International Standard 6353/1

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Reagents for chemical analysis — Part 1 : General test methods

Réactifs pour analyse chimique — Partie 1 : Méthodes générales d'essai

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Foreword

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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 6353/1 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in May 1980.

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

Belgium	Hungary	Poland
Brazil	India	Romania
China	Italy	South Africa, Rep. of
Czechoslovakia	Korea, Rep. of	Switzerland
Egypt, Arab Rep. of	Mexico	United Kingdom
France	Netherlands	
Germany, F. R.	Philippines	

The member bodies of the following countries expressed disapproval of the document on technical grounds :

Australia
USSR

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INTERNATIONAL STANDARD ISO 6353/1-1982 (E)

Reagents for chemical analysis — Part 1 : General test methods

1 Scope and field of application

This part of ISO 6353 specifies general test methods for verifying the compliance of reagents for chemical analysis with the specifications given in other parts of this International Standard.

2 References

ISO 31, *Quantities, units and symbols.*

ISO 758, *Liquid chemical products for industrial use — Determination of density at* 20 °C.

ISO 759, *Volatile organic liquids for industrial use — Determination of dry residue after evaporation on a water bath — General method.*

ISO 760, *Determination of water — Karl Fischer method (General method).*

ISO 918, *Volatile organic liquids for industrial use — Determination of distillation characteristics — General method.*[1)]

ISO 1392, *Determination of crystallizing point — General method.*

ISO 2211, *Liquid chemical products — Measurement of colour in Hazen units (platinum-cobalt scale).*

ISO 2718, *Standard layout for a method of chemical analysis by gas chromatography.*

ISO 6685, *Chemical products for industrial use — General method for determination of iron content — 1,10-Phenanthroline spectrophotometric method.*[2)]

3 General information

3.1 The nomenclature for chemical compounds used in this International Standard in general conforms to the rules published by the International Union of Pure and Applied Chemistry (IUPAC).

3.2 In all reactions or operations described, use only distilled or deionized water. Carbon dioxide-free water, if required, may be prepared by boiling water of the above grade for about 10 min and protecting from the atmosphere during cooling and storing.

3.3 Unless otherwise stated, solutions are aqueous and, dilutions shall be made with water.

3.4 The symbol "%" indicates percentage by mass (m/m), unless otherwise stated.

3.5 The reference number of a general test method, abbreviated GM, as given in the individual tests, refers to the number of the method in clause 5.

3.6 The reagents used shall conform to the specifications in ISO 6353. In the absence of such a specification, reagents of suitable analytical grade be shall be used.

NOTE — Reagents specified in this International Standard are identified R .., e. g. sodium chloride is R 31.

3.7 Unless otherwise stated, values for density refer to the density at 20 °C.

3.8 Temperatures are expressed in degrees Celsius (°C).

1) At present at the stage of draft. (Revision of ISO/R 918.)

2) At present at the stage of draft.

3.9 The following additional abbreviations are used in this International Standard :

AgDDTC	silver diethyldithiocarbamate
APDC	ammonium pyrrolidine-1-carbodithioate
EDTA	ethylenediaminetetraacetic acid, *di*sodium salt
AAS	atomic absorption spectroscopy
FES	flame emission spectroscopy
GC	gas chromatography
SS	standard solution
IS	indicator solution
RS	reagent solution
GM	general test method
R	reagent
MAS	molecular absorption spectrophotometry

3.10 Warning

The physical and chemical properties of the chemicals being handled, in particular those relating to physiological effects, combustibility and explosive tendencies, may be such as to present significant health and safety hazards. Although the degree of risk is extremely variable, it should be assumed, in the absence of specific information to the contrary, that the handling of any chemical will involve hazards of this kind.

The provision of exhaustive details in respect of hazards and associated safety procedures is not considered to fall within the scope of this International Standard as most manufactures of chemicals are very willing to advise prospective users on the handling of their products. In addition, national regulations on the packaging and labelling of hazardous chemicals should ensure that adequate information is given on the hazards associated with the use of chemicals.

4 Solutions for use in test methods

4.1 Standard solutions

Prepare stock standard solutions (4.1.1) and dilute standard solutions (4.1.2) as follows.

4.1.1 Stock standard solutions

Dissolve the constituents indicated in column 2 of table 1, dilute to the mark in a 1 000 ml one-mark volumetric flask and mix.

It is recommended that all stock standard solutions of inorganic compounds be stored in bottles of suitable plastic material, unless otherwise stated.

4.1.2 Dilute standard solutions

Prepare dilute standard solutions I, II and III at the time of use by diluting the stock standard solutions (4.1.1) in one-mark volumetric flasks of appropriate capacity and in the precise volume ratios 1/10, 1/100, 1/1 000, respectively.

4.2 Reagent solutions

Prepare the reagent solutions as follows.

4.2.1 Ammonium metavanadate (RS)

Dissolve 2,5 g of ammonium metavanadate in 500 ml of boiling water, cool, add 20 ml of nitric acid solution (R 19), cool and dilute to 1 000 ml. Store in a polyethylene bottle.

4.2.2 Borate standard buffer (RS)

Using the carbon dioxide-free water (see 3.2), dissolve 3,81 g of sodium tetraborate decahydrate and dilute to 1 000 ml. Store protected from atmospheric carbon dioxide.

4.2.3 Calcium hydroxide standard buffer (RS)

Prepare a saturated solution at 25 °C. Determine the calcium hydroxide concentration by titration with standard volumetric hydrochloric acid solution, $c(HCl) = 0,1$ mol/l, using phenol red (IS 4.3.10) as indicator. The concentration $c[1/2\ Ca(OH)_2]$ shall be between 0,040 0 and 0,041 2 mol/l. Store protected from atmospheric carbon dioxide and reject the solution as soon any turbidity appears.

4.2.4 Chromic acid (RS)

Dissolve 100 g of chromium trioxide in sulphuric acid solution (35 %) and dilute to 1 000 ml with the same acid.

4.2.5 Cobalt(II) chloride (RS)

4.2.5.1 Preparation

Dissolve 60 g of cobalt(II) chloride hexahydrate in about 900 ml of a mixture of 25 ml of hydrochloric acid solution (R 13) and 975 ml of water and dilute to 1 000 ml with the same mixture. Determine the concentration by the method specified in 4.2.5.2 and adjust it to 59,5 mg of $CoCl_2 \cdot 6H_2O$ per millilitre using a calculated quantity of diluted hydrochloric acid solution.

4.2.5.2 Titration

Place 5,0 ml of the solution (4.2.5.1) , 5 ml of hydrogen peroxide solution (3 %) and 10 ml of sodium hydroxide solution (27 %) in a 200 ml conical flask fitted with a ground glass stopper. With the stopper removed, boil gently for 10 min, allow to cool, add 60 ml of sulphuric acid (10 %) and 2 g of potassium iodide (R 25). Stopper the flask and dissolve the precipitate by shaking gently. Titrate the liberated iodine with standard volumetric sodium thiosulphate solution, $c(Na_2S_2O_3) = 0,1$ mol/l, adding 10 drops of the starch solution (IS 4.3.11) towards the end of the titration.

The end-point is reached when the blue colour has just been discharged.

1 ml of sodium thiosulphate solution, $c(Na_2S_2O_3) = 0,1$ mol/l, corresponds to 23,79 mg of $CoCl_2 \cdot 6H_2O$.

Table 1 — Preparations of stock standard solutions

Reagent name	Mass of substance required to prepare 1 000 ml of solution	1 ml of solution corresponds to
Acetaldehyde	1,00 g of CH_3CHO	0,001 g of CH_3CHO
Aluminium	17,60 g of $KAl(SO_4)_2 \cdot 12H_2O$ + 10 ml H_2SO_4 (25 %)	0,001 g of Al
Ammonium	2,97 g of NH_4Cl (R 5)	0,001 g of NH_4 or 0,000 776 6 g of N
Arsenic	1,32 g of As_2O_3 dissolved in 3 ml of NaOH solution (27 %) by warming.	0,001 g of As
Barium	1,78 g of $BaCl_2 \cdot 2H_2O$ (R 6)	0,001 g of Ba
Bismuth	1,00 g of Bi dissolved in 6 ml of HNO_3 (R 19), and nitrous gases removed by boiling.	0,001 g of Bi
Bromate	1,31 g of $KBrO_3$	0,001 g of BrO_3
Bromide	1,49 g of KBr	0,001 g of Br
Calcium	3,67 g of $CaCl_2 \cdot 2H_2O$. Alternatively, 2,50 g of $CaCO_3$ dissolved in 25 ml of HCl (10 %) solution and CO_2 removed by boiling.	0,001 g of Ca
Carbonate	2,41 g of Na_2CO_3 (R 30)	0,001 g of CO_2 or 0,000 27 g of C
Carbonyl	10,43 g of acetone (R 2) corresponding to 5,0 g of CO, weighed into a 100 ml one-mark volumetric flask containing 50 ml of carbonyl-free methanol (RS 4.2.11), diluted to the mark with the same methanol and mixed thoroughly. Take 20,0 ml of this solution and dilute to 1 000 ml. Use the same methanol for all dilutions.	0,001 g of CO
Chlorate	1,47 g of $KClO_3$	0,001 g of ClO_3
Chloride	1,65 g of NaCl (R 32)	0,001 g of Cl
Chlorine	3,97 g of Chloramine T (trihydrate)	0,001 g of active chlorine
Chromium	2,83 g of $K_2Cr_2O_7$ (R 23)	0,001 g of Cr
Cobalt	4,94 g of $Co(NO_3)_2 \cdot 6H_2O$	0,001 g of Co
Copper	3,93g of $CuSO_4 \cdot 5H_2O$ (R 9)	0,001 g of Cu
Fluoride	2,21 g of NaF	0,001 g of F
Formaldehyde	2,86 g of formaldehyde solution (35 %)	0,001 g of HCHO
Hexacyanoferrate(II)	1,99 g of $K_4[Fe(CN)_6] \cdot 3\ H_2O$	0,001 g of $Fe(CN)_6$
Hexafluorosilicate	3,38 g of H_2SiF_6 (30 %) solution	0,001 g of SiF_6
Iron	8,63 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ + 10 ml of H_2SO_4 (25 %) solution	0,001 g of Fe
Iodate	1,22 g of KIO_3	0,001 g of IO_3
Iodide	1,31 g of KI (R 25)	0,001 g of I
Lead	1,60 g of $Pb(NO_3)_2$ + 1 ml of HNO_3 (R 19)	0,001 g of Pb
Magnesium	10,14 g of $MgSO_4 \cdot 7H_2O$	0,001 g of Mg
Manganese	3,08 g of $MnSO_4 \cdot H_2O$	0,001 g of Mn
Mercury	1,62 g of $Hg(NO_3)_2$ + 10 ml of HNO_3 (R 19)	0,001 g of Hg
Molybdenum	1,84 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0,001 g of Mo
Nickel	4,48 g of $NiSO_4 \cdot 6H_2O$ or 4,78 g of $NiSO_4 \cdot 7H_2O$	0,001 g of Ni
Nitrate	1,37 g of $NaNO_3$	0,001 g of NO_3
Nitrite	1,50 g of $NaNO_2$	0,001 g of NO_2
Nitrogen	6,07 g of $NaNO_3$	0,001 g of N
Oxalate	1,43 g of $C_2H_2O_4 \cdot 2H_2O$ (R 20)	0,001 g of C_2O_4
Phosphate	1,43 g of KH_2PO_4	0,001 g of PO_4
Phosphorus	4,39 g of KH_2PO_4	0,001 g of P
Potassium	2,59 g of KNO_3	0,001 g of K
Silicate	1,00 g of silicic acid heated at 900 °C and dissolved in 8 ml of NaOH solution (27 %)	0,001 g of SiO_2
Silver	1,58 g of $AgNO_3$ (R 28). Store the solution in a dark glass bottle.	0,001 g of Ag
Sodium	2,54 g of NaCl (R 32)	0,001 g of Na
Sulphate	1,81 g of K_2SO_4	0,001 g of SO_4
Sulphide	7,49 g of $Na_2S \cdot 9H_2O$	0,001 g of S
Sulphur	5,44 g of K_2SO_4	0,001 g of S
Thiocyanate	1,31 g of NH_4SCN	0,001 g of SCN
Thiosulphate	2,21 g of $Na_2S_2O_3 \cdot 5H_2O$ (R 36)	0,001 g of S_2O_3
Titanium	21,47 g of $TiCl_3$ solution (15 %) + 20 ml of HCl solution (25 %)	0,001 g of Ti
Zinc	4,40 g of $ZnSO_4 \cdot 7H_2O$	0,001 g of Zn

4.2.6 Copper(II) sulphate (RS)

4.2.6.1 Preparation

Dissolve 63 g of copper(II) sulphate pentahydrate (R 9) in about 900 ml of a mixture of 25 ml of hydrochloric acid solution (R 13) and 975 ml of water and dilute to 1 000 ml with the same mixture. Determine the concentration by the method specified in 4.2.6.2 and adjust it to 62,4 mg of $CuSO_4 \cdot 5H_2O$ per millilitre using a calculated quantity of the diluted hydrochloric acid solution.

4.2.6.2 Titration

Place 10,0 ml of the solution (4.2.6.1), 50 ml of water, 12 ml of approximately 12 % acetic acid solution and 3 g of potassium iodide (R 25), in a 200 ml conical flask fitted with a ground glass stopper. Titrate the liberated iodine with standard volumetric sodium thiosulphate solution, $c(Na_2S_2O_3)$ = 0,1 mol/l, using 10 drops of the starch solutions (IS 4.3.11) towards the end of the titration.

The end-point is reached when the blue colour has just been discharged.

1 ml of sodium thiosulphate solution, $c(Na_2S_2O_3)$ = 0,1 mol/l, corresponds to 24,97 mg of $CuSO_4 \cdot 5H_2O$.

4.2.7 2,4-Dinitrophenylhydrazine (RS)

Dissolve 50 mg of 2,4-dinitrophenylhydrazine in 25 ml of carbonyl-free methanol (RS 4.2.11) and 2 ml of hydrochloric acid solution (R 13), and dilute to 50 ml with water. Discard after 2 weeks.

4.2.8 Iron(III) chloride (RS)

4.2.8.1 Preparation

Dissolve 46 g of iron(III) chloride hexahydrate in about 900 ml of a mixture of 25 ml of hydrochloric acid solution (R 13) and 975 ml of water and dilute to 1 000 ml with the same mixture. Determine the concentration by the method specified in 4.2.8.2 and adjust it to 45,0 mg of $FeCl_3 \cdot 6H_2O$ per millilitre using a calculated quantity of the diluted hydrochloric acid solution.

4.2.8.2 Titration

Place 10,0 ml of the solution (4.2.8.1), 15 ml of water, 5 ml of the hydrochloric acid solution (R 13) and 4 g of potassium iodide (R 25) in a 200 ml conical flask fitted with a ground glass stopper. Stopper the flask, allow to stand in the dark for 15 min and add 100 ml of water; titrate the liberated iodine with standard volumetric sodium thiosulphate solution, $c(Na_2S_2O_3)$ = 0,1 mol/l, using 10 drops of the starch solution (IS 4.3.11) towards the end of the titration.

The end-point is reached when the blue colour has just been discharged.

1 ml of sodium thiosulphate solution, $c(Na_2S_2O_3)$ = 0,1 mol/l, corresponds to 27,03 mg of $FeCl_3 \cdot 6H_2O$.

4.2.9 Iron(II)/iron(III) mixture (RS)

Dissolve 10 g of ammonium iron(II) sulphate hexahydrate and 1 g of ammonium iron(III) sulphate dodecahydrate in water, add 5 ml of sulphuric acid solution (20 %), and dilute to 100 ml.

4.2.10 Lead acetate (basic) (RS)

Dissove 5 g of lead(II) acetate trihydrate and 15 g of sodium hydroxide (R 34) in 80 ml of water and dilute to 100 ml.

4.2.11 Methanol, carbonyl-free (RS)

Add 10 g of 2,4-dinitrophenylhydrazine and 0,5 ml of hydrochloric acid solution (R 13) to 2 litres of methanol (R 18), reflux for 2 h and then distil, rejecting the first 50 ml of distillate. Stir the methanol during the distillation using a magnetic stirrer to avoid bumping. Stored in a tightly stoppered bottle, the methanol will remain carbonyl-free indefinitely.

4.2.12 Oxalate standard buffer (RS)

Dissolve 12,71 g of potassium tetraoxalate dihydrate in water and dilute to 1 000 ml.

4.2.13 Phosphate standard buffer (RS)

Dissolve 3,40 g of potassium dihydrogen phosphate and 3,55 g of *di*sodium hydrogen phosphate, both previously dried for 2 h at 120 ± 10 °C, in the carbon dioxide-free water (see 3.2) and dilute to 1 000 ml with the same water.

4.2.14 Phthalate standard buffer (RS)

Dissolve 10,21 g of potassium hydrogen phthalate, previously dried for 1 h at 110 °C, in water and dilute to 1 000 ml.

4.2.15 Potassium hydroxide methanolic solution (RS)

Mix 15,0 ml of potassium hydroxide solution (33 %) with 50 ml of carbonyl-free methanol (RS 4.2.11). Discard after 2 weeks.

4.2.16 Sodium dihydrogen phosphate (RS)

Dissolve 20 g of sodium dihydrogen phosphate monohydrate in water, add 1 ml of sulphuric acid solution (20 %), and dilute to 100 ml.

4.2.17 Tartrate standard buffer (RS)

Prepare a saturated solution of racemic potassium hydrogen tartrate by shaking an excess vigorously with water at 25 °C. The solution has a limited shelf life which may be extended by adding a small crystal of thymol.

4.3 Indicator solutions

Prepare the indicator solutions as follows.

4.3.1 Ammonium iron(III) sulphate (IS)

Dissolve 33 g of ammonium iron(III) sulphate dodecahydrate in 67 ml of nitric acid solution (12 %).

4.3.2 Bromophenol blue (IS)

Warm 0,1 g of bromophenol blue with 3,0 ml of 0,2 % sodium hydroxide solution and 5 ml of 95 % (*V*/*V*) ethanol. When dissolution is complete, add 50 ml of 95 % (*V*/*V*) ethanol and dilute to 250 ml with water.

4.3.3 Crystal violet (IS)

Dissolve 1,25 g of crystal violet C.I. 42.555 in 250 ml of acetic acid (R 1).

4.3.4 Isatin (IS)

Dissolve 0,50 g of isatin in 50 ml of sulphuric acid solution (R 37) (solution A).

Dissolve 0,50 g of iron(III) chloride hexahydrate in 2 ml of water and dilute to 100 ml with sulphuric acid solution (R 37) stirring until the evolution of gas ceases (solution B).

Immediately before use, add 5,0 ml of solution B to 2,5 ml of solution A and dilute to 100 ml with sulphuric acid solution (R 37).

4.3.5 Methyl orange (IS)

Dissolve 0,1 g of methyl orange C.I. 13025 in 50 ml of 95 % (*V*/*V*) ethanol and dilute to 250 ml with water.

4.3.6 Methyl red (IS)

Warm 25 mg of finely powdered methyl red C.I. 13020 with 0,95 ml of 0,2 % sodium hydroxide solution and 5 ml of 95 % (*V*/*V*) ethanol. When dissolution is complete, add 125 ml of 95 % (*V*/*V*) ethanol and dilute to 250 ml with water.

4.3.7 Methylthymol blue mixture

Triturate 1 g of methylthymol blue with 100 g of potassium nitrate to a fine powder.

4.3.8 Mordant black 11 mixture

Triturate 1 g of Mordant black 11 C.I. 14645 and 100 g of sodium chloride to a fine powder.

4.3.9 Phenolphthalein (IS)

Dissolve 2,5 g of phenolphthalein in 250 ml of 95 % (*V*/*V*) ethanol.

4.3.10 Phenol red (IS)

Warm 50 mg of phenol red with 2,85 ml of 0,2 % sodium hydroxide solution and 5 ml of 95 % (*V*/*V*) ethanol. After solution is effected, add 50 ml of 95 % (*V*/*V*) ethanol and dilute to 250 ml with water.

4.3.11 Starch (IS)

Make a paste of 1,0 g of soluble starch with 5 ml of water and add the paste to 100 ml of boiling water, with stirring. Boil for a few minutes and cool. Discard the solution after 2 weeks.

NOTE — The shelf life of the solution may be extended to several months by adding a few drops of formaldehyde solution.

4.3.12 Thymolphthalein (IS)

Dissolve 0,50 g of thymolphthalein in 60 ml of 95 % (*V*/*V*) ethanol and dilute to 250 ml with water.

5 General test methods (GM)

5.1 Water-insoluble matter (GM 1)

Dissolve the specified test portion as completely as possible in a suitable volume of boiling water, cool and filter through a sintered glass filter porosity P 40 (pore size diameter 16 to 40 µm), previously dried for 1 h at 105 ± 2 °C, cooled in a desiccator and weighed to the nearest 0,1 mg. Wash the residue with water, dry for 1 h at 105 ± 2 °C, cool in a desiccator and then reweigh to the nearest 0,1 mg. Calculate the mass of residue.

5.2 Chloride (GM 2)

Acidify the specified volume of the test solution with 1 ml of nitric acid solution (25 %) and add 1 ml of approximately 1,7 % silver nitrate solution.

Allow to stand for 2 min. Compare the opalescence with that obtained with the specified standard matching solution.

5.3 Sulphate (GM 3)

Mix 0,25 ml of 0,02 % potassium sulphate solution in 30 % (*V*/*V*) ethanol with 1 ml of 25 % barium chloride dihydrate solution (seeding solution). To this mixture add, after exactly 1 min, the specified volume of the test solution which has previously been acidified with 0,5 ml of 20 % hydrochloric acid solution.

Allow to stand for 5 min and compare the turbidity with that obtained with the specified standard matching solution.

5.4 Phosphate (GM 4)

Add 5 ml of 10 % ammonium molybdate solution to the specified volume of the test solution. Adjust the pH to 1,8 and heat the solution to boiling. Cool, add 12,5 ml of 15 % hydrochloric acid solution and extract with 20 ml of diethyl ether. Wash the organic phase with 5 % hydrochloric acid solution and reduce with 0,2 ml of 2 % tin(II) chloride dihydrate solution in hydrochloric acid solution (R 13).

Compare the blue colour of the organic phase with that obtained with the specified standard matching solution.

5.5 Silicate (GM 5)

Mix the specified volume of the test solution with 4,5 ml of 5 % sulphuric acid solution and 1 ml of 10 % ammonium molybdate solution. After 5 min, add 5 ml of 5 % oxalic acid solution and after a further 5 min, add 0,2 ml of 2 % tin(II) chloride dihydrate solution in hydrochloric acid solution (R 13).

Compare the blue colour with that obtained with the specified standard matching solution.

5.6 Total nitrogen (GM 6)

To the specified volume of the test solution, diluted if necessary to 140 ml, in a Kjeldahl apparatus consisting of a Kjeldahl flask fitted with a distillation unit, add 5 ml of 32 % sodium hydroxide solution and 1,0 g of Devarda's alloy or aluminium wire. Allow to stand for 1 h. Distil 75 ml of the reaction mixture into a graduated cylinder containing 5,0 ml of 0,5 % sulphuric acid solution. Add 3 ml of 32 % sodium hydroxide solution and 2 ml of Nessler's reagent and dilute to 100 ml.

Compare the yellow colour with that obtained with the specified standard matching solution.

5.7 Heavy metals (as Pb) (GM 7)

Add 0,2 ml of 30 % acetic acid solution to the specified volume of the test solution and saturate with hydrogen sulphide or use a suitable quantity of aqueous solution of hydrogen sulphide.

Compare the brown colour with that obtained with the specified standard matching solution.

5.8 Iron (GM 8)

5.8.1 1,10-Phenanthroline method (GM 8.1)

See ISO 6685.

5.8.2 Bathophenanthroline method (GM 8.2)

5.8.2.1 Buffer solution (pH 4,5)

Dissolve 164 g of sodium acetate trihydrate (R 29) and 115 ml of acetic acid (R 1) in water. Dilute to 1 000 ml.

5.8.2.2 Procedure

Add 1 ml of 10 % ascorbic acid solution, 15 ml of buffer solution (5.8.2.1) and 1 ml of 0,1 % solution of bathophenanthroline disulphonic acid *di*sodium salt to the specified volume of the test solution. Dilute to 50 ml and allow to stand for 15 min. Compare the red colour with that obtained with the specified standard matching solution.

5.9 Aluminium (GM 9)

5.9.1 Aluminon reagent

Add 0,25 g of aluminon (ammonium aurine tricarboxylate) and 5 g of gum acacia in 250 ml of water and warm to dissolve. Add 87 g of ammonium acetate (R 4) and dissolve. Add 145 ml of 15 % hydrochloric acid solution and dilute to 500 ml. Filter if necessary. Discard the solution after 1 month.

5.9.2 Procedure

Neutralize the specified volume of the test solution using litmus, add 1 ml of 30 % acetic acid solution and adjust the pH of the solution to 4,5 with 10 % ammonia solution. Add 0,1 ml of thioacetic acid and 3 ml of the aluminon reagent (5.9.1), heat at about 100 °C for 10 min and cool.

Compare the red colour with that obtained with the specified standard matching solution.

5.10 Ammonia (GM 10)

Dilute the specified volume of the test solution to 75 ml. Add 3 ml of 32 % sodium hydroxide solution and 2 ml of Nessler's reagent and dilute to 100 ml.

Compare the yellow colour with that obtained with the specified standard matching solution.

5.11 Arsenic (GM 11)

To the sample solution, add 10 ml of 0,4 % tin(II) chloride dihydrate solution in hydrochloric acid solution (R 13), 5 ml of 15 % potassium iodide solution and 1 ml of 2 % copper(II) sulphate pentahydrate solution. Allow this mixture to react with 8 g of zinc granules (R 40). Trap the arsine formed in an absorption vessel containing 5 ml of 0,5 % AgDDTC solution in pyridine (see the figure).

Measure the red colour with that obtained with the specified standard matching solution.

5.12 Water — Karl Fischer method (GM 12)

See ISO 760.

5.13 Acidity and alkalinity (GM 13)

5.13.1 Acidity or alkalinity in water-miscible liquid products (GM 13.1)

5.13.1.1 Procedure

Place 100 ml of water in a 250 ml conical flask and boil for 5 min in order to eliminate carbon dioxide. After cooling slightly, add the specified volume of the test solution and boil gently for a further 5 min. Then close the flask with a stopper fitted with a soda-lime guard tube and allow the solution to cool to room temperature. Finally, add the specified indicator and titrate with the specified titrant solution, to reach the appropriate end-point stable for at least 15 s.

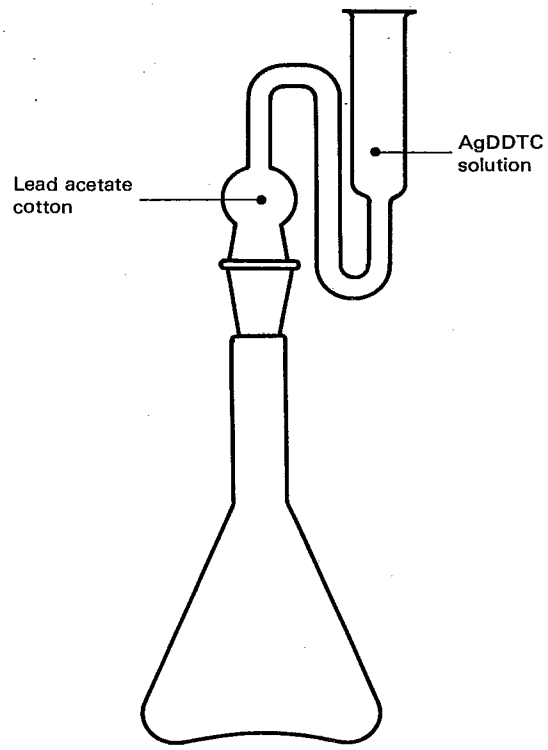

Figure — Absorption apparatus for use in arsenic test

5.13.1.2 Expression of results

The acidity or alkalinity, in millimoles of H^+ or OH^-, as appropriate, per 100 g of product, is given by the formula

$$\frac{V \times c}{m} \times 100$$

where

V is the volume, in millilitres, of the standard volumetric solution used;

c is the concentration, in moles of H^+ or OH^- per litre, of the standard volumetric solution;

m is the mass, in grams, of sample present in the specified volume of the test solution.

5.13.2 Acidity or alkalinity in water-immiscible liquid products (GM 13.2)

5.13.2.1 Procedure

Add 100 ml of water, previously neutralized against the specified indicator, to the specified volume of the test solution in a separating funnel, and shake for 3 min. Allow the two phases to separate, titrate 50 ml of the aqueous phase with the specified titrant solution, to reach the appropriate end-point stable for at least 15 s.

5.13.2.2 Expression of results

The acidity or alkalinity, in millimoles of H^+ or OH^-, as appropriate, per 100 g of product, is given by the formula

$$\frac{V \times c \times 100}{m \times 50} \times 100$$

$$= \frac{V \times c}{m} \times 200$$

where

V is the volume, in millilitres, of the standard volumetric solution used;

c is the concentration, in moles of H^+ or OH^- per litre, of the standard volumetric solution;

m is the mass, in grams, of sample present in the specified volume of test solution.

5.14 Residue on evaporation (GM 14) (see also ISO 759)

Evaporate the specified test portion to dryness on a boiling water bath, using a suitable weighed evaporation dish of about 150 ml capacity (platinum, glass, silica). Dry to constant mass at 105 ± 2 °C, as specified in the specification for each product concerned.

5.15 Residue on heating (GM 15)

Place the specified test portion in a suitable crucible or dish, previously heated in an oven, controlled at 650 ± 50 °C, for 15 min, cooled in a desiccator and weighed to the nearest 0,1 mg. Heat by increasing the temperature slowly, until the test portion is completely volatilized or charred. In the case of liquid products, heat without boiling until the test portion is completely evaporated, avoiding the ignition of organic products. Finally, heat the dish and residue in the oven, controlled at 650 ± 50 °C, for 15 min (unless otherwise specified), cool in a desiccator, and weigh to the nearest 0,1 mg.

NOTE — If may be more convenient to volatilize or char larger test portions in successive fractions.

5.16 Sulphated ash in solid products (GM 16)

Place the specified test portion in a suitable crucible or dish, previously heated in an oven, controlled at 650 ± 50 °C, for 15 min, cooled in a desiccator and weighed to the nearest 0,1 mg. Heat by increasing the temperature slowly, until the test portion is completely volatilized or charred, avoiding the ignition of organic products. Allow to cool, add 0,25 ml of sulphuric acid solution (R 37) to the residue and continue heating gently until all fumes have disappeared. Then heat the dish and the residue in the oven, controlled at 650 ± 50 °C, for 15 min (unless otherwise specified), cool in a desiccator and weigh to the nearest 0,1 mg.

NOTE — It may be more convient to volatilize or char larger test portions in successive fractions.

5.17 Sulphated ash in liquid products (GM 17)

Place the specified test portion in a suitable crucible or dish, previously heated in an oven, controlled at 650 ± 50 °C, for 15 min, cooled in a desiccator and weighed to the nearest 0,1 mg. Add 0,25 ml of sulphuric acid solution (R 37) and warm, without boiling, in a well-ventilated fume cupboard, until the test portion is completely evaporated, avoiding the ignition of organic products. If necessary, continue heating gently until all fumes have disappeared, then heat in the oven, controlled at 650 ± 50 °C, for 15 min (unless otherwise specified), cool in a desiccator and weigh to the nearest 0,1 mg.

NOTE — If the test portion is large, it may be more convenient to operate on several successive portions, after adding 0,5 ml of sulphuric acid solution (R 37) to the whole test portion.

5.18 Readily carbonizable substances (GM 18)

5.18.1 Standard colours

Using cobalt(II) chloride (RS 4.2.5), iron(III) chloride (RS 4.2.8), and copper(II) sulphate (RS 4.2.6) reagent solutions, prepare the appropriate standard matching solutions using the quantities of materials specified in table 2. Store these solutions, covered with a 50 mm thick layer of paraffin wax in stoppered test tubes, sealed with paraffin wax.

Table 2 — Preparation of standard matching solutions

Standard matching solution	Cobalt(II) chloride solution (RS 4.2.5)	Iron(III) chloride solution (RS 4.2.8)	Copper(II) sulphate solution (RS 4.2.6)	Water
	ml	ml	ml	ml
A	0,1	0,4	0,1	4,4
B	0,3	0,9	0,3	3,5
C	0,1	0,6	0,1	4,2
D	0,3	0,6	0,4	3,7
E	0,4	1,2	0,3	3,1
F	0,3	1,2	0,0	3,5
G	0,5	1,2	0,2	3,1
H	0,2	1,5	0,0	3,3
I	0,4	2,2	0,1	2,3
J	0,4	3,5	0,1	1,0
K	0,5	4,5	0,0	0,0
L	0,8	3,8	0,1	0,3
M	0,1	2,0	0,1	2,8
N	0,0	4,9	0,1	0,0
O	0,1	4,8	0,1	0,0
P	0,2	0,4	0,1	4,3
Q	0,2	0,3	0,1	4,4
R	0,3	0,4	0,2	4,1
S	0,2	0,1	0,0	4,7
T	0,5	0,5	0,4	3,6

5.18.2 Procedure

Add the specified test portion, finely powdered if solid, to the specified amount of 95 ± 0,5 % sulphuric acid solution, shake to homogenize the mixture or to dissolve the test portion completely and allow to stand for 15 min at 25 °C (unless otherwise specified). It is particularly important that the concentration of the sulphuric acid solution should fall within the specified range.

Compare the colour intensity of the test solution with that of the specified standard matching solution. For comparison, the test liquid shall be contained in a test tube matching that containing the standard matching solution.

5.19 Permanganate-reducing substances (GM 19)

5.19.1 Direct method (GM 19.1)

Place the specified test portion or its solution in a suitable colourless glass container fitted with a ground glass stopper, and add the specified volume of potassium permanganate solution, $c(1/5\ KMnO_4) = 0,1$ mol/l. Stopper the container and allow it to stand, protected from light, at the specified temperature for the specified time.

Check that the colour of the resulting solution is not completely discharged.

5.19.2 Indirect method (GM 19.2)

5.19.2.1 Procedure

Add the specified test portion or its solution and 10,0 ml of potassium permanganate solution, ($c(1/5\ KMnO_4) \approx 0,1$ mol/l) to 50 ml of 5 % sulphuric acid solution contained in a conical flask fitted with a ground glass stopper. Stopper the flask and allow to stand, protected from light, at the specified temperature for the specified time. Then add 10 ml of 10 % potassium iodide solution and titrate the liberated iodine with standard volumetric sodium thiosulphate solution, $c(Na_2S_2O_3) = 0,05$ mol/l, using the starch solution (IS 4.3.11) as indicator and a burette graduated in 0,05 ml or smaller divisions. Carry out a blank test at the same time as the determination using the same procedure and the same quantities of reagents as in the determination, but omitting the test portion.

5.19.2.2 Expression of results

The content of permanganate-reducing substances, expressed as a percentage by mass of oxygen (O), is given by the formula

$$(V_0 - V_1) \times 0,05 \times \frac{100}{m} \times 8 \times \frac{1}{1\,000}$$

$$= \frac{(V_0 - V_1)}{m} \times 0,04$$

where

V_0 is the volume, in millilitres, of the standard volumetric sodium thiosulphate solution used for the blank test;

V_1 is the volume, in millilitres, of the standard volumetric sodium thiosulphate solution used for the determination;

m is the mass, in grams, of the test portion;

8 is the mass, in milligrams, of oxygen corresponding to 1,00 ml of potassium permanganate solution, $c(1/5\ KMnO_4) = 1{,}00$ mol/l.

5.20 Aldehydes (GM 20)

Add 5 ml of water and 0,15 ml of 5 % dimedone solution in 95 % (*V*/*V*) ethanol to the specified volume of the test solution and warm on a boiling water-bath until the sample is completely dissolved. Dilute with hot water quickly to 10 ml and cool.

Compare the turbidity with that obtained with the specified standard matching solution.

5.21 Sulphur compounds (GM 21)

Place in a suitable distillation flask the specified volume of the test solution, add 10 ml of 3 % ethanolic potassium hydroxide solution and boil under reflux for 30 min, avoiding the use of rubber connections. Add, through the condenser, 20 ml of water, remove the condenser, and evaporate off all organic materials. Add 5 ml of a saturated bromine solution, heat on a boiling water-bath for 15 min, and then neutralize with 10 % hydrochloric acid solution. Add 1 ml of the acid in excess and boil until all bromine is eliminated. Finally, evaporate the solution to about 5 ml, neutralize with 10 % sodium hydroxide solution and proceed in accordance with GM 3.

Prepare a standard matching solution from a mixture of 10 ml of 3 % ethanolic potassium hydroxide solution and the specified volume of the sulphur standard solution (SS).

5.22 Oxalates (GM 22)

Add 2 ml of the hydrochloric acid solution (R 13) and 1 g of the zinc granules (R 40) to the specified test portion or to the specified volume of the test solution and boil for 1 min; allow to stand for 2 min, filter and collect the filtrate in a test tube containing 0,25 ml of 1 % phenylhydrazine hydrochloride solution. Heat to boiling, cool quickly, add an equal volume of hydrochloric acid solution (R 13) and 0,25 ml of 5 % potassium hexacyanoferrate(III) solution and shake.

Compare the pink colour with that obtained with the specified standard matching solution.

5.23 Carbonyl compounds (GM 23)

Place the specified test portion or its solution in a colourless glass cylinder fitted with a ground glass stopper add 1 ml of 2,4-dinitrophenylhydrazine solution (RS 4.2.7), stopper the cylinder, shake, and allow to stand for 30 min. Then add 8 ml of pyridine, 2 ml of water and 2 ml of methanolic potassium hydroxide solution (RS 4.2.15). Shake, allow to stand for 10 min, and dilute to 25 ml with carbonyl-free methanol (RS 4.2.11).

Compare the dark red colour with that obtained with the specified standard matching solution.

5.24 Densitometry (GM 24)

5.24.1 Pyknometric method (GM 24.1) (see also ISO 758)

5.24.1.1 Procedure

Weigh a dry density bottle (volume preferably 25 to 50 ml) to the nearest 0,2 mg. Fill the bottle with freshly boiled and cooled distilled water, and determine the apparent mass of the contents at 20 ± 0,1 °C (m_2). Empty the bottle and after cleaning and drying it, fill it with the sample under test and, using the same procedure, determine the apparent mass of the sample at 20 ± 0,1 °C (m_1).

5.24.1.2 Expression of results

The density, expressed in grams per millilitre and calculated to the third decimal place, is given by the formula

$$\frac{m_1 + A}{m_2 + A} \times \varrho_w$$

where

m_1 is the apparent mass, in grams, of the test portion;

m_2 is the apparent mass, in grams, of the water;

ϱ_w is the density of water at 20 °C (= 0,998 2 g/ml);

A is the buoyancy correction

$$\varrho_a \times V$$

where ϱ_a is the density of air (approximately 0,001 2 g/ml);

V is the volume, in millilitres, of sample taken.

5.24.2 Hydrostatic method (GM 24.2)

5.24.2.1 Principle

Measurement of the buoyancy of a body immersed first in water and then in the liquid to be tested, using the Mohr-Westphal balance.

5.24.2.2 Procedure

By using a thin platinum wire, suspend the float at the end of the beam of a Mohr-Westphal balance and set the apparatus to zero by operating the screw on the base tripod; then immerse the float in water at the required temperature, and return the pointer to zero by suitably adjusting the riders of the balance. Remove the float, dry it thoroughly, and repeat the operation using the liquid being tested, at the same temperature as the water.

5.24.2.3 Expression of results

The density, expressed in grams per millilitre, is given by the formula

$$\frac{P_2}{P_1} \times \varrho_w$$

where

P_1 and P_2 are the readings corresponding to the position of the riders for the water and for the liquid being tested respectively;

ϱ_w has the same meaning as in 5.24.1.2.

5.25 Measurement of phase change temperatures (GM 25)

The thermometers used in these tests shall be graduated in accordance with the requirements of the appropriate International Standards and shall have official certificates of calibration.

5.25.1 Distillation range (GM 25.1)

See ISO 918.

5.25.2 Melting range (GM 25.2)

5.25.2.1 Principle

This conventionally indicates the temperature interval from the point at which the test portion begins to melt to the point at which it becomes completely molten, as indicated by the formation of a meniscus.

5.25.2.2 Apparatus

This consists of a capillary tube, made of soft glass, sealed at one end, and of an appropriate instrument for temperature measurement. The latter may be a simple thermometer, or it may consist, for example, of a photocell sensor and a digital temperature read-out system. In any case, it is necessary to be able to read temperatures with an accuracy and precision of 0,05 °C.

It is further necessary to provide a controlled source of heat, which may be either an electrical source or a bath containing a liquid having a boiling point higher than the melting range of the substance. Some liquids which may be used in the heating bath are

up to 100 °C : water;

up to 150 °C : glycerol;

up to 300 °C : silicone oil.

5.25.2.3 Procedure

Unless otherwise indicated, grind the sample to a very fine powder and dry it either in a desiccator over sulphuric acid or in an oven at a temperature well below the expected melting point. Alternatively, use a sample on which the "loss on drying" test has been carried out.

Place sufficient of the dry powder in the capillary tube to form a column in the bottom of the tube about 2 to 3 mm in height, when packed as closely as possible by gentle tapping on a solid surface.

Mount the capillary tube in the heating apparatus (in the case of a mercury thermometer, place the capillary with the sealed end level with the middle of the mercury bulb), pre-heated to a temperature 10 °C below the expected lower end of the melting range. Carefully regulate the rate of heating to between 1 and 2 °C/min.

Record the temperature, first when the subtance begins to form small drops on the capillary tube, and then when the substance is completely melted, usually forming a distinct meniscus.

5.25.3 Crystallizing point (GM 25.3)

See ISO 1392.

5.26 Polarimetry (GM 26)

This clause specifies methods based on the determination of angular rotation of the plane of polarized light.

5.26.1 Definitions and symbols

5.26.1.1 optical rotation (α) : The angle through which the plane of polarization is rotated when polarized light passes through a layer of liquid. Unless otherwise stated, this rotation measured at the wavelength of the sodium D line at 20 ± 0,5 °C on a layer 1 dm in length.

5.26.1.2 specific optical rotation of a liquid : The angle of rotation at the wavelength of the sodium D line at 20 ± 0,5 °C, unless otherwise stated, calculating the optical rotation with reference to a layer 1 dm in length, and dividing by the density, in grams per millilitre, at 20 °C of the liquid.

5.26.1.3 specific optical rotation of a solution : The angle of rotation at the wavelength of the sodium D line at 20 ± 0,5 °C, unless otherwise stated, calculating the optical rotation with reference of a layer 1 dm in length, and dividing by the concentration, in grams per millilitre, of the solution.

5.26.2 Apparatus

5.26.2.1 Polarimeter, capable of measuring with an accuracy of at least ± 2′ (± 0,03°).

5.26.2.2 Polarimeter tubes, the lengths of which are known to an accuracy of ± 0,05 mm.

5.26.3 Procedure

5.26.3.1 Calibration

Calibrate the instrument using substances of known optical rotation, e. g. water gives a reading of 0° or 180°; a 260,0 g/l solution of anhydrous sucrose gives a reading of + 34 ° 37′ 2′′ (+ 34,62 °) at 20 °C using a 2 dm tube. In addition, transparent sheets of known optical rotation may also be used.

5.26.3.2 Test portion

Use either the liquid or the solution prepared, as specified, from the finely powdered, dry test sample. In latter case, the sample from the "loss on drying" test may be used for this purpose.

5.26.3.3 Determination

Place the test liquid in one of the thoroughly clean and dry polarimeter tubes, taking care to exclude air bubbles and bring both the liquid and the apparatus to the required temperature. Take the reading of optical rotation.

5.26.4 Expression of results

For pure liquids, the specific optical rotation is given by the formula

$$(\alpha)_{\mathrm{D}}^{t^\circ} = \frac{\alpha}{l\varrho}$$

For solutions, the specific optical rotation is given by the formula

$$(\alpha)_{\mathrm{D}}^{t^\circ} = \frac{100\,\alpha}{lc}$$

where

α is the optical rotation observed, in arc degrees;

l is the length, in decimetres, of the polarimeter tube;

ϱ is the density, in grams per millilitre, of the liquid at t °C;

c is the concentration, in grams per 100 ml, of the active ingredient;

t° is the temperature of measurement, in degrees Celsius.

5.27 Refractometry (GM 27)

5.27.1 Definition and symbols

See ISO 31.

5.27.2 Apparatus

Refractometer, capable of directly measuring the refractive index over the range 1,300 0 to 1,700 0, with a precision of ± 0,000 2.

5.27.3 Procedure

5.27.3.1 Calibration

Calibrate the instrument using either sheets or liquids of known refractive index.

5.27.3.2 Determination

Bring both the liquid being tested and the apparatus to the required temperature and carry out the determination. The refractive index decreases with increase of temperature and for most liquids, the decrease is about 0,000 5 K^{-1} (for water 0,000 1 K^{-1}).

5.28 Molecular absorption spectrophotometry (MAS) (ultraviolet and visible) (GM 28)

5.28.1 Principle

Measurement of the absorption resulting from the passage of a monochromatic beam of parallel rays, of wavelength between 185 and 380 nm (UV) and 380 and 780 nm (visible), through a known depth of test solution.

5.28.2 Apparatus

5.28.2.1 Spectrophotometer, fitted with a monochromator capable of measuring the transmittance or, preferably, the absorbance at a given wavelength through a known depth of solution.

5.28.2.2 Optical cells, of appropriate optical path length, made of silica for reading in the UV spectrum, and silica or glass for reading in the visible spectrum.

5.28.3 Procedure

Carry out the procedure given in the specification for the reagent concerned.

5.29 Atomic absorption spectroscopy (AAS) (GM 29)

5.29.1 General

The sample or its solution is aspirated and atomized into a high-temperature flame, maintained by an appropriate fuel and support gas mixture so as to effect evaporation, vaporization and dissociation. Alternatively, a flameless heating device may be used. The light source consisting of a hollow-cathode lamp or a microwave-activated, electrodeless discharge tube, emits radiations at the same wavelength as the excitation energy of the sample atoms. The atoms of the element to be determined absorb a certain fraction of this radiation, proportionally to their ground state population, and the absorbance is measured by means of a suitable atomic absorption spectrometer.

5.29.2 Procedure

Because of the nature of the method, the range of instruments available, the number of variable sample and instrumental parameters and the great diversity of interferences, it is not possible to give detailed instructions.

The choice of a procedure depends upon the degree of precision that is required. The possibility of interference from flame and non-flame sources should be taken into account. If the apparatus is fitted with a flame atom source, the determinations are usually carried out on aqueous solutions of the products being tested, slightly acidified with nitric or hydrochloric acid.

In order to detect any matrix effects, it is advisable to use the procedure of standard additions. This consists of carrying out the determination on a number (dependent on the precision required, but at least two) of aliquot portions of the test solution to which have been added known amounts of the substances to be determined.

The wavelengths of the resonance lines and other special information are given in the specification for the reagent concerned.

5.30 Flame emission spectroscopy (FES) (GM 30)

5.30.1 General

This technique is based upon the measurement of the luminous radiations emitted by some atomic species when passing from an excited to a lower energy level. The energy necessary for reaching the excited level is usually supplied by a flame obtained with an appropriate fuel and support gas mixture, and the emitted radiation is measured with a suitable photometric system, either with filters or with a monochromator.

NOTE — Alternative flame mixtures different from those specified may be used, in which case the concentrations of the solutions recommended in the appropriate specifications may need to be changed.

5.30.2 Procedure

The procedure is very similar to that used for the atomic absorption spectroscopy (see 5.29) and it is again only possible to give general guidance.

Conditions for each determination are given in the specification for the reagent concerned.

5.31 Potentiometry (GM 31)

5.31.0 General

Potentiometric methods are generally based on the measurement of the electromotive force of a galvanic cell incorporating the following electrodes or half cells :

a) the indicator electrode, immersed in the test solution. Its potential depends upon the nature of the sample and the concentration of the test solution;

b) the reference electrode, displaying a constant potential.

The electromotive force of such a galvanic cell depends upon the concentration of the test solution. If the potential of the reference electrode with respect to a standard hydrogen electrode is known, the concentration of the test solution may be calculated from the measured value of the electromotive force. If, however, the concentration of the test solution changes, as happens during a titration, the value of the electromotive force will also change in such a way that it is possible to determine the endpoint of the titration from a graph plotting the potential against the volume or mass of titrant added, or against the time of electrolysis.

5.31.1 Determination of pH (GM 31.1)

5.31.1.1 General

Consider the galvanic cell reference electrode/saturated KCl solution/solution R/Pt·H_2. Let solutions R_1 and R_2 be standard buffer solutions having respectively : known pH values pH_{R1} and pH_{R2}; measured potential differences E_1 and E_2.

If the solution R is replaced by a test solution of unknown pH, the potential difference measured is related to the pH of the test solution.

If all measurements are carried out at the same temperature and potassium chloride solution concentration, the pH may be calculated using the expressions :

$$\frac{E_1 - E_{test}}{S} + pH_{R1}$$

$$\frac{E_2 - E_{test}}{S} + pH_{R2}$$

where S is the slope factor $\left(\frac{mV}{pH}\right) = \frac{E - E_2}{pH_{R1} - pH_{R2}}$

5.31.1.2 Apparatus

pH meter, consisting of a glass electrode rather than a hydrogen electrode connected to a high impedance millivoltmeter having a scale calibrated in pH-units. This permits direct reading of pH by sensing the potential difference between the pH-dependent electrode (glass, antimony) and a reference electrode, the two being connected by an electrolytic solution bridge (for example saturated KCl solution).

5.31.1.3 Calibration

Calibrate the pH-meter using appropriate pH standards (hydrogen ion activity standards), some of which are listed below :

a) oxalate standard buffer (RS) (4.2.12);

b) tartrate standard buffer (RS) (4.2.17);

c) phthalate standard buffer (RS) (4.2.14);

d) phosphate standard buffer (RS) (4.2.13);

e) borate standard buffer (4.2.2);

f) calcium hydroxide standard buffer (4.2.3).

Table 3 gives the pH values of the above-mentioned standard buffer solutions in the temperature range 15 to 35 °C.

Table 3 — pH values

Temperature °C	Standard buffer solution					
	a)	b)	c)	d)	e)	f)
15	1,67	—	4,00	6,90	9,27	12,81
20	1,68	—	4,00	6,88	9,22	12,63
25	1,68	3,56	4,01	6,86	9,18	12,45
30	1,69	3,55	4,01	6,85	9,14	12,30
35	1,69	3,55	4,02	6,84	9,10	12,14

5.31.1.4 Procedure

Except when the determination is carried out upon the reagent itself, prepare a test solution of specified concentration, using the carbon dioxide free water (see 3.2).

At the same time, prepare two buffer solutions, bridging the expected pH of the test solution. Adjust the temperatures of these three solutions and of the reference cell to 25 ± 1 °C.

Calibrate the instrument with the two buffer solutions, washing the measuring electrode with the buffer solution before taking the reading. After washing the electrode with water and then with the test solution, measure the pH of the test solution.

In order to obtain exact results, it is necessary to repeat the measurement with different portions of the test solution, without washing the electrode between consecutive readings until the pH reading remains constant for at least 1 min.

5.31.2 Titrations (GM 31.2)

5.31.2.1 Apparatus

5.31.2.1.1 Potentiometer or **pH-meter,** accurate to 2 mV, with a hydrogen or glass working electrode and a calomel reference electrode.

5.31.2.1.2 Burette.

5.31.2.1.3 Magnetic stirrer.

NOTE — Automatic titration apparatus may be used as an alternative.

5.31.2.2 Procedure

Insert the electrodes of the potentiometer or the pH-meter (5.31.2.1.1) into the test solution and titrate rapidly, with constant stirring, to approximately 2 to 3 ml from the end-point; continue the titration by adding small and equal volumes of the titrant and recording the e.m.f. or the pH after each addition.

The end-point occurs when ΔE is a maximum or where the second differential $\Delta' E$ is zero. A typical example is given in table 4.

Table 4 — Typical titration end-point

V	E	ΔE	$\Delta' E$
ml	mV	mV	mV
10,0	320	32	
10,5	352	42	+ 10
11,0	394	66	+ 24
11,5	460	26	− 40
12,0	486	16	− 10
12,5	502		

The volume V_E, in millilitres, of titrant corresponding to the end-point is given by the formula

$$V + V' \times \frac{a}{a - b}$$

where

V is the volume, in millilitres, of titrant corresponding to the last positive value of $\Delta' E$ (in the example 11,0 ml);

V' is the successively added volume, in millilitres, of titrant (in the example, 0,5 ml);

a is the final positive value of $\Delta' E$ (in the example, + 24);

b is the first negative value of $\Delta' E$ (in the example, − 40).

In the example, therefore

$$V_E = 11{,}0 + 0{,}5 \times \frac{24}{24 + 40}$$

$$= 11{,}19 \text{ ml}$$

5.32 Single-sweep polarography (GM 32)

5.32.1 General

Single-sweep polarography is a form of d.c. polarography using a dropping mercury electrode. The potential sweep is applied to every mercury drop at a very late moment of the drop's lifetime and is initiated by the falling of the drop

If an electrochemical reaction occurs within the potential range applied to the electrode, a peak-shaped current signal is obtained on the screen of the cathode ray tube. The shape of the signal and its high sensitivity derive from the rapid potential sweep. As the size of the drop is almost constant during the potential sweep, the capacitative current is small relative to the electrochemical (faradaic) current. The method is rapid and gives greater sensitivity and resolution than normal d.c. polarography.

5.32.2 Procedure

Prepare a test solution, containing a given amount of support electrolyte, as described in the specification for the reagent concerned. Transfer this solution to the polarographic vessel, placed in a water-bath. Bubble purified nitrogen through the

test solution to remove dissolved oxygen and select the appropriate starting potential and current sensitivity. Read the appropriate peak heights from the cathode ray screen.

The appropriate experimental details are given in the specification for the reagent concerned.

5.33 Anodic stripping voltammetry (GM 33)

5.33.1 General

Anodic (or cathodic) stripping or inverse voltammetry is used for the determination of traces of ions, especially those of heavy metals. It uses a stationary electrode which may consist of a suspended mercury drop or a solid electrode made, for example, of carbon or platinum.

The ions being determined are first electrodeposited from the stirred test solution onto the stationary electrode while a constant potential is applied to the electrode. In the case of heavy metal cations, they are then reduced to the metal, forming amalgams on the surface of the suspended mercury drop. During this step, an enrichment of the ions at the electrode takes place.

The potential is then reversed anodically in the case of heavy metals, and varied with time. Peak-shaped graphs relating current to voltage are recorded while the metals are being stripped anodically from the electrode. A particular metal has a characteristic peak potential and the peak height is proportional to the concentration of the ions in the solution, provided that all other test conditions are kept constant.

5.33.2 Procedure

Prepare a test solution, including a specified amount of support electrolyte, as described in the specification for the reagent concerned. Transfer this solution to a clean polarographic vessel. Insert a magnetic stirrer bar into the solution and stir at a constant speed. Insert the electrodes into the test solution and bubble purified nitrogen through it for at least 5 min. Apply the relevant starting potential between the working and reference electrodes and adjust the period of electrolysis of the polarographic equipment available.

The appropriate experimental details are given in the specification for the reagent concerned.

5.34 Gas chromatography (GM 34)

Carry out the determination using a suitable gas chromatograph and the conditions given in the specification for the reagent concerned.

NOTE — ISO 2718 describes a standard layout for writing a method of chemical analysis by gas chromatography.

5.35 Determination of metals by solvent extraction followed by AAS (GM 35)

Prepare 150 ml of test solution, adding sufficient of the acetic acid (R 1) or 20 % sodium hydroxide solution to adjust the pH to 5. Divide the solution into three equal portions in three separating funnels and to two of them add standard solutions of those metals to be determined equivalent to the limit and twice the limit, respectively. Treat the content of each of the three funnels as follows : Add 1 ml of 1 % ammonium pyrrolidine-1-carbodithioate (APDC) solution, mix, add 10 ml of 4-methylpentan-2-one and shake for 30 s. Allow to separate and discard the aqueous layer. Transfer the organic layer to a 10 ml one-mark volumetric flask and dilute to the mark with 95 % (*V*/*V*) ethanol. Use these solutions to apply GM 29.

5.36 Measurement of colour in Hazen units (GM 36)

Measure by the method specified in ISO 2211.