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भारतीय मानक मसौदा

विस्फोटक और आतिशबाज़ी उद्योग में उपयोग के लिए ज़िरकोनियम पाउडर की विशिष्टि

(*पहला पुनरीक्षण*)

Draft Indian Standard

SPECIFICATION FOR ZIRCONIUM POWDER FOR USE IN EXPLOSIVE AND PYROTECHNIC INDUSTRY

(*First Revision*)

ICS 71.100.30

Explosives and Pyrotechnics Sectional Committee, CHD 26

Last date for Comments: 16th Dec, 2023

FOREWORD

(*Formal clause may be added later*)

Zirconium powder is used as a fuse-head for electric detonation and for incendiary compositions.

This Indian Standard was originally published in 1988. This first revision of the standard has been taken up to update the ICS No and several other editorial changes in order to bring out the standard in the latest style and format of the Indian Standards.

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.

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Draft Indian Standard

SPECIFICATION FOR ZIRCONIUM POWDER FOR USE IN EXPLOSIVE AND PYROTECHNIC INDUSTRY

(*First Revision*)

1 SCOPE

This standard prescribes the requirements and the method of sampling and test for zirconium powder for use in explosive and pyrotechnic industry.

2 REFERENCES

The standards listed below 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.	*IS Title*
IS 264 : 2005	Nitric acid — Specification (*third revision*)
IS 1070 : 2023	Reagent Grade Water Specification (*fourth revision*)
IS 4905 : 2015	Random sampling and randomization procedures (*first revision*)

3 REQUIREMENTS

3.1 Description — The material shall be in the form of grey crystalline fine powder, free from grit, impurities and foreign matter.

3.2 Particle Size — The material shall have an average particle size between 2 and 10 microns or as agreed to between the purchaser and the supplier.

3.3 The material shall also comply with the requirements specified in Table 1, when tested according to the methods prescribed in **Annex A**. Reference to the relevant clauses of Annex A is given in col 4 of Table 1.

3.4 Safety precautions in handling of zirconium powder are given in **Annex B**.

4 PACKING AND MARKING

4.1 Packing —The material in completely dried form shall be packed in double metallic container under argon or helium atmosphere with inner container of wall thickness 1.3 mm minimum and capacity 1 kg maximum. Annular space of not less than 2.5 cm between the inner and outer containers shall be fitted with fine dry sand. Not more than six such containers shall be packed in wooden box completely surrounded by all sides with inert cushioning material.

4.1.1 The material shall be supplied in containers with net mass not exceeding 1 kg.

4.2 Marking — The containers shall be legibly and indelibly marked with the following information:

a) Name of the material;

b) Manufacturer's name and/or his recognized trademark, if any;

c) Identification in code or otherwise to enable the lot of manufacture to be traced from records;

d) Tare and net mass; and

e) Year and month of manufacture.

TABLE 1 REQUIREMENTS FOR ZIRCONIUMPOWDER FOR EXPLOSIVE ANDPYROTECHNIC INDUSTRY

(*Clause* 3.3)

SL No. **(1)**	**CHARACTERISTIC** **(2)**	**REQUIREMENT** **(3)**	**METHOD OF TEST REF TO CL NO.** **(4)**
i)	Assay, percent by mass, *Min*	96.5	A-2
ii)	Volatile matter at (105 ± 2)°C for 1 hour, percent by mass, *Max*	0.5	A-3
iii)	Ignition temperature	270 °C to 370 °C	A-4
iv)	Insoluble matter, percent by mass, *Max*	3.0	A-5
v)	Apparent density, *g/ml*	2.0 to 2.5	A-6
vi)	Iron (as Fe), percent by mass, *Max*	0.5	A-7
vii)	Calcium (as Ca), percent by mass, *Max*	0.1	A-8
viii)	Magnesium (as Mg), percent by mass, *Max*	0.1	A-9

4.2.1 BIS *Certification Marking*

The containers may also be marked with Standard Mark. The use of the Standard Mark is governed by the provisions of The Bureau of Indian Standards Act, 2016 and the Rules and Regulations made thereunder. The details of the conditions under which the licence for use of the Standard Mark may be granted to manufacturers or producers, may be obtained from the Bureau of Indian Standards.

5 SAMPLING

The method of drawing representative samples of the material, number of tests to be performed and the method of determining criteria for conformity of the material to the requirements of this specification shall be as prescribed in **Annex C**.

ANNEX A

METHODS OF TEST FOR ZIRCONIUM POWDER FOR EXPLOSIVE AND PYROTECHNIC INDUSTRY

(*Clause* 3.3; and *Table* 1)

A-1 QUALITY OF REAGENTS

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

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

A-2 ASSAY

Two methods have been prescribed for determination of assay. In case of any dispute, Method I shall be the referee method.

A-2.1 Method I

A-2.1.1 *Procedure* — Weigh about 0.1 g of zirconium powder accurately and transfer to a 250 ml beaker. Dissolve it in 25 mi of sulphuric acid (1 : 1) by heating on a sand bath in a fume chamber. Cool and dilute with 25 ml of distilled water. Filter and wash the insoluble matter through Whatman No. 42 filter paper. Collect the filtrate and the washings, and dilute to about 150 ml with distilled water. Add a freshly prepared 10 percent aqueous di-ammonium hydrogen phosphate or ammonium phosphate solution in 50 to 100 fold excess (use 10 ml for every 10 mg of zirconium present, but not less than 20 ml). Boil the solution for a few minutes, allow to digest for 30 minutes on a water bath and allow to cool to about 60 °C. Filter the precipitate through Whatman No. 42 filter paper, wash first with 100 ml to 150 ml of 2N sulphuric acid containing 2.5 g di-ammonium hydrogen phosphate in 150 ml and finally with cold five percent ammonium nitrate solution, until the filtrate is sulphate free. Dry the precipitate at 100 °C to 110 °C. Ignite the filter paper along with the precipitate in a silica crucible. Heat the silica crucible in an electric muffle at about 800 °C till constant mass. Weigh as zirconium pyrophosphate (ZrP_2O_7).

A-2.1.2 *Calculation*

$$\text{Zirconium content percent by mass} = \frac{0.344\,1 \times M_2 \times 100}{M_1}$$

where

M_2 = mass of precipitate, and

M_1= mass of sample

A-2.2 Method II

A-2.2.1 *Procedure* — Weigh 0.2 g (M_1) of sample into a previously dried and weighed crucible with lid. Heat on a Bunsen burner on low flame till the sample is completely burnt (flame is extinguished). Introduce into muffle furnace and gently heat at 800 °C to 850 °C, and keep for one hour. Cool and weigh (M_2).

A-2.2.2 *Calculation*

$$\text{Assay, percent by mass} = \frac{M_2 \times 100}{M_1 \times 1.35}$$

A-3 DETERMINATION OF VOLATILE MATTER

A-3.1 Procedure — Heat a flat bottomed clean glass or aluminium dish with cover, about 6 cm in diameter and 3 cm in depth, in an oven at (105 ± 2) °C for half an hour. Cool it in a desiccator and weigh. Place about 10 g of the material in the dish, replace the cover and weigh accurately. Uncover the dish and heat the sample, and cover in an oven maintained at (105 ± 2) °C for 2 hours. At the end of this period, replace the cover, cool the dish and the cover in a desiccator to room temperature and weigh. Repeat the operation till constant mass is obtained.

A-3.2 Calculation — Calculate the volatile matter as follows:

$$\text{Volatile matter, percent by mass} = \frac{100 \times (M_2 - M_3)}{(M_2 - M_1)}$$

where

M_2 = mass in g of the dish and the cover with the sample taken,

M_3 = mass in g of the dish and the cover with the sample after heating, and

M_1 = mass in g of the empty dish and the cover.

A-4 IGNITION TEMPERATURE

Two methods have been prescribed. In case of any dispute, Method II shall be the referee method.

A-4.1 Method I

A-4.1.1 *Apparatus* — This test is performed in a device consisting of a brass cylinder (40 mm high and 50 mm in dia). This cylinder is equipped with two identical recesses. (Dia 7 mm and 10 mm deep).

A-4.1.2 *Procedure* — A thermometer (200 °C to 400 °C) is placed in one recess and into the other one, the weighed out quantity of zirconium powder. The device is placed in an electric furnace. This device is heated to a temperature which is above the expected ignition temperature.

0.05 g of the sample is put into the recess. If this catches fire, the experiment is repeated at a temperature of 5 °C below this temperature and the sample is again observed for ignition. The temperature is lowered in decrements of 5 °C till the sample does not catch fire. The lowest temperature at which the sample catches fire (to the nearest 5 °C) is the ignition temperature.

A-4.2 Method II — In this method, standard Julius Peters Equipment is used.

A-4.2.1 *Apparatus*— The apparatus is suitable for three specimens at a time. A circular gap is provided at the centre of a round block of non-scaling steel with a three step electric heating installed in a casing of steel sheet. Automatic regulation of the increase of the temperature at the rate of 5°C per minute and 20°C per minute by means of a contact thermometer is done by two synchronous motors for the desired rate. The apparatus is provided with a protective shield in the front.

A-4.2.1.1 In the absence of this apparatus, the one with similar arrangements may be used.

A-4.2.2 *Procedure* — Take approximately 0.05 g of the material in each of the two thick-walled test tubes meant for the test and place into the appropriate test. Connect the contact thermometer and adjust to 380 °C Commence heating at random rate up to 250 °C and 5 °C per minute thereafter. Note the temperature at which the specimen in each test tube gets ignited and record as the mean temperature nearest to 5 °C. Disconnect the thermometer immediately after ignition of the sample.

NOTE — Ensure that sufficient wood metal is there in the recess before commencing the test.

A-5 INSOLUBLE MATTER

A-5.1 Procedure — Weigh about 0.1 g zirconium powder accurately and transfer to a 250ml beaker. Dissolve it in 25 ml of sulphuric acid (1 : 1) by heating on a sand bath in a fume chamber. Cool and dilute with 25 ml of distilled water. Fitter and wash the insoluble matter through Whatman No. 42 filter paper. Dry the filter paper with residue at (100 ± 5) °C. Ignite the dried residue/filter paper in a previously weighed silica crucible. When most of the carbon has been burnt off, heat the silica crucible in an electric muffle at 300 °C to 500 °C for about 30 minutes. Cool and weigh.

Insoluble matter, percent by mass = Mass of ash × 100 Mass of the sample

A-6 DETERMINATION OF APPARENT DENSITY

20 g of the material is introduced into a stoppered glass cylinder, graduated in 0.5 ml, the cylinder being approximately 15 cm high and having an internal diameter of 2 cm. The cylinder is dropped vertically 30 times from a height of 6.5 cm on to a hard leather pad. The surface of the column of zirconium powder is levelled off by the minimum amount of the side tapping, and the total value is read off and expressed as g/ml.

A-7 DETERMINATION OF IRON

A-7.1 Outline of the Method — Ferric (but not ferrous) iron reacts with thiocyanate to give a series of intensely red coloured complexes which remain in true solution. In the colorimetric determination, excess of thiocyanate should be used since this increases the intensity and also stability of the colour. Strong acid (hydrochloric or nitric acid, concentration 0.052 M to 0.05 M) should be present to suppress the hydrolysis of ferric iron.

A-7.2 Reagents

A-7.2.1 *Potassium Thiocyanate Solution*— Dissolve 20 g of potassium thiocyanate in 100 ml of water.

A-7.2.2 *Concentrated Nitric Acid* — *See* IS 264.

A-7.2.3 *Standard Solution of Iron* (*Ferric*) — Dissolve 0.864 g of ferric ammonium sulphate in water, add 10 ml of concentrated nitric acid and dilute to one litre. 1.0 ml of this solution is equivalent to 0.1 mg of iron (Fe).

A-7.3 Procedure — Dissolve accurately 5 g of the material in (1 : 1) water-nitric acid mixture and evaporate to nearly dryness to expel excess of acid. Dilute slightly with water, oxidize any ferrous ion to the ferric state with dilute potassium permanganate solution (2 g/l), adding slowly dropwise until a slight pink colour remains after stirring well. Make up the solution to 250 ml or other suitable volume. Place 50 ml of the solution in a Nessler cylinder, add 5 ml of thiocyanate solution and 2 ml to 4 ml of 4 N nitric acid. Add the same amounts of reagents to 50 ml of water contained in a similar Nessler cylinder and run in standard iron solution from burette (use long glass rod with flattened end for mixing) until colours arc matched. Note the exact volume (X ml) of the standard iron solution added. Repeat determination using 50 X ml of water. Comparison of the standard and unknown should be made soon after preparation since the colour may fade on standing for a long time.

For estimating the concentration of ferric iron more accurately, the use of photoelectric colorimeter may be resorted to. A filter showing maximum transmission at or near 480 nm should be used. Standard solutions of ferric to be present in zirconium powder sample are prepared and the transmittance of each such solution measured with photoelectric colorimeter. A reference curve is then prepared by plotting the concentration versus transmittance. Now the transmittance of the sample solution is also measured and from the reference curve, the concentration of ferric iron is directly read.

A-7.4 Calculation

$$\text{Iron content (as Fe), percent by mass } = \frac{m}{M} \times 100$$

where

m = mass in g of ferric iron as $Fe(NO_3)_3$ as found from the reference curve, and

M = mass in g of the material taken for the test.

A-8 DETERMINATION OF CALCIUM

A-8.1 Outline of the Method — Calcium, like some other metal ions, is complexed by EDTA by choosing the proper pH and indicator. Using calcon as indicator, calcium can be estimated in the presence of magnesium since magnesium is precipitated quantitatively as magnesium hydroxide in the *p*H range of the reaction.

A-8.2 Reagents

A-8.2.1 *Diethylamine*

A-8.2.2 *Calcon Indicator* — Prepared by dissolving 0.2 g of the dyestuff in 50 ml of methyl alcohol.

A-8.2.3 *Standard EDTA* (*Disodium Dihydrogen Ethylenediamine Tetra Acetate Solution*) — Weigh 3.772 5 g of EDTA, dissolve in water free from polyvalent ions (distilled water for this purpose should be passed through a column of cation exchange resins in the sodium form) and make up to a volume of 1 000 ml. Concentration of the resulting solution will be 0.01 M. (If the EDTA is not of analytical reagent grade, then the solution prepared needs to be standardized against standard zinc chloride solution or magnesium chloride solution which is prepared from analytical reagent grade material or corresponding metal pellets of analytical reagent grade).

A-8.2.4 *Sample Solution* — Weigh about 1 g of the material accurately, dissolve in water free from polyvalent ions, filter and make up to 100 ml.

A-8.3 Procedure — Pipette out 10 ml of the sample solution into 250 ml conical flask. Add about 40 ml of water and 5 ml of diethylamine, giving the mixture a *p*H of about 12.5. Under these conditions, magnesium, if present, precipitates quantitatively as the hydroxide. Add four drops of calcon indicator to the solution and titrate with standard EDTA solution with shaking until the colour changes from pink to a pure blue.

A-8.4 Calculation

$$\text{Calcium (as Ca), percent by mass } = \frac{0.4 \times V \times M}{A}$$

where

V = volume in ml of standard EDTA solution,

M = molarity of standard EDTA solution, and

A = mass in g of material taken

A-9 DETERMINATION OF MAGNESIUM

A-9.1 Outline of the Method — Calcium is precipitated as calcium oxalate and magnesium, if any, is estimated by complexing with EDTA using *Eriochrome Black T*.

A-9.2 Reagents

A-9.2.1 *EDTA* — 0.01 M.

A-9.2.2 *Eriochrome Black T* — Dissolve 0.2 g of the dyestuflf in 15 ml of triethanolamine and 5 ml of absolute ethanol.

A-9.2.3 *Standard Magnesium Solution* — 0.01 M. Weigh 6.1 g of magnesium sulphate heptahydrate and dissolve in 50 ml of water. Make up to 250 ml with water in a volumetric flask.

A-9.2.4 *Ammonium Oxalate*

A-9.2.5 *Ammonium Chloride*

A-9.2.6 *Dilute Ammonium Hydroxide* — 1 : 1 by volume.

A-9.2.7 *Ammonia — Ammonium Chloride Buffer Solution* — *p*H 10. Add 142 ml of concentrated ammonium hydroxide to 17.5 g of ammonium chloride and dilute to 250 ml with water.

A-9.2.8 *Dilute Hydrochloric Acid* — 1 : 1 by volume.

A-9.2.9 *Calcium Precipitating Buffer Solution* — Dissolve 5 g of ammonium oxalate in about 100 ml of water, add 144 g of ammonium chloride and 13 ml of concentrated ammonium hydroxide, and dilute the resulting solution to 1 litre.

A-9.3 Standardization of EDTA Solution — Pipette out 25 ml of standard magnesium solution into a conical flask and dilute to 100 ml with water. Add 5 ml of buffer followed by the addition of 6 drops of *Eriochrome Black T* indicator and titrate with EDTA solution until the colour changes from red to pure blue.

1 ml of 0.01 M EDTA = 0.243 2 mg of Mg.

A-9.3.1 *Procedure* — Weigh 1 g of the material into a 250 ml beaker and add 40 ml of water. Add 5 ml of dilute hydrochloric acid slowly with constant stirring. Once the material is dissolved, add another 5 ml of dilute hydrochloric acid. Add a few drops of methyl red indicator. Heat the solution to boiling. Add a clear solution of 6 g of ammonium oxalate dissolved in 100 ml of water slowly with constant stirring. To the hot solution 70 ºC to 80 °C, add dilute ammonium hydroxide (1 : 1) dropwise until the solution becomes fairly alkaline. Digest on water bath for 1 hour.

A-9.3.2 Decant the supernatant liquid through Whatman No. 42 filter paper and collect the filtrate. Transfer the precipitate quantitatively to the filter paper and wash three times with 25 ml to 30 ml of water. Collect the washings along with the filtrate. Evaporate the solution to 100 ml. Add 2 ml of buffer solution followed by the addition of 3 to 4 drops of *Eriochrome Black T* indicator. Titrate the solution with EDTA solution at 40 °C until the colour changes from red to pure blue. (The last traces of reddish shade should disappear at the end point. Complex formation does not take place instantaneously. Titration, therefore, should be conducted slowly near the end point.)

A-9.4 Calculation — Calculate magnesium content on the basis that one millilitre of 0.01 M EDTA solution is equivalent to 0.243 2 mg of magnesium (Mg).

ANNEX B

SAFETY PRECAUTIONS IN HANDLING OF ZIRCONIUM POWDER

(*Clause* 3.4)

B-1 Zirconium powder is a big fire hazard.

B-2 Partly wet zirconium powder is most dangerous since it burns with nearly explosive speed and disperses flaming zirconium over a wide area. Zirconium powder with 30 percent water is sufficiently wet to prevent ignition.

B-3 Ignited dry zirconium powder fire may be controlled by covering with powdered limestone or similar material, preferably 'Ansul'. Small zirconium fires can be isolated and allowed to burn out. Extinguishers containing water, carbon dioxide, carbon tetrachloride or foam extinguishers must not be used in controlling a zirconium powder fire.

B-4 Spilling or dust accumulations in work areas should be avoided.

B-5 Drying of zirconium powder, if required, should be done in small quantities under vacuum at moderate heat, 60 ºC to 80°C. Zirconium powder spontaneously ignites in air at about 240 °C. If exposure of dry zirconium powder to air is required, zirconium should not be above room temperature.

B-6 Persons handling zirconium powder should not use synthetic fibre clothes and should use safety goggles.

B-7 Zirconium powder is safe to handle with due precautions above 10 micron size.

B-8 In presence of air or oxygen, it may spontaneously catch fire even at ambient temperature.

B-9 Zirconium powder is not toxic.

ANNEX C

SAMPLING OF ZIRCONIUM POWDER FOR USE IN EXPLOSIVE AND PYROTECHNIC INDUSTRY

(*Clause* 5)

C-1 GENERAL REQUIREMENTS OF SAMPLING

C-1.1 In drawing, preparing, storing and handling test samples, the following precautions and directions shall be observed.

C-1.2 Samples shall not be taken in an exposed place.

C-1.3 Precautions shall be taken to protect the samples, the material being sampled, the sampling instrument and the containers for samples from adventitious contamination.

C-1.4 To draw a representative sample, the contents of each container selected for sampling shall be mixed thoroughly by suitable means.

C-1.5 The samples shall be placed in clean, dry airtight glass or other suitable containers which have no action on the material.

C-1.6 The sample containers shall be of such a size that they are almost completely filled by the sample.

C-1.7 Each sample container shall be sealed air-tight with a stopper after filling, and marked with all particulars of the material (*see* **4.2**) and date of sampling.

C-1.8 Samples shall be stored in such a manner that the temperature of the material does not vary unduly from the ambient temperature.

C-2 SCALE OF SAMPLING

C-2.1 Lot — In any consignment, all the containers belonging to the same batch of manufacture shall constitute a lot.

C-2.1.1 For ascertaining the conformity of the material in a lot to the requirements of the specification, samples shall be tested from each lot separately.

C-2.1.2 The number of containers to be selected from a lot shall depend upon its size and shall be in accordance with Table 2.

TABLE 2 NUMBER OF CONTAINERS TO BE SELECTED FOR SAMPLING

(*Clause* C-2.1.2)

Sl No. **(1)**	**Lot Size** *N* **(2)**	**Sample Size** *n* **(3)**
i.	2 to 15	2
ii.	16 to 25	3
iii.	26 to 100	5
iv.	101 to 150	8
v.	151 and above	13

C-2.1.3 These containers shall be selected at random. In order to ensure the randomness of selection, procedures given in IS 4905 may be followed.

C-3 PREPARATION OF TEST SAMPLES AND REFEREE SAMPLES

C-3.1 From each of the containers selected according to **C-2.1.3** a small representative portion of the material not less than 100 g shall be taken out.

C-3.2 Out of these portions, small but equal quantities of the material shall be taken and thoroughly mixed to form a composite sample not less than 150 g. The composite sample shall be divided into three equal parts, one for the purchaser, another for the supplier and the third to be used as a referee sample.

C-3.3 The remaining portion of the material from each container shall be divided into three equal parts, each forming an individual sample. One set of the individual samples representing the containers shall be marked for the purchaser, another for the supplier and third to be used as referee sample.

C-3.4 All the individual samples and composite samples shall be immediately transferred to thoroughly dried containers which are sealed airtight with stoppers. These shall be labelled with all the particulars of sample given under **4.2**.

C-4 NUMBER OF TESTS

C-4.1 Tests for determination of volatile matter shall be performed on the individual samples.

C-4.2 Tests for all other characteristics given in **3** shall be performed on the composite sample.

C-5 CRITERIA FOR CONFORMITY

C-5.1 For Individual Samples — From each set of test results for volatile matter, the mean ($\bar{X}$) and range (R) of test results shall be computed separately (the range being defined as the difference between the maximum and the minimum values of the test results).

C-5.1.1 The lot shall be declared as conforming to the requirements of volatile matter if ($\bar{X}$ + 0.6 R) as calculated from the relevant test results is less than or equal to the maximum value specified in **3**.

C-5.2 For Composite Sample — For declaring the conformity of the lot to the requirements of the specification, all the test results on the composite sample satisfy the corresponding requirements given in **4**.