409	*91 067*
$Ce(C_2H_3O_2)_3$ (acetate)	,,	1·8431	*26 556*
$Ce_2(C_2O_4)_3$ (oxalate)	,,	1·5811	*19 896*
$Ce_2(C_2O_4)_3 \cdot 9\ H_2O$	,,	2·0521	*31 220*
$CeCl_3$	,,	1·4321	*15 596*
$Ce(ClO_4)_4$	,,	3·1253	*49 489*
$Ce(NO_3)_3$	,,	1·8948	*27 757*
$Ce(NO_3)_3 \cdot 6\ H_2O$	,,	2·5228	*40 188*
Ce_2O_3	,,	0·95352	*97 933*
$CePO_4$	,,	1·3659	*13 541*
$Ce(SO_4)_2$	,,	1·9303	*28 562*
$Ce(SO_4)_2 \cdot 4\ H_2O$	,,	2·3490	*37 088*
$Ce_2(SO_4)_3$	,,	1·6512	*21 780*
$Ce_2(SO_4)_3 \cdot 8\ H_2O$	,,	2·0699	*31 594*
Ce	Ce_2O_3	0·85377	*93 134*
CeO_2	,,	1·0487	*02 067*
Ag	AgCN	0·80568	*90 616*
CN	,,	0·19432	*28 851*
HCN	,,	0·20185	*30 502*
KCN	,,	0·48633	*68 693*
NaCN	,,	0·36605	*56 354*
NH_4CN	,,	0·32905	*51 726*
CNS	AgCNS	0·34998	*54 405*
AgCNS	CuCNS	1·3646	*13 499*
$BaSO_4$	,,	1·9192	*28 312*
CNS	,,	0·47757	*67 904*
HCNS	,,	0·48586	*68 651*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
KCNS	CuCNS	0·79905	*90 258*
NH_4CNS	,,	0·62590	*79 650*
NaCNS	,,	0·66661	*82 387*
CNS	$BaSO_4$	0·24884	*39 593*
HCNS	,,	0·25316	*40 340*
KCNS	,,	0·41635	*61 946*
NH_4CNS	,,	0·32613	*51 339*
NaCNS	,,	0·34734	*54 075*
ClO_4	$C_{20}H_{16}N_4 \cdot HClO_4$ (nitron perchlorate)	0·24091	*38 185*
$HClO_4$	,,	0·24335	*38 623*
$KClO_4$	,,	0·33562	*52 584*
$NaClO_4$	,,	0·29660	*47 217*
$CoCl_2$	Co	2·2031	*34 303*
$Co(NO_3)_2$	,,	3·1041	*49 193*
$Co(NO_3)_2 \cdot 6\ H_2O$	,,	4·9381	*69 356*
CoO	,,	1·2715	*10 430*
Co_3O_4	,,	1·3620	*13 416*
$Co(OH)_2$	,,	1·5772	*19 789*
$Co_2P_2O_7$	,,	2·4757	*39 369*
$CoSO_4$	,,	2·6300	*41 995*
$CoSO_4 \cdot 7\ H_2O$	,,	4·7696	*67 848*
$K_3[Co(NO_2)_6]$	,,	7·6737	*88 501*
Co	$Co(C_5H_5N)_4(SCN)_2$ (pyridine thiocyanate)	0·11991	*07 887*
Co_3O_4	,,	0·16332	*21 303*
$CoSO_4$	,,	0·31537	*49 882*
Co	$Co(C_9H_6ON)_2$ (oxinate)	0·16973	*22 977*
Co_3O_4	,,	0·23117	*36 393*
$CoSO_4$	,,	0·44639	*64 972*
Co	$Co(C_9H_6ON)_2 \cdot 2\ H_2O$ (oxinate)	0·15378	*18 689*
Co_3O_4	,,	0·20944	*32 105*
$CoSO_4$	,,	0·40443	*60 684*
Co	$Co(C_{10}H_6ONO)_3$ (α-nitroso-β-naphthol)	0·10243	*01 041*
Co_3O_4	,,	0·13950	*14 458*
$CoSO_4$	,,	0·26938	*43 036*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Co	$Co(NH_2 \cdot C_6H_4 \cdot CO_2)_2$ (anthranilate)	0·17796	*25 031*
Co_3O_4	,,	0·24237	*38 447*
$CoSO_4$	,,	0·46802	*67 026*
Co	Co_3O_4	0·73424	*86 584*
$CoSO_4$	,,	1·9310	*28 579*
Co	$Co_2P_2O_7$	0·40393	*60 631*
Co_3O_4	,,	0·55014	*74 047*
$CoSO_4$	,,	1·0623	*02 626*
Co	$CoSO_4$	0·38023	*58 005*
$CoCl_2$	,,	0·83769	*92 308*
$Co(NO_3)_2$	,,	1·1803	*07 198*
$Co(NO_3)_2 \cdot 6\ H_2O$	,,	1·8776	*27 361*
CoO	,,	0·48345	*68 435*
Co_3O_4	,,	0·51786	*71 421*
$Co(OH)_2$	,,	0·59970	*77 794*
$Co_2P_2O_7$	,,	0·94133	*97 374*
$CoSO_4 \cdot 7\ H_2O$	,,	1·8136	*25 853*
$K_3[Co(NO_2)_6]$	,,	2·9179	*46 507*
Co	$K_3[Co(NO_2)_6]$	0·13032	*11 500*
Co_3O_4	,,	0·17748	*24 916*
$CoSO_4$	,,	0·34272	*53 493*
Cr	Ag_2CrO_4	0·15677	*19 525*
CrO_3	,,	0·30144	*47 921*
Cr_2O_3	,,	0·22910	*36 003*
CrO_4	,,	0·34967	*54 366*
Cr_2O_7	,,	0·32556	*51 263*
Cr	$BaCrO_4$	0·20527	*31 233*
CrO_3	,,	0·39472	*59 629*
Cr_2O_3	,,	0·30000	*47 712*
CrO_4	,,	0·45787	*66 074*
Cr_2O_7	,,	0·42629	*62 971*
Cr	$Cr(C_9H_6ON)_3$ (oxinate)	0·10735	*03 082*
Cr_2O_3	,,	0·15689	*19 560*
Ag_2CrO_4	Cr_2O_3	4·3648	*63 997*
$BaCrO_4$	,,	3·3334	*52 288*
Cr	,,	0·68425	*83 522*
$CrCl_2$	,,	1·6172	*20 875*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
$CrCl_3$	Cr_2O_3	2·0837	*31 883*
$CrCl_3 \cdot 6\ H_2O$	,,	3·5059	*54 479*
CrO_2Cl_2	,,	2·0382	*30 924*
CrO_3	,,	1·3157	*11 917*
CrO_4	,,	1·5262	*18 362*
Cr_2O_7	,,	1·4210	*15 259*
$Cr(OH)_3$	,,	1·3555	*13 209*
$CrPO_4$	,,	1·9338	*28 640*
$CrSO_4$	,,	1·9481	*28 961*
$CrSO_4 \cdot 7\ H_2O$	,,	3·6072	*55 717*
$Cr_2(SO_4)_3$	,,	2·5799	*41 161*
$Cr_2(SO_4)_3 \cdot 18\ H_2O$	,,	4·7131	*67 331*
K_2CrO_4	,,	2·5551	*40 740*
$K_2Cr_2O_7$	,,	1·9354	*28 677*
$KCr(SO_4)_2 \cdot 12\ H_2O$	,,	6·5705	*81 760*
$(NH_4)Cr(SO_4)_2 \cdot 12\ H_2O$	,,	6·2936	*79 889*
$PbCrO_4$	,,	4·2523	*62 863*
Cr	$CrPO_4$	0·35385	*54 881*
Cr_2O_3	,,	0·51713	*71 360*
Cr	$PbCrO_4$	0·16091	*20 659*
Cr (empirical)	,,	0·1593	*20 222*
CrO_3	,,	0·30942	*49 054*
Cr_2O_3	,,	0·23516	*37 137*
CrO_4	,,	0·35892	*55 500*
Cr_2O_7	,,	0·33417	*52 397*
CsCl	AgCl	1·1746	*06 991*
Cs	$CsClO_4$	0·57198	*75 738*
Cs_2PtCl_6	,,	1·4495	*16 123*
Cs	$Cs_3[Co(NO_2)_6] \cdot H_2O$	0·53041	*72 461*
Cs_2PtCl_6	,,	1·3442	*12 846*
Cs	Cs_2PtCl_6	0·39460	*59 615*
Cs_2CO_3	,,	0·48368	*68 455*
CsCl	,,	0·49987	*69 886*
$CsClO_4$	,,	0·68988	*83 877*
$Cs_3[Co(NO_2)_6] \cdot H_2O$	,,	0·74394	*87 154*
$CsNO_3$	,,	0·57870	*76 245*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Cs_2O	Cs_2PtCl_6	0·41835	*62 153*
Cs_2SO_4	,,	0·53721	*73 014*
$Cs_2[SnCl_6]$	,,	0·88660	*94 773*
Cs	Cs_2SO_4	0·73453	*86 601*
Cs_2PtCl_6	,,	1·8615	*26 986*
Cs	$Cs_2[SnCl_6]$	0·44506	*64 842*
Cs_2PtCl_6	,,	1·1279	*05 227*
$Cu(C_2H_3O_2)_2$ (acetate)	Cu	2·8585	*45 615*
CuCl	,,	1·5580	*19 257*
$CuCl_2$	,,	2·1160	*32 551*
$Cu_2[Fe(CN)_6] \cdot 7\ H_2O$	,,	3·6603	*56 352*
$Cu_3[Fe(CN)_6]_2$	,,	3·2239	*50 839*
CuI	,,	2·9973	*47 673*
$Cu(IO_3)_2$	,,	6·5055	*81 328*
$Cu(NO_3)_2$	,,	2·9518	*47 008*
$Cu(NO_3)_2 \cdot 3\ H_2O$	,,	3·8024	*58 005*
CuO	,,	1·2518	*09 754*
Cu_2O	,,	1·1259	*05 150*
$Cu(OH)_2$	,,	1·5353	*18 621*
CuS	,,	1·5047	*17 744*
Cu_2S	,,	1·2523	*09 772*
CuSCN	,,	1·9141	*28 198*
$CuSO_4$	,,	2·5120	*40 001*
$CuSO_4 \cdot 5\ H_2O$	,,	3·9297	*59 435*
$CuSO_4 \cdot 4\ NH_3 \cdot H_2O$	,,	3·8677	*58 745*
Cu	$Cu(C_5H_5N)_2(SCN)_2$ (pyridine thiocyanate)	0·18803	*27 424*
CuO	,,	0·23538	*37 178*
Cu	$Cu(C_6H_5O_2N_2)_2$ (cupferrate)	0·18811	*27 441*
CuO	,,	0·23548	*37 195*
Cu	$Cu(C_7H_6O_2N)_2$ (anthranilate)	0·18922	*27 696*
CuO	,,	0·23686	*37 450*
Cu	$Cu(C_7H_6O_2N)_2$ (salicyl aldoxime)	0·18922	*27 696*
CuO	,,	0·23686	*37 450*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Cu	$Cu(C_9H_6ON)_2$ (oxinate)	0·18059	*25 669*
CuO	,,	0·22606	*35 423*
Cu	$Cu(C_{10}H_6O_2N)_2 \cdot H_2O$ (quinaldinate)	0·14919	*17 375*
CuO	,,	0·18676	*27 129*
Cu	$Cu(C_{12}H_{10}ONS)_2$ (thionalide)	0·12808	*10 747*
CuO	,,	0·16033	*20 501*
Cu	$Cu(C_{13}H_8O_2N)_2$ (benzoxazole)	0·13129	*11 823*
CuO	,,	0·16435	*21 577*
Cu	$Cu(C_{14}H_{11}O_2N)$ (benzoinoxime)	0·22002	*34 247*
CuO	,,	0·27543	*44 000*
Cu	CuI	0·33363	*52 327*
CuO	,,	0·41764	*62 080*
Cu	$Cu(IO_3)_2$	0·15372	*18 672*
CuO	,,	0·19242	*28 426*
Cu	CuO	0·79884	*90 246*
$Cu(C_2H_3O_2)_2$ (acetate)	,,	2·2835	*35 861*
CuCl	,,	1·2446	*09 504*
$CuCl_2$	,,	1·6903	*22 798*
$Cu_2[Fe(CN)_6] \cdot 7\,H_2O$	,,	2·9240	*46 598*
$Cu[Fe(CN)_6]_2$	,,	2·5754	*41 085*
CuI	,,	2·3944	*37 920*
$Cu(IO_3)_2$	,,	5·1969	*71 574*
$Cu(NO_3)_2$	,,	2·3580	*37 255*
$Cu(NO_3)_2 \cdot 3\,H_2O$	,,	3·0375	*48 251*
Cu_2O	,,	0·89942	*95 396*
$Cu(OH)_2$	,,	1·2265	*08 867*
CuS	,,	1·2020	*07 990*
Cu_2S	,,	1·0004	*00 018*
CuSCN	,,	1·5291	*18 444*
$CuSO_4$	,,	2·0067	*30 247*
$CuSO_4 \cdot 5\,H_2O$	,,	3·1392	*49 682*
$CuSO_4 \cdot 4\,NH_3 \cdot H_2O$	,,	3·0897	*48 992*
Cu	Cu_2S	0·79851	*90 228*
CuO	,,	0·99959	*99 982*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
$CuSO_4$	CuS	2·0058	*30 229*
$CuSO_4 \cdot 5\,H_2O$	,,	3·1379	*49 664*
Cu	CuSCN	0·52243	*71 802*
CuO	,,	0·65398	*81 556*
$CuSO_4$	,,	1·3123	*11 804*
$CuSO_4 \cdot 5\,H_2O$	,,	2·0529	*31 238*
Cu	$CuSO_4$	0·39810	*59 999*
CuO	,,	0·49834	*69 753*
$CuSO_4 \cdot 5\,H_2O$	,,	1·5644	*19 434*
CaF_2	BaF_2	0·44526	*64 861*
F	,,	0·21670	*33 585*
CaF_2	$Ba[SiF_6]$	0·83822	*92 336*
F	,,	0·40794	*61 060*
CaF_2	BiF_3	0·44030	*64 375*
F	,,	0·21429	*33 099*
CaF_2	$(C_6H_5)_3SnF$	0·10579	*02 446*
F	,,	0·051488	*71 171*
BaF_2	CaF_2	2·2459	*35 139*
$BaSiF_6$	,,	1·1930	*07 664*
BiF_3	,,	2·2712	*35 625*
F	,,	0·48668	*68 724*
HF	,,	0·51250	*70 969*
$H_2[SiF_6]$	,,	0·61521	*78 902*
KBF_4	,,	0·80638	*90 654*
KF	,,	1·4882	*17 267*
$K_2[SiF_6]$	,,	0·94045	*97 333*
NH_4F	,,	0·94877	*97 716*
$Na_3[AlF_6]$	,,	0·89632	*95 246*
NaF	,,	1·0756	*03 165*
PbClF	,,	6·7025	*82 624*
SiF_4	,,	0·66656	*82 384*
SiF_6	,,	0·60660	*78 290*
U_3O_8	,,	3·5955	*55 576*
CaF_2	$K_2[SiF_6]$	1·0633	*02 667*
F	,,	0·51750	*71 391*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
CaF_2	$La_2F_3 \cdot La_2O_3$	0·17727	*24 864*
F	,,	0·086275	*93 588*
CaF_2	PbClF	0·14920	*17 376*
F	,,	0·072611	*86 100*
CaF_2	U_3O_8	0·27813	*44 424*
F	,,	0·13536	*13 148*
Fe	$Fe(C_9H_6ON)_3$ (oxinate)	0·11437	*05 832*
Fe_2O_3	,,	0·16352	*21 357*
Fe	Fe_2O_3	0·69944	*84 475*
FeC_2O_4 (oxalate)	,,	1·8018	*25 570*
$FeC_2O_4 \cdot 2\ H_2O$	,,	2·2530	*35 277*
$Fe_2(C_2O_4)_3$	,,	2·3529	*37 161*
$Fe(CN)_6$	,,	2·6545	*42 399*
$FeCO_3$	,,	1·4510	*16 166*
$FeCl_2$	,,	1·5875	*20 072*
$FeCl_2 \cdot 4\ H_2O$	,,	2·4900	*39 620*
$FeCl_3$	,,	2·0316	*30 783*
$FeCl_3 \cdot 6\ H_2O$	,,	3·3853	*52 960*
$Fe_3[Fe(CN)_6]_2$	,,	1·4815	*17 069*
$Fe_4[Fe(CN)_6]_3$	,,	1·5373	*18 677*
$Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$	,,	4·9112	*69 119*
$Fe(NO_3)_2$	,,	2·2525	*35 267*
$Fe(NO_3)_2 \cdot 6\ H_2O$	,,	3·6063	*55 706*
$Fe(NO_3)_3$	,,	3·0291	*48 131*
$Fe(NO_3)_3 \cdot 6\ H_2O$	,,	4·3828	*64 176*
$Fe(NO_3)_3 \cdot 9\ H_2O$	,,	5·0597	*70 413*
FeO	,,	0·89981	*95 415*
Fe_3O_4	,,	0·96660	*98 525*
$Fe(OH)_2$	,,	1·1254	*05 132*
$Fe(OH)_3$	,,	1·3384	*12 660*
$FePO_4$	,,	1·8889	*27 620*
FeS	,,	1·1010	*04 179*
$FeSO_4$	,,	1·9025	*27 933*
$FeSO_4 \cdot 7\ H_2O$	,,	3·4819	*54 181*
$Fe_2(SO_4)_3$	,,	2·5041	*39 864*
$Fe_2(SO_4)_3 \cdot 9\ H_2O$	,,	3·5194	*54 646*
$K_3[Fe(CN)_6]$	,,	4·1235	*61 527*
$K_4[Fe(CN)_6]$	,,	4·6132	*66 400*
$NH_4Fe(SO_4)_2 \cdot 12\ H_2O$	,,	6·0390	*78 096*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Fe	$FePO_4$	0·37030	*56 855*
Fe_2O_3	,,	0·52942	*72 380*
Ga	$Ga(C_9H_4Br_2ON)_3$ (dibromo oxinate)	0·071461	*85 407*
Ga_2O_3	,,	0·096061	*98 255*
Ga	Ga_2O_3	0·74392	*87 153*
$GaCl_3$	,,	1·8789	*27 390*
$Ga(NO_3)_3$	,,	2·7288	*43 597*
$Ga(OH)_3$	,,	1·2883	*11 002*
Ga_2S_3	,,	1·2570	*09 935*
$Ga_2(SO_4)_3$	,,	2·2814	*35 820*
Ga	Ga_2S_3	0·59180	*77 218*
Ga_2O_3	,,	0·79552	*90 065*
Ge	GeO_2	0·69407	*84 140*
$GeCl_4$	,,	2·0500	*31 175*
GeK_2F_6	,,	2·5315	*40 337*
GeS_2	,,	1·3071	*11 630*
Hf	HfO_2	0·84798	*92 839*
Hg	$Co[Hg(SCN)_4]$	0·40784	*61 048*
HgS	,,	0·47301	*67 487*
$Hg(CN)_2$	Hg	1·2594	*10 015*
$Hg(CN)_2 \cdot HgO$	,,	1·1696	*06 802*
$HgCl_2$	,,	1·3535	*13 145*
Hg_2Cl_2	,,	1·1768	*07 069*
HgI_2	,,	2·2653	*35 513*
Hg_2MoO_4	,,	1·3987	*14 571*
$Hg(NO_3)_2$	,,	1·6182	*20 903*
$Hg(NO_3)_2 \cdot \frac{1}{2} H_2O$	,,	1·6631	*22 091*
$Hg_2(NO_3)_2$	,,	1·3091	*11 697*
$Hg_2(NO_3)_2 \cdot 2 H_2O$	,,	1·3989	*14 578*
HgO	,,	1·0798	*03 333*
HgS	,,	1·1598	*06 439*
$Hg(SCN)_2$	,,	1·5790	*19 839*
$Hg_2(SCN)_2$	,,	1·2895	*11 043*
$HgSO_4$	,,	1·4788	*16 992*
Hg_2SO_4	,,	1·2394	*09 322*
Hg_2WO_4	,,	1·6178	*20 892*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Hg	$Hg_3(AsO_4)_2$	0·68417	*83 516*
HgS	,,	0·79351	*89 955*
Hg	$Hg_2C_2O_4$ (oxalate)	0·82009	*91 386*
HgS	,,	0·95115	*97 825*
Hg	$Hg(C_5H_5N)Cl_2$ (pyridine chloride)	0·57215	*75 751*
HgS	,,	0·66358	*82 190*
Hg	$Hg(C_6H_4NCS_2)_2$ (mercaptobenzothiazole)	0·37630	*57 554*
HgS	,,	0·43645	*63 994*
Hg	$Hg_2(C_6H_5O_2N_2)_2$ (cupferrate)	0·59399	*77 378*
HgS	,,	0·68894	*83 818*
Hg	$Hg(C_7H_6O_2N)_2$ (anthranilate)	0·42423	*62 760*
HgS	,,	0·49203	*69 199*
Hg	$Hg(C_{12}H_{10}ONS)_2$ (thionalide)	0·31683	*50 083*
HgS	,,	0·36746	*56 521*
Hg	Hg_2Cl_2	0·84979	*92 931*
HgS	,,	0·98560	*99 370*
Hg	Hg_2CrO_4	0·77571	*88 970*
HgS	,,	0·89968	*95 409*
Hg	HgI_2	0·44145	*64 489*
HgS	,,	0·51200	*70 927*
Hg	$Hg_2(IO_3)_2$	0·53422	*72 772*
HgS	,,	0·61959	*79 211*
Hg	HgS	0·86221	*93 561*
$Hg(CN)_2$	,,	1·0858	*03 576*
$Hg(CN)_2 \cdot HgO$	,,	1·0084	*00 363*
$HgCl_2$	,,	1·1670	*06 706*
Hg_2Cl_2	,,	1·0146	*00 630*
HgI_2	,,	1·9531	*29 073*
Hg_2MoO_4	,,	1·2059	*08 132*
$Hg(NO_3)_2$	,,	1·3952	*14 464*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
$Hg(NO_3)_2 \cdot \frac{1}{2} H_2O$	HgS	1·4339	*15 652*
$Hg_2(NO_3)_2$	,,	1·1287	*05 258*
$Hg_2(NO_3)_2 \cdot 2 H_2O$	,,	1·2061	*08 139*
HgO	,,	0·93098	*96 894*
Hg_2O	,,	0·89657	*95 258*
$Hg(SCN)_2$	,,	1·3615	*13 400*
$Hg_2(SCN)_2$	,,	1·1118	*04 604*
$HgSO_4$	,,	1·2751	*10 553*
Hg_2SO_4	,,	1·0686	*02 883*
Hg_2WO_4	,,	1·3949	*14 453*
Hg	$Zn[Hg(SCN)_4]$	0·40256	*60 484*
HgS	,,	0·46690	*66 922*
In	$In(C_9H_6ON)_3$ (oxinate)	0·20980	*32 180*
In_2O_3	,,	0·25365	*40 424*
In	In_2O_3	0·82711	*91 757*
$InCl_3$	,,	1·5934	*20 232*
In_2S_3	,,	1·1736	*06 952*
In	In_2S_3	0·70477	*84 805*
In_2O_3	,,	0·85208	*93 048*
AgI	Ag	2·1764	*33 774*
I	,,	1·1764	*07 055*
$AgIO_3$	AgI	1·2044	*08 078*
CuI	,,	0·81115	*90 910*
HIO_3	,,	0·74926	*87 463*
IO_3	,,	0·74496	*87 214*
IO_4	,,	0·81311	*91 015*
I_2O_5	,,	0·71089	*85 180*
I_2O_7	,,	0·77904	*89 156*
$KH(IO_3)_2$	,,	0·83038	*91 927*
KIO_3	,,	0·91150	*95 975*
KIO_4	,,	0·97964	*99 107*
$NaIO_3$	,,	0·84289	*92 577*
PbI_2	,,	0·98179	*99 202*
PdI_2	,,	0·76711	*88 486*
TlI	,,	1·4110	*14 954*
AgI	$AgIO_3$	0·83026	*91 922*
I	,,	0·44878	*65 203*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
AgI	CuI	1·2328	*09 090*
I	,,	0·66637	*82 371*
AgI	PbI_2	1·0185	*00 798*
I	,,	0·55055	*74 080*
AgI	PdI_2	1·3036	*11 514*
I	,,	0·70462	*84 796*
IO_3	,,	0·97113	*98 728*
I_2O_5	,,	0·92671	*96 694*
AgI	TlI	0·70869	*85 046*
I	,,	0·38307	*58 327*
K	$C_6H_2(NO_2)_3 \cdot OK$ (picrate)	0·14633	*16 533*
KCl	,,	0·27902	*44 564*
K	$K[B(C_6H_5)_4]$ (tetraphenylborate)	0·10911	*03 788*
KCl	,,	0·20806	*31 819*
K_2SO_4	,,	0·24315	*38 588*
K	KBO_2	0·47729	*67 879*
KCl	,,	0·91012	*95 910*
K	KCl	0·52443	*71 969*
$K_2(AlO_2)_2 \cdot 3\ H_2O$	,,	1·6780	*22 478*
$KAl(SO_4)_2 \cdot 12\ H_2O$	,,	6·3630	*80 366*
$K[B(C_6H_5)_4]$ (tetraphenylborate)	,,	4·8063	*68 181*
KBF_4	,,	1·6889	*22 761*
KBO_2	,,	1·0988	*04 090*
KBr	,,	1·5963	*20 312*
$KBrO_3$	,,	2·2401	*35 027*
$K_2C_2O_4$ (oxalate)	,,	1·1147	*04 717*
KCN	,,	0·87341	*94 122*
K_2CO_3	,,	0·92688	*96 702*
$KHCO_3$	,,	1·3429	*12 803*
$KClO_3$	,,	1·6438	*21 585*
$KClO_4$	,,	1·8584	*26 914*
K_2CrO_4	,,	1·3024	*11 475*
$K_2Cr_2O_7$	,,	1·9731	*29 515*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
$KCr(SO_4)_2 \cdot 12\,H_2O$	KCl	6·6987	*82 599*
KF	,,	0·77927	*89 169*
$K_3[Fe(CN)_6]$	,,	1·4721	*16 793*
$K_4[Fe(CN)_6]$	,,	1·2352	*09 173*
$KHC_4H_4O_6$ (tartrate)	,,	2·5240	*40 209*
KI	,,	2·2266	*34 765*
KIO_3	,,	2·8704	*45 795*
$KH(IO_3)_2$	,,	5·2299	*71 850*
KNO_3	,,	1·3561	*13 230*
K_2O	,,	0·63173	*80 853*
KOH	,,	0·75255	*87 654*
K_3PO_4	,,	0·94905	*97 729*
K_2HPO_4	,,	1·1681	*06 749*
KH_2PO_4	,,	1·8253	*26 134*
K_2PtCl_6	,,	3·2595	*51 315*
K_2SO_4	,,	1·1687	*06 769*
$KHSO_4$	,,	1·8264	*26 161*
$K_2S_2O_8$	,,	1·8129	*25 838*
KSCN	,,	1·3035	*11 511*
K_2SiF_6	,,	1·4773	*16 948*
ClO_4	$KClO_4$	0·71781	*85 601*
K	,,	0·28219	*45 055*
KCl	,,	0·53810	*73 086*
K_2O	,,	0·33993	*53 139*
K	$K_3[Co(NO_2)_6] \cdot 3\,H_2O$	0·23166	*36 486*
KCl	,,	0·44174	*64 517*
K	$KHC_4H_4O_6$ (tartrate)	0·20778	*31 759*
KCl	,,	0·39619	*59 791*
K	KIO_4	0·16999	*23 043*
KCl	,,	0·32415	*51 074*
K	K_2PtCl_6	0·16089	*20 654*
KCl	,,	0·30680	*48 685*
K	K_2SO_4	0·44874	*65 199*
KCl	,,	0·85567	*93 231*
K	Pt	0·40084	*60 297*
KCl	,,	0·76433	*88 328*
K_2O	,,	0·48285	*68 382*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
La	La_2O_3	0·85269	*93 079*
$LaCl_3$	,,	1·5056	*17 771*
Li	LiCl	0·16369	*21 402*
Li_2O	,,	0·35238	*54 702*
Li_2SO_4	,,	1·2966	*11 281*
Li	$Li_2O \cdot 5\ Al_2O_3$	0·048739	*68 788*
Li_2SO_4	,,	0·38607	*58 667*
Li	Li_3PO_4	0·17980	*25 479*
LiCl	,,	1·0984	*04 077*
Li_2SO_4	,,	1·4242	*15 358*
Li	Li_2SO_4	0·12624	*10 121*
LiBr	,,	1·5800	*19 865*
Li_2CO_3	,,	0·67207	*82 741*
LiCl	,,	0·77123	*88 719*
$LiNO_3$	,,	1·2542	*09 837*
$LiNO_3 \cdot 3\ H_2O$	,,	2·2374	*34 974*
Li_2O	,,	0·27177	*43 420*
LiOH	,,	0·43563	*63 912*
Li_3PO_4	,,	0·70213	*84 642*
Li	$Zn(UO_2)_3Li(CH_3COO)_9$ (zinc uranyl acetate)	0·0049083	*69 093*
Li_2SO_4	,,	0·038879	*58 972*
Li	$ZnU_2O_7 \cdot Li_2U_2O_7$	0·0072706	*86 157*
Li_2SO_4	,,	0·057592	*76 036*
$MgCO_3$	CO_2	1·9161	*28 242*
MgO	,,	0·91613	*96 196*
As_2O_7	$Mg_2As_2O_7$	0·84333	*92 600*
Mg	,,	0·15667	*19 499*
$Mg(NH_4)PO_4 \cdot 6\ H_2O$	,,	1·5811	*19 895*
MgO	,,	0·25974	*41 454*
$Mg_2P_2O_7$	,,	0·71697	*85 550*
Mg	$MgC_2O_4 \cdot 2\ H_2O$ (oxalate)	0·16391	*21 461*
$Mg(NH_4)PO_4 \cdot 6\ H_2O$	,,	1·6541	*21 857*
MgO	,,	0·27175	*43 416*
$Mg_2P_2O_7$	,,	0·75010	*87 512*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Mg	$Mg(C_9H_6ON)_2$ (oxinate)	0·077792	*89 093*
$Mg(NH_4)PO_4 \cdot 6\ H_2O$	,,	0·78505	*89 490*
MgO	,,	0·12897	*11 049*
$Mg_2P_2O_7$	,,	0·35600	*55 145*
Mg	$Mg(C_9H_6ON)_2 \cdot 2\ H_2O$	0·69752	*84 356*
$Mg(NH_4)PO_4 \cdot 6\ H_2O$	,,	0·70392	*84 752*
MgO	,,	0·11564	*06 312*
$Mg_2P_2O_7$	,,	0·31921	*50 407*
AsO_4	$Mg(NH_4)AsO_4 \cdot 6\ H_2O$	0·48004	*68 128*
Mg	,,	0·084045	*92 451*
$Mg(NH_4)PO_4 \cdot 6\ H_2O$	,,	0·84815	*92 847*
MgO	,,	0·13934	*14 407*
$Mg_2P_2O_7$	,,	0·38461	*58 502*
Mg	$Mg(NH_4)PO_4 \cdot 6\ H_2O$	0·099091	*99 603*
$Mg_2As_2O_7$	,,	0·63248	*80 105*
$MgCO_3$	,,	0·34360	*53 605*
$MgC_2O_4 \cdot 2\ H_2O$ (oxalate)	,,	0·60455	*78 143*
$MgCl_2$	,,	0·38801	*58 885*
$MgCl_2 \cdot 6\ H_2O$	,,	0·82846	*91 827*
$MgCl_2 \cdot KCl \cdot 6\ H_2O$	,,	1·1322	*05 394*
MgF_2	,,	0·25392	*40 470*
$Mg(NH_4)AsO_4 \cdot 6\ H_2O$	,,	1·1790	*07 152*
MgO	,,	0·16428	*21 559*
$Mg(OH)_2$	,,	0·23771	*37 604*
$Mg_2P_2O_7$	,,	0·45347	*65 655*
$MgSO_4$	,,	0·49051	*69 065*
$MgSO_4 \cdot 7\ H_2O$	,,	1·0044	*00 189*
P_2O_5	,,	0·28919	*46 118*
Mg	MgO	0·60317	*78 044*
$Mg(NH_4)PO_4 \cdot 6\ H_2O$	,,	6·0871	*78 441*
$Mg_2P_2O_7$	,,	2·7603	*44 096*
Mg	$Mg_2P_2O_7$	0·21852	*33 949*
$Mg_2As_2O_7$	,,	1·3948	*14 450*
$MgC_2O_4 \cdot 2\ H_2O$ (oxalate)	,,	1·3332	*12 488*
$MgCO_3$	,,	0·75772	*87 951*
$MgCl_2$	,,	0·85565	*93 230*
$MgCl_2 \cdot 6\ H_2O$	,,	1·8269	*26 173*
$MgCl_2 \cdot KCl \cdot 6\ H_2O$	,,	2·4969	*39 739*
MgF_2	,,	0·55995	*74 815*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
$Mg(NH_4)AsO_4 \cdot 6\ H_2O$	$Mg_2P_2O_7$	2·6000	*41 497*
$Mg(NH_4)PO_4 \cdot 6\ H_2O$	,,	2·2052	*34 345*
MgO	,,	0·36228	*55 904*
$Mg(OH)_2$	,,	0·52419	*71 949*
$MgSO_4$	,,	1·0817	*03 410*
$MgSO_4 \cdot 7\ H_2O$	,,	2·2148	*34 534*
P_2O_5	,,	0·63772	*80 463*
$MnCO_3$	CO_2	2·6119	*41 695*
MnO	,,	1·6119	*20 733*
Mn	MnC_2O_4 (oxalate)	0·38430	*58 467*
$Mn_2P_2O_7$	,,	0·99268	*99 681*
$MnSO_4$	,,	1·0563	*02 377*
Mn	$Mn(C_9H_6ON)_2$ (oxinate)	0·16006	*20 428*
$Mn_2P_2O_7$	,,	0·41345	*61 642*
$MnSO_4$	,,	0·43993	*64 338*
Mn	$Mn(NH_4)PO_4 \cdot H_2O$	0·29542	*47 044*
$Mn_2P_2O_7$	,,	0·76310	*88 258*
$MnSO_4$	,,	0·81199	*90 955*
Mn	Mn_3O_4	0·72030	*85 752*
$Mn_2P_2O_7$	,,	1·8606	*26 966*
$MnSO_4$	,,	1·9798	*29 662*
Mn	$Mn_2P_2O_7$	0·38713	*58 786*
$MnCO_3$	,	0·81000	*90 848*
MnC_2O_4 (oxalate)	,,	1·0074	*00 319*
$MnCl_2$	,,	0·88683	*94 784*
$MnCl_2 \cdot 4\ H_2O$	,,	1·3946	*14 446*
$Mn(NH_4)AsO_4 \cdot 6\ H_2O$	,,	2·2548	*35 310*
$Mn(NH_4)PO_4 \cdot H_2O$	,,	1·3104	*11 742*
MnO	,,	0·49988	*69 886*
MnO_2	,,	0·61262	*78 719*
Mn_2O_3	,,	0·55624	*74 527*
Mn_2O_7	,,	0·78174	*89 306*
Mn_3O_4	,,	0·53746	*73 034*
$Mn(OH)_2$	,,	0·62683	*79 715*
$MnPO_4$	,,	1·0564	*02 382*
MnS	,,	0·61309	*78 752*
$MnSO_4$	,,	1·0641	*02 697*
$MnSO_4 \cdot 4\ H_2O$	,,	1·5719	*19 641*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Mn	MnS	0·63145	*80 034*
$Mn_2P_2O_7$	,,	1·6311	*21 248*
$MnSO_4$	,,	1·7356	*23 945*
Mn	$MnSO_4$	0·36383	*56 089*
$MnCO_3$	,,	0·76123	*88 152*
MnC_2O_4 (oxalate)	,,	0·94673	*97 623*
$MnCl_2$	,,	0·83344	*92 087*
$MnCl_2 \cdot 4\,H_2O$	,,	1·3107	*11 749*
$Mn(NH_4)AsO_4 \cdot 6\,H_2O$	,,	2·1190	*32 614*
$Mn(NH_4)PO_4 \cdot H_2O$	,,	1·2315	*09 045*
MnO	,,	0·46978	*67 190*
MnO_2	,,	0·57574	*76 023*
Mn_2O_3	,,	0·52276	*71 830*
Mn_2O_7	,,	0·73467	*86 609*
Mn_3O_4	,,	0·50510	*70 338*
$Mn(OH)_2$	,,	0·58909	*77 018*
$MnPO_4$	,,	0·99278	*99 685*
$Mn_2P_2O_7$	,,	0·93980	*97 303*
MnS	,,	0·57618	*76 056*
$MnSO_4 \cdot 4\,H_2O$	,,	1·4772	*16 945*
Mo	Ag_2MoO_4	0·25538	*40 719*
MoO_3	,,	0·38314	*58 336*
Mo	$BaMoO_4$	0·32273	*50 884*
MoO_3	,,	0·48417	*68 500*
Mo	$CaMoO_4$	0·47968	*68 095*
MoO_3	,,	0·71964	*85 712*
Mo	$CdMoO_4$	0·35229	*54 690*
MoO_3	,,	0·52853	*72 307*
Mo	$MoO_2(C_9H_6ON)_2$ (oxinate)	0·23050	*36 268*
MoO_3	,,	0·34582	*53 885*
Ag_2MoO_4	MoO_3	2·6100	*41 664*
$BaMoO_4$	,,	2·0654	*31 500*
$CaMoO_4$	,,	1·3896	*14 288*
H_2MoO_4	,,	1·1252	*05 121*
Mo	,,	0·66655	*82 383*
MoO_4	,,	1·1111	*04 577*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
MoS_2	MoO_3	1·1121	*04 613*
MoS_3	,,	1·3348	*12 542*
$(NH_4)_2MoO_4$	,,	1·3618	*13 411*
$(NH_4)_3PO_4 \cdot 12\ MoO_3$	,,	1·0863	*03 596*
$PbMoO_4$	,,	2·5506	*40 664*
Mo	$PbMoO_4$	0·26133	*41 719*
MoO_3	,,	0·39206	*59 336*
HNO_3	$C_{20}H_{16}N_4 \cdot HNO_3$ (nitron nitrate)	0·16787	*22 496*
KNO_3	,,	0·26934	*43 030*
$NaNO_3$	,,	0·22642	*35 492*
NO_3	,,	0·16518	*21 796*
N_2O_5	,,	0·14387	*15 797*
$(NH_4)_2SO_4$	$BaSO_4$	0·56612	*75 290*
NH_3	$NH_4[B(C_6H_5)_4]$ (tetraphenyl borate)	0·050498	*70 327*
$(NH_4)_2PtCl_6$	,,	0·65807	*81 827*
N	$(NH_4)_2PtCl_6$	0·063112	*80 011*
NH_3	,,	0·076736	*88 500*
NH_4	,,	0·081277	*90 997*
$(NH_4)_2CO_3$	,,	0·21646	*33 539*
NH_4Cl	,,	0·24102	*38 205*
NH_4NO_3	,,	0·36065	*55 708*
NH_4OH	,,	0·15791	*19 840*
$(NH_4)_2SO_4$	,,	0·29769	*47 376*
NH_3	Pt	0·17461	*24 206*
$(NH_4)_2PtCl_6$	,,	2·2754	*35 706*
$Na_2B_4O_7$	B_2O_3	1·4450	*15 987*
$Na_2B_4O_7 \cdot 10\ H_2O$	,,	2·7385	*43 752*
Na_2S	$BaSO_4$	0·33436	*52 421*
$Na_2S \cdot 9\ H_2O$	,,	1·0290	*01 241*
Na_2SO_3	,,	0·53999	*73 239*
$Na_2SO_3 \cdot 7\ H_2O$	,,	1·0803	*03 353*
$NaHSO_4$	,,	0·51436	*71 127*
$NaHSO_4 \cdot H_2O$	,,	0·59154	*77 198*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Na_2SO_4	$BaSO_4$	0·60854	*78 429*
$Na_2SO_4 \cdot 10\ H_2O$	,,	1·3803	*13 999*
Na_2CO_3	CO_2	2·4083	*38 172*
$Na_2CO_3 \cdot 10\ H_2O$	,,	6·5019	*81 304*
Na_2O	,,	1·4083	*14 870*
Na_2HAsO_3	$Mg_2As_2O_7$	1·0945	*03 922*
Na_2HAsO_4	,,	1·1976	*07 830*
Na_3PO_4	$Mg_2P_2O_7$	1·4732	*16 827*
NaH_2PO_4	,,	1·0782	*03 268*
Na_2HPO_4	,,	1·2757	*10 574*
$Na_2HPO_4 \cdot 12\ H_2O$	,,	3·2184	*50 764*
$Na_4P_2O_7$	,,	1·1947	*07 727*
Na	NaCl	0·39336	*59 479*
Na_3AlF_6	,,	1·1974	*07 823*
$NaBO_3$	,,	1·3997	*14 604*
$Na_2B_4O_7$	,,	1·7217	*23 596*
$Na_2B_4O_7 \cdot 10\ H_2O$	,,	3·2629	*51 361*
NaBr	,,	1·7607	*24 568*
$NaBrO_3$	,,	2·5819	*41 194*
$NaC_2H_3O_2$ (acetate)	,,	1·4036	*14 724*
$Na_2C_2O_4$ (oxalate)	,,	1·1549	*06 255*
NaCN	,,	0·83852	*92 352*
Na_2CO_3	,,	0·90673	*95 748*
$Na_2CO_3 \cdot 10\ H_2O$	,,	2·4479	*38 880*
$NaHCO_3$	,,	1·4373	*15 756*
$NaClO_3$	,,	1·8212	*26 037*
$NaClO_4$	,,	2·0950	*32 118*
Na_2CrO_4	,,	1·3858	*14 169*
$Na_2Cr_2O_7$	,,	2·2413	*35 050*
NaF	,,	0·71843	*85 639*
Na_2HAsO_4	,,	1·5903	*20 148*
NaI	,,	2·5647	*40 903*
$NaIO_3$	,,	3·3859	*52 968*
$NaNO_2$	,,	1·1805	*07 207*
$NaNO_3$	,,	1·4543	*16 264*
Na_2O	,,	0·53023	*72 447*
Na_2O_2	,,	0·66711	*82 419*
NaOH	,,	0·68435	*83 528*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Na_3PO_4	NaCl	0·93501	*97 082*
Na_2HPO_4	,,	1·2145	*08 438*
NaH_2PO_4	,,	2·0528	*31 235*
$Na_4P_2O_7$	,,	1·1374	*05 591*
Na_2S	,,	0·66767	*82 456*
$Na_2S \cdot 9\ H_2O$	,,	2·0547	*31 276*
Na_2SO_3	,,	1·0783	*03 274*
$Na_2SO_3 \cdot 7\ H_2O$	,,	2·1571	*33 388*
$NaHSO_3$	,,	1·7805	*25 054*
$NaHSO_4$	,,	2·0542	*31 265*
Na_2SO_4	,,	1·2152	*08 464*
$Na_2SO_4 \cdot 10\ H_2O$	,,	2·7564	*44 034*
$Na_2S_2O_3$	,,	1·3526	*13 117*
$Na_2S_2O_3 \cdot 5\ H_2O$	,,	2·1232	*32 699*
$NaSbO_2$	,,	3·0241	*48 059*
$Na\{Mg[UO_2(CH_3COO)_3]_3\} \cdot 6{\cdot}5\ H_2O$	,,	25·767	*41 107*
$Na_2U_2O_7(MgU_2O_7)_2$	,,	15·903	*20 149*
$Na\{Zn[UO_2(CH_3COO)_3]_3\} \cdot 6{\cdot}5\ H_2O$	,,	26·470	*42 275*
$Na_2U_2O_7(ZnU_2O_7)_2$	,,	16·606	*22 026*
Na	Na_2SO_4	0·32371	*51 015*
Na_2CO_3	,,	0·74618	*87 284*
NaCl	,,	0·82293	*91 536*
Na_2O	,,	0·43635	*63 983*
Na	$Na\{Mg[UO_2(CH_3COO)_3]_3\} \cdot 6{\cdot}5\ H_2O$	0·015266	*18 372*
NaCl	,,	0·038809	*58 893*
Na	$Na_2U_2O_7(MgU_2O_7)_2$	0·024734	*39 330*
NaCl	,,	0·062880	*79 851*
Na	$Na\{Z\ [UO_2(CH_3COO)_3]_3\} \cdot 6{\cdot}5\ H_2O$	0·014861	*17 204*
NaCl	,,	0·037779	*57 725*
Na	$Na_2U_2O_7(ZnU_2O_7)_2$	0·023688	*37 453*
NaCl	,,	0·060220	*77 974*
Nb	Nb_2O_5	0·69904	*84 450*
Nd	Nd_2O_3	0·85737	*93 317*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
NiO	Ni	1·2725	*10 467*
Ni	$Ni(C_5H_5N)_4(SCN)_2$ (pyridine thiocyanate)	0·11950	*07 737*
NiO	,,	0·15207	*18 204*
Ni	$NiC_8H_{14}N_4O_4$ (diacetyl dioxime)	0·20319	*30 790*
$NiCO_3$	,,	0·41088	*61 372*
$Ni(NO_3)_2$	,,	0·63240	*80 099*
$Ni(NO_3)_2 \cdot 6\ H_2O$	,,	1·0065	*00 282*
NiO	,,	0·25856	*41 257*
$Ni(OH)_2$	,,	0·32092	*50 639*
$NiSO_4$	,,	0·53566	*72 889*
$NiSO_4 \cdot 6\ H_2O$	,,	0·90977	*95 893*
Ni	$Ni(C_9H_6ON)_2$ (oxinate)	0·16918	*22 836*
NiO	,,	0·21529	*33 302*
Ni	$Ni(NH_2 \cdot C_6H_4 \cdot CO_2)_2$ (anthranilate)	0·17738	*24 892*
NiO	,,	0·22573	*35 358*
Ni	NiO	0·78584	*89 533*
Os	OsO_4	0·74823	*87 404*
P	$(C_9H_7ON)_3 \cdot H_7[P(Mo_2O_7)_6] \cdot 2\ H_2O$ (quinoline phosphormolybdate)	0·013277	*12 311*
P_2O_5	,,	0·030423	*48 320*
P_2O_5 (empirical)	,,	0·0306	*48 572*
P	$BiPO_4$	0·10190	*00 817*
$Mg_2P_2O_7$	,,	0·36613	*56 364*
P_2O_5	,,	0·23349	*36 827*
H_3PO_3	Hg_2Cl_2	0·17368	*23 974*
PO_2	,,	0·13338	*12 510*
PO_3	,,	0·16727	*22 342*
$Mg_2P_2O_7$	$Mg(NH_4)PO_4 \cdot 6\ H_2O$	0·45347	*65 655*
P	,,	0·12621	*10 108*
P_2O_5	,,	0·28919	*46 118*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Ag_3PO_4	$Mg_2P_2O_7$	3·7613	*57 534*
$AlPO_4$	,,	1·0958	*03 972*
$Ca_3(PO_4)_2$	,,	1·3935	*14 412*
$Ca(H_2PO_4)_2$	,,	1·0515	*02 183*
$CaHPO_4$	,,	1·2225	*08 726*
$FePO_4$	,,	1·3552	*13 200*
H_3PO_3	,,	0·73677	*86 733*
KH_2PO_4	,,	1·2228	*08 735*
$Mg(NH_4)PO_4 \cdot 6\ H_2O$	,,	2·2052	*34 345*
$(NH_4)_3P(Mo_3O_{10})_4$	,,	16·861	*22 687*
Na_3PO_4	,,	1·4731	*16 823*
Na_2HPO_4	,,	1·2756	*10 571*
NaH_2PO_4	,,	1·0781	*03 264*
P	,,	0·27831	*44 454*
PO_3	,,	0·70960	*85 101*
PO_4	,,	0·85336	*93 113*
P_2O_5	,,	0·63772	*80 463*
$P_2O_5 \cdot 24\ MoO_3$	,,	16·159	*20 840*
P_2O_7	,,	0·78148	*89 292*
$Zn_2P_2O_7$	,,	1·3689	*13 638*
$Mg_2P_2O_7$	$(NH_4)_3P(Mo_3O_{10})_4$	0·059310	*77 313*
P	,,	0·016507	*21 766*
(empirical)	,,	0·01639	*21 458*
PO_4	,,	0·050613	*70 426*
PO_4 (empirical)	,,	0·05025	*70 114*
P_2O_5	,,	0·037823	*57 776*
P_2O_5 (according to Finkener)	,,	0·03755	*57 461*
P_2O_5 (according to Lorenz)	,,	0·03295	*51 786*
$Mg_2P_2O_7$	$P_2O_5 \cdot 24\ MoO_3$	0·061886	*79 160*
P	,,	0·017224	*23 613*
P_2O_5	,,	0·039466	*59 623*
$Mg_2P_2O_7$	$Zn_2P_2O_7$	0·73050	*86 362*
P	,,	0·20331	*30 815*
P_2O_5	,,	0·46585	*66 825*
Pb	$PbCO_3$	0·77543	*88 945*
PbO	,,	0·83530	*92 184*
$PbSO_4$	,,	1·1349	*05 497*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Pb	PbC_2O_4 (oxalate)	0·70185	*84 625*
PbO	,,	0·75605	*87 855*
$PbSO_4$	,,	1·0272	*01 167*
Pb	$Pb(C_7H_4NS_2)OH$ (mercaptobenzothiazole)	0·53067	*72 483*
		0·57165	*75 713*
PbO	,,	0·77670	*89 025*
$PbSO_4$	,,		
Pb	$Pb(C_7H_5O_3)_2$ (salicylate)	0·43039	*63 386*
PbO	,,	0·46363	*66 617*
$PbSO_4$	,,	0·62993	*79 929*
Pb	$Pb(C_7H_6O_2N)_2$ (anthranilate)	0·43216	*63 564*
PbO	,,	0·46553	*66 795*
$PbSO_4$	,,	0·63252	*80 107*
Pb	$Pb(C_8H_4O_4)$ (phthalate)	0·55802	*74 665*
PbO	,,	0·60111	*77 895*
$PbSO_4$	,,	0·81673	*91 208*
Pb	$Pb(C_9H_6ON)_2$ (oxinate)	0·41817	*62 135*
PbO	,,	0·45046	*65 365*
$PbSO_4$	,,	0·61204	*78 678*
Pb	$Pb(C_9H_4ONBr_2)_2$ (dibromo oxinate)	0·25545	*40 731*
PbO	,,	0·27518	*43 961*
$PbSO_4$	,,	0·37388	*57 274*
Pb	$Pb(C_{10}H_7N_4O_5)_2$ (picrolonate)	0·28245	*45 095*
PbO	,,	0·30426	*48 325*
$PbSO_4$	,,	0·41340	*61 638*
Pb	$Pb(C_{12}H_{10}ONS)_2$ (thionalide)	0·32388	*51 038*
PbO	,,	0·34888	*54 268*
$PbSO_4$	,,	0·47403	*67 581*
Pb	$PbCl_2$	0·74503	*87 217*
PbO	,,	0·80256	*90 448*
$PbSO_4$	,,	1·0904	*03 760*
Pb	$PbCrO_4$	0·64108	*80 691*
Pb (empirical)	,,	0·6378	*80 468*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
PbO	$PbCrO_4$	0·69058	*83 922*
$PbSO_4$	,,	0·93830	*97 234*
Pb	$Pb(IO_3)_2$	0·37199	*57 053*
PbO	,,	0·40071	*60 284*
$PbSO_4$	,,	0·54445	*73 596*
Pb	$PbMoO_4$	0·56436	*75 156*
PbO	,,	0·60794	*78 386*
$PbSO_4$	,,	0·82601	*91 698*
Pb	PbO	0·92832	*96 770*
$PbSO_4$	,,	1·3587	*13 312*
Pb	PbO_2	0·86623	*93 763*
PbO	,,	0·93311	*96 993*
$PbSO_4$	,,	1·2678	*10 306*
Pb	$Pb_3(PO_4)_2$	0·76595	*88 420*
PbO	,,	0·82509	*91 650*
$PbSO_4$	,,	1·1211	*04 963*
Pb	PbS	0·86599	*93 751*
PbO	,,	0·93286	*96 981*
$PbSO_4$	,,	1·2675	*10 294*
Pb	$PbSO_3$	0·72129	*85 811*
PbO	,,	0·77699	*89 041*
$PbSO_4$	,,	1·0557	*02 354*
Pb	$PbSO_4$	0·68324	*83 457*
$PbCO_3$	,,	0·88111	*94 503*
$(PbCO_3)_2 \cdot Pb(OH)_2$	,,	0·85254	*93 072*
$Pb(C_2H_3O_2)_2$ (acetate)	,,	1·0726	*03 045*
$Pb(C_2H_3O_2)_2 \cdot 3\,H_2O$	,,	1·2508	*09 720*
$Pb(C_2H_5)_4$ (tetraethyl)	,,	1·0665	*02 798*
PbC_2O_4 (oxalate)	,,	0·97348	*98 833*
$PbCl_2$	,,	0·91707	*96 240*
$PbCrO_4$	,,	1·0658	*02 766*
$Pb(IO_3)_2$	,,	1·8367	*26 404*
$PbMoO_4$	,,	1·2106	*08 302*
$Pb(NO_3)_2$	,,	1·0922	*03 829*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
PbO	$PbSO_4$	0·73600	*86 688*
PbO_2	,,	0·78875	*89 694*
Pb_3O_4	,,	0·75358	*87 713*
$Pb_3(PO_4)_2$	,,	0·89201	*95 037*
PbS	,,	0·78897	*89 706*
$PbSO_3$	,,	0·94724	*97 646*
$PbWO_4$	,,	1·5005	*17 624*
K_2PdCl_6	Pd	3·7344	*57 222*
$Pd(CN)_2$	,,	1·4891	*17 292*
$PdCl_2$	,,	1·6665	*22 180*
$PdCl_2 \cdot 2\,H_2O$	,,	2·0051	*30 214*
PdI_2	,,	3·3855	*52 963*
$Pd(NO_3)_2$	,,	2·1656	*33 557*
PdO	,,	1·1504	*06 084*
Pd	$Pd(C_7H_6O_2N)_2$ (salicyl aldoxime)	0·28099	*44 869*
Pd	$Pd(C_8H_{14}O_4N_4)$ (diacetyldioxime)	0·31607	*49 979*
Pd	$Pd(C_{10}H_6ONO)_2$ (α-nitroso-β-naphthol)	0·23606	*37 302*
Pd	$Pd[C_{10}H_6O(NO_2)]_2$ (α-nitro-β-naphthol)	0·22041	*34 324*
Pr	Pr_2O_3	0·85447	*93 170*
Pt	K_2PtCl_6	0·40139	*60 357*
Pt	$(NH_4)_2PtCl_6$	0·43948	*64 294*
H_2PtCl_6	Pt	2·1008	*32 239*
$H_2PtCl_6 \cdot 6\,H_2O$	,,	2·6549	*42 405*
K_2PtCl_6	,,	2·4913	*39 643*
$(NH_4)_2PtCl_6$	,,	2·2754	*35 706*
$PtCl_4$	,,	1·7270	*23 729*
$PtCl_4 \cdot 5\,H_2O$	,,	2·1887	*34 019*
PtS_2	,,	1·3287	*12 344*
Pt	PtS_2	0·75260	*87 656*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Rb	AgCl	0·59636	*77 551*
RbCl	,,	0·84372	*92 620*
Rb	Rb_2PtCl_6	0·29537	*47 037*
Rb_2CO_3	,,	0·39906	*60 104*
$RbHCO_3$	,,	0·50622	*70 434*
RbCl	,,	0·41789	*62 107*
Rb_2O	,,	0·32302	*50 923*
Rb_2SO_4	,,	0·46135	*66 403*
Rb	Rb_2SO_4	0·64024	*80 634*
Rb_2PtCl_6	,,	2·1675	*33 597*
FeS_2	$BaSO_4$	0·25700	*40 994*
H_2S	,,	0·14601	*16 438*
H_2SO_3	,,	0·35167	*54 613*
H_2SO_4	,,	0·42018	*62 344*
K_2SO_4	,,	0·74656	*87 306*
$(NH_4)_2SO_4$	,,	0·56612	*75 290*
Na_2S	,,	0·33436	*52 421*
$Na_2S \cdot 9\,H_2O$	,,	1·0290	*01 241*
$NaHSO_3$	,,	0·44582	*64 916*
Na_2SO_3	,,	0·53999	*73 239*
$Na_2SO_3 \cdot 7\,H_2O$	,,	1·0803	*03 353*
Na_2SO_4	,,	0·60854	*78 429*
$Na_2S_2O_3$	,,	0·33868	*52 979*
$Na_2S_2O_3 \cdot 5\,H_2O$	,,	0·53163	*72 561*
$Na_2S_2O_4$	,,	0·37295	*57 165*
S	,,	0·13737	*13 790*
SO_2	,,	0·27446	*43 848*
SO_3	,,	0·34300	*53 530*
SO_4	,,	0·41155	*61 442*
S_2O_3	,,	0·24019	*38 055*
S_2O_4	,,	0·27446	*43 848*
$BaSO_4$	$C_{12}H_{12}N_2 \cdot H_2SO_4$ (benzidine sulphate)	0·82680	*91 740*
S	,,	0·11358	*05 529*
$BaSO_4$	CuO	2·9347	*45 756*
H_2S	,,	0·42849	*63 194*
S	,,	0·40314	*60 546*
S	CuS	0·33540	*52 556*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Sb_2O_4	Sb	1·2628	*10 134*
Sb	$Sb(C_9H_6ON)_3$ (oxinate)	0·21969	*34 182*
Sb_2O_4	,,	0·27743	*44 316*
Sb	$Sb(C_{12}H_{10}ONS)$ (thionalide)	0·15800	*19 867*
Sb_2O_4	,,	0·19953	*30 000*
Sb	$(SbOH)C_6H_3O_3$ (pyrogallate)	0·46498	*66 744*
Sb_2O_4	,,	0·58719	*76 878*
$KSbO \cdot C_4H_4O_6 \cdot \frac{1}{2} H_2O$ (tartrate)	Sb_2O_4	2·1719	*33 683*
$Na_3SbS_4 \cdot 9 H_2O$	,,	3·1292	*49 543*
Sb	,,	0·79188	*89 866*
Sb (empirical)	,,	0·7922	*89 884*
$SbCl_3$	,,	1·4837	*17 134*
$SbCl_5$	,,	1·9449	*28 889*
SbOCl	,,	1·1265	*05 175*
$SbOCl_3$	,,	1·5877	*20 078*
Sb_2O_3	,,	0·94797	*97 680*
Sb_2O_3 (empirical)	,,	0·9484	*97 698*
Sb_2S_3	,,	1·1047	*04 325*
Sb_2S_3 (empirical)	,,	1·105	*04 341*
Sb_2S_5	,,	1·3132	*11 835*
$Sb_2(SO_4)_3$	,,	1·7291	*23 781*
Sb	Sb_2S_3	0·71683	*85 542*
Sb (empirical)	,,	0·7173	*85 568*
Sb_2O_4	,,	0·90522	*95 675*
Sb	Sb_2S_5	0·60300	*78 031*
Sb_2O_3	,,	0·72185	*85 845*
Sb_2O_4	,,	0·76147	*88 165*
Sc	Sc_2O_3	0·65197	*81 423*
H_2SeO_3	Se	1·6334	*21 310*
H_2SeO_4	,,	1·8361	*26 389*
Na_2SeO_3	,,	2·1902	*34 049*
Na_2SeO_4	,,	2·3929	*37 892*
SeO_2	,,	1·4053	*14 776*
SeO_3	,,	1·6079	*20 626*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Se	$PbSeO_4$	0·22549	*35 313*
Si	$(C_9H_7N)_4 \cdot H_4Si(Mo_3O_{10})_4$ (quinoline molybdosilicate)	0·012003	*07 930*
SiO_2	,,	0·025678	*40 955*
Si	K_2SiF_6	0·12751	*10 556*
SiO_2	,,	0·27278	*43 581*
$BaSiF_6$	SiO_2	4·6505	*66 750*
H_2SiO_3	,,	1·2998	*11 388*
K_2SiF_6	,,	3·6660	*56 419*
Na_2SiO_3	,,	2·0315	*30 781*
Si	,,	0·46747	*66 975*
SiF_4	,,	1·7322	*23 861*
SiO_3	,,	1·2663	*10 253*
SiO_4	,,	1·5325	*18 541*
Si_2O_7	,,	1·3994	*14 594*
SnO_2	Sn	1·2696	*10 366*
$(NH_4)_2SnCl_6$	SnO_2	2·4388	*38 717*
Sn	,,	0·78766	*89 634*
$SnCl_2$	,,	1·2582	*09 976*
$SnCl_2 \cdot 2\,H_2O$	,,	1·4973	*17 531*
$SnCl_4$	,,	1·7288	*23 774*
SnO	,,	0·89383	*95 125*
Sr	$Sr_2As_2O_7$	0·40098	*60 312*
$SrSO_4$	,,	0·84056	*92 457*
Sr	SrC_2O_4 (oxalate)	0·49888	*69 800*
$SrSO_4$	,,	1·0458	*01 945*
Sr	$SrC_2O_4 \cdot H_2O$	0·45248	*65 559*
$SrSO_4$	,,	0·94851	*97 704*
Sr	$SrCO_3$	0·59353	*77 345*
$SrSO_4$	,,	1·2442	*09 489*
Sr	$SrC_4H_4O_6 \cdot 4\,H_2O$ (tartrate)	0·28473	*45 443*
$SrSO_4$	,,	0·59686	*77 587*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Sr	$SrCrO_4$	0·43032	*63 379*
$SrSO_4$	,,	0·90206	*95 524*
Sr	SrF_2	0·69752	*84 356*
$SrSO_4$	,,	1·4622	*16 501*
Sr	$Sr(IO_3)_2$	0·20032	*30 172*
$SrSO_4$	,,	0·41992	*62 317*
SO_3	$SrSO_4$	0·43586	*63 935*
Sr	,,	0·47704	*67 855*
$Sr_2As_2O_7$	,,	1·1897	*07 543*
SrC_2O_4 (oxalate)	,,	0·95621	*98 055*
$SrC_2O_4 \cdot H_2O$	,,	1·0543	*02 296*
$SrCl_2$	,,	0·86308	*93 605*
$SrCl_2 \cdot 6\ H_2O$	,,	1·4515	*16 183*
$SrCrO_4$	,,	1·1086	*04 476*
SrF_2	,,	0·68390	*83 499*
$Sr(IO_3)_2$	,,	2·3814	*37 683*
$Sr(NO_3)_2$	,,	1·1522	*06 151*
$Sr(NO_3)_2 \cdot 4\ H_2O$	,,	1·5445	*18 877*
SrO	,,	0·56414	*75 139*
SrS	,,	0·65160	*81 398*
SrS_2O_3	,,	1·0875	*03 641*
Ta	Ta_2O_5	0·81896	*91 326*
$TaCl_5$	,,	1·6213	*20 987*
Te	$PbTeO_4$	0·31997	*50 511*
$PbTeO_4$	Te	3·1253	*49 489*
H_2TeO_3	,,	1·3919	*14 362*
H_2TeO_4	,,	1·5173	*18 108*
$H_2TeO_4 \cdot 2\ H_2O$	,,	1·7997	*25 520*
TeO_2	,,	1·2508	*09 718*
TeO_3	,,	1·3761	*13 866*
Th	$Th(C_9H_6ON)_4$ (oxinate)	0·28695	*45 781*
ThO_2	,,	0·32652	*51 391*
Th	$Th(C_{10}H_7O_5N_4)_4 \cdot H_2O$ (picrolonate)	0·17811	*25 068*
ThO	,,	0·20267	*30 679*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Th	ThO_2	0·87881	*94 390*
$ThCl_4$	,,	1·4159	*15 104*
$Th(NO_3)_4$	,,	1·8181	*25 963*
$Th(NO_3)_4 \cdot 4\,H_2O$	,,	2·0911	*32 037*
$Th(SO_4)_2$	,,	1·6064	*20 587*
Ti	TiO_2	0·59950	*77 779*
$TiCl_3$	,,	1·9308	*28 574*
$TiCl_4$	,,	2·3746	*37 558*
$Ti_3(PO_4)_4$	,,	2·1844	*33 933*
$Ti_2(SO_4)_3$	,,	2·4030	*38 075*
Ti	$TiO(C_9H_6ON)_2$ (oxinate)	0·13600	*13 353*
TiO_2	,,	0·22685	*35 575*
Ti	$TiO(C_9H_4Br_2ON)_2$ (dibromooxinate)	0·071724	*85 566*
TiO_2	,,	0·11964	*07 787*
Tl	$TlC_7H_4NS_2$ (mercaptobenzothiazole)	0·55145	*74 151*
TlI	,,	0·89386	*95 127*
Tl	$TlC_{12}H_{10}ONS$ (thionalide)	0·48586	*68 651*
TlI	,,	0·78754	*89 627*
Tl	TlCl	0·85216	*93 052*
TlI	,,	1·3813	*14 028*
Tl	Tl_2CrO_4	0·77894	*89 150*
TlI	,,	1·2626	*10 127*
Tl	TlI	0·61693	*79 024*
Tl_2CO_3	,,	0·70750	*84 973*
TlCl	,,	0·72397	*85 972*
$TlCl_3$	,,	0·93800	*97 221*
$TlCl_3 \cdot 4\,H_2O$	,,	1·1555	*06 278*
Tl_2CrO_4	,,	0·79202	*89 873*
$TlIO_3$	,,	1·1449	*05 876*
$TlNO_3$	,,	0·80410	*90 531*
$Tl(NO_3)_3$	,,	1·1784	*07 130*
$Tl(NO_3)_3 \cdot 3\,H_2O$	,,	1·3416	*12 761*
Tl_2O_3	,,	0·68938	*83 846*
TlOH	,,	0·66827	*82 495*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
$Tl(OH)_3$	TlI	0·77094	*88 702*
Tl_3PO_4	,,	0·71249	*85 278*
Tl_2PtCl_6	,,	1·2324	*09 076*
Tl_2SO_4	,,	0·76192	*88 191*
Tl	$TlIO_3$	0·53886	*73 148*
TlI	,,	0·87345	*94 124*
Tl	Tl_2O_3	0·89492	*95 178*
TlI	,,	1·4506	*16 154*
Tl	Tl_2PtCl_6	0·50058	*69 947*
TlI	,,	0·81140	*90 924*
U	$U(C_2O_4)_2$ (oxalate)	0·57489	*75 958*
U_3O_8	,,	0·67792	*83 118*
U	$UO_2(C_9H_6ON)_2$ (oxinate)	0·42636	*62 977*
U_3O_8	,,	0·50277	*70 137*
U	$UO_2(C_9H_6ON)_2C_9H_7ON$ (oxinate)	0·33839	*52 941*
U_3O_8	,,	0·39903	*60 101*
U	UOF_2	0·81511	*91 122*
U_3O_8	,,	0·96120	*98 281*
$Na_2U_2O_7$	U_3O_8	1·1294	*05 284*
U	,,	0·84802	*92 841*
$U(C_2O_4)_2$ (oxalate)	,,	1·4751	*16 882*
UF_4	,,	1·1187	*04 873*
UOF_2	,,	1·0439	*01 867*
UO_2	,,	0·96200	*98 318*
$UO_2(C_2H_3O_2) \cdot 2\,H_2O$ (acetate)	,,	1·5110	*17 926*
$UO_2(NO_3)_2 \cdot 6\,H_2O$	,,	1·7888	*25 256*
$(UO_2)_2P_2O_7$	,,	1·2718	*10 442*
$UO_2SO_4 \cdot 3\,H_2O$	,,	1·4967	*17 514*
U	$(UO_2)_2P_2O_7$	0·66678	*82 398*
U_3O_8	,,	0·78628	*89 558*
V	$AgVO_3$	0·24634	*39 153*
V_2O_5	,,	0·43973	*64 319*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
V	Ag_3VO_4	0·11617	*06 509*
V_2O_5	,,	0·20737	*31 674*
V	$Ba(VO_3)_2$	0·30394	*48 279*
V_2O_5	,,	0·54256	*73 445*
V	$V_2O_3(C_9H_6ON)_4$ (oxinate)	0·14026	*14 693*
V_2O_5	,,	0·25037	*39 859*
$AgVO_3$	V_2O_5	2·2741	*35 681*
Ag_3VO_4	,,	4·8223	*68 326*
$Ba(VO_3)_2$	,,	1·8431	*26 555*
HVO_3	,,	1·0990	*04 101*
NH_4VO_3	,,	1·2863	*10 935*
V	,,	0·56020	*74 834*
VCl_2	,,	1·3399	*12 707*
$VOCl_2$	,,	1·5158	*18 065*
$VOCl_3$	,,	1·9057	*28 005*
VO_4	,,	1·2639	*10 171*
V_2O_2	,,	0·73612	*86 695*
V_2O_3	,,	0·82408	*91 597*
V_2O_4	,,	0·91204	*96 001*
V_2O_7	,,	1·1759	*07 038*
V_2S_3	,,	1·0890	*03 705*
W	$BaWO_4$	0·47729	*67 878*
WO_3	,,	0·60189	*77 952*
W	$CaWO_4$	0·63854	*80 519*
WO_3	,,	0·80524	*90 592*
W	$PbWO_4$	0·40403	*60 641*
WO_3	,,	0·50950	*70 715*
$BaWO_4$	WO_3	1·6614	*22 048*
$CaWO_4$	,,	1·2419	*09 408*
H_2WO_4	,,	1·0777	*03 250*
Na_2WO_4	,,	1·2673	*10 289*
$Na_2WO_4 \cdot 2\,H_2O$	,,	1·4227	*15 312*
$PbWO_4$	,,	1·9627	*29 285*
W	,,	0·79298	*89 926*
WO_2	,,	0·93099	*96 895*
WS_2	,,	1·0696	*02 921*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
W	$WO_2(C_9H_6ON)_2$ (oxinate)	0·36468	*56 191*
WO_3	,,	0·45988	*66 265*
Y	Y_2O_3	0·78746	*89 623*
YCl_3	,,	1·7295	*23 791*
$Y(NO_3)_3$	,,	2·4349	*38 647*
$Y(NO_3)_3 \cdot 3\ H_2O$	,,	2·6742	*42 719*
$Y(OH)_3$	,,	1·2393	*09 318*
$Y_2(SO_4)_3$	,,	2·0636	*31 462*
ZnO	Zn	1·2447	*09 507*
Zn	$Zn(C_7H_6O_2N)_2$ (anthranilate)	0·19363	*28 698*
ZnO	,,	0·24102	*38 206*
Zn	$Zn(C_9H_6ON)_2$ (oxinate)	0·18485	*26 682*
ZnO	,,	0·23009	*36 189*
Zn	$Zn(C_{10}H_6O_2N)_2 \cdot H_2O$ (quinaldinate)	0·15285	*18 428*
ZnO	,,	0·19026	*27 935*
Zn	$Zn[Hg(SCN)_4]$	0·13120	*11 793*
ZnO	,,	0·16331	*21 300*
Zn	$Zn(NH_4)PO_4$	0·36649	*56 406*
ZnO	,,	0·45618	*65 914*
Zn	ZnO	0·80339	*90 493*
$Zn(C_2H_3O_2)_2$ (acetate)	,,	2·2545	*35 305*
$Zn(C_2H_3O_2)_2 \cdot 2\ H_2O$	,,	2·6973	*43 092*
ZnC_2O_4 (oxalate)	,,	1·8850	*27 531*
$ZnCl_2$	,,	1·6748	*22 396*
$ZnCl_2 \cdot \frac{1}{2}\ H_2O$	,,	1·7855	*25 175*
$Zn(NH_4)PO_4$	,,	2·1921	*34 087*
$Zn(NO_3)_2$	,,	2·3273	*36 685*
$Zn(OH)_2$	,,	1·2214	*08 685*
$Zn_2P_2O_7$	,,	1·8721	*27 234*
ZnS	,,	1·1974	*07 825*
$ZnSO_4$	,,	1·9839	*29 751*
$ZnSO_4 \cdot 7\ H_2O$	,,	3·5335	*54 821*
Zn	$Zn_2P_2O_7$	0·42913	*63 259*
ZnO	,,	0·53415	*72 766*

TABLE 60.2 *(contd.)*

Required	Found	Factor	log
Zn	ZnS	0·67094	*82 668*
ZnO	,,	0·83513	*92 175*
Zn	$ZnSO_4$	0·40497	*60 742*
ZnO	,,	0·50407	*70 249*
Zr	$Zr(C_6H_5CHOHCOO)_4$ (tetramandelate)	0·13110	*11 761*
ZrO_2	,,	0·17709	*24 820*
Zr	$Zr(BrC_6H_4CHOHCOO)_4$ (*p*-bromo tetramandelate)	0·090189	*95 516*
ZrO_2	,,	0·12183	*08 575*
Zr	ZrO_2	0·74030	*86 941*
$ZrCl_4$	,,	1·8913	*27 676*
$Zr(NO_3)_4$	,,	2·7532	*43 984*
$Zr(NO_3)_4 \cdot 5\ H_2O$	,,	3·4843	*54 211*
$Zr(OH)_4$	,,	1·2924	*11 140*
ZrP_2O_7	,,	2·1520	*33 284*
$Zr(SO_4)_2$	,,	2·2996	*36 165*
$Zr(SO_4)_2 \cdot 4\ H_2O$	,,	2·8844	*46 006*
$Zr(SeO_3)_2$	,,	2·8010	*44 731*
Zr	ZrP_2O_7	0·34401	*53 657*
ZrO_2	,,	0·46468	*66 716*
Zr	$Zr(SeO_3)_2$	0·26430	*42 209*
ZrO_2	,,	0·35701	*55 269*

TABLE

Shortened five figure

Number	0	$_0\Delta_1$	1	$_1\Delta_2$	2	$_2\Delta_3$	3	$_3\Delta_4$	4	$_4\Delta_5$	Number
10	00000	**432**	00432	**428**	00860	**424**	01284	**419**	01703	**416**	10
11	04139	**393**	04532	**390**	04922	**386**	05308	**382**	05690	**380**	11
12	07918	**361**	08279	**357**	08636	**355**	08991	**351**	09342	**349**	12
13	11394	**333**	11727	**330**	12057	**328**	12385	**325**	12710	**323**	13
14	14613	**309**	14922	**307**	15229	**305**	15534	**302**	15836	**301**	14
15	17609	**289**	17898	**286**	18184	**285**	18469	**283**	18752	**281**	15
16	20412	**271**	20683	**269**	20952	**267**	21219	**265**	21484	**264**	16
17	23045	**255**	23300	**253**	23553	**252**	23805	**250**	24055	**249**	17
18	25527	**241**	25768	**239**	26007	**238**	26245	**237**	26482	**235**	18
19	27875	**228**	28103	**227**	28330	**226**	28556	**224**	28780	**223**	19
20	30103	**217**	30320	**215**	30535	**215**	30750	**213**	30963	**212**	20
21	32222	**206**	32428	**206**	32634	**204**	32838	**203**	33041	**203**	21
22	34242	**197**	34439	**196**	34635	**195**	34830	**195**	35025	**193**	22
23	36173	**188**	36361	**188**	36549	**187**	36736	**186**	36922	**185**	23
24	38021	**181**	38202	**180**	38382	**179**	38561	**178**	38739	**178**	24
25	39794	**173**	39967	**173**	40140	**172**	40312	**171**	40483	**171**	25
26	41497	**167**	41664	**166**	41830	**166**	41996	**164**	42160	**165**	26
27	43136	**161**	43297	**160**	43457	**159**	43616	**159**	43775	**158**	27
28	44716	**155**	44871	**154**	45025	**154**	45179	**153**	45332	**152**	28
29	46240	**149**	46389	**149**	46538	**149**	46687	**148**	46835	**147**	29
30	47712	**145**	47857	**144**	48001	**143**	48144	**143**	48287	**143**	30
31	49136	**140**	49276	**139**	49415	**139**	49554	**139**	49693	**138**	31
32	50515	**136**	50651	**135**	50786	**134**	50920	**135**	51055	**133**	32
33	51851	**132**	51983	**131**	52114	**130**	52244	**131**	52375	**129**	33
34	53148	**127**	53275	**128**	53403	**126**	53529	**127**	53656	**126**	34
35	54407	**124**	54531	**123**	54654	**123**	54777	**123**	54900	**123**	35
36	55630	**121**	55751	**120**	55871	**120**	55991	**119**	56110	**119**	36
37	56820	**117**	56937	**117**	57054	**117**	57171	**116**	57287	**116**	37
38	57978	**114**	58092	**114**	58206	**114**	58320	**113**	58433	**113**	38
39	59106	**112**	59218	**111**	59329	**110**	59439	**111**	59550	**110**	39
40	60206	**108**	60314	**109**	60423	**108**	60531	**107**	60638	**108**	40
41	61278	**106**	61384	**106**	61490	**105**	61595	**105**	61700	**105**	41
42	62325	**103**	62428	**103**	62531	**103**	62634	**103**	62737	**102**	42
43	63347	**101**	63448	**100**	63548	**101**	63649	**100**	63749	**100**	43
44	64345	**99**	64444	**98**	64542	**98**	64640	**98**	64738	**98**	44
	0		1		2		3		4		

60.4

logarithms

Number	5	$_5\Delta_6$	6	$_6\Delta_7$	7	$_7\Delta_8$	8	$_8\Delta_9$	9	$_9\Delta_0$	Number
10	02119	**412**	02531	**407**	02938	**404**	03342	**401**	03743	**396**	10
11	06070	**376**	06446	**373**	06819	**369**	07188	**367**	07555	**363**	11
12	09691	**346**	10037	**343**	10380	**341**	10721	**338**	11059	**335**	12
13	13033	**321**	13354	**318**	13672	**316**	13988	**313**	14301	**312**	13
14	16137	**298**	16435	**297**	16732	**294**	17026	**293**	17319	**290**	14
15	19033	**279**	19312	**278**	19590	**276**	19866	**274**	20140	**272**	15
16	21748	**263**	22011	**261**	22272	**259**	22531	**258**	22789	**256**	16
17	24304	**247**	24551	**246**	24797	**245**	25042	**243**	25285	**242**	17
18	26717	**234**	26951	**233**	27184	**232**	27416	**230**	27646	**229**	18
19	29003	**223**	29226	**221**	29447	**220**	29667	**218**	29885	**218**	19
20	31175	**212**	31387	**210**	31597	**209**	31806	**209**	32015	**207**	20
21	33244	**201**	33445	**201**	33646	**200**	33846	**198**	34044	**198**	21
22	35218	**193**	35411	**192**	35603	**190**	35793	**191**	35984	**189**	22
23	37107	**184**	37291	**184**	37475	**183**	37658	**182**	37840	**181**	23
24	38917	**177**	39094	**176**	39270	**175**	39445	**175**	39620	**174**	24
25	40654	**170**	40824	**169**	40993	**169**	41162	**168**	41330	**167**	25
26	42325	**163**	42488	**163**	42651	**162**	42813	**162**	42975	**161**	26
27	43933	**158**	44091	**157**	44248	**156**	44404	**156**	44560	**156**	27
28	45484	**153**	45637	**151**	45788	**151**	45939	**151**	46090	**150**	28
29	46982	**147**	47129	**147**	47276	**146**	47422	**145**	47567	**145**	29
30	48430	**142**	48572	**142**	48714	**141**	48855	**141**	48996	**140**	30
31	49831	**138**	49969	**137**	50106	**137**	50243	**136**	50379	**136**	31
32	51188	**134**	51322	**133**	51455	**132**	51587	**133**	51720	**131**	32
33	52504	**130**	52634	**129**	52763	**129**	52892	**128**	53020	**128**	33
34	53782	**126**	53908	**125**	54033	**125**	54158	**125**	54283	**124**	34
35	55023	**122**	55145	**122**	55267	**121**	55388	**121**	55509	**121**	35
36	56229	**119**	56348	**119**	56467	**118**	56585	**118**	56703	**117**	36
37	57403	**116**	57519	**115**	57634	**115**	57749	**115**	57864	**114**	37
38	58546	**113**	58659	**112**	58771	**112**	58883	**112**	58995	**111**	38
39	59660	**110**	59770	**109**	59879	**109**	59988	**109**	60097	**109**	39
40	60746	**107**	60853	**106**	60959	**107**	61066	**106**	61172	**106**	40
41	61805	**104**	61909	**105**	62014	**104**	62118	**103**	62221	**104**	41
42	62839	**102**	62941	**102**	63043	**101**	63144	**102**	63246	**101**	42
43	63849	**100**	63949	**99**	64048	**99**	64147	**99**	64246	**99**	43
44	64836	**97**	64933	**98**	65031	**97**	65128	**97**	65225	**96**	44
	5		6		7		8		9		

TABLE

Shortened five figure

Number	0	$_0\Delta_1$	1	$_1\Delta_2$	2	$_2\Delta_3$	3	$_3\Delta_4$	4	$_4\Delta_5$	Number
45	65321	97	65418	96	65514	96	65610	96	65706	95	45
46	66276	94	66370	94	66464	94	66558	94	66652	93	46
47	67210	92	67302	92	67394	92	67486	92	67578	91	47
48	68124	91	68215	90	68305	90	68395	90	68485	89	48
49	69020	88	69108	89	69197	88	69285	88	69373	88	49
50	69897	87	69984	86	70070	87	70157	86	70243	86	50
51	70757	85	70842	85	70927	85	71012	84	71096	85	51
52	71600	84	71684	83	71767	83	71850	83	71933	83	52
53	72428	81	72509	82	72591	82	72673	81	72754	81	53
54	73239	81	73320	80	73400	80	73480	80	73560	80	54
55	74036	79	74115	79	74194	79	74273	78	74351	78	55
56	74819	77	74896	78	74974	77	75051	77	75128	77	56
57	75587	77	75664	76	75740	75	75815	76	75891	76	57
58	76343	75	76418	74	76492	75	75567	74	76641	75	58
59	77085	74	77159	73	77232	73	77305	74	77379	73	59
60	77815	72	77887	73	77960	72	78032	72	78104	72	60
61	78533	71	78604	71	78675	71	78746	71	78817	71	61
62	79239	70	79309	70	79379	70	79449	69	79518	70	62
63	79934	69	80003	69	80072	68	80140	69	80209	68	63
64	80618	68	80686	68	80754	67	80821	68	80889	67	64
65	81291	67	81358	67	81425	66	81491	67	81558	66	65
66	81954	66	82020	66	82086	65	82151	66	82217	65	66
67	82607	65	82672	65	82737	65	82802	64	82866	64	67
68	83251	64	83315	63	83378	64	83442	64	83506	63	68
69	83885	63	83948	63	84011	62	84073	63	84136	62	69
70	84510	62	84572	62	84634	62	84696	61	84757	62	70
71	85126	61	85187	61	85248	61	85309	61	85370	61	71
72	85733	61	85794	60	85854	60	85914	60	85974	60	72
73	86332	60	86392	59	86451	59	86510	60	86570	59	73
74	86923	59	86982	58	87040	59	87099	58	87157	59	74
75	87506	58	87564	58	87622	57	87679	58	87737	58	75
76	88081	57	88138	57	88195	57	88252	57	88309	57	76
77	88649	56	88705	57	88762	56	88818	56	88874	56	77
78	89209	56	89265	56	89321	55	89376	56	89432	55	78
79	89763	55	89818	55	89873	54	89927	55	89982	55	79
	0		1		2		3		4		

60.4 *(contd.)*

logarithms

Number	5	$_5\Delta_6$	6	$_6\Delta_7$	7	$_7\Delta_8$	8	$_8\Delta_9$	9	$_9\Delta_0$	Number
45	65801	**95**	65896	**96**	65992	**95**	66087	**94**	66181	**95**	45
46	66745	**94**	66839	**93**	66932	**93**	67025	**92**	67117	**93**	46
47	67669	**92**	67761	**91**	67852	**91**	67943	**91**	68034	**90**	47
48	68574	**90**	68664	**89**	68753	**89**	68842	**89**	68931	**89**	48
49	69461	**87**	69548	**88**	69636	**87**	69723	**87**	69810	**87**	49
50	70329	**86**	70415	**86**	70501	**85**	70586	**86**	70672	**85**	50
51	71181	**84**	71265	**84**	71349	**84**	71433	**84**	71517	**83**	51
52	72016	**83**	72099	**82**	72181	**82**	72263	**83**	72346	**82**	52
53	72835	**81**	72916	**81**	72997	**81**	73078	**81**	73159	**80**	53
54	73640	**79**	73719	**80**	73799	**79**	73878	**79**	73957	**79**	54
55	74429	**78**	74507	**79**	74586	**77**	74663	**78**	74741	**78**	55
56	75205	**77**	75282	**76**	75358	**77**	75435	**76**	75511	**76**	56
57	75967	**75**	76042	**76**	76118	**75**	76193	**75**	76268	**75**	57
58	76716	**74**	76790	**74**	76864	**74**	76938	**74**	77012	**73**	58
59	77452	**73**	77525	**72**	77597	**73**	77670	**73**	77743	**72**	59
60	78176	**71**	78247	**72**	78319	**71**	78390	**72**	78462	**71**	60
61	78888	**70**	78958	**71**	79029	**70**	79099	**70**	79169	**70**	61
62	79588	**69**	79657	**70**	79727	**69**	79796	**69**	79865	**69**	62
63	80277	**69**	80346	**68**	80414	**68**	80482	**68**	80550	**68**	63
64	80956	**67**	81023	**67**	81090	**68**	81158	**66**	81224	**67**	64
65	81624	**66**	81690	**67**	81757	**66**	81823	**66**	81889	**65**	65
66	82282	**65**	82347	**66**	82413	**65**	82478	**65**	82543	**64**	66
67	82930	**65**	82995	**64**	83059	**64**	83123	**64**	83187	**64**	67
68	83569	**63**	83632	**64**	83696	**63**	83759	**63**	83822	**63**	68
69	84198	**63**	84261	**62**	84323	**63**	84386	**62**	84448	**62**	69
70	84819	**61**	84880	**62**	84942	**61**	85003	**62**	85065	**61**	70
71	85431	**60**	85491	**61**	85552	**60**	85612	**61**	85673	**60**	71
72	86034	**60**	86094	**59**	86153	**60**	86213	**60**	86273	**59**	72
73	86629	**59**	86688	**59**	86747	**59**	86806	**58**	86864	**59**	73
74	87216	**58**	87274	**58**	87332	**58**	87390	**58**	87448	**58**	74
75	87795	**57**	87852	**58**	87910	**57**	87967	**57**	88024	**57**	75
76	88366	**57**	88423	**57**	88480	**56**	88536	**57**	88593	**56**	76
77	88930	**56**	88986	**56**	89042	**56**	89098	**56**	89154	**55**	77
78	89487	**55**	89542	**55**	89597	**56**	89653	**55**	89708	**55**	78
79	90037	**54**	90091	**55**	90146	**54**	90200	**55**	90255	**54**	79
	5		6		7		8		9		

TABLE

Shortened five figure

Number	0	$_0\Delta_1$	1	$_1\Delta_2$	2	$_2\Delta_3$	3	$_3\Delta_4$	4	$_4\Delta_5$	Number
80	90309	54	90363	54	90417	55	90472	54	90526	54	80
81	90849	53	90902	54	90956	53	91009	53	91062	54	81
82	91381	53	91434	53	91487	53	91540	53	91593	52	82
83	91908	52	91960	52	92012	53	92065	52	92117	52	83
84	92428	52	92480	51	92531	52	92583	51	92634	52	84
85	92942	51	92993	51	93044	51	93095	51	93146	51	85
86	93450	50	93500	51	93551	50	93601	50	93651	51	86
87	93952	50	94002	50	94052	49	94101	50	94151	50	87
88	94448	50	94498	49	94547	49	94596	49	94645	49	88
89	94939	49	94988	48	95036	49	95085	49	95134	48	89
90	95424	48	95472	49	95521	48	95569	48	95617	48	90
91	95904	48	95952	47	95999	48	96047	48	96095	47	91
92	96379	47	96426	47	96473	47	96520	47	96567	47	92
93	96848	47	96895	47	96942	46	96988	47	97035	46	93
94	97313	46	97359	46	97405	46	97451	46	97497	46	94
95	97772	46	97818	46	97864	45	97909	46	97955	45	95
96	98227	45	98272	46	98318	45	98363	45	98408	45	96
97	98677	45	98722	45	98767	44	98811	45	98856	44	97
98	99123	44	99167	44	99211	44	99255	45	99300	44	98
99	99564	43	99607	44	99651	44	99695	44	99739	43	99
	0		1		2		3		4		

60.4 *(contd.)*

logarithms

Number	5	$_5\Delta_6$	6	$_6\Delta_7$	7	$_7\Delta_8$	8	$_8\Delta_9$	9	$_9\Delta_0$	Number
80	90580	54	90634	53	90687	54	90741	54	90795	54	80
81	91116	53	91169	53	91222	53	91275	53	91328	53	81
82	91645	53	91698	53	91751	52	91803	52	91855	53	82
83	92169	52	92221	52	92273	51	92324	52	92376	52	83
84	92686	51	92737	51	92788	52	92840	51	92891	51	84
85	93197	50	93247	51	93298	51	93349	50	93399	51	85
86	93702	50	93752	50	93802	50	93852	50	93902	50	86
87	94201	49	94250	50	94300	49	94349	50	94399	49	87
88	94694	49	94743	49	94792	49	94841	49	94890	49	88
89	95182	49	95231	48	95279	49	95328	48	95376	48	89
90	95665	48	95713	48	95761	48	95809	47	95856	48	90
91	96142	48	96190	47	96237	47	96284	48	96332	47	91
92	96614	47	96661	47	96708	47	96755	47	96802	46	92
93	97081	47	97128	46	97174	46	97220	47	97267	46	93
94	97543	46	97589	46	97635	46	97681	46	97727	45	94
95	98000	46	98046	45	98091	46	98137	45	98182	45	95
96	98453	45	98498	45	98543	45	98588	44	98632	45	96
97	98900	45	98945	44	98989	45	99034	44	99078	45	97
98	99344	44	99388	44	99432	44	99476	44	99520	44	98
99	99782	44	99826	44	99870	43	99913	44	99957	43	99
	5		6		7		8		9		

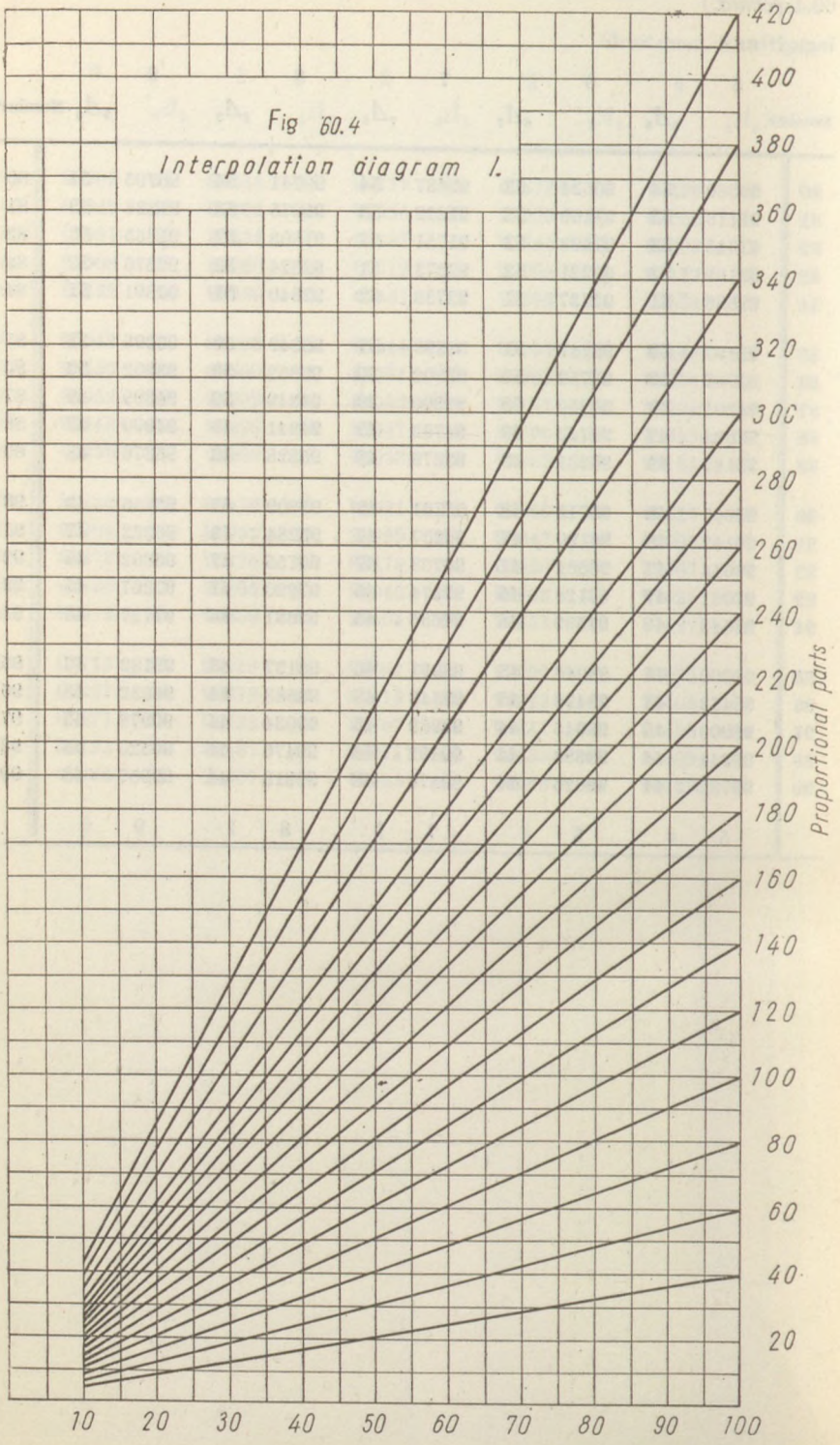


Fig 60.4
Interpolation diagram I.
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
Proportional parts
10
20
30
40
50
60
70
80
90
100

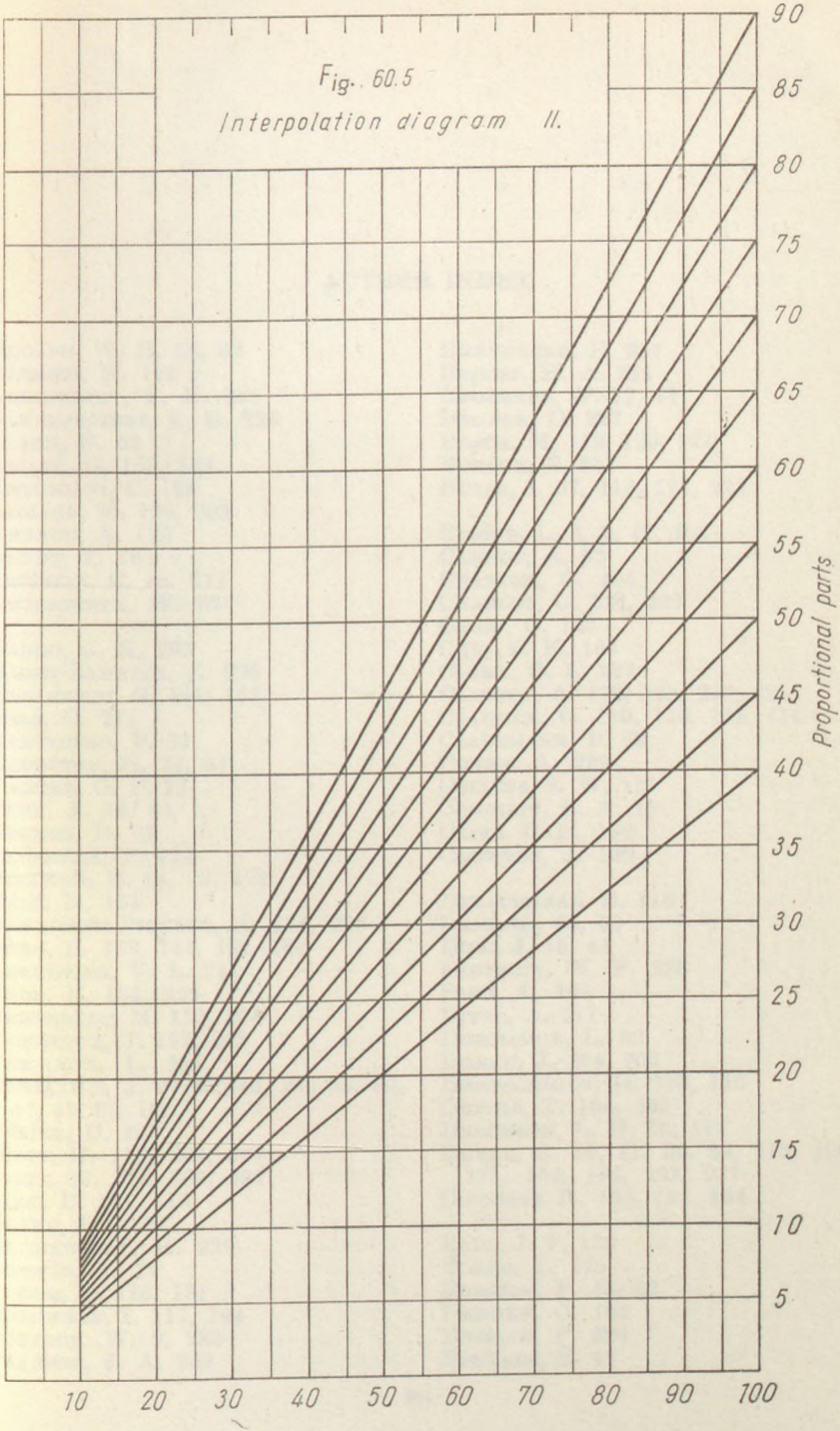
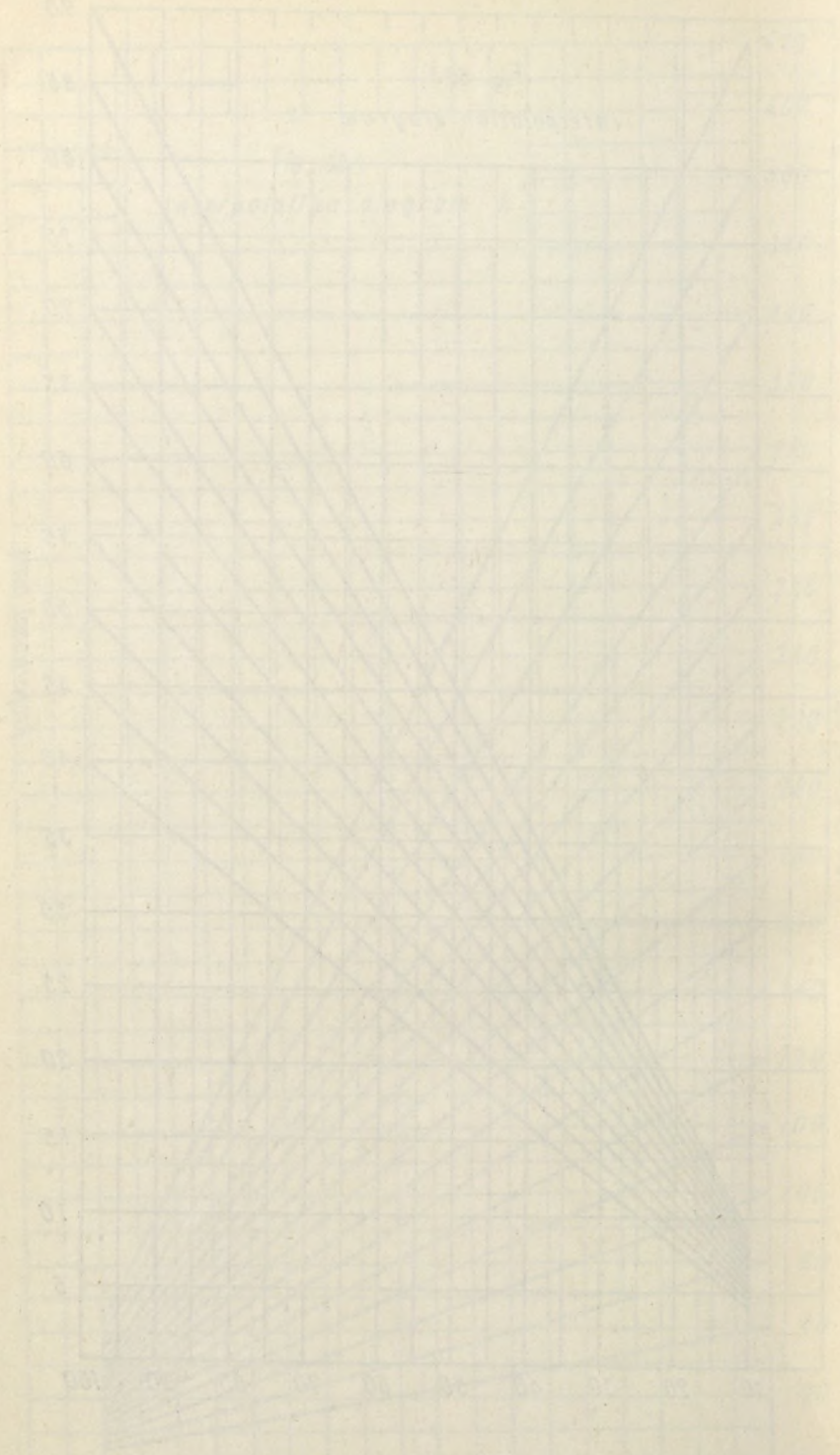


Fig. 60.5
Interpolation diagram II.
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
Proportional parts
10
20
30
40
50
60
70
80
90
100



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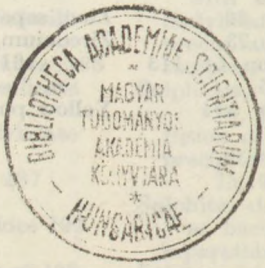
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