*Draft Indian Standard*

# METHODS OF CHEMICAL ANALYSIS OF NICKEL ANODES

First Reprint FEBRUARY 1977

(Incorporating Amendment No. 1)

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*Indian Standard*

# METHODS OF CHEMICAL ANALYSIS OF NICKEL ANODES

## 0. FOREWORD

**0.1** This Indian standard was adopted by the Indian Standards Institution on 1 July 1963, after the draft finalized by the methods of Chemical Analysis Sectional committee had been approved by the Structural and Metal Division Council.

**0.2** Since nickel anodes used in electroplating should be of the highest possible purity, from 99 to 100 percent nickel, the correct analysis of the impurities is necessary to determine its purity. The sectional committee, therefore, felt the need for formulating this standard which lays down standard methods for analyzing nickel anodes.

**0.3** The methods of analysis prescribed in this standard have been prepared with a view that they shall be useful primarily as referee methods and could also be used by laboratories for their day to day work.

**0.4** While preparing this standard, the views of producers, consumers and testing authorities, relating to the technological methods followed in the country in this field were taken into account. Due weightage has also been given to the need for international co-ordination among standards prevailing in different countries of the world in this field. With these views, assistance has been derived from the following publications:

B.S. 558 & 564: 1953 NICKEL ANODES AND NICKEL SALTS FOR ELECTRO-PLATING. British Standards Institution.

1962 BOOK OF ASTM MITHODS rot CHIMICAL ANALYSIS or MILTALS. American Society for Testing and Materials.

FURMAN N. H. (Ed). SCOTT, W. W. Standard Methods of Chemical Analysis. 5th ed. New York. D. Van Nostrand COMPANY Inc., 1962.

HILLEBRAND, W. F., LUNDELL G. E. F. & BRIGHT, H. A. Applied Inorganic Analysis. 2nd ed. New York. John Wiley & Sons, 1955.

**0.5** Wherever a reference to any Indian Standard appears in this standard, it shall be taken as a reference to the latest version of the standard.

0.6 In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960 Rules for Rounding off Numerical Values (*Revised*).

## 1. SCOPE

**1.1** This standard prescribes methods for determination of nickel, cobalt, copper, lead, iron, manganese, silicon, sulphur, carbon and zinc within the ranged as specified in *IS 1958-1961 Specification for Nickel Anodes for Electroplating.

## 2. SAMPLING

**2.1** Sampling for chemical analysis of nickel anodes shell be done in accordance with *IS : 1958-1961 Specification for Nickel Anodes for Electroplating.

## 3. QUALITY OF REAGENTS

**3.1** Unless specified otherwise, pure chemicals and distilled water [*see* IS : 1070-1960 Specification for Water, Distilled Quality (*Revised*)] shall be employed in the tests.

NOTE – ‘Pure chemicals’ shall mean chemicals that do not contain impurities which affect the results of analysis

## 4. GENERAL

**4.1 Use of Filter Paper** — In some of the methods given in this standard, only relative numbers of Whatman filter papers have been given since they are commonly used. However, any other brand of filter paper of corresponding porosity may also be used.

## 5. DETERMINATION OF NICKEL BY THE DIMETHYLGLYOXIME (GRAVIMETRIC) METROD

**5.1 Outline of the Method** - The sample is dissolved in nitric acid and silicic acid is dehydrated by means of perchloric acid. Nickel in the solution of the sample is precipitated by diamethylglyoxime in ammoniacal medium, filtered, dried and weighed as nickel dimethylglyoxime.

### 5.2 Reagents

**5.2.1** *Dilute Nitric Acid* -1:1 (*v/v*).

**5.2.2** *Perchloric Acid* — 70 percent.

**5.2.3** *Dilute Hydrochloric Acid* — 1:5 (*v/v*).

**5.2.4** *Tartaric Acid Solution* — 20 percent (*w/v*).

**5.2.5** *Concentrated Ammonium Hydroxide* — 20 percent.

**5.2.6** *Dimethylglyoxime Solution* — one percent (*w/v*). Dissolve one gram of dimethylglyoxime in 100 ml of rectified spirit [conforming to IS : 323-1959 Specification for Rectified Spirit (*Revised*)]. Filter the solution before use.

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*Since revised.

### 5.3 Procedure

**5.3.1** Transfer accurately one gram of the sample to a 400-ml beaker and add 20 ml of dilute nitric acid. Heat gently until action ceases. Add 10 ml of perchloric acid and evaporate the solution to white fumes. Heat till silicic acid has been dehydrated. Cool and add 100 ml of water and heat to dissolve the nickel salt. Filter the solution into a 600-ml beaker. Wash the paper and the residue with hot dilute hydrochloric acid. Discard the residue and transfer the filtrate to a one-litre volumetric flask. Make up the volume to the mark.

**5.3.2** Take 25 ml from the solution prepared under **5.3.1** in a beaker and add 20 ml of tartaric acid solution. Neutralize with concentrated ammonium hydroxide and add dilute hydrochloric acid until slightly acidic. Dilute the solution to about 500 ml and heat to 60° to 80°C. Add 40 ml of the dimethylglyoxime solution for each 0.1 g of the nickel present. Add 5 to 10 ml in excess. Render the solution slightly alkaline with concentrated ammonium hydroxide and digest at 60°C for about 30 minutes. Stir vigorously and allow to cool to room temperature slowly while stirring occasionally. Filter the precipitate on a weighed sintered crucible (G-3; 30 to 50-ml capacity) and wash it with cold water. Keep the filtrate overnight to make sure that nickel has been completely precipitated.

**5.3.3** Dry the precipitate obtained under **5.3.2** at 110° to 120°C to constant weight. Cool in a desiccator and weigh as nickel dimethyl-glyoxime.

### 5.4 Calculation

$$\text{Nickel, percent} = \frac{A \times 20.32}{B}$$

where

$A$ = weight in g of nickel dimethylglyoxime, and

$B$ = weight in g of the sample represented by the aliquot taken.

## 6. DETERMINATION OF COBALT BY THE NITROSO-R-SALT (PHOTOMETRIC) METHOD

**6.1 Outline of the method** — After the removal of interfering elements like copper, iron, etc, the hot solution of the sample buffered with sodium acetate is complexed with nitroso-R-salt and photometric measurement is made of an orange coloured complex at approximately 520 mμ.

### 6.2 Reagents

**6.2.1** *Dilute Nitric Acid* — 1:1 (*v/v*).

**6.2.2** *Hydrofluoric Acid* — 40 percent.

**6.2.3** *Hydrogen Sulphide* — gas.

**6.2.4** *Dilute Hydrochloric Acid* — 1:1 (*v/v*).

**6.2.5** *Nitroso-R-Salt Solution* — one percent (*w/v*). Dissolve 0.10 g of nitroso-R-salt in water, filter and dilute to 100 ml. Do not keep the solution for more than a week.

**6.2.6** *Sodium Acetate* — solid.

**6.2.7** *Concentrated Hydrochloric Acid* — sp 1.16 [conforming to IS : 263-1962 Specification for Hydrochloric Acid ( *Revised*)].

**6.2.8** *Standard Cobalt Solution (1 ml = 0.1 mg of Co)* — Dissolve 0.67 g of pure cobalt ammonium sulphate (AR) [$CoSO_4 . (NH_4)_2SO_4 . 6H_2O$] in water and dilute to one litre.

**6.3 Procedure**

**6.3.1** Transfer 2 g of an accurately weighed sample to a 400-ml beaker and dissolve it in 25 to 30 ml of dilute nitric acid. Cover the beaker with a watch-glass, heat on a steam bath and boil gently. If silicic acid appears, add few drops of hydrofluoric acid to dissolve it. Continue heating until action ceases. Evaporate the solution until it becomes syrupy and a thin scum forms on the surface. Add 50 ml of hot water and heat until the syrup dissolves. Filter and wash the residue with hot water.

**6.3.2** Dilute the filtrate to about 100 ml and heat to 60°C. Pass hydrogen sulphide through the hot solution and continue passing the gas till the solution cools down. Add a small amount of paper pulp and filter the sulphides. Transfer the solution to a one-litre volumetric flask and make up the volume to the mark.

**6.2.3** Take a suitable aliquot from the solution so that it contains between 0.001 and 0.02 mg of cobalt. Evaporate almost to dryness; dissolve the residue in 10 ml of water containing 0.5 ml each of dilute hydrochloric acid and nitroso-R-salt solution. Add 2 g of sodium acetate. The *p*H of the solution at this point should be 5.5. Boil for a minute, cool and add 1.5 ml of concentrated hydrochloric acid. Boll further for a minute, cool and dilute to 50 ml in a volumetric flask.

**6.3.4** Transfer a suitable portion of the solution prepared under **6.3.3** to an absorption cell and take the photometric reading using light filter at 520 mμ.

**6.3.5** Take a series of standard solutions of cobalt and a reagent blank. Using the same quantities of reagents, carry through all stages as described under **6.3.3** and **6.3.4**, and record the photometric readings of all the standard solutions along with the blank. Construct a calibration curve by plotting the photometric readings of standard solutions against the quantities of cobalt.

**6.3.6** Convert the photometric reading of the sample to milligrams of cobalt by means of the calibration curve and calculate as under **6.4**.

**6.4 Calculation**

$$\text{Cobalt, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A$ = weight in mg of cobalt found in the aliquot of the solution, and

*B* = weight in g of the sample represented by the aliquot taken.

## 7. DETERMINATION OF COPPER AND LEAD BY THE COLORMETRIC METHOD

**7.1 Outline of the Method** — After removal of silica, the solution of the sample is electrolyzed. Copper and lead are deposited on cathode and anode respectively, dissolved in nitric acid and determined Colorimetrically.

### 7.2 Apparatus

**7.2.1** *Platinum Electrodes* — with or without rotating stirrer.

**7.2.1.1** *Cathode* — It shall be formed either from a sheet or wire gauze and shall have a depositing surface of about 100 sq cm.

**7.2.1.2** *Anode* — It shall be in the form of a spiral.

### 7.3 Reagents

**7.3.1** *Dilute Nitric Acid* — 1:1 (*v/v*).

**7.3.2** *Concentrated Nitric Acid* — sp gr 1.42 (conforming to *IS : 264-1950 Specification for Nitric Acid).

**7.3.3** *Perchloric Acid* — 70 percent.

**7.3.4** *Dilute Hydrochloric Acid* — 1:1 (*v/v*)

**7.3.5** *Dilute Ammonium Hydroxide* — 1:1 (*v/v*).

**7.3.6** *Standard Copper Solution (*1 *m* = 0.0001 *g of Cu)* — Dissolve 0.1000 g of copper in 10 ml of dilute nitric acid (1:3). Add 5 ml of concentrated sulphuric acid, cover and evaporate to dense white fumes, cool, wash down the cover and walls of the vessel with 20 ml of water and again evaporate to white fumes. Add 200 ml of dilute sulphuric acid (1:1), cool and dilute to one litre in a volumetric flask.

**7.3.7** *Hydrogen Peroxide* — 3 percent.

**7.3.8** *Ammonium Acetate Solution (*3 *N approx)* — Dissolve 23 g of ammonium acetate in water and 3 ml of glacial acetic acid and dilute to 100 ml.

**7.3.9** *Sucrose Solution* — 50 percent (*w/v*).

**7.3.10** *Hydrogen Sulphide Solution* — Saturate dilute sulphuric acid (1:99) with hydrogen sulphide gas.

**7.3.11** *Standard Lead Acetate Solution* — Dissolve 0.1831 g of lead acetate $[Pb(C_2H_3O_2)_2\ 3H_2O]$ in water containing a little acetic acid, and dilute to one litre.

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*Since revised.

### 7.4 Procedure

**7.4.1** Transfer 5 g of the accurately weighed sample to a 600-m1 beaker and dissolve it in 50 ml of dilute nitric acid. Further, carry out the procedure as given in **6.3.1** and **6.3.2** for separating the sulphides. Preserve the precipitate.

**7.4.2** Transfer the precipitate to the original beaker and add 15 ml of concentrated nitric acid followed by 5 ml of perchloric acid. Evaporate the mixture to dense white fumes. Boil gently for 5 minutes taking care that most of perchloric acid is retained. Allow the solution to cool and add 50 ml of water and 2 ml of concentrated nitric acid. Boil until the salts dissolve.

**7.4.3** Transfer the solution to a 250-m1 electrolytic beaker, filter if necessary, and wash the residue with hot water and discard it.

**7.4.4** Dilute the solution to 125 ml and add one drop of dilute hydro-chloric acid. Electrolyze overnight using platinum gauze electrodes and a current density of 0.3 to 0.4 A/$dm^2$ until deposition of copper is complete. This will be indicated by the failure to plate on the new exposed surface of the cathode when the level of the solution is raised. When no copper appears, it can be assumed that all the lead has also been deposited on the anode. Without breaking the current, raise the electrode assembly and rinse thoroughly with water.

**7.4.5** Dissolve the cathodic deposit in 25 ml of dilute nitric acid. Make the solution alkaline with dilute ammonia and add 10 ml in excess. Dilute to 50 ml in a graduated flask and transfer the solution or a suitable aliquot to a Nessler tube ($N_1$). In another Nessler tube ($N_2$), take an equal volume of water and dilute ammonium hydroxide. Add from a graduated pipette standard copper solution slowly to the Nessler tube ($N_2$) until the colours in both the tubes match approximately. Dilute the contents of both the tubes to the mark and stir. Compare the intensities of colours in a suitable type of colorimeter and calculate the copper content as given in **7.5**.

**7.4.6** Dissolve the deposit of lead peroxide obtained under **7.4.4** in 5 ml of dilute nitric acid and a few drops of hydrogen peroxide. Evaporate to dryness and take up with water. Transfer to a 50-ml graduated flask and dilute to the mark and mix well.

**7.4.7** Pipette out a suitable aliquot into a 100-ml Nessler tube ($N_1$). In another Nessler tube ($N_2$), take an equal quantity of water. Add 6 ml of ammonium acetate solution, 3 drops of dilute nitric acid, one millilitre of sucrose solution and 6 ml of hydrogen sulphide solution to both the tubes. Add from a graduated pipette standard lead solution to the Nessler tube ($N_2$) until the colours in both the tubes match approximately. Dilute the contents of both the tubes to the mark and stir. Compare the intensities of colours in a suitable type of colorimeter and calculate the lead content as given in **7.5**.

### 7.5 Calculations

$$\text{Copper, percent} = \frac{A}{B} \times 0.01$$

$$\text{Lead, percent} = \frac{C}{D} \times 0.01$$

where

*A* = volume in ml of standard copper solution required for matching the colour of the test solution,

*B* = weight in g of the sample represented by the aliquot taken,

*C* = volume in ml of standard lead solution required for matching the colour of the test solution, and

*D* = weight in g of the sample represented by the aliquot taken.

## 8. DETERMINATION OF IRON BY THE DICHROMATE (VOLUMETRIC) METHOD

**8.1 Outline of the Method** — Iron is reduced in a boiling solution with stannous chloride solution adding a slight excess of the latter. The excess of stannous chloride is destroyed with mercuric chloride solution and the reduced iron is titrated with standard potassium dichromate solution, using sodium diphenylamine sulphonate as an internal indicator.

### 8.2 Reagents

**8.2.1** *Concentrated Nitric Acid* — *see* **7.3.2**.

**8.2.2** *Concentrated Ammonium Hydroxide* — 20 percent.

**8.2.3** *Dilute Ammonium Hydroxide* — 5:95 (*v/v*).

**8.2.4** *Dilute Hydrochloric Acid* — 1:1, 1:3 and 5:95 (*v/v*).

**8.2.5** *Stannous Chloride Solution* — Dissolve by heating 60 g of pure stannous chloride in a mixture of 400 ml of concentrated hydrochloric acid and 600 ml of water until the solution is complete. Cool, add a few pieces of granulated tin and present the solution in an air-tight amber-coloured bottle to prevent oxidation.

**8.2.6** *Mercuric Chloride Solution* — Prepare a saturated solution of mercuric chloride in water.

**8.2.7** *Concentrated Sulphuric Acid* — sp gr 1.84 [conforming to IS: 266-1961 Specification for Sulphuric Acid (*Revised*)].

**8.2.8** *Phosphoric Acid* — 85 percent.

**8.2.9** *Sulphuric-Phosphoric Acid Mixture* — Add slowly 150 ml of concentrated sulphuric acid to 700 ml of water with continuous stirring. Add to this 150 ml of syrupy phosphoric acid. Destroy any oxidizable impurities by adding potassium permanganate solution (0.1 N), drop by drop, until the pink colour of permanganate persists, and cool the solution.

**8.2.10** *Sodium Diphenylamine Sulphonate Indicator Solution* — Dissolve 0.32 g of barium diphenylamine sulphonate in 100 ml of hot water. Add 0.5 g of sodium sulphate, stir, allow to settle, and filter off the precipitate of barium sulphate. Store in a dark-coloured bottle.

**8.2.11** *Standard Potassium Dichromate Solution* — 0.02 N. Dry pure potassium dichromate in an oven at 105° to 110°C for one and a half hours. Cool in a desiccator and transfer exactly 0.9806 g to a one-litre volumetric flask carefully through a funnel using water at room temperature. Wash the funnel thoroughly and dissolve the salt by shaking until the solution is complete. Make up to the mark and mix well. Preserve the solution in an amber-coloured bottle.

### 8.3 Procedure

**8.3.1** Dissolve 5 g of the sample in a 600-m1 baker in 35 ml of concentrated nitric acid. Heat the solution gently until action ceases. When solution is clear, boil it until brown fumes are no longer evolved, and dilute to 100 ml. Make the solution strongly ammoniacal, adding sufficient amount of concentrated ammonium hydroxide and boil for one minute. Filter the precipitate through filter paper No. 41 and wash with dilute ammonium hydroxide. Dissolve the precipitate with hot dilute hydrochloric acid (1:1) and reprecipitate iron and filter it. Dissolve the precipitate in 40 ml of hot dilute hydrochloric acid (1:3) receiving the solution in a 500-ml conical flask and washing the paper with hot dilute hydrochloric acid (5:95).

**8.3.2** Heat the solution to boiling and to the boiling solution add stannous chloride solution, drop by drop, with continuous stirring until the solution just becomes colourless. Add 2 to 3 drops excess of stannous chloride solution and wash down the sides with a little water. Cool the flask rapidly under running tap water until the contents have cooled down to room temperature.

**8.3.3** Add excess of mercuric chloride solution (about 5 ml) and shake the flask. At this stage, a silky white precipitate appears. If it fails to appear or if a blackish precipitate appears, reject the test. If the precipitate is too much, add further 5 ml of mercuric chloride solution. Keep for about 2 to 5 minutes and add 15 ml of sulphuric-phosphoric acid mixture, and dilute to about 250 ml, washing down the sides of the flask. Add 3 to 4 drops of sodium diphenylamine sulphonate indicator solution and titrate slowly with standard potassium dichromate solution stirring continuously until the green colour begins to darken. Continue the titration slowly till a drop of the dichromate solution produces a reddish violet colouration.

**8.3.4** Carry out a blank determination following the same procedure and using the same amounts of all reagents, but without the sample.

### 8.4 Calculation

$$\text{Iron, percent} = \frac{(A - B)\,C \times 5.585}{D}$$

where

$A$ = volume in ml of the standard dichromate solution required for titration of the sample,

$B$ = volume in ml of the standard dichromate solution required for the blank titration,

$C$ = normality of the standard dichromate solution, and

$D$ = weight in g of the sample taken.

## 9. DETERMINATION OF MANGANESE BY THE PERSULPHATE-ARSENITE METHOD

**9.1 Outline of the Method** — After the removal of iron, manganese in the solution of the sample is oxidized with ammonium persulphate in the presence of silver nitrate and titrated with sodium arsenite solution.

### 9.2 Reagents

**9.2.1** *Concentrated Nitric Acid* — see **7.3.2**.

**9.2.2** *Zinc Oxide* — emulsion.

**9.2.3** *Dilute Nitric Acid* — 1:1 (*v/v*).

**9.2.4** *Ammonium Persulphate Solution* [$(NH_4)_2S_2O_8$] — Dissolve 250 g of the reagent in water and dilute to one litre. If the salt is of less than 95 percent strength, the necessary equivalent shall be used. Prepare the solution immediately before use.

**9.2.5** *Silver Nitrate Solution* — 0.1 percent (*w/v*).

**9.2.6** *Sodium Chloride Solution* — 10 percent (*w/v*).

**9.2.7** *Standard Sodium Arsenite (Stock) Solution* — To 15 g of arsenous oxide in a 500-ml flask, add 45 g of sodium carbonate and 150 ml of distilled water. Heat the flask and contents on the steam-bath until the arsenous oxide is dissolved, Cool the solution, filter and make up to one litre with distilled water.

**9.2.8** *Standard Sodium Arsenite Solution* — Mix 200 ml of the sodium arsenite (stock) solution with 2500 ml of distilled water and standardize against potassium permanganate (0.01 N) or a standard manganese alloy containing about one percent manganese, by dissolving 0.2 g of the latter in 30 ml of mixed acids (200 ml water, 400 ml each of concentrated sulphuric acid and concentrated nitric acid) and carry through procedure indicated below.

### 9.3 Procedure

**9.3.1** Dissolve *one gram of the accurately weighed sample in 10 ml of concentrated nitric acid in a 400-m1 beaker. Heat gently till the dissolution is complete. To the boiling solution add zinc oxide emulsion in small increments until an excess of zinc oxide is present. Heat the beaker on a steam bath for 15 minutes. Filter the solution through filter paper No. 40 into a 500-ml conical desk. Wash the precipitate and the filter paper with hot water.

**9.3.2** Heat the solution to boiling and add 10 ml of dilute nitric acid. Keep boiling for some time Add 10 ml of ammonium persulphate solution and 5 ml of silver nitrate solution. Boil briskly for one to two minutes. Add 50 ml of water and cool to about 30ºC. Add a few drops of sodium chloride solution and filter out the silver chloride precipitate, if necessary. Titrate rapidly (*see*

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*If the manganese contents is below 0.1 percent, 2 to 8 g of sample should be taken.

Note) with standard sodium arsenite solution to clear yellow end point that remains unchanged on further addition of standard arsenite solution.

NOTE — If the titration is not carried out rapidly, part of manganese may, be reoxidized by ammonium persulphate during the titration, thus yielding high results.

### 9.4 Calculation

$$\text{Manganese, percent} = \frac{A \times B}{C} \times 100$$

where

$A$ = volume in ml of the standard arsenite solution,

$B$ = manganese equivalent of the sodium arsenite solution in g per ml, and

$C$ = weight in g of the sample taken.

## 10. DETERMINATION OF SILICON BY THE PERCHLORIC ACID METHOD

**10.1 Outline of the Method** — The sample 11 dissolved in nitric acid and perchloric acid and the solution evaporated to dehydrate silica. The residue is filtered and ignited. The silica is volatilized by treatment with hydrofluoric acid. Loss in weight of the residue represents silica.

### 10.2 Reagents

**10.2.1** *Concentrated Nitric Acid — see* **7.3.2**.

**10.2.2** *Perchloric Acid* — 70 percent.

**10.2.3** *Dilute Hydrochloric Acid* — 5:95 (*v/v*).

**10.2.4** *Concentrated Sulphuric Acid — see* **8.2.7**.

**10.2.5** *Hydrofluoric Acid* — 40 percent.

### 10.3 Procedure

**10.3.1** Dissolve 15 to 20 g of the sample in a 400-ml beaker in 35 ml of concentrated nitric acid. When action ceases, add 25 ml of perchloric acid. Evaporate the solution to dense white fumes. Then boil the solution gently for 10 minutes at such a rate that the bulk of the perchloric acid vapour condenses on the beaker wall and is retained. Allow the solution to cool, add 100 ml of warm water and stir until the perchlorates have dissolved. Filter the residue through filter paper No. 41 and wash thoroughly with hot dilute hydrochloric acid and then with hot water, till all perchloric acid is washed off.

**10.3.2** Transfer the filter paper and residue to a platinum crucible. Ignite the crucible at low temperature until the paper has been consumed and then ignite for 10 to 15 minutes. Cool in a desiccator and weigh.

**10.3.3** Add one or two drops of concentrated sulphuric acid and about 10 ml of hydrofluoric acid to dissolve the residue. Evaporate the solution slowly to dense white fumes. Continue to heat the crucible till sulphuric acid has been expelled. Ignite at 900° to 950°C for five minutes. Cool in a desiccator and weigh. The loss in weight represents silica.

**10.3.4** Carry out a blank determination following the same procedure and using the same amount of all reagents, but without the sample.

### 10.4 Calculation

$$\text{Silicon, percent} = \frac{(A - B) \times 46.72}{C}$$

where

*A* = weight in g of silica obtained under **10.3.3**,

*B* = weight in g of silica obtained from the blank determination, and

*C* = weight in g of the sample taken.

## 11. DETERMINATION OF SULPHUR BY THE EVOLUTION (IODIMETRIC) METHOD

**11.1 Outline of the Method** — By dissolving the sample in hydrochloric acid, hydrogen sulphide is liberated from the sample. This is swept from the flask by a stream of hydrogen gas into an ammoniacal zinc sulphate solution when sulphur is estimated by titration.

**11.2 Apparatus** — An all-glass apparatus as shown in Fig. 1 shall be used. Hydrogen supplied from a Kipp's generator or a cylinder of hydrogen is freed from hydrogen sulphide by passing through lead acetate solution held in bottle (*A*). The decomposition flask (*D*) shall be provided with a funnel (*B*) and a ground glass stop cock (*C*). The tube (*E*) dips just beneath the surface of 25 ml of water in 125-m1 flask (*F*). An ammoniacal solution of zinc sulphate shall be placed in 125-m1 flask (*G*). The water serves to collect the hydrochloric acid that distills over and prevents the absorbent solution in flask (*G*) from becoming acid.

### 11.3 Reagents

**11.3.1** *Hydrogen* — gas

**11.3.2** *Ammoniacal Zinc Sulphate Solution* — Dissolve 10 g of zinc sulphate in 100 ml of dilute ammonium hydroxide solution (1:1).

**11.3.3** *Dilute Hydrochloric Acid* — 1:1 (*v/v*).

**11.3.4** *Starch Solution* — Make a suspension of one gram of soluble starch in about 10 ml of water and add it carefully to 100 ml of boiling water. Boil for 2 to 3 minutes and cool. Prepare the solution fresh as needed.

**11.3.5** *Standard Potassium Iodate Solution* — 0.02 N. Dissolve 0.7134 g of potassium iodate in 150 ml of water containing 0.2 g of sodium hydroxide and add 4 g of potassium iodide. When the solution is complete, dilute to one litre in a volumetric flask.

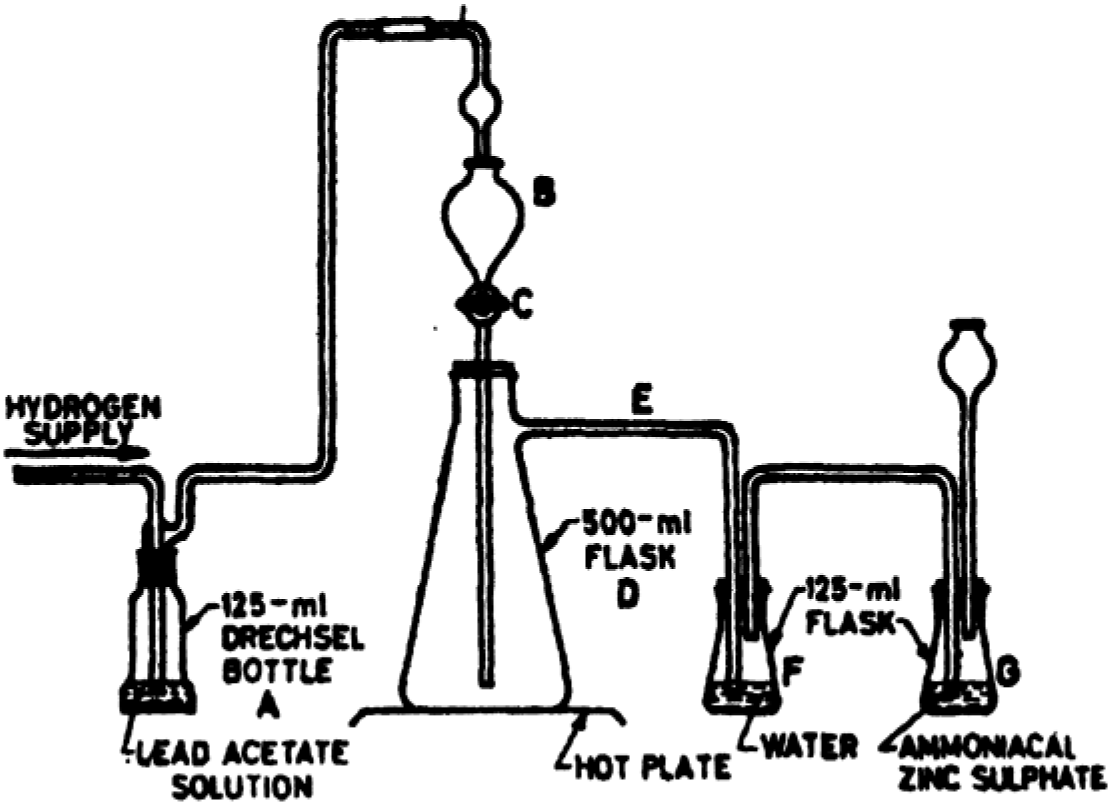

FIG. 1 APPARATUS FOR THE DETERMINATION OF SULPHUR BY THE EVOLUTION (IODIMETRIC) METHOD

**11.3.6** *Standard Sodium Thiosulphate Solution* — 0.2 N. Dissolve about 4.96 g of sodium thiosulphate ($Na_2S_2O_3$, $5H_2O$) in one litre of freshly boiled and cooled water. Store the solution in an amber coloured bottle. Standardize the solution with potassium iodate.

## 11.4 Procedure

**11.4.1** Transfer 5 g of the accurately weighed sample to a 500-m1 decomposition flask (*D*) and assemble the apparatus as shown in Fig 1. Displace the air in the system with hydrogen, close stop cock (*C*), and shut off the hydrogen at its source. Disconnect the hydrogen line from the funnel (*B*), transfer 100 ml of dilute hydrochloric acid to the funnel and then replace the hydrogen at its source. Warm the decomposition flask (*D*) to 40° to 50°C in order to hasten the solution. When the solution is complete, heat to boiling for two minutes, and continue the flow of hydrogen for five minutes more.

**11.4.2** Disconnect flasks (*F*) and (*G*) from the train, and then turn off the hydrogen and the source of heat. Add a measured excess of standard potassium iodate solution in flask (*G*) and also add 40 ml of dilute hydrochloric acid. Titrate the excess potassium iodate solution with standard sodium thiosulphate solution in presence of one millilitre of starch solution which should be added near the end point when the solution is of straw colour.

### 11.5 Calculation

$$\text{Sulphur, percent} = \frac{(A - B) \times C \times 1.6}{D}$$

when

$A$ = volume in ml of the total standard potassium iodate solution added,

$B$ = volume in ml of the standard potassium iodate solution left,

$C$ = normality of the standard potassium iodate solution, and

$D$ = weight in g of the sample taken.

## 12. DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION (GRAVIMETRIC) METHOD

**12.1 Outline of the Method** — The sample is burnt in a stream of pure oxygen, and the resulting carbon dioxide is absorbed in soda asbestos after removal of the contaminants. The increase in weight of the absorbent is proportional to the carbon content of the sample.

**12.2 Apparatus** — The assembly of apparatus is shown in Fig. 2.

**12.2.1** *Source of Oxygen Supply* — gas holder (*A*) capacity 8 to 10 litres containing 99.5 percent oxygen free from carbonaceous matter connected by rubber tubing with the gas purifying train. The gas holder should be filled up before starting the operation.

**12.2.2** *Oxygen Purification Train* — consists of Arnold bottles (*B*) and (*C*), the latter containing concentrated sulphuric acid, the exit bulb of which is packed with glass wool and another absorption bottle (*D*) containing soda asbestos which passes through IS Sieve 1.40 mm (width of aperture 1.40 mm) but is retained on IS Sieve 500 micron (width of aperture 0.500 mm) [*see* IS: 460-1962 Specification for Test Sieves (*Revised*)], and "anhydrone" in layers, connected in series between the gas holder and the inlet end of the combustion tube. A layer of about 12 mm of anhydrone is placed on top for removing moisture in the gas and the soda asbestos removes carbon dioxide in the gas.

**12.2.3** *Furnace* — a horizontal tube furnace (*E*) heated to about 1350°C by electricity.

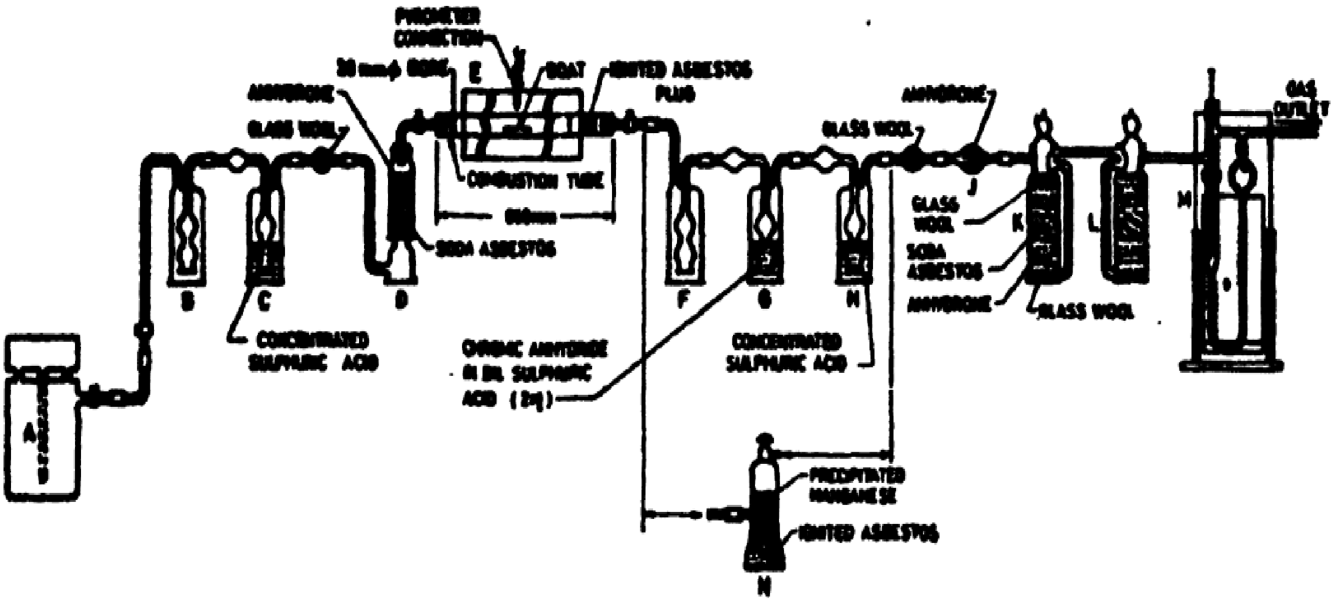

FIG. 2 APPARATUS FOR THE DETERMINATION OF CARBON (TOTAL) BY THE DIRECT COMBUSTION (GRAVIMETRIC) METHOD

**12.2.4** *Combustion Tube* — A combustion tube approximately 650 mm long and of 20 mm inner diameter, made of fused silica, fire-clay or any other suitable material should be used. In the exit end of the tube an ignited asbestos plug 75 mm long is placed lightly to retain ferric oxide carried over by the gas stream.

**12.2.5** *Absorption Train* — consists of an Arnold bottle (*F*) to prevent back suction, a gas absorption bottle (*G*) filled with chromic anhydride in dilute sulphuric acid [2:1 (*v/v*)] to remove oxides of sulphur from the gas stream, a bottle (*H*) containing about 10 ml of concentrated sulphuric acid to remove most of the moisture from exit gas. The exit end of this bottle is filled with glass wool to remove sulphuric acid mist, one tube (*J*) containing "anhydrone" or any other suitable desiccant and carbon dioxide absorption bottle (*K*) (80 ml capacity) containing a layer of soda asbestos or ascarite, which should be uniformly graded and evenly packed with a layer of anhydrone on the top, all connected in series with the exit end of the combustion furnace and the atmosphere. The fillings in (*K*) are held in position by small plugs of glass wool. A bottle (*L*), packed similarly to bottle (*K*), acts as a guard against atmospheric gases. Its exit end is attached to a flowmeter. Bottles (*F*), (*G*) and (*H*) may be replaced by a Midvale or Nesbitt bulb (*N*) containing precipitated manganese dioxide over ignited asbestos.

## 12.3 Reagents

**12.3.1** *Concentrated Sulphuric Acid* — *see* **8.2.7**.

**12.3.2** *Dilute Sulphuric Acid* — 2:98 (*v/v*).

**12.3.3** *Chromic-Sulphuric Acid Solution* — Saturate 100 ml of dilute sulphuric acid (2:1) with chromic anhydride.

**12.3.4** *Manganese Sulphate* — solid.

**12.3.5** *Concentrated Ammonium Hydroxide* — 20 percent.

**12.3.6** *Ammonium Persulphate Solution* — 25 and 22.5 percent (*w/v*).

**12.3.7** *Precipitated Manganese Dioxide*— a) Dissolve 200 g of manganese sulphate ($MnSO_4$, $4H_2O$) in 2500 ml of water, add concentrated ammonium hydroxide until ammoniacal, followed by 1000 ml of freshly prepared ammonium persulphate solution (22.5 percent) and heat to boiling. Boil for 10 minutes, adding more of concentrated ammonium hydroxide to maintain the ammoniacal condition. Further addition of solutions of ammonium persulphate and ammonium hydroxide may be required until precipitation is judged to be complete.

b) Discontinue boiling and allow the precipitate to settle; wash by decantation 6 to 8 times with 500 to 600-m1 portions of water, allowing the precipitate to settle thoroughly between washings. Finally wash 2 to 3 times by decantation with 500 to 600-ml portions of dilute sulphuric acid. Transfer the precipitate to a Buchner funnel and wash with hot water until free from sulphates. Dry the residue at 105° to 110°C, grind to pass through IS Sieve 850 micron (width of aperture 0.850 mm) but retain on IS Sieve 710 micron (width of aperture 0.710 mm) [*see* IS : 460-1962 Specification for Test Sieves ( *Revised*)], and again dry thoroughly at 105° to 110°C.

**12.3.8** *Soda Asbestos* — It should be graded to pass through IS Sieve 1.40 mm (width of aperture l.40 mm) but retain on IS Sieve 500 micron (width of aperture 0.500 mm) [*see* IS : 460-1962 Specification for Test Sieves (*Revised*)].

**12.3.9** *Anhydrone or Magnesium Perchlorate* $Mg(ClO)_4$ — The supply bottle should be well stoppered.

**12.3.10** *Lead Foil* — This should be of assay grade and 0.127 mm in thickness.

**12.3.11** *Magnesite Brick Powder* — Magnesite brick powder which has passed through IS Sieve 500 micron (width of aperture 0.500 mm) shall be used for spreading in the boat on which the sample is to be placed before combustion. This powder shall be calcined in the open muffle furnace prior to use, in order to eliminate any carbonaceous matter.

**12.4 Procedure**

**12.4.1** Heat the furnace to a temperature between 1200° to 1300°C. Before starting an analysis, test the apparatus for any leaks. Pass a slow stream of oxygen for about 13 minutes through the whole train of the apparatus and then weigh the carbon dioxide absorption tube. A counter-poise of a similar tube is recommended in a balance for weighing. After taking the first weight, connect it back to the apparatus, pass oxygen for 15 minutes and weigh again. If constant weight is obtained, the apparatus is ready for use.

**12.4.2** Weigh 2.0 g of the sample mixed with 2.0 g of tin millings and place in a previously ignited combustion boat made of either porcelain, refractory, clay, nickel sheet or alumina and of dimensions 100 x 20 x 15 mm (or near about), with walls as thin as possible, and cover the sample with lead foil (1.5 g twice folded). Before placing the sample in the boat, sprinkle in the bottom of the boat some burnt magnesite brick dust which has been tested by the blank run (*see* **12.4.3**). Insert the boat quickly into the hot zone of the furnace, with the rubber stopper replaced at the end of the combustion tube, wait for about a minute so that the boat attains the temperature of the furnace and pass a rapid stream (150 to 200 ml per minute) of oxygen for 10 to 15 minutes to sweep out carbon dioxide. At the end of this period, remove the carbon dioxide absorption bulb, cool in a desiccator and weigh quickly against a similar tube used as a counterpoise. The increase in weight represents carbon dioxide.

**12.4.3** Carry out a blank determination on 2.0 g of tin millings which were used with the sample.

### 12.5 Calculation

$$\text{Carbon, percent} = \frac{(A - B) \times 27.29}{C}$$

where

$A$ = weight in g of carbon dioxide absorption tube after test,

$B$ = weight in g of carbon dioxide absorption tube in blank run, and

$C$ = weight in g of the sample taken.

## 13. DETERMINATION OF ZINC BY THE DITHIZONE (PHOTOMETRIC) METHOD

**13.1 Outline of the Method** — Zinc is extracted from the solution of the sample with diphenylcarbazone-amyl alcohol solution, and determined photometrically at about 530 mµ.

### 13.2 Reagents

**13.2.1** *Concentrated Hydrochloric Acid* — *see* **6.2.7**.

**13.2.2** *Concentrated Nitric Acid* — *see* **7.3.2**.

**13.2.3** *Concentrated Ammonium Hydroxide* — 20 percent.

**13.2.4** *Cobalt Sulphate Solution* — 10 g/litre.

**13.2.5** *Acridine Hydrochloride Solution* — 10 g/litre (*w/v*).

**13.2.6** *Ammonium Thiocyanate Solution* — 100 g/litre (*w/v*).

**13.2.7** *Ammonium Thiocyanate Wash Solution* — 10 g/litre. Just before use add 5 ml acridine hydrochloride solution per 200 ml of wash solution.

**13.2.8** *Ammonium Chloride Solution* — 200 g/litre (*w/v*).

**13.2.9** *Sodium Carbonate Solution* — 1 N.

**13.2.10** *Hydrogen Peroxide* — 20 volumes.

**13.2.11** *Ammonium Chloride Wash Solution* — 10 g/litre containing a few drops of N sodium carbonate.

**13.2.12** *Potassium Cyanide Solution* — 2.5 g/litre.

**13.2.13** *Diphenylcarbazone Extracting Solution* — 2 g/litre of pure amyl alcohol.

**13.2.14** *Amyl Alcohol* — High purity amyl alcohol shall be used. Test the reagent as follows:

To one millilitre of 2 g/litre diphenylcarbazone add 9 ml of the amyl alcohol under test. The resulting solution should be pale yellow. If there is any trace of pink colour, the amyl alcohol shall be redistilled.

**13.2.15** *Standard Zinc Solution* (1 *ml* = 0.01 *mg of* Zn) — Dissolve 0.1 g of pure zinc in 5 to 10 ml of dilute hydrochloric acid (1:1). Cool and dilute to one litre in a volumetric flask. Transfer 10 ml of this solution to a 100-m1 volumetric flask and make up the volume to the mark.

### 13.3 Procedure

**13.3.1** Dissolve 0.2 g of the accurately weighed sample in a mixture of 10 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid. Evaporate to dryness, add 5 ml of concentrated hydrochloric acid, warm to dissolve salts and evaporate to low bulk. Dilute the solution to about 5 ml and neutralize to litmus with concentrated ammonium hydroxide.

**13.3.2** Add 5 ml of cobalt sulphate, followed by 25 ml of acridine hydrochloride solution and mix. Add slowly, with constant stirring, 25 ml of ammonium thiocyanate solution. Shake vigorously to coagulate the green cobalt complex. Let stand for 10 minutes and filter on a hardened solid low ash filter paper*. Wash the beaker three times and the paper four times with ammonium thiocyanate wash solution.

**13.3.3** Transfer the funnel and filter paper to the neck of the original beaker and pierce a hole in the paper. Wash the precipitate thoroughly with hot water. Pour 10 ml of ammonium chloride solution through the funnel and wash several times with hot water until the paper is colourless. Keep the volume of water used for washing as low as possible.

**13.3.4** Warm the beaker containing the precipitate on the hot plate, shaking frequently until a clear solution is obtained. Remove from the hot plate. To the warm solution (60º-70ºC), add from a pipette 10 ml of sodium carbonate solution and then 5 ml of hydrogen peroxide. Allow to stand, warm for 5 minutes and then allow to cool for a further 20 minutes.

**13.3.5** It is essential that the time of standing with hydrogen peroxide is strictly adhered to if cobalt interference is to be avoided. Filter off the acridine and ferric hydroxide through filter paper No. 541 and collect the filtrate in a beaker marked at 100 ml. Wash several times with cold ammonium chloride wash solution. Dilute the filtrate to 100 ml. Add 5 ml of potassium cyanide solution. Shake and add 5 ml of acetone.

**13.3.6** Transfer the solution to a 250-m1 separating funnel. Add 20 ml of diphenylcarbazone solution and extract for about 30 seconds. Run off the aqueous layer and transfer the alcoholic layer to a dry beaker. Repeat the extraction with a further 20 ml of diphenylcarbazone solution and

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*Filter paper No. 541 is suitable.

combine the extracts. Pipette 2 ml from the 40 ml of extract and dilute to 10 ml with pure amyl alcohol. Mix thoroughly.

**13.3.7** Transfer a suitable portion of the solution prepared under **13.3.6** to an absorption cell and take photometric reading using light filter at about 530 mμ.

**13.3.8** Take a series of standard solutions of zinc and a reagent blank. Using same quantities of reagents, carry through all the stages as prescribed in **13.3.6** and **13.3.7** and record the photometric readings of all the standard solutions along with the blank. Construct a calibration curve by plotting the photometric readings of the standard solutions against the quantities of zinc.

**13.3.9** Convert the photometric reading of the sample to milligrams of zinc by means of calibration curve and calculate as given under **13.4**.

### 13.4 Calculation

$$\text{Zinc, percent} = \frac{A}{B} \times \frac{1}{10}$$

where

$A$ = weight in mg of zinc found in aliquot of the solution, and

$B$ = weight in g of sample represented by aliquot taken.