BRITISH STANDARD

BS 3031 : 1996

Specification for

Sulfuric acid used in lead-acid batteries

ICS 29.220 : 71.060 30

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by Technical Committee CII/8, Sulfuric acid for accumulators, upon which the following bodies were represented:

Chemical Industries Association
Ministry of Defence
National Sulfuric Acid Association
Society of British Battery Manufacturers

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Foreword

This British Standard has been prepared by Technical Committee CII/8. It supersedes BS 3031 : 1972, which is withdrawn.

This edition of BS 3031 incorporates specifications for nickel, chromium and cadmium and the specifications for manganese have been revised. A flame atomic absorption spectrophotometric method has been added for the determination of copper, manganese, nickel, chromium and cadmium. This edition also introduces up-to-date terminology.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Specification

1 Scope

This British Standard specifies the limits for impurities in sulfuric acid suitable for use in lead-acid batteries and details procedures for the determination of those impurities.

This edition covers sulfuric acid of any relative density.

NOTE. This is a matter for agreement between purchaser and supplier. Clauses and relevant appendices are worded accordingly.

All of the numerical limits refer to sulfuric acid of relative density 1.215 at 20 °C. Conversions to 100 % and other commonly used acid bases are given in annex K. Useful tables relating density to percentage composition will be found in BS 753 .

2 References

2.1 Normative references

This British Standard incorporates, by reference, provisions from specific editions of other publications. These normative references are cited at the appropriate points in the text and the publications are listed on the inside back cover. Subsequent amendments to, or revisions of, any of these publications apply to this British Standard only when incorporated in it by updating or revision.

2.2 Informative references

This British Standard refers to other publications that provide information or guidance. Editions of these publications current at the time of issue of this standard are listed on the inside back cover, but reference should be made to the latest editions.

3 Definition

For the purposes of this British Standard the following definition applies.

reference acid

Sulfuric acid of relative density 1.215 at 20 °C.

4 Description

The material shall consist essentially of an aqueous solution of sulfuric acid, H_2SO_4, having a relative density not less than 1.215 at 20 °C. When diluted to a relative density of 1.215 at 20 °C with water conforming to Grade 3 of BS EN ISO 3696 : 1995, it shall be clear and colourless when viewed through a depth of 300 mm.

5 Sample

A representative sample of not less than 1 l of the material shall be taken from the bulk. The sample shall be placed in a clean, dry and airtight stoppered glass bottle of such a size that it is nearly filled by the sample. When it is necessary to seal the bottle, care shall be taken to avoid contaminating the contents in any way.

The mass of test portion required for each test is given in the appropriate annex.

Since all numerical limits refer to acid having a relative density of 1.215 at 20 °C, all results obtained on the sample of acid as received to their equivalents, based on an acid of that relative density, shall be converted by use of a conversion factor, *F*. The calculation of the conversion factor is given in annex A.

6 Residue on ignition

When determined and calculated by the method described in annex B, the residue, on ignition of the material, shall not exceed the equivalent of 150 $mg{\cdot}kg^{-1}$ of the reference acid.

7 Chloride content

When determined and calculated by the method described in annex C, the chloride content of the material, expressed as C_{Cl}, shall not exceed the equivalent of 7 $mg{\cdot}kg^{-1}$ of the reference acid.

8 Sulfur dioxide content

When determined and calculated by the method described in annex D, the sulfur dioxide content of the material, expressed as C_{SO2}, shall not exceed the equivalent of 5 $mg{\cdot}kg^{-1}$ of the reference acid .

9 Ammoniacal nitrogen content

When determined and calculated by the method described in annex E, the ammoniacal nitrogen content of the material, expressed as C_{NH3}, shall not exceed the equivalent of 50 $mg{\cdot}kg^{-1}$ of the reference acid.

10 Nitrogen oxides content

When determined and calculated by the method described in annex F, the nitrogen oxides content of the material, expressed as C_N, shall not exceed the equivalent of 5 $mg{\cdot}kg^{-1}$ of the reference acid.

11 Iron content

When determined and calculated by the method described in annex G, the iron content of the material, expressed as C_{Fe}, shall not exceed the equivalent of 12 mg·kg^{-1} of the reference acid.

12 Arsenic content

When determined and calculated by the method described in annex H, the arsenic content of the material expressed as C_{As}, shall not exceed the equivalent of 2 mg·kg^{-1} of the reference acid.

13 Copper content

When determined and calculated by the method described in annex J, the copper content of the material, expressed as C_{Cu}, shall not exceed the equivalent of 7 mg·kg^{-1} of the reference acid.

14 Manganese content

When determined and calculated by the method described in annex J, the manganese content of the material, expressed as C_{Mn}, shall not exceed the equivalent of 0.1 mg·kg^{-1} of the reference acid.

15 Nickel content

When determined and calculated by the method described in annex J, the nickel content of the material, expressed as C_{Ni}, shall not exceed the equivalent of 0.6 mg·kg^{-1} of the reference acid.

16 Chromium content

When determined and calculated by the method described in annex J, the chromium content of the material, expressed as C_{Cr}, shall not exceed the equivalent of 0.2 mg·kg^{-1} of the reference acid.

17 Cadmium content

When determined and calculated by the method described in annex J, the cadmium content of the material, expressed as C_{Cd}, shall not exceed the equivalent of 0.2 mg·kg^{-1} of the reference acid.

18 Test report

The test report shall include the following information:

a) a complete identification of the sample;

b) a reference to this British Standard;

c) the results of the determinations;

d) any unusual features noted during the determination.

Annexes

Annex A (normative)

Calculation of conversion factor for each method

Calculate the conversion factor, F, using the equation:

$$F = \frac{29.6}{g}$$

where

g is the percentage by mass of H_2SO_4 in the sample acid, derived from its relative density at 20 °C.

NOTE. 29.6 is the percentage by mass of H_2SO_4 in reference acid.

Annex B (normative)

Method for the determination of residue on ignition

B.1 Apparatus

B.1.1 Platinum dish, approximately 50 mm in diameter.

B.2 Procedure

Weigh to the nearest 0.01 g a test portion of approximately 50 g into the tared dish and evaporate to dryness on a sand bath in a fume cupboard until no further fumes are evolved. Finally ignite to constant mass at (850 ± 50) °C.

B.3 Calculation

Calculate the residue on ignition, R, in percentage by mass, using the equation:

$$R = \frac{M_2 \times 100 \times F}{m}$$

where

M_2 is mass of residue found, in grams;

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

F is the conversion factor (see annex A).

Report the result as the mean of duplicate determinations, to two significant figures.

Annex C (normative)

Method for the determination of chloride content

C.1 Principle

The chloride present is determined nephelometrically using silver nitrate.

C.2 Apparatus

C.2.1 *Ordinary laboratory apparatus.*

C.2.2 *Matched Nessler cylinders*, conforming to BS 612.

C.2.3 *Thirteen one-mark volumetric flasks*, conforming to BS 1792, 100 ml capacity.

C.3 Reagents

C.3.1 *General.* All reagents shall be of analytical quality and water shall conform to Grade 3 of BS EN ISO 3696 : 1995.

C.3.2 *Sulfuric acid*, relative density 1.215 at 20 °C. Add slowly, with constant stirring, 200 ml of sulfuric acid, concentrated, 98 % (*m/m*), to 750 ml of water. Cool to room temperature, then dilute to 1000 ml.

C.3.3 *Nitric acid*, concentrated, approximately 70 % (*m/m*).

C.3.4 *Silver nitrate solution*, approximately 17 g $AgN0_3$ per litre.

C.3.5 *Standard chloride solution.* Dissolve 1.648 g of previously dried sodium chloride in water and dilute to 1000 ml. Mix well. Further dilute 10 ml of this solution to 1000 ml with water. Mix well. 1 ml of this diluted solution corresponds to 10 µg of Cl.

C.4 Procedure

C.4.1 ***Preparation of standard solutions***

Into 11 of the 100 ml one-mark volumetric flasks, each containing 10 g (8.2 ml) of the sulfuric acid (**C.3.2**), transfer known amounts of the standard chloride solution (**C.3.5**), containing from 0 to 100 µg of chloride increasing by stages of 10 µg and treat each solution as follows.

Dilute to about 95 ml, add 1 ml of the nitric acid (**C.3.3**) and 2 ml of the silver nitrate solution (**C.3.4**), dilute to the mark with water, mix well and allow to stand in the dark at room temperature, for not less than 5 min and not more than 15 min.

These solutions are used directly for visual comparison.

C.4.2 ***Determination***

Weigh, to the nearest 0.01 g, a test portion of approximately 10 g containing not more than 100 μg Cl and dilute to about 75 ml with water, avoiding a temperature higher than 40 °C. Cool, transfer to a 100 ml one-mark volumetric flask and dilute to about 95 ml with water. Add 1 ml of the nitric acid (**C.3.3**) and 2 ml of the silver nitrate solution (**C.3.4**), dilute to the mark with water, mix well and allow to stand in the dark at room temperature for not less than 5 min and not more than 15 min. At the same time carry out a blank determination on the reagents alone.

Compare the turbidity of the test solution and the blank test solution with the series of prepared standard solutions in matched Nessler cylinders. Note the chloride content of the standard solution that most nearly matches each solution. Correct for the blank test solution.

C.5 Calculation

Calculate the chloride content, C_{Cl} milligrams per kilogram, using the equation:

$$C_{\mathrm{cl}} = \frac{M_3 \times F}{m}$$

where

M_3 is the mass of chloride found, in micrograms;

F is the conversion factor (see annex A);

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

Report the result as the mean of duplicate determinations to two significant figures.

Annex D (normative)

Method for the determination of sulfur dioxide content

D.1 Principle

Sulfur dioxide is removed from the sample by means of a current of nitrogen and absorbed in sodium hydroxide solution. An excess of potassium iodate/iodide is added to the latter, the solution is acidified and the liberated iodine is titrated with standard sodium thiosulfate solution.

D.2 Apparatus

D.2.1 *Ordinary laboratory apparatus.*

D.2.2 *Conical flask*, 250 ml capacity, fitted with a ground glass stopper through which pass inlet and outlet tubes. The inlet tube reaches almost to the bottom of the flask and is connected through a trap and safety lute to a cylinder of nitrogen fitted with a needle valve. The outlet tube is connected by a glass-to-glass joint to a coarse sintered-glass bubbler reaching nearly to the bottom of a Drechsel bottle conforming to BS 2461.

D.2.3 *Burette*, Class A, 5 ml capacity, conforming to BS 846.

D.3 Reagents

D.3.1 *General.* All reagents shall be of analytical quality and water shall conform to Grade 3 of BS EN ISO 3696 : 1995.

D.3.2 *Nitrogen*, conforming to BS 4366, from a cylinder.

D.3.3 *Sulfuric acid solution*, approximately 250 g H_2SO_4 per litre.

D.3.4 *Sodium hydroxide solution*, approximately 0.4 g NaOH per litre.

D.3.5 *Sodium thiosulfate solution*, $c(Na_2S_2O_3.5H_2O) = 0.01$ mol·l $^{-1}$ exactly.

D.3.6 *Potassium iodate/iodide solution*, approximately 0.36 g KIO_3 per litre, containing approximately 50 g/l of potassium iodide.

D.3.7 *Starch indicator solution*, approximately 2.5 g/l aqueous solution of soluble starch.

D.4 Procedure

Weigh to the nearest 0.01 g, a test portion of approximately 60 g, containing not more than 600 μg SO_2 and place it in the 250 ml flask. Place 100 ml of the sodium hydroxide solution (**D.3.4**) in the Drechsel bottle. Open the needle valve on the inlet tube to the flask, adjust the flow of nitrogen (**D.3.2**) to 20 l per hour and maintain this rate for 3 h.

At the end of this period, disconnect the Drechsel bottle from the outlet tube and then turn off the nitrogen. Rinse the solution remaining in the sintered glass bubbler into the bottle, add 2.0 ml of the potassium iodate/iodide solution (**D.3.6**) and add 5 ml of the sulfuric acid solution (**D.3.3**). Add 2 ml of the starch indicator solution (**D.3.7**) and titrate with the sodium thiosulfate solution (**D.3.5**) until the blue colour is just discharged.

Carry out a blank test, using the same procedure and adding exactly the same volume of potassium iodate/iodide solution, omitting only the sample.

D.5 Calculation

Calculate the sulfur dioxide content, C_{SO2} in milligrams per kilogram, using the equation:

$$C_{SO2} = \frac{(T_1 - T_0) \times 320 \times F}{m}$$

where

T_0 is the volume of sodium thiosulfate solution used in the blank test, in millilitres;

T_1 is the volume of sodium thiosulfate solution used in the determination, in millilitres;

F is the conversion factor (see annex A);

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

NOTE. 320 is the mass of SO_2 corresponding to 1 ml of the sodium thiosulfate solution, in micrograms (**D.3.4**).

Report the result as the mean of duplicate determinations to two significant figures.

Annex E (normative)

Method for the determination of ammoniacal nitrogen content

E.1 Principle

The sample is made alkaline with sodium hydroxide solution and any ammonia present is determined colorimetrically using Nessler's reagent.

E.2 Apparatus

E.2.1 *Ordinary laboratory apparatus.*

E.2.2 *Spectrophotometer*, with 4 cm cells.

NOTE. As an alternative, use matched Nessler cylinders conforming to BS 612.

E.2.3 *Twelve one-mark volumetric flasks*, conforming to BS 1792, 100 ml capacity.

E.3 Reagents

E.3.1 *General.* All reagents shall be of analytical quality and water shall conform to Grade 3 of BS EN ISO 3696 : 1995[1]

E.3.2 *Sulfuric acid solution*, relative density 1.215 at 20 °C. Add slowly, with constant stirring, 200 ml of sulfuric acid, concentrated, 98 % *(m/m)*, to 750 ml of water. Cool to room temperature, then dilute to 1000 ml and mix well.

E.3.3 *Sodium hydroxide solution*, approximately 200 g NaOH per litre.

E.3.4 *Nessler's reagent.* Dissolve 3.5 g of potassium iodide and 1.25 g of mercury(II) chloride in 80 ml of water. Add a cold saturated aqueous solution of mercury(II) chloride, stirring constantly, until a slight red precipitate remains, then add 12 g of sodium hydroxide. Allow this to dissolve, add a little more of the saturated mercury(II) chloride solution until a slight turbidity is obtained, and dilute to 100 ml with water. Allow to settle, decant and store in the dark.

E.3.5 *Standard ammonia solution.* Dissolve 3.141 g of ammonium chloride in water and dilute to 1000 ml. Mix well. Further dilute 10 ml to 1000 ml with water. Mix well. 1 ml of the diluted solution corresponds to 10 μg of ammonia, NH_3.

E.4 Procedure

E.4.1 ***Preparation of colour standards***

Into 11 of the 100 ml one-mark volumetric flasks, each containing 60 ml of water, transfer known amounts of the standard ammonia solution (**E.3.5**), containing from 0 to 100 μg of ammonia increasing by stages of 10 μg, and treat each solution as follows.

Add 1 g (0.82 ml) of the sulfuric acid (**E.3.2**), neutralize with about 1.2 ml of the sodium hydroxide solution (**E.3.3**), add 3 ml in excess and dilute to about 95 ml. Add 2 ml of the Nessler's reagent (**E.3.4**), dilute to the mark, mix thoroughly and allow to stand for a period of 10 min to 15 min.

These standards are used directly for visual comparison. If an instrument is to be used, measure the absorbance of each solution at a wavelength of 370 nm using the zero standard as reference, and prepare a calibration graph having, for example, micrograms of ammonia as abscissa and absorbance as ordinate.

E.4.2 ***Determination***

Weigh to the nearest 0.01 g a test portion having a mass of approximately 10 g, containing not more than 100 μg NH_3, and dilute to about 75 ml with water. Cool, transfer to a 100 ml volumetric flask and dilute to the mark. Mix well. Transfer a 10 ml aliquot portion to another 100 ml volumetric flask containing 60 ml of water. Neutralize with the sodium hydroxide solution (**E.3.3**), add 3 ml in excess and dilute to about 95 ml. Add 2 ml of the Nessler's reagent (**E.3.4**), dilute to the mark, mix thoroughly and allow to stand for a period of 10 min to 15 min.

At the same time, carry out a blank test using the reagents alone.

Measure the absorbance of the test solution and that of the blank test solution at a wavelength of 370 nm using distilled water as reference solution. Correct the reading of the test solution for that of the blank test solution and read the amount of ammonia present from the calibration graph (**see E.4.1**).

Alternatively, compare the colour of the two solutions with the series of prepared colour standards in matched Nessler cylinders, noting the ammonia content of the standard that most nearly matches each solution. Correct for the blank.

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[1] Further purified if necessary to free it from ammonia.

E.5 Calculation

Calculate the ammoniacal nitrogen content, C_{NH3}, in milligrams per kilogram, using the equation:

$$C_{NH3} = \frac{M_4 \times 100 \times F}{m \times 10}$$

where

M_4 is the mass of ammonia found in the aliquot portion of the sample taken, in micrograms;

F is the conversion factor (see annex A);

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

Report the result as the mean of duplicate determinations to two significant figures.

Annex F (normative)

Method for the determination of nitrogen oxides content

F.1 Principle

The nitrogen oxides present are first oxidized using potassium permanganate solution and then treated with 2,4-xylenol reagent. The resulting nitro-xylenol is distilled and the amount present in the distillate is determined photometrically.

F.2 Apparatus

F.2.1 *Ordinary laboratory apparatus.*

F.2.2 *Spectrophotometer,* with 4 cm cells.

NOTE. As an alternative, use matched Nessler cylinders conforming to BS 612.

F.2.3 *Water bath,* maintained at (35 ± 1) °C.

F.2.4 *Twelve one-mark volumetric flasks,* conforming to BS 1792, 100 ml capacity.

F.2.5 *All-glass distillation assembly,* with 250 ml distillation flask.

F.3 Reagents

F.3.1 *General.* All reagents shall be of analytical quality and water shall conform to Grade 3 of BS EN ISO 3696 : 1995.

F.3.2 *Mercury (II) acetate.*

F.3.3 *Sulfuric acid solution,* concentrated, 98 % (*m/m*).

F.3.4 *Hydrogen peroxide solution,* approximately 1 g H_2O_2 per litre. Dilute 3.5 ml of 30 % H_2O_2 (100 volumes) to 1 l with water.

F.3.5 *2,4-xylenol solution,* 10 g/l in glacial acetic acid, freshly prepared.

F.3.6 *Sodium hydroxide solution,* approximately 80 g NaOH per litre.

F.3.7 *Sodium hydroxide, dilute solution,* approximately 8 g NaOH per litre. Dilute 100 ml of the sodium hydroxide solution (**F.3.6**) to 1000 ml with water. Mix well.

F.3.8 *Potassium permanganate solution,* approximately 3 g $KMnO_4$ per litre.

F.3.9 *Standard nitrogen solution.* Dissolve 0.3609 g of potassium nitrate in water and dilute to 100 ml. Mix well. 1 ml of this solution corresponds to 500 μg of nitrogen.

F.4 Procedure

F.4.1 *Preparation of standard distillate*

To 9 ml of water contained in a small flask, carefully add 15 ml of the concentrated sulfuric acid solution (**F.3.3**). Cool to 35 °C, then pour the diluted acid into a 100 ml ground glass stoppered boiling tube containing 1.00 ml of the standard nitrogen solution (**F.3.9**). Add 1 ml of the 2,4-xylenol solution (**F.3.5**) and mix well. Transfer the tube to the water bath and maintain at (35 ± 1) °C for 30 min. At the end of this period, remove from the bath, transfer the contents of the tube completely to the distillation flask and dilute to 100 ml with water.

Connect the flask to the distillation assembly, heat to boiling and collect 60 ml of the distillate in a 100 ml one-mark volumetric flask containing 10 ml of the sodium hydroxide solution (**F.3.6**). Cut the water supply to the condenser towards the end of the distillation to ensure that no nitrated 2,4-xylenol remains in the condenser. Dilute to the mark with water and mix thoroughly.

F.4.2 *Preparation of colour standards*

Into 10 of the 100 ml one-mark volumetric flasks, transfer known amounts of the standard distillate from 1 ml to 10 ml increasing in stages of 1 ml, corresponding to nitrogen contents from 5 μg to 50 μg. Dilute each solution to the mark with the dilute sodium hydroxide solution (**F.3.6**) and mix thoroughly.

These standards are used directly for visual comparison. If an instrument is to be used, measure the absorbance of each solution at a wavelength of 445 nm using the dilute sodium hydroxide solution as reference solution, and prepare a calibration graph, having for example micrograms of nitrogen as abscissa and absorbance as ordinate.

F.4.3 *Determination*

Weigh to the nearest 0.01 g a test portion of approximately 6 g containing not more than 50 μg nitrogen and transfer it to a 50 ml ground glass stoppered boiling tube. Immerse the tube in a bath of ice water, dilute to 5.0 ml with water and carefully add 6.0 ml of the sulfuric acid solution (**F.3.3**). Keep the temperature below 40 °C while making these additions.

Add 0.2 g of the mercury (II) acetate solution (**F.3.2**) followed by the potassium permanganate solution (**F.3.8**) drop by drop until a permanent pink coloration is obtained, then just decolorize with the hydrogen peroxide solution (**F.3.4**).

Add 1 ml of the 2,4-xylenol solution (**F.3.5**), mix well, insert the stopper and immerse the tube in the water bath (**F.2.3**) maintained at (35 ± 1) °C for 30 min. At the end of this period, remove from the bath, transfer the contents of the tube completely to the distillation flask and dilute to 100 ml with water.

Connect the flask to the distillation assembly, heat to boiling and collect 60 ml of the distillate in a 100 ml one-mark volumetric flask containing 10 ml of the sodium hydroxide solution (**F.3.6**). Turn off the water supply to the condenser towards the end of the distillation to ensure that no nitrated 2,4-xylenol remains in the condenser. Dilute to the mark with water and mix thoroughly.

Carry out a blank test on 6.0 ml of the reagent sulfuric acid (**F.3.3**), carefully adding it to 4.0 ml of water, ensuring that the temperature does not rise above 40 °C.

Measure the absorbance of the test solution and that of the blank test solution at a wavelength of 445 nm using the dilute sodium hydroxide solution (**F.3.6**) as reference solution. Correct the absorbance of the test solution for that of the blank test solution and read the amount of nitrogen present from the calibration graph (see **F.4.2**).

Alternatively, compare the colour of the two solutions with the series of prepared colour standards in matched Nessler cylinders, noting the nitrogen content of the standard that most nearly matches each solution. Correct for the blank.

F.5 Calculation

Calculate the nitrogen oxides content, C_N, in micrograms per kilogram, using the equation:

$$C_N = \frac{M_5 \times F}{m}$$

where

M_5 is the mass of nitrogen found, in micrograms;

F is the conversion factor (see annex A);

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

Report the result as the mean of duplicate determinations to two significant figures.

Annex G (normative)

Method for the determination of iron content

G.1 Principle

The iron present is reduced to the ferrous state and determined photometrically using 2,2'-bipyridyl.

G.2 Apparatus

G.2.1 *Ordinary laboratory apparatus.*

G.2.2 *Spectrophotometer,* with 4 cm cells, or matched Nessler cylinders conforming to BS 612.

G.2.3 *Fifteen one-mark volumetric flasks,* conforming to BS 1792, 100 ml capacity.

G.3 Reagents

G.3.1 *General.* All reagents shall be of analytical quality and water shall conform to Grade 3 of BS EN ISO 3696 : 1995.

G.3.2 *Hydrochloric acid solution,* approximately 36.5 g HCl per litre.

G.3.3 *Hydroxylammonium chloride,* 50 g/l solution.

G.3.4 *Ammonium acetate,* 400 g/l solution.

G.3.5 *2,2'-Bipyridyl,* 1 g/l solution. Dissolve 0.1 g of the reagent in 50 ml of water containing 2 ml of the hydrochloric acid solution (**G.3.2**) and dilute to 100 ml.

G.3.6 *Standard iron solution.* Dissolve 7.022 g of diammonium iron(II) sulfate 6-hydrate in a mixture of 600 ml of water and 350 ml of concentrated sulfuric acid solution, 98 % (*m/m*), and dilute to 1000 ml with water. Mix well. Further dilute 10 ml of the solution so obtained to 1000 ml with water. Mix well. 1 ml of the diluted solution corresponds to 10 µg of iron.

G.4 Procedure

G.4.1 *Preparation of colour standards*

Into 13 of the 100 ml one-mark volumetric flasks, each containing 50 ml of water and 2 ml of the hydrochloric acid solution (**G.3.2**), transfer known amounts of the standard iron solution (**G.3.6**), containing from 0 to 120 µg of iron, increasing by stages of 10 µg, and treat each solution as follows.

Add 4 ml of the hydroxylammonium chloride solution (**G.3.3**) and allow to stand for 1 min. Add 5 ml of the ammonium acetate solution (**G.3.4**) and 3 ml of the 2,2'-bipyridyl solution (**G.3.5**). Dilute the contents of each flask to 100 ml and mix thoroughly.

These standards are used directly for visual comparison. If an instrument is to be used, measure the absorbance of each solution at a wavelength of 515 nm using the zero standard solution as reference standard, and prepare a calibration graph having, for example, micrograms of iron as abscissa and absorbance as ordinate.

G.4.2 *Determination*

Weigh, to the nearest 0.01 g, a test portion of approximately 8 g containing not more than 120 µg Fe, transfer it to a silica basin and evaporate just to dryness on a sand bath in a fume cupboard. Cool, dissolve the residue in 2 ml of the hydrochloric acid solution (**G.3.2**) and transfer to a 100 ml one-mark volumetric flask.

Add 4 ml of the hydroxylammonium chloride solution (**G.3.3**), and allow to stand for 1 min. Add 5 ml of the ammonium acetate solution (**G.3.4**), mix, and add 3 ml of the 2,2'-bipyridyl solution (**G.3.5**). Dilute to 100 ml with water and mix thoroughly.

At the same time carry out a blank test on the reagents alone.

Measure the absorbance of the test solution and that of the blank test solution at a wavelength of 515 nm, using distilled water as reference solution. Correct the absorbance of the test solution for that of the blank test solution and read the amount of iron present from the calibration graph (see **G.4.1**).

Alternatively, compare the colour of the two solutions with the series of prepared colour standards in matched Nessler cylinders, noting the iron content of the standard that most nearly matches the test solution. Correct for the blank.

G.5 Calculation

Calculate the iron content, C_{Fe}, in milligrams per kilogram, using the equation:

$$C_{\mathrm{Fe}} = \frac{M_6 \times F}{m}$$

where

M_6 is the mass of iron found, in micrograms;

F is the conversion factor (see annex A);

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

Report the result as the mean of duplicate determinations to two significant figures.

Annex H (normative)

Method for the determination of arsenic content

H.1 Principle

The arsenic in the sample is reduced with zinc, the arsine evolved is absorbed in a solution of silver diethyldithiocarbamate in pyridine, and the optical relative density of the complex is measured spectrophotometrically.

H.2 Procedure

Follow the procedure described in BS 4404 : 1968. For the preparation of the test solution, dilute 7 ml of the concentrated hydrochloric acid (**5.2 (1)** of BS 4404 : 1968) to 30 ml with water, add a test portion of approximately 4 g, weighed to the nearest 0.001 g, and dilute to 40 ml with water.

H.3 Calculation

Calculate the arsenic content, C_{As}, in milligrams per kilogram, using the equation:

$$C_{\mathrm{As}} = \frac{M_7 \times F}{m}$$

where

M_7 is the mass of arsenic found (less the blank correction),in micrograms;

F is the correction factor (see annex A);

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

Annex J (normative)

Method for the determination of copper, manganese, chromium, nickel and cadmium by flame atomic absorption spectrometry

J.1 Principle

The copper, manganese, chromium and nickel and cadmium contents are determined by flame atomic absorption spectrometry.

J.2 Apparatus

J.2.1 *Atomic absorption spectrometer*, with hollow cathode lamps for copper, manganese, chromium, nickel and cadmium, with provision for supplies of air and acetylene. It shall be sufficiently pure to give a clear blue flame, free from water and oil and have provision for hydrogen or deuterium background correction.

The atomic absorption spectrometer used shall be regarded as satisfactory if, after optimization, the limit of detection and the characteristic concentration are compatible with the values given by the manufacturer.

The characteristic concentration, limit of detection and the linearity for the elements are given in table J.1.

Table J.1 limit of detection and linearity

Element	**Characteristic concentration** $\mu g \cdot ml^{-1}$	**Limit of detection** $\mu g \cdot ml^{-1}$	**Linearity** $\mu g \cdot ml^{-1}$
Copper	0.032	0.01	2.0
Manganese	0.03	0.01	2.0
Chromium	0.041	0.02	3.0
Nickel	0.042	0.02	1.0
Cadmium	0.016	0.01	1.0

NOTE. The figures given in table J.1 were obtained using an impact bead in aqueous solutions. For solutions of sulfuric acid, at the dilution of the test, the limit of detection is approximately double those given in the table for all elements.

J.3 Reagents

J.3.1 *General.* All reagents shall be of analytical quality and water shall conform to Grade 3 of BS EN ISO 3696 : 1995.

J.3.2 *Sulfuric acid solution,* concentrated, 98 % *(m/m)*

J.3.3 *Nitric acid solution.* Dilute concentrated nitric acid, 70 % *(m/m)*, with an equal volume of water.

J.3.4 *Dilute hydrochloric acid solution.* Dilute concentrated hydrochloric acid, 36 % (m/m) with an equal volume of water.

J.3.5 *Standard copper solution.* Dissolve (1.000 ± 0.001) g of copper metal in (50 ± 2) ml of dilute nitric acid (**J.3.3**). Cool. Make up to 1000 ml in a graduated flask and mix well. Further dilute 10 ml of this solution to 100 ml in a graduated flask. Mix well. 1 ml of the diluted solution corresponds to 100 µg of copper, Cu.

J.3.6 *Standard manganese solution.* Dissolve (1.000 ± 0.001) g of manganese metal in (50 ± 2) ml of dilute nitric acid (**J.3.3**). Cool. Make up to 1000 ml in a graduated flask adding 50 ml concentrated hydrochloric acid 36 % (m/m) before making up to the mark. Further dilute 10 ml of this solution to 100 ml in a graduated flask. Mix well. 1 ml of the diluted solution corresponds to 100 µg of manganese, Mn.

J.3.7 *Standard chromium solution.* Dissolve (1.000 ± 0.001) g of chromium metal in (50 ± 2) ml of concentrated hydrochloric acid (36 % m/m). Cool. Make up to 1000 ml in a graduated flask and mix well. Further dilute 10 ml of this solution to 100 ml in a graduated flask. Mix well. 1 ml of the diluted solution corresponds to 100 µg of chromium, Cr.

J.3.8 *Standard nickel solution.* Dissolve (1.000 ± 0.001) g of nickel metal in (50 ± 2) ml of the dilute nitric acid (**J.3.3**). Cool. Make up to 1000 ml in a graduated flask and mix well. Further dilute 10 ml of this solution to 100 ml in a graduated flask. Mix well. 1 ml of the diluted solution corresponds to 100 µg of nickel, Ni.

J.3.9 *Standard cadmium solution.* Dissolve (1.000 ± 0.001) g of cadmium metal in a minimum of dilute hydrochloric acid solution (**J.3.4**). Cool. Make up to 1000 ml in a graduated flask and mix well. Further dilute 10 ml of this solution to 100 ml in a graduated flask. Mix well. 1 ml of the diluted solution corresponds to 100 µg of cadmium, Cd.

NOTE 1. A composite standard of the metals can be made up by diluting 10 ml of each of the metal stock solutions in a single 100 ml graduated flask. 1 ml of the standard solution corresponds to 100 µg of each element.

NOTE 2. Commercial solutions can be obtained from recognized suppliers for each of the above elements.

J.4 Procedure

J.4.1 *Preparation of Standards*

Into three 250 ml beakers, add 18 g of the concentrated sulfuric acid (**J.3.2**). Carefully add approximately 30 ml of water and cool. Then add 0, 1.0 ml and 2.0 ml of each of the standard solutions (**J.3.5** to **J.3.9**) or the same volumes of the composite metal standard (see note table J.1). Transfer quantitatively each standard to a separate 100 ml one mark volumetric flask. Add 2 ml of the dilute nitric acid (**J.3.3**). Make up to the mark and mix. These standard solutions contain 0, 1.0 and 2.0 $\mu g \cdot ml^{-1}$ of each element.

J.4.2 *Calibration*

J.4.2.1 Aspirate the standards (**J.4.1**) in turn, including the blank, and obtain a calibration curve for each element using the settings given in table J.2 for each element.

J.4.2.2 Prepare a calibration graph for each element, having micrograms per millilitre as abscissa and absorbance as ordinate.

Table J.2 Instrument settings for each element

Element	Copper	Manganese	Chromium	Nickel	Cadmium
Wavelength (nm)	324.8	279.5	357.9	232.0	228.8
Background correction	No	Yes	No	Yes	No
Flame	All air/acetylene optimized for each element.				
Lamp current	Follow manufacturers recommended settings.				
Slit width	Follow manufacturers recommended settings.				

NOTE. Modern instruments have the facility to generate their own calibration curves either by an internal microprocessor or an external computer. If an instrument without such facility is used, a graph of absorbance against metal content should be drawn.

J.4.3 *Determination*

J.4.3.1 *Preparation of the sample solution*

The sulfate content of the solutions causes an interference effect on the absorption of these elements because of viscosity effects. It is therefore essential to matrix match the standards with the sample under test.

Take a volume of the acid under test as given in table J.3.

Table J.3 Volume of acid

Relative density at 20 °C	Volume ml
1.700	25 ± 1
1.400	42 ± 1
1.280	63 ± 1

NOTE. These volumes are calculated from the equation:

$$v = \frac{29.6 \times 1}{g\rho}$$

where

- g is the percentage by mass of sulfuric acid in the sample, derived from its relative density 20 °C;
- ρ is the relative density of the sample at 20 °C.

NOTE. 29.6 is the percentage by mass of sulfuric acid in the reference acid (sulfuric acid of relative density 1.215 at 20 °C) and 100 is the mass in grams of sulfuric acid in the reference acid (sulfuric acid of relative density 1.215 at 20 °C).

Prepare the test portion by adding the required volume carefully to a tared 250 ml beaker and reweighing to the nearest 0.01 g. With acids of relative density 1.700 g/ml and 1.400 g/ml carefully dilute the test portion with water to approximately 70 ml and cool.

Prepare the sample solution by transferring the test portion or diluted test portion quantitatively to a 100 ml one mark graduated flask and make up to the mark with water.

J.4.3.2 *Measurement of sample solution*

Aspirate the test solution several times, alternating with the blank solution. Obtain a net absorbance and refer to the calibration graphs to obtain the concentration of each element.

NOTE. In the event that any solution gives a reading outside the range of the calibration graph, take a new, test portion, reduced to the volume that will bring it into the range of the calibration graph and repeat the determination. New standards should also be made to reflect the dilution of the sample.

J.5 Calculation

The element content, expressed in micrograms per kilogram at 1.215 g·ml -1 is given by the equation:

$$\text{Element} = \frac{M \times 100 \times F}{m}$$

where

- M is the concentration of element in the test solution, in micrograms per millilitre;
- F is the correction factor (see annex A);
- m is the mass of the test portion in grams.

Report the result as the mean of duplicate determinations to two significant figures.

Annex K (normative)

Summary of specification requirements and conversions to other acid concentrations

Table K.1 gives a list of the limits specified on reference acid (acid of relative density 1.215 at 20 °C) and their conversion to an equivalent limit for commonly used 100 %, 77 % and 50 % sulfuric acid.

Table K.1 Limits specified on reference acid (acid of relative density 1.215 at 20 °C) and their conversion to an equivalent limit for 100 %, 77 % and 50 % sulfuric acid

Impurity	**Limit specified on acid of relative density 1.215 at 20 °C** mg·kg^{-1}	**Equivalent limit for 50 % H_2SO_4 relative density 1.400 at 20 °C** mg·kg^{-1}	**Equivalent limit for 77 % H_2SO_4 relative density 1.700 at 20 °C** mg·kg^{-1}	**Equivalent limit for 100 % H_2SO_4 relative density 1.840 at 20 °C** mg·kg^{-1}
Residue on ignition	150	275	424	550
Chloride	7.0	12	18	24
Sulfur dioxide	5.0	9	13	17
Ammoniacal nitrogen	50	85	131	170
Nitrogen oxides	5.0	9	13	17
Iron	12	21	32	41
Copper	7.0	12	18	24
Manganese	0.1	0.2	0.2	0.3
Arsenic	2.0	3.4	5.2	6.8
Nickel	0.6	1.0	2.0	2.0
Chromium	0.2	0.5	0.8	1.0
Cadmium	0.2	0.4	0.5	0.7

blank

List of references

Normative references

BSI publications

BRITISH STANDARDS INSTITUTION, London

BS 612 : 1966	*Specification for Nessler cylinders*
BS 846 : 1985	*Specification for burettes*
BS 1792 : 1982	*Specification for one-mark volumetric flasks*
BS 2461 : 1983	*Specification for gas washing bottles*
BS 4366 : 1993	*Specification for industrial nitrogen*
BS 4404 : 1968	*Method for the determination of arsenic (silver diethyldithiocarbamate procedure)*
BS EN ISO 3696 : 1995	*Water for analytical laboratory use. Specification and test methods*

Informative references

BSI publications

BRITISH STANDARDS INSTITUTION, London

BS 753 : 1987	*Schedule for density-composition tables for aqueous solutions of sulphuric acid*

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