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Chemical products for industrial use — General method for determination of traces of sulphur compounds, as sulphate, by reduction and titrimetry

ERRATUM

Page 3

Table

Delete "From 4,5 to 450", and substitute :

"From 45 to 450"

International Standard 6228

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Chemical products for industrial use — General method for determination of traces of sulphur compounds, as sulphate, by reduction and titrimetry

Produits chimiques à usage industriel — Méthode générale de dosage, à l'état de sulfate, de traces de composés soufrés, par réduction et titrimétrie

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 6228 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in November 1978.

It has been approved by the member bodies of the following countries :

Australia
Austria
Belgium
Bulgaria
China
Czechoslovakia
Egypt, Arab Rep. of
France
Germany, F. R.
Hungary
India
Israel
Italy
Korea, Rep. of
Mexico
Netherlands
New Zealand
Poland
Romania
South Africa, Rep. of
Switzerland
Turkey
United Kingdom
USSR
Yugoslavia

No member body expressed disapproval of the document.

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

Printed in Switzerland

Chemical products for industrial use — General method for determination of traces of sulphur compounds, as sulphate, by reduction and titrimetry

1 Scope

This International Standard specifies a general reduction and titrimetric method for the determination, as sulphate, of trace quantities of sulphur compounds in chemical products for industrial use.

The International Standard relating to the chemical product to which the method is to be applied shall specify the method by which the test portion should be treated in order to convert the sulphur compounds to sulphate, if necessary, together with any modifications to the general procedure that may be needed.

2 Field of application

The method is applicable to the determination of amounts of sulphate (SO_4^{2-}) of between 4,5 and 450 µg, either in solution or, in some cases, directly in the test portion. The volume of solution taken for the determination shall not contain more than 2 ml of water; the test portion shall not contain more than the acceptable limits of interfering elements, as specified in the International Standard relating to the chemical product to which the method is to be applied.

The sulphate can be present as such in the product or can be produced by suitable pre-treatment of a sample containing other sulphur compounds to give a test solution.

The precision that can be expected is ± 5 %.

NOTE — By replacing the reducing solution by hydrochloric acid, it is possible to determine sulphides (but not polysulphides) in the presence of other sulphur compounds.

3 Principle

Prior conversion of the sulphur compounds in a test portion to sulphate, if required, and reduction of the sulphate ions to hydrogen sulphide by a mixture of hydriodic and phosphinic (hypophosphorous) acids in the presence of hydrochloric acid. Entrainment of the hydrogen sulphide in a current of nitrogen and absorption in a solution of sodium hydroxide in aqueous acetone. Titration of the sulphide ions with standard volumetric mercury(II) acetate or nitrate solution in the presence of 1,5-diphenyl-3-thiocarbazone (dithizone) as indicator.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Acetone.

4.2 Nitrogen, oxygen free.

4.3 Sodium hydroxide, 40 g/l solution.

4.4 Reducing solution.

Place in a 1 000 ml flask, fitted with three ground necks and a bulb reflux condenser (see, for example, figure 2), in the following order and under a current of the nitrogen (4.2),

- 100 ml of hydriodic acid solution, ϱ approximately 1,71 g/ml, about 57 % (*m*/*m*) solution;
- 25 ml of phosphinic (hypophosphorous) acid (H_3PO_2) solution, ϱ approximately 1,21 g/ml, about 50 % (*m*/*m*) solution;
- 100 ml of hydrochloric acid solution, ϱ approximately 1,19 g/ml, about 38 % (*m*/*m*) solution.

Fit the reflux condenser to the flask and, while bubbling a gentle current of the nitrogen (4.2) through the mixture, boil under reflux for about 4 h.

Cool to ambient temperature, maintaining the current of nitrogen.

Store the reagent away from direct sunlight in a dark glass flask fitted with a ground glass stopper, and under a nitrogen atmosphere obtained by purging the flask initially with the nitrogen (4.2).

The solution is stable for several weeks.

NOTE — This reagent should be prepared in a fume cupboard so as to remove liberated hydrogen chloride.

4.5 Sodium sulphate, standard reference solution, $c(Na_2SO_4) = 0{,}001$ mol/l.

Weigh, to the nearest 0,000 1 g, 0,142 0 g of anhydrous sodium sulphate, previously dried for 2 h at about 110 °C and allowed to cool in a desiccator. Dissolve in about 100 ml of water and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 96 µg of SO_4^{2-}.

4.6 Sodium sulphate, standard reference solution, $c(Na_2SO_4) = 0{,}000\ 1$ mol/l.

Transfer 100,0 ml of the standard reference sodium sulphate solution (4.5), to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 9,6 µg of SO_4^{2-}.

Prepare this solution at the time of use.

4.7 Mercury(II) acetate, standard volumetric solution, $c[Hg(CH_3COO)_2] = 0{,}001$ mol/l.

Weigh, to the nearest 0,000 1 g, 0,318 7 g of mercury(II) acetate $[Hg(CH_3COO)_2]$. Dissolve in about 100 ml of water and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix.

The following solution can be used as an alternative.

4.7.1 Mercury(II) nitrate, standard volumetric solution, $c[Hg(NO_3)_2] = 0{,}001$ mol/l.

Weigh 10,83 ± 0,01 g of mercury(II) oxide (HgO), place in a beaker of convenient capacity (for example 100 ml) and dissolve in 10 ml of nitric acid solution, ϱ approximately 1,40 g/ml, about 68 % (*m/m*) solution. Dilute the solution, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

NOTE — This solution may also be prepared by dissolution of a mass of 17,13 g of mercury(II) nitrate monohydrate $[Hg(NO_3)_2 \cdot H_2O]$ in water acidified with 1 ml of nitric acid solution, ϱ approximately 1,40 g/ml.

Transfer 20,00 ml of this solution, to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare the latter solution at the time of use.

4.8 Mercury(II) acetate, standard volumetric solution, $c[Hg(CH_3COO)_2] = 0{,}000\ 1$ mol/l.

Transfer 100,0 ml of the mercury(II) acetate solution (4.7), to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.

The following solution can be used as an alternative.

4.8.1 Mercury(II) nitrate, standard volumetric solution, $c[Hg(NO_3)_2] = 0{,}000\ 1$ mol/l.

Transfer 100,0 ml of the mercury(II) nitrate solution (4.7.1), to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.

NOTE — The concentration of the solutions (4.7, 4.7.1, 4.8 and 4.8.1) as prepared are sufficiently exact, taking into account the low levels of sulphate ions to be determined. Standardization is, therefore, not necessary.

4.9 1,5-Diphenyl-3-thiocarbazone (dithizone), 0,5 g/l solution in the acetone (4.1).

Discard the solution after 2 weeks.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Apparatus for reduction and entrainment (of the type, for example, shown in figure 1), of which all the components are connected by means of ground glass joints, with the exception of the flexible joint.

5.2 Microburette, graduated in 0,01 ml.

6 Procedure

WARNING — Mercury compounds are toxic and must be handled with precaution. Store the residual solutions obtained from the titrations, and treat them as specified in annex C, so as to avoid the pollution of waste water by the mercury.

6.1 Test portion and preparation of the test solution

Weigh a mass of the test sample and prepare the test solution following the procedure specified in the International Standard relating to the product to which the method is to be applied. The test solution shall meet the following requirements :

a) It shall contain either in its total volume or in the aliquot portion taken for the determination not more than 2 ml of water and between 4,5 and 450 µg of sulphate ions (SO_4^{2-}).

b) It shall be free from the interferences listed in annex B or shall have been treated to eliminate their influence.

NOTE — If the product is liquid or is a solid soluble in acids, of which the expected sulphate ions content of the test portion is between 4,5 and 450 µg, the test portion shall be introduced directly into the flask of the reduction apparatus (5.1).

6.2 Check test

Check the gas-tightness and functioning of the apparatus (reduction of sulphur compounds and quantitative recovery of the hydrogen sulphide liberated) as follows.

Introduce 5 ml of the sodium hydroxide solution (4.3), 5 ml of the acetone (4.1) and 0,1 ml of the dithizone solution (4.9) into the test tube of the apparatus. Mix and add, drop by drop, the appropriate mercury(II) acetate or nitrate solution, as indicated in the table below, until the colour changes from yellow to pink.

Expected SO_4^{2-} content	Standard volumetric mercury(II) acetate or nitrate solution	Standard reference sodium sulphate solution
µg		
From 4,5 to 60	4.8 or 4.8.1	4.6
From 4,5 to 450	4.7 or 4.7.1	4.5

NOTE — If too small a volume of the 0,000 1 mol/l titration solution is required (in the order of 1 ml), reduce to 1 drop the addition of the dithizone solution so as to detect more easily the end-point of the reaction.

Introduce 2,00 ml of the appropriate standard reference sodium sulphate solution (4.5 or 4.6) into the clean and dry reduction flask (5.1).

Assemble the apparatus (5.1) as shown, for example, in figure 1, having first smeared the ground glass cones lightly with silicone grease. With stopcock **3** closed, remove the cone from the top of the dropping funnel, pour in 15 ml of the reducing solution (4.4) and replace the cone. Fit clips to all the ground glass joints to ensure gas tightness. Open stopcock **1** and pass the nitrogen (4.2) gently through the inlet tube so as to give 2 or 3 bubbles per second through the tube in the receiver. Open stopcocks **2** and **3** and allow the reducing solution (4.4) in the dropping funnel to flow into the reduction flask. Close stopcocks **2** and **3**.

Maintaining the current of the nitrogen through the inlet tube, immerse the reduction flask to a depth of about 70 mm in a boiling water bath for 30 min. Then open stopcocks **2** and **3** and allow the nitrogen to flow through the dropping funnel for 5 min.

The hydrogen sulphide liberated by the reduction is absorbed in the solution contained in the receiver, which becomes yellow.

NOTE — Development of a blue-green coloration indicates that a large quantity of hydrochloric acid has been entrained. The test should therefore be repeated, checking carefully the nitrogen flow and the cooling efficiency of the condenser.

Disconnect the apparatus (5.1) and wash the connection tube with several millilitres of a mixture of equal volumes of water and the acetone (4.1), collecting the washings in the test tube. Titrate the solution obtained with the mercury(II) acetate solution (4.7 or 4.8, as appropriate), or with the mercury(II) nitrate solution (4.7.1 or 4.8.1, as appropriate), contained in the microburette (5.2), until the re-appearance of a pink colour.

Carry out a blank test on the reagents, using the same procedure as for the check test but omitting the standard reference sodium sulphate solution (4.5 or 4.6, as appropriate).

The result of the check test is considered satisfactory if the volume of the standard volumetric mercury(II) acetate or nitrate solution used for the titration is between 1,90 and 2,10 ml after making allowance for the blank test on the reagents. If the results are outside these limits, the reason shall be sought and eliminated, for example by checking the apparatus for leaks.

6.3 Determination

Carry out the determination using the procedure specified in 6.2, taking care

- to replace the 2,00 ml of the appropriate standard reference sodium sulphate solution by the test portion (6.1) or the aliquot portion of the test solution (containing in either case not more than 2 ml of water);
- to heat the reduction flask by means of a boiling water bath for the period of time specified in the International Standard appropriate to the product being analysed to ensure that the sulphate ions are fully converted to hydrogen sulphide.

6.4 Blank test

Carry out a blank test using the same reagents (including those for preparation of the test solution) as used in the determination (6.3), and following the same procedure, but omitting the test portion (6.1).

7 Expression of results

The International Standard relating to the product in question will give the formulae to be applied for the calculation.

8 Test report

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the general method used and to the International Standard relating to the product being analysed;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or in the International Standard relating to the product being analysed, or regarded as optional.

Dimensions in millimetres

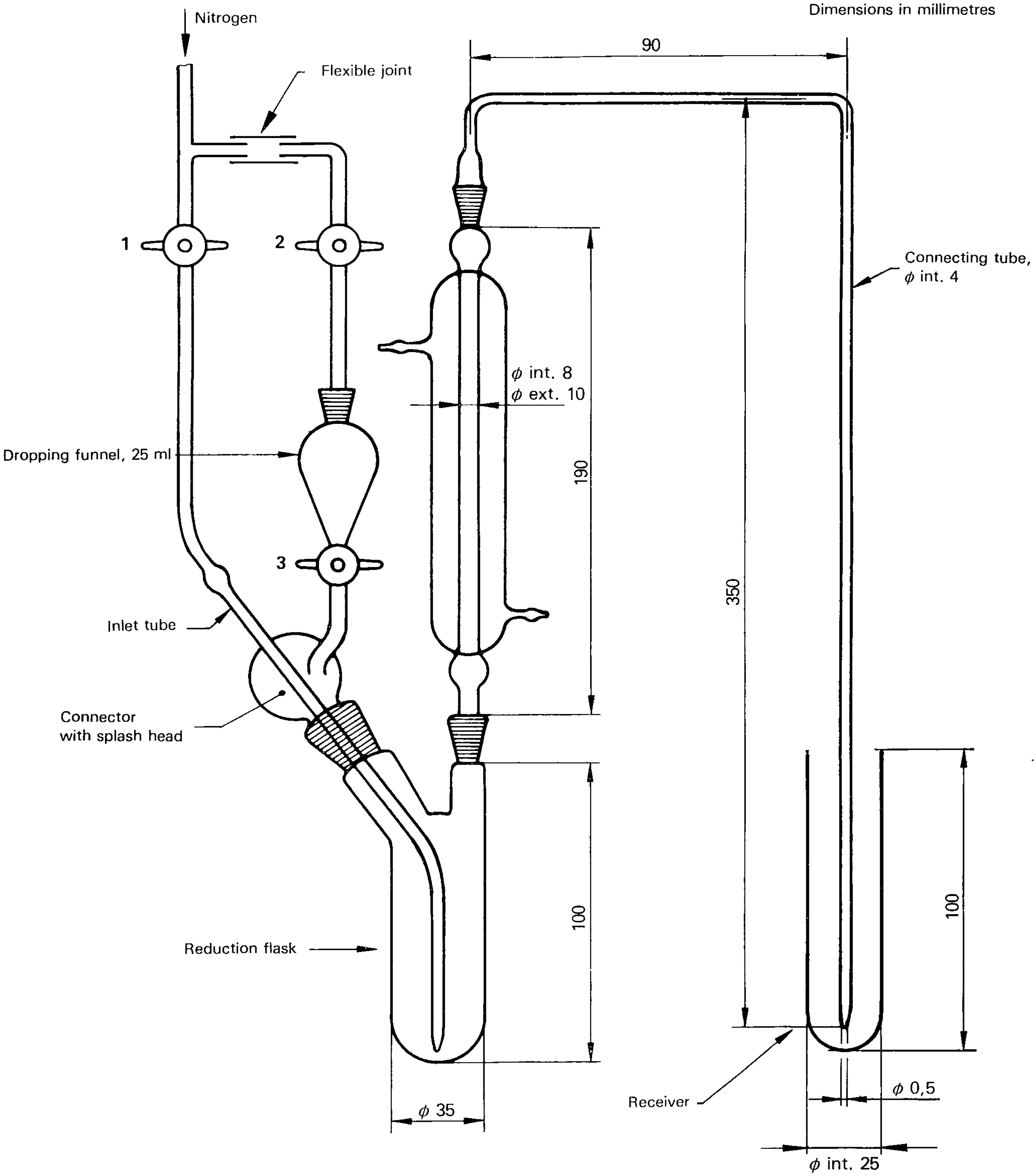

Figure 1 — Typical apparatus for reduction and entrainment

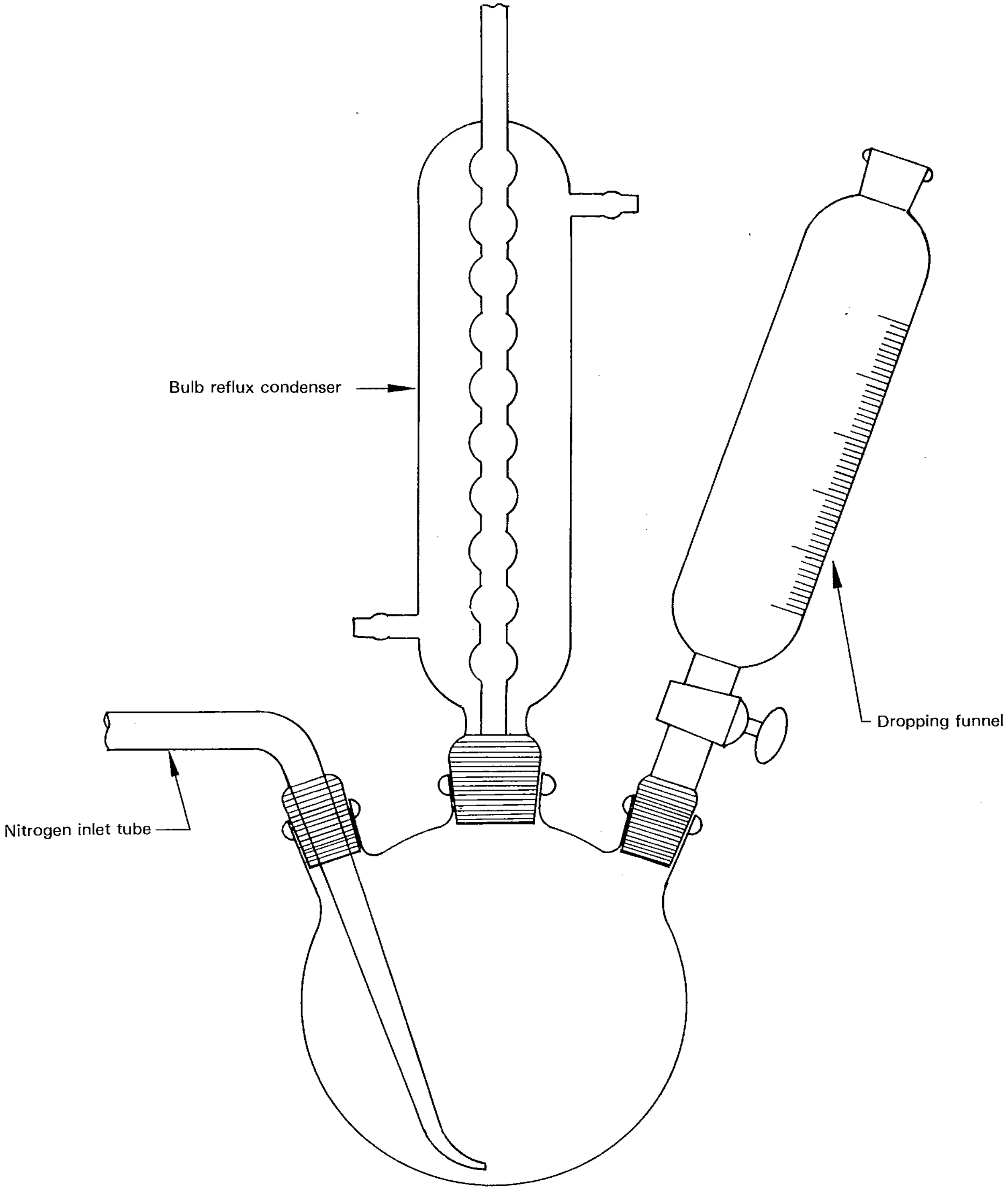

Figure 2 — Typical apparatus for the preparation of the reducing solution

Annex A

Methods for the mineralization of organic compounds for the determination of low contents of sulphur

A.0 This annex is not comprehensive. The following methods may be suitable for preparing test solutions from organic compounds.

A.1 Combustion in a Grote apparatus, which comprises a silica tube fitted with two fitted silica discs and a third pierced plate. The end of the tube is connected to an absorbant flask with a porous plate. Combustion is carried out in a current of air or oxygen.

This method is applicable to all organic products especially liquid and gaseous compounds.

A.2 Combustion in the Wickbold apparatus, which comprises a silica tube fitted with a condenser and an absorber. The apparatus should be fitted with a safety device to prevent flashback and with flowmeters for oxygen and hydrogen.

This method is applicable to volatile liquid and gaseous compounds.

A.3 Combustion in a bomb with sodium peroxide (the Parr bomb or its equivalent). With this method, the test portion is limited to about 200 to 300 mg.

This method is applicable to non-volatile liquid compounds and to solid compounds.

A.4 Combustion of organic liquids and solids in the Berthelot-Mahler-Kroecker bomb calorimeter under pressurized oxygen.

This method is applicable to liquid and solid compounds.

A.5 Fusion of the test portion with anhydrous sodium carbonate in a platinum crucible or dish.

This method is applicable to non-volatile compounds.

A.6 Fusion of the test portion with Eschka mixture.

This method is applicable to non-volatile compounds.

A.7 Combustion in oxygen in a Schoeniger flask. With this method, the mass of the test portion is very limited.

This method is applicable to solid compounds and, by using gelatine capsules, also to liquid compounds.

The choice of method depends on the nature of the organic compound and of its physical state (solid, liquid or gaseous). Furthermore, the mass of the test portion to be mineralized depends on the expected sulphur content of the sample.

All the methods should be compatible with the titrimetric method of determination. In this respect, the introduction of oxidizing agents should be avoided and if they are already present they should be destroyed before the reduction. In particular, the presence of nitric acid or hydrogen peroxide should be avoided.

When dissolving the mineralized product, the solution should contain between 4,5 and 450 µg of sulphate ions (SO_4^{2-}) in the aliquot portion taken for the determination.

Annex B

Interferences

This annex is not comprehensive. A check for possible interferences should always be carried out. Furthermore, the treatment may not cover all possible cases.

Interfering species	Acceptable limits for the aliquot portion taken for the determination	Possible treatments if the acceptable limits are exceeded
Peroxides	nil	Prolonged boiling in alkaline solution and addition of tin(II) chloride solution
Cr^{6+}	nil	Addition of tin(II) chloride solution in acid medium
NO_3^-	nil	Repeated evaporations in hydrochloric acid medium
NO_2^-	nil	Repeated evaporations in hydrochloric acid medium
Oxidizing agents in general	nil	Reduction by tin(II) chloride solution
Organic compounds	—	See annex A
Fe^{3+}	0,1 g	Reduction with tin(II) chloride solution in acid medium
Cu^{2+}	1 mg	Precipitation in alkaline medium by sodium hydroxide or sodium carbonate followed by filtration of copper(II) oxide
Water	2 ml	Evaporation of the water in alkaline medium
Mo	—	The presence of molybdates reduces the completeness of the reduction by an amount depending directly on the molybdenum content. In the presence of 200 mg of tin(II) chloride, the reduction will be complete.
Hg, Cd, Bi, Pb, Sn, Sb and As	1 mg	Do not interfere. Interference by quantities greater than 1 mg has not been checked.

Annex C

Removal of mercury from residual solutions

Collect the residual solutions obtained from the titrations and any other solution containing mercury compounds in a container of sufficient capacity.

Precipitate the mercury in an alkaline medium with excess sodium sulphide.

Oxidize this excess by hydrogen peroxide to prevent the mercury from re-dissolving in the form of polysulphides.

Decant and filter the mercury-free solution before disposal to waste.

Transfer the insoluble residues to a storage container with a view to subsequent recovery of the mercury by specialist firms.