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BUREAU OF INDIAN STANDARDS

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(*आइ एस 15848 का पहला पुनरीक्षण*)

Draft *Indian Standard*

ZINC SULPHATE, MONOHYDRATE, AGRICULTURAL GRADE — SPECIFICATION

(*First Revision of IS 15848*)

ICS 65.080

Soil Quality and Fertilizers Sectional Committee, FAD 07	**Last date of comments:** 26 November 2024

FOREWORD

(*Adoption clause will be added later*)

Zinc sulphate monohydrate is a white, crystalline chemical compound which is used in agriculture to correct zinc deficiencies in the plants. It helps in increasing plant growth and development.

This standard was first published in 2009. In this revision, the following major changes have been made to harmonize with *Fertilizer Control Order*, 1985:

a) The method for determination of zinc by ethylene diamine tetra acetate (EDTA) method has been removed.
b) The limits for sulphate sulphur, cadmium and arsenic along with their test methods have been incorporated.

In the preparation of this standard, due consideration has been given to the *Fertilizer Control Order*, 1985. However, this standard is subject to restrictions imposed under these, wherever applicable.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 2022 ‘Rules for rounding off numerical values (*second revision*)’. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

1 SCOPE

This standard prescribes the requirements and methods of sampling and test for zinc sulphate, monohydrate agricultural grade.

2 REFERENCES

The following standards contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

IS No.	*Title*
IS 1070 : 1992	Reagent grade water- Specification (*fourth revision*)
IS 5985 : 1985	Code of practice for handling and storage of bagged fertilizers (*first revision*)
IS 6092 (Part 1) :1985	Methods of sampling and test for fertilizers: Part 1 Sampling (*first revision*)
IS 6092 (Part 5) : 1985	Methods of sampling and test for fertilizers: Part 5 Determination of secondary elements and micronutrients (*first revision*)
IS 7017 : 1973	Method of colorimetric determination of traces of heavy metals by dithizone
IS 7212 : 2023	Methods of determination of copper (*first revision*)

3 REQUIREMENTS

3.1 Description

The material shall be dry, in the form of free-flowing powder or crystals consisting essentially of $ZnSO_4.H_2O$.

3.2 The material shall also comply with the requirements given in Table 1.

Table 1 Requirements for Zinc Sulphate, Monohydrate, Agricultural Grade
(*Clauses* 3.2. 7.2.2, 7.2.3. 7.2.4 and 8)

Sl No.	**Characteristic**	**Requirement**	**Method of Test, Ref to**
(1)	(2)	(3)	(4)
i)	Zinc (as Zn), percent by mass. *Min*	33.0	Annex A
ii)	Magnesium (as Mg). percent by mass, *Max*	0.5	Annex B
iii)	Copper (as Cu), percent by mass, *Max*	0.1	Annex C

iv)	Lead (as Pb). percent by mass, *Max*	0.003	Annex D
v)	*p*H of 5 percent solution (*m*/*v*)	Not less than 4.0	Annex E
vi)	Matter insoluble in water, percent by mass, *Max*	1.0	Annex F
vii)	Iron (as Fe), percent by mass, *Max*	0.5	Annex G
viii)	Sulphur (as S), percent by mass, *Max*	15	IS 6092 (Part 5)
ix)	Cadmium (as Cd), percent by mass, *Max*	0.0025	Annex H
x)	Arsenic (as As_2O_3), percent by mass, *Max*	0.01	Annex J

4 PACKING

The material shall be packed in the manner as agreed to between the purchaser and the supplier. Each bag shall be securely closed.

5 MARKING

5.1 Each bag shall bear legibly the following information:

a) Name of the fertilizer;
b) Indication of the source of manufacture;
c) Percentage of zinc by mass;
d) Gross and net quantity in kg;
e) Batch number, in code or otherwise to enable the lot of manufacture to be traced back from records; and
f) Any other requirements as specified under the *Fertilizer Control Order*, 1985 and the *Legal Metrology* (*Packaged Commodities*) *Rules*, 2011.

5.2 BIS Certification Marking

The product(s) conforming to the requirements of this standard may be certified as per the conformity assessment schemes under the provisions of the *Bureau of Indian Standards Act*, 2016 and the Rules and Regulations framed thereunder, and the products may be marked with the Standard Mark.

6 HANDLING AND STORAGE

Factors to be taken in view in the handling and storage of the material shall be as presented in IS 5985.

7 SAMPLING

7.1 Representative sample of the material shall be drawn as, prescribed in IS 6092 (Part 1)

7.2 Number of Tests and Criteria for Conformity

7.2.1 Zinc shall be tested on each of the individual samples**.**

7.2.2 The remaining characteristics given in Table 1 shall be tested on the composite sample.

7.2.3 The lot shall he considered to have satisfied the requirement for zinc, if test results on each of the individual samples meet the corresponding requirement given in Table 1.

7.2.4 The lot shall be considered to have met the remaining requirements given in Table 1 if each of the test results on the composite sample satisfies the corresponding requirement given in Table 1.

7.3 The lot shall be declared as conforming to the requirements of the specification if requirements in **7 .2 3** and 7**.2.4** are satisfied.

8 TEST METHODS

Test shall be carried out according to method prescribed in col (4) of Table 1

9 QUALITY OF REAGENTS

Unless otherwise specified pure chemicals and distilled water (*see* IS 1070) shall be employed in tests.

NOTE - 'Pure chemicals' shall mean chemicals that do not contain impurities, which affect the results of analysis

ANNEX A

[*Table*1, *Sl No.* (i)]

DETERMINATION OF ZINC

A-1 GENERAL

Two methods have been prescribed for determination ion of zinc in zinc sulphate monohydrate, agricultural grade. Both the methods can be used for determination of zinc on routine basis. However, in the event of any dispute Method 2 should be treated as a referee method.

A-2 METHOD 1 - MODIFIED ETHYLENE DIAMINE TETRA ACETATE (EDTA)

A-2.1 Reagents

A-2.1.1 *Disodium Ethylene Diamine Tetra Acetate* (*EDTA*) — Dissolve 3.72 g of disodium ethylene diamine tetraacetate dihydrate in distilled water and make up the volume to one litre in a volumetric flask.

A-2.1.2 *Standard Zinc Solution* — Weigh about 1.0 g of zinc metal analytical reagent grade accurately. Dissolve in 20 ml of hydrochloric acid (1: l), keep it for few hours and allow it to dissolve completely. Make up the volume of the solution to exactly 1000 ml.

A-2.1.3 *Ammonium Hydroxide*, 20 percent (*m*/*m*).

A-2.1.4 *Ammonium Chloride*, AR grade

A-2.1.5 *Sodium Cyanide,* AR grade

A-2.1.6 *Sodium Chloride*, AR grade

NOTE – Sodium cyanide is very poisonous. It should be used with extreme care.

A-2.1.7 *Eriochrome Black T Indicator Mixture* — Mix thoroughly 1 g of Eriochrome black T indicator with 100 g of sodium chloride.

A-2.1.8 *Formaldehyde — Acetic Acid Solution (4 Percent)* — Dissolve 100 ml of formaldehyde 37-40 percent in about 100 ml of distilled water. Add 40 ml glacial acetic acid and make volume to one litre with distilled water.

A-2.1.9 *Hydroxylamine Hydrochloride*, AR grade

A-2.2 Procedure

A-2.2.1 *Standardization of EDTA Solution*

Take 10 ml of standard zinc solution. Add about 0.1 g of ammonium chloride and 30 ml of ammonium hydroxide solution (20 percent). Dilute it by adding about 30 ml distilled water. Add a pinch of Eriochrome Black T indicator mixture. It will give red colour. Titrate it with EDTA solution to obtain clear blue end point. Note the volume of EDTA used as V_1 ml.

A-2.2.2 *Estimation of Zinc in Samples*

Weigh accurately 1.0 g of a given zinc sulphate sample and dissolve it in 100 ml of distilled water in a volumetric flask. Take 10 ml of aliquot in a beaker. Add 0.1 g of hydroxylamine hydrochloride and 0.1 g of ammonium chloride. Continuously add small quantity of sodium cyanide. White precipitate will appear. Continue adding sodium cyanide till white precipitate disappears while swirling the beaker with hand. Add about 0.5 g excess of sodium cyanide. Dilute it by adding about 30 ml of ammonium hydroxide (20 percent) and add about 30 ml of distilled water.

Add a pinch of Eriochrome Black T indicator mixture. It will give red colour. Titrate with EDTA solution till there is a sharp change to violet colour. Note the volume of EDTA used as V_2 ml. Add 20 ml of formaldehyde acetic acid solution to above titrated solution and mix well. Red colour will reappear. Titrate it with EDTA solution to get blue end point without red tinge. Note the volume of EDTA used in second titration as V_3 ml.

A-2.3 Calculation

$$\text{Zinc (as Zn), percent by mass} = \frac{10 \times V_3 \times M}{V_1}$$

Where

M = mass, in g, of piece of zinc metal taken for preparation of standard zinc solution.
V_1 = volume of EDTA solution, in ml, used for 10 ml of standard zinc solution and;
V_3 = volume of EDTA solution, in ml, used for second titration.

A-3 METHOD 2 - ABSORPTION SPECTROPHOTOMETRIC METHOD

A-3 .1 Reagents

Unless otherwise specified, pure chemicals and glass distilled or demineralized water shall be used in test.

NOTE - 'Demineralized water' means the water obtained after passing distilled water through a cation and an anion exchanger or a combined cation-anion exchange resin.

A-3.1.1 *Standard Zinc Solution* —Weigh 0.4398 g of zinc sulphate ($ZnSO_4.7\ H_2O$) A.R. grade on a clear watch glass and transfer it to one litre flask through the funnel giving several washings to watch glass and funnel with glass distilled or demineralized water. Add 1 ml of 10 percent sulphuric acid (A.R. grade) and make the volume up to the mark. Stopper the flask and shake the solution well. This is 100 ppm zinc solution hereinafter called Standard A. This solution should be stored in a clean bottle for further use. Dilute 10 ml of 100 ppm standard zinc solution (Standard A) to 100 ml to get 10 ppm standard zinc solution designated as Standard B.

A-3.1.2 *Glass Distilled or Demineralized Water of pH 2.5 ± 0.5* — Dilute 1 ml of 10 percent sulphuric acid to one litre with glass distilled or demineralized water and adjust the *p*H to 2.5 with a *p*H meter using H_2SO_4 or NaOH. This solution is called acidified water and 5 to 10 litres of this solution should be prepared at a time.

A-3.2 Preparation of Working Standards

Pipette the following volume of Standard B solution in 50 ml numbered volumetric flasks and make the volume with acidified water (*see* Table 2).

Table 2 Preparation of Working Standards

Flask No.	*Volume of standard B solutions Taken*	*Concentration of Zinc After making Volume to 50ml (ppm)*
(1)	(2)	(3)
1	0.0	0.0
2	1.0	0.2
3	2.0	0.4
4	3.0	0.6
5	4.0	0.8
6	5.0	1.0
7	7.0	1.4
8	9.0	1.8
9	10.0	2.0

A-3.3 Procedure

A-3.3.1 *Preparation of Zinc Sulphate Fertilizer Samples*

Weigh 0.25 g of the material on a clean watch glass and transfer it to one-litre volumetric flask through the funnel giving repeated washings with glass distilled water and dissolve the material by shaking well. Then make the volume up to mark with glass distilled water and shake well.

Take 5 ml of the prepared solution in 250 ml volumetric flask and make the volume with acidified water. Shake the solution well and filter Whatman No.42 filter paper in dry clean flask. The flasks should be rinsed with a 10 to 15 ml of the filtrate and then continue filtration.

A-3.3.2 *Flaming the Solutions*

Flame the standards and the filtered samples on atomic absorption spectrophotometer at a wavelength of 213.8 nm (Zn line of the instrument).

A-3.4 Calculation

Prepare a standard curve of known concentrations of zinc solution by plotting the absorbance values of Y-axis against their respective zinc concentration on X-axis. Calculate the percentage zinc in zinc fertilizer by multiplying zinc concentration value calculated from standard curve by 20.

Example:

Mass of the fertilizer sample : 0.25 g

Volume made : 1000 ml

Further dilution : 50 times

Reading of the samples from atomic absorption : Y

Corresponding concentration value of zinc from standard curve against Y absorbance : X ppm

Percentage zinc in the fertilizer : 20 (X)

A-3.5 Precautions

a) Weighing shall be done on an electronic balance.
b) All the glass apparatus to be used should be neutral and washed with dilute hydrochloric acid (1:4) and washed thoroughly with distilled water and then with demineralized water.
c) The pipette should be rinsed with the same solution to be measured.
d) The outside of the pipette should be wiped with filler paper after taking out from the solution to be measured.
e) After using the pipette, place them on a clean dry filter paper in order to prevent contamination
f) To start filtration, only a few drops should be added first in order to wet the filler paper and then continue further filtration.

Stopper the flasks and shake them well. Prepare the standard solution in duplicate. The same acidified water should be used for preparing the solution of unknown fertilizer samples. Fresh standard solution should be prepared every time when a fresh lot of acidified water is prepared.

ANNEX B

[*Table* 1, *SI No.* (ii)]

DETERMINATION OF MAGNESIUM

B-1 GENERAL

Two methods have been prescribed for the determination of magnesium in zinc sulphate monohydrate, agricultural grade. Both the methods can be used for the determination of magnesium.

B-2 METHOD I - EDTA METHOD

B-2.1 Reagents

B-2.1.1 *Dilute Sulphuric Acid*, approximately 5 N**.**

B-2.1.2 *Dilute Nitric Acid***,** approximately 10 percent (*v/v*).

B-2.1.3 *Sodium Sulphide Solution*, 10 percent**.**

B-2.1.4 *Eriochrome Black T Indicator* — Dissolve 0.1 g of Eriochrome black T in 25 ml of methyl alcohol.

B-2.1.5 *Diammonium Hydrogen Phosphate*, 10 percent (*m/m*).

B-2.1.6 *Ammonium Hydroxide — Ammonium Chloride Buffer Solution* — Mix 350 ml of ammonium hydroxide (20 percent, *m/m*) with 54 g of ammonium chloride. Dilute with water and make up the volume to 1000 ml. (The *p*H of the solution should be not more than 10)

B-2.1.7 *Standard Magnesium Solution, 0.01 M* — Weigh 2.4640 g of magnesium sulphate ($MgSO_4.7H_2O$) and dissolve it in water. Make up the volume to one litre.

B-2.1.8 *Ethylene Diamine Tetra Acetate (EDTA) Solution* — Dissolve 3.72 g of disodium ethylene diamine tetraacetate dihydrate in water and make up the volume to one litre.

B-2.1.8.1 *Standardization of EDTA Solution*

Take 10 ml of standard magnesium solution in a conical flask. Add 20 ml of water, 1 ml of Eriochrome black T indicator and 25 ml of ammonium hydroxide ammonium chloride buffer solution. Heat to 40 °C to 50 °C and then titrate with EDTA solution, maintaining the temperature between 40 °C and 50 °C until the colour changes from wine red to distinct blue. Calculate the molarity of EDTA solution as follows:

$$\text{Molarity of EDTA solution} = \frac{10\ M_1}{V_1}$$

where

M_1 = molarity of standard magnesium solution; and
V_1 = volume, in ml, of EDTA solution used for titration.

B-2.2 Procedure

B-2.2.1 Weigh accurately about 5 g of the sample, dissolve in water and add 1 ml of dilute sulphuric acid. Filter the solution and make up to 250 ml with water in a volumetric flask. Take 50 ml of the above solution in a beaker, heat, pass hydrogen sulphide gas or add sodium sulphide solution and ensure complete precipitation. Filter hot and keep the filtrate for the determination of magnesium. Boil the residue with dilute nitric acid and filter if necessary. To the filtered solution add dilute sulphuric acid, evaporate, dilute and filter. Use the filtrate for the determination of copper and the residue for the determination of lead.

B-2.2.2 Take the filtrate obtained in **B-2.2.1** after precipitation of sulphides, add a few drops of concentrated nitric acid, boil and cool and then add solid ammonium chloride (about 2 g), boil and cool, add ammonium hydroxide till strong smell of ammonia comes and filler the precipitate through sintered crucible. Take the filtrate and add dilute sulphuric acid till the solution is acidic (test with methyl red), heat the solution to boil and add excess of diammonium hydrogen phosphate with continuous stirring. Add 10 percent ammonia solution with continuous stirring till the solution is just alkaline (test with methyl red); white precipitate of zinc ammonium phosphate will be formed (the optimum *p*H of precipitation is 6 to 7). Allow it to stand for 3 to 4 h, then filter through filter paper (Whatman No. 40 or equivalent). Collect the filtrate in a volumetric flask and make up the volume (say to 100 ml), and take a suitable aliquot (say 10 ml) for the determination of magnesium. Add 20 ml of water, 1 ml of Eriochrome black T indicator and 20 ml of ammonium hydroxide-ammonium chloride buffer solution. Heat to 40 °C to 50 °C and titrate with standard EDTA solution, maintaining the temperature between 40 °C and 50 °C until the colour changes from wine red to distinct blue.

B-2.3 Calculation

1 ml of 0.01 M EDTA = 0.2432 mg of 'Mg'

Magnesium (as Mg), percent by mass = $\frac{V \times 0.2432}{5}$

where

V = volume of 0.01 M EDTA solution used for titration.

The calculation factor 5 is derived presuming that 5 g of material is taken for test in **B-2.2.1** and the filtrate obtained in **B-2.2.2** is 100 ml out of which 10 ml is titrated.

B-3 METHOD 2 – ATOMIC ABSORPTION METHOD

B-3.1 Reagents

B-3.1.1 *Strontium Chloride* — Dissolve 7.5 g of strontium chloride ($SrCl_2.6H_2O$) in a litre of glass distilled water.

B-3.1.2 *Standard Magnesium Solution* — Weigh 0.507 g of magnesium sulphate ($MgSO_4.7H_2O$) on a clean watch glass and transfer it to one litre flask through the funnel giving several washings to watch glass and the funnel with glass distilled or demineralized water. This is 50 ppm Mg solution. Dilute 10 ml of 50 ppm solution of Mg to 100 ml to get 5 ppm standard Mg solution.

B-3.1.3 *Preparation of Working Standard* — Pipette the following volume of 5 ppm standard Mg solution in 50 ml numbered volumetric flasks. Add 10 ml of strontium chloride solution to each flask and make up the volume to 50 ml.

Stopper the flasks and shake them well. Prepare fresh standards every fortnight.

Flask No.	*Volume of 5ppm Mg Solution Taken (ml)*	*Volume of Strontium Chloride Added (ml)*	*Concentration of Magnesium After Making the Volume to 50 ml (ppm)*
1	0.0	10.0	0.0

2	2.0	10.0	0.2
3	4.0	10.0	0.4
4	6.0	10.0	0.6
5	8.0	10.0	0.8
6	10.0	10.0	1.0

B-3.2 Procedure

B-3.2.1 Pipette 20 ml of the solution which was prepared for the determination of zinc by dissolving 0.25 g of the fertilizer sample in one litre flask. Add 10 ml of strontium chloride. Make up the volume to 50 ml.

B-3.2.2 Flame the standards and the samples on atomic absorption spectrophotometer at a wavelength of 285.5 nm (Mg line of the instrument).

Prepare a standard curve of known concentrations of Mg solutions by plotting the absorbance value on Y-axis against their respective concentration values on X-axis. Percentage magnesium in the zinc fertilizer will correspond to the concentration values calculated from the standard curve.

Example:

Mass of the fertilizer sample : 0.255 g

Volume made : 1000 ml

Further dilution : 2.5 times

Reading of the samples from atomic absorption : *Y*

Corresponding concentration value of zinc from standard curve against *Y* absorbance : *X* ppm

Percentage zinc in the fertilizer : *X*

ANNEX C

[*Table* 1, *Sl No.* (iii)]

DETERMINATION OF COPPER

C-1 GENERAL

Two methods have been prescribed for the determination of copper in zinc sulphate, monohydrate, agricultural grade. Both the methods can be used for the determination of copper.

C-2 METHOD 1 – DIETHYL DITHIOCARBONATE METHOD

Make up the filtrate reserved in **B-2.2.1** for determination of copper, to 200 ml with water in a volumetric flask. Take a suitable aliquot of the solution containing not more than 0.05 mg of copper. Determine copper by diethyl dithiocarbonate method or by biquinoline method as prescribed in IS 7212.

C-3 METHOD 2 – ATOMIC ABSORPTION METHOD

C-3.1 Reagents

C-3.1.1 *Standard Copper Solution* — Weigh 0.1965 g of copper sulphate ($CuSO_4.5H_2O$) on a clean watch glass and transfer it to one-litre flask through the funnel giving several washings to watch glass and the funnel with glass distilled water. Add 1 ml of 10 percent sulphuric acid and make up the volume up to the mark. Stopper the flask and shake the solution well. This is 50 ppm Cu solution and should be stored in a clean bottle for further use. Dilute 10 ml of 50 ppm solution of copper to 100 ml to get 5 ppm standard copper solution.

C-3.1.2 *Glass Distilled or Mineralized Acidified, Water p*H 2.5 ± 0.5

C-3.1.3 *Preparation of Working Standards* – Pipette the following volume of 5 ppm standard copper solution in 50 ml numbered volumetric flasks and make the volume with acidified water:

Flask No.	*Volume of 5 ppm Standard Cu Solution Taken (ml)*	*Concentration of Copper After Making Volume of 50 ml (ppm)*
1.	10.0	1.0
2.	8.0	0.8
3.	6.0	0.6
4.	4.0	0.4
5.	2.0	0.2
6.	0.0	0.0

Stopper the flasks and shake them well. Prepare fresh standards every fortnight.

C-3.2 Procedure

C-3.2.1 The solution, which was prepared for the determination of zinc by dissolving 0.25 g of the fertilizer sample in one-litre flask as described in **A-3.3.1**, should be used for the determination of copper.

C-3.2.2 Flame the standards and the samples on an atomic absorption spectrophotometer at a wavelength of 324.8 nm (Cu line of the instrument).

C-3.3 Calculation

C-3.3.1 Prepare a standard curve of known concentrations of copper solutions by plotting the absorbance values on Y-axis against their respective concentration values on X-axis. Calculate the percentage copper in the zinc fertilizer by multiplying the copper concentration value calculated from the standard curve by 0.4.

Example:

Mass of the fertilizer sample	:	0.25 g
Volume made	:	1000 ml
Reading of the samples from atomic absorption	:	Y
Corresponding concentration value of zinc from standard curve against Y absorbance	:	X ppm
Percentage zinc in the fertilizer	:	$X (0.4)$

ANNEX D

[*Table* 1, *Sl No.* (iv)]

DETERMINATION OF LEAD

D-1 GENERAL

Two methods have been prescribed for the determination of lead in zinc sulphate, monohydrate, agricultural grade. Both the methods can be used for the determination of lead.

D-2 METHOD 1 – DITHIOZONE METHOD

Dissolve the residue reserved in **B-2.2.1** for determination of lead, in dilute nitric acid, and make up to a known volume with water in a volumetric flask. Take a suitable aliquot of the solution and determine lead by the colorimetric method using dithizone as prescribed in IS 7017.

D-3 METHOD 2 – ATOMIC ABSORPTION METHOD

D-3.1 Reagents

D-3.1.1 *Standard Lead Solution* — Weigh 0.1599 g of lead nitrate [$Pb(NO_3)_2$] on a clean watch glass and transfer it to one litre flask through the funnel giving several washings to watch glass and funnel with glass distilled or demineralized water. Add 10 ml of concentrated distilled nitric acid and make the volume up to the mark. Stopper the flask and shake the solution well. This is 100 ppm lead solution and should be stored in a clean bottle for further use. Dilute 10 ml of 100 ppm solution of lead to 100 ml with one percent nitric acid solution to get 100 ppm standard lead solution.

D-3.1.2 *Nitric Acid Solution, 1 Percent* — Dilute 10 ml of concentrated distilled nitric acid to one litre with glass distilled water.

D-3.1.3 *Zinc Sulphate Solution, 20 Percent* — Weigh 20 g of zinc sulphate ($ZnSO_4.7H_2O$) and dilute to 100 ml with one percent nitric solution.

D-3.1.4 *Preparation of Working Standards* — Pipette the following volume of 10 ppm standard lead solution in 50 ml numbered volumetric flasks. Add 5 ml of 20 percent zinc sulphate solution to each flask and make the volume with one percent nitric acid solution:

Flask No.	*Volume of 10 ppm Standard Lead Solution Taken (ml)*	*Volume of 20 percent Zinc Sulphate Solution Added (ml)*	*Concentration of Lead After Making Volume of 50 ml (ppm)*
1	0.0	5.0	0.0
2	2.0	5.0	0.4
3	4.0	5.0	0.8
4	6.0	5.0	1.2
5	8.0	5.0	1.6
6	10.0	5.0	2.0

Stopper the flasks and shake them well.

D-3.2 Procedure

D-3.2.1 *Preparation of Zinc Sulphate Fertilizer Samples* — Weigh 1 g of the material on a clean watch glass and transfer to 50 ml volumetric flask through the funnel giving washing with 1 percent nitric acid solution. Dissolve the material and make the volume with 1 percent nitric acid solution. Samples should be prepared in duplicate.

D-3.2.2 *Flaming the Solutions* – Flame the standards and the samples on atomic absorption spectrophotometer at a wavelength of 217 nm (Lead line of the instrument).

D-3.3 Calculations

Prepare a standard curve of known concentrations of lead solution by plotting the absorbance values on Y-axis against their respective lead concentration on X-axis. Calculate the percentage lead in zinc fertilizer by multiplying lead concentration value calculated from standard curve by 0.005.

ANNEX E

[*Table* 1, *Sl No.* (v)]

DETERMINATION OF *p*H

Dissolve 5 g of the material in freshly boiled and cooled water, dilute to 100 ml and mix. Determine the *p*H value of the solution with a pH meter.

ANNEX F

[*Table* 1, *Sl No*. (vi)]

DETERMINATION OF MATTER INSOLUBLE IN WATER

F-1 REAGENT

F-1.1 Dilute Sulphuric Acid, 10 percent.

F-2 PROCEDURE

Dissolve 25.0 g of the material in 125 ml of water and add 1 ml of dilute sulphuric acid. Heat the solution to boiling. Filter through a weighed and prepared Gooch crucible or sintered glass crucible (G No. 4) and wash the residue thoroughly with hot water. Dry the crucible at (110 ± 5) °C to constant mass.

F-3 CALCULATION

Matter insoluble in water = 4 A

Where

A= mass, in g, of the residue.

ANNEX G

[*Table* 1, *Sl No*. (vii)]

DETERMINATION OF IRON

G-1 GENERAL

Two methods have been prescribed - Spectrophotometric method and Atomic Absorption Method. spectrophotometric method is for routine analysis and in case of dispute atomic absorption method shall be taken as a referee method.

G-2 METHOD 1 – SPECTROPHOTOMETRIC METHOD

G-2.1 Outline of the Method

In test solution, iron is determined spectrophotometrically as ferrous iron forms red complex with ortho-phenanthroline.

G-2.2 Apparatus, photoelectric-colorimeter.

G-2.3 Reagents

G-2.3.1 *Bromophenol Blue Indicator Solution,* 0.4 percent solution in 95 percent ethanol.

G-2.3.*2 Sodium Citrate Solution*, 25 percent.

G-2.3.3 *Hydroquinone Solution*, 1 percent in an acetic acid buffer of *p*H 4.5 obtained by mixing 65 ml of 0.1 M acetic acid with 35 ml of 0.1 M sodium acetate solution.

G-2.3.4 *Ortho-phenanthroline Solution*, 0.25 percent in 25 percent ethanol.

G-2.3.5 *Dilute Hydrochloric Acid*, 1:3 (*v*/*v*).

G-2.3.6 *Standard Iron Solution* — Dissolve 0.7002 g of ammonium ferrous sulphate (AR) in distilled water containing 2 ml of perchloric acid and dilute to 100 ml with water. One millilitre of this solution contains 1 mg of iron.

G-2.4 Preparation of Sample Solution

Boil 1 g of sample in 20 ml of hydrochloric acid (1:1) for 30 min and filter through Whatman No. 40 filter paper in 100 ml volumetric flask. Follow with repeated extraction with boiling dilute hydrochloric acid (1:5) decanting the solution each time through the same filter paper. Dilute the filtrate to 100 ml.

G-2.5 Procedure

G-2.5.1 Take 5 ml of the sample solution, add bromophenol blue indicator solution and titrate with sodium citrate solution until yellow colour changes to blue.

G-2.5.2 Take another 5 ml of sample solution in a 25 ml volumetric flask. Add 1 ml of hydroquinone solution, 3 ml of ortho-phenanthroline solution and an amount of sodium citrate solution equivalent to the above titration in **G-2.5.1**. Dilute with distilled water to 25 ml. Allow the solution to stand for 1 h.

G-2.5.3 Measure the absorbance of test solution at 510 nm using 1 cm cell and also blank with water.

G-2.5.4 Place 4 ml, 8 ml, 12 ml, 16 ml and 20 ml of standard iron solution in a series of 100 ml volumetric flasks. To each, add 40 ml of dilute hydrochloric acid and dilute to 100 ml with water.

G-2.5.5 Using 5 aliquot proceed as for sample solution.

G-2.5.6 Measure the absorbance of the solution and plot a graph relating absorbance and mg of iron.

G-2.6 Calculation

$$\text{Fe, percent} = \frac{2X}{W}$$

where

X= concentration, in mg, of iron in final sample solution aliquot as determined from the graph, and
W= weight, in g, of material taken for the preparation of sample solution.

G-3 METHOD 2 – ATOMIC ABSORPTION METHOD

G-3.1 Reagents

G-3.1.1 *Standard Iron Solution* (*1000 ppm*) — Weigh accurately 1 g pure iron wire and put it in approximately 30 ml of 6 N hydrochloric acid in a beaker and boil. Transfer it to one litre volumetric flask through the funnel giving several washings to the beaker and funnel with glass distilled water. Make the volume up to the mark. Stopper the flask and shake the solution well. This is 1000 ppm iron solution.

G-3.1.2 *Glass Distilled or Demineralized Water*, of *p*H 2.5 ± 0.5.

G-3.1.3 *Preparation of Working Standards* — Pipette 10 ml iron stock solution in 100 ml volumetric flask and dilute to volume. This is 100 ppm iron solution. Pipette the following volumes of 100 ppm iron solution in 50 ml of volumetric flask and make the volume with acidified water:

Flask No.	*Volume of 100 ppm Standard Iron Solution*	*Concentration of Iron After Making Volume to 50 ml (ppm)*
1	0.0	0.0
2	1.0	2.0
3	2.0	4.0
4	3 .0	6.0
5	4.0	8.0
6	5.0	10.0
7	6 .0	12.0
8	7 .0	14.0
9	8.0	16.0
10	9.0	18.0
11	10.0	20.0

Stopper the flask and shake the solution well.

G-3.2 Procedure

G-3.2.1 *Preparation of Fertilizer Sample Solution*

Weigh exactly 1 g of the material on a clean watch glass and transfer it to a one litre volumetric flask through the funnel giving repeated washings with acidified water and dissolve the material by shaking well. Make the volume up to the mark with acidified water and shake well and filter through Whatman No. 42 filter and then continue filtration.

G-3.2.2 *Flamming the Solution*

Flame the standards and the filtered sample on atomic absorption spectrophotometer at a wavelength of 248.3 nm using clean air acetylene flame.

G-3.3 Calculation

Prepare a standard curve of known concentrations of iron solution by plotting the absorption value on Y-axis against the respective iron concentration on X-axis. Determine the concentration of iron in the sample solution from the graph.

$$\text{Total iron (as Fe), percent} = \frac{X}{10}$$

where

X = concentration of iron, in ppm, obtained from the standard curve.

ANNEX H

[*Table* 1, *Sl No.* (ix)]

DETERMINATION OF CADMIUM

H-1 REAGENTS

H-1.1 Standard Cadmium Solution

Weigh out 1 g of pure cadmium metal and transfer it to a 250 ml beaker. Add 50 ml of water and 10 ml of concentrated nitric acid to dissolve the metal completely. Transfer the cadmium solution to a one litre flask with necessary washing. Make up the volume up to the mark. Shake well. This is a 1000 ppm solution of cadmium, (hereinafter called standard A). Dilute 1 ml of standard A to 100 ml in a volumetric flask. This is a 10 ppm solution of cadmium, (hereinafter called standard B).

H-1.2 Glass distilled water of *p*H 2.5 + 0.5

Dilute 1 ml of 10 percent sulphuric acid to one litre with glass distilled water and adjust the *p*H to 2.5 + 0.5 with a pH meter using sulphuric acid or sodium hydroxide solution. The water so obtained is called acidified water.

H-2 PREPARATION OF WORKING STANDARDS

Pipette out the following volume of standard B in 100 ml of numbered volumetric flask and make up the volume with acidified water. Stopper the flask and shake them well. The same acidified water should be used for the preparation of the sample solution. Fresh standards should be prepared and used every time.

Flask No.	*Volume of standard (B) taken in ml*	*Concentration of cadmium after making volume to 100 ml (in ppm)*
1	0	0.0
2	2.0	0.2
3	4.0	0.4
4	8.0	0.8
5	12.0	1.2

6	16.0	1.6
7	20.0	2.0

H-3 PROCEDURE

H-3.1 Preparation of Sample Solution

Weigh 2 g of zinc sulphate and transfer it to a 100 ml volumetric flask giving repeated washings with acidified water. Dissolve the material by shaking well, make up the volume and mix thoroughly. Filter a portion if necessary. For higher concentration of cadmium adjust the weight and dilution such that the absorbance of final flaming solution is not more than a 2 ppm solution of cadmium.

Aspirate the standards as well as the sample solution in an atomic absorption spectrophotometer at a wave length of 228.8 nm using air acetylene flame and note the corresponding absorbance value for each solution.

H-4 CALCULATION

Draw a graph using concentration (ppm) as the X-axis and absorbance as the Y-axis. Determine the concentration of cadmium in ppm in the sample solution from the graph.

Cadmium (as Cd), concentration in ppm = $\frac{C \times F}{M}$

where,

C = concentration in ppm of final sample solution
M = mass of the sample
F = dilution factor.

ANNEX J

[*Table* 1, *Sl No.* (x)]

DETERMINATION OF ARSENIC

J-1 PRINCIPLE

Arsenic V is reduced by KI to Arsenic III and the iodine thus released is reduced in turn by $SnC1_2$. Hydrogen is liberated by the reduction of zinc with HC1 in a nascent state. It also converts Arsenic V to Arsenic III. Acidity of the solution plays a key role in this case. The arsenic produced is swept out of the solution as arsine by brisk evolution of hydrogen and it passes through a plug impregnated with lead acetate, which removes any hydrogen sulphide that may be liberated from the solution. H_2S discolours the $HgC1_2$ paper. As the concentration of liberated arsenic as arsine increases, the yellow spot of ($HgC1_2$) turns to brown spot of ($HgC1_3$) and finally to black Hg_3As_2 with further increase in concentration of arsine.

J-2 REAGENT

J-2.1 Concentrated Hydrochloric Acid – A.R. grade

J-2.2 0.5 M HCl – Mix 20 ml concentrated HCl with 420 ml water.

J-2.3 Potassium Iodide Solution – Dissolve 10 g KI in 400 ml water (2.5%).

J-2.4 10 percent Stannous Chloride Solution

Dissolve 25 g $SnCl_2.5H_2O$ in 250 ml concentrated HCl

J-2.5 0.75 percent Stannous Chloride Solution

Mix 75 ml of the 10 percent stannous chloride solution with 375 ml of concentrated hydrochloric acid and 550 ml of water. Do not keep this solution for a period of more than two days.

J-2.6 Ethyl Alcohol (Absolute) – 95 percent.

J-2.7 Mercuric Chloride Solution – Dissolve 25 g $HgC1_2$ in 100 ml of ethyl alcohol.

J-2.8 Filter paper (Whatman No. 40) – 9 cm diameter or comparable grade.

J-2.9 Mercuric chloride paper

Allow 15 Filter paper to soak for 1 h in alcoholic $HgC1_2$ solution. Leave it in the dark to dry, then cut into 1 cm square avoiding the edges of each circle. Store in an air tight and light proof container. Prepare freshly each week.

J-2.10 Lead Acetate Solution – Dissolve 15 g lead acetate trihydrate in 100 ml glacial acetic acid.

J-2.11 Glass Wool – Saturate glass wool with above lead acetate solution and allow it to dry. Pack loose plug of this into the tube of each Gutzeit apparatus (*see* Fig. 1). Replenish when this is discoloured along half of the length of the tube.

J-2.12 Zinc Pellets (Arsenic Free Zinc Pellets) – AR grade.

J-2.13 Preparation of Arsenic Solution

Dissolve 0.416 g of sodium Arsenate ($Na_2HAsO_4.7H_2O$) in 1000 ml distilled water in volumetric flask after addition of 1 ml of concentrated hydrochloric acid. This is a 100 ppm arsenic solution which may be called Standard *A*.

Take 1 ml of standard *A* and dilute to 100 ml in a volumetric flask. This is a 1 ppm arsenic solution which may be called Standard *B*.

J-2.14 Preparation of Working Solution

Take 5 ml, 10 ml, 15 ml, 20 ml, and 25 ml solution of Standard *B* in respective Gutzeit bottle. The solution taken in Gutzeit bottles contain 5 ppm, 10 ppm, 20 ppm, 25 ppm of arsenic respectively as shown in Fig 1 and proceed as given in **J-3** except **J-3 a)**.

J-3 PROCEDURE

a) Weigh minimum 10 g of fertilizer sample in a Gutzeit bottle.
b) Add 120 ml of water and dissolve the material.
c) Add 25 ml of 0.5 M HCl and shake.
d) Add 3 ml potassium iodide solution and wait for 5 min.

e) Add 10 ml of 0.75% stannous chloride. Add 1 g to 2 g zinc pellets and connect the Gutzeit bottle to the tube without delay, having previously placed a mercuric chloride paper in the head of the arsenic apparatus.

f) Leave for 30 min or till the reaction ceases, remove the mercuric chloride paper immediately, compare the confined spots with standard spot and ascertain the nearest concentration of Arsenic.

g) Carry out blank analysis to ensure that reagents are free from arsenic.

J-6 CALCULATION

$$\text{Arsenic (as } As_2O_3\text{), percent by mass} = \frac{Conc.\ in\ ppm \times 1.32}{Mass\ of\ the\ sample \times 10000}$$

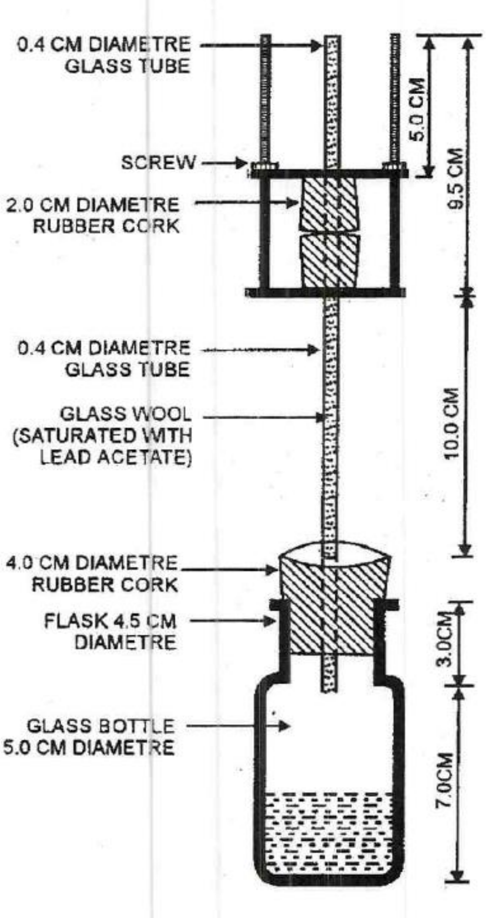

Fig. 1 Modified Gutzeit Apparatus For Arsenic Estimation