Specification no. : HEMRL/PYRO/FS&CD/FS/R0/5, Rev-03

PROVISIONAL SPECIFICATION FOR AMORPHOUS STABILIZED RED PHOSPHORUS

High Energy Materials Research Laboratory

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1) FOREWORD:

This specification has been prepared by Director, HEMRL, Sutarwadi, Pune-411021. For additional copies or any other enquiry regarding this specification, reference should be made to the Inspecting Authority named in the tender or contract.

2) SCOPE:

This specification govern the manufacture, supply and inspection of amorphous stabilized Red Phosphorus for processing of composition for 81 mm AT-AL Smoke Grenade.

3) TEST REQUIREMENTS:

Sr. No.	Characteristics	Passing standard	Specification/Test Methods
1	Appearance	Reddish violet amorphous powder	Visual
2	Total Red Phosphorus content	95-97%	Appendix-'A'
3	Phosphorus (yellow) content % by mass	0.01% max	Appendix-'B'
4	Acidity (as H_2SO4) % by mass	0.1% max	Appendix-'C'
5	Free moisture % by mass	0.2 % max	Appendix-'D'
6	Iron content (as Fe)	<100 ppm	Appendix-'E'
7	Copper content (as Cu)	<50 ppm	Appendix-'E'
8	Particle size (sieve test), % by mass. Passing through 240 mesh (63µm IS Test sieve)	Minimum 90%	Appendix-'F'
9	Stabilizer (as $Mg(OH)_2$) content	3±0.5 %	Appendix-'G'

Appendix-'A'

4) DETERMINATION OF RED PHOSPHORUS (Ref. JSS:6810-56:2014):

Reagents:

(a) Magnesia Mixture Preparation of

Constituents:

(aa) 50 g of hydrated Magnesium chloride ($MgCl_2.6H_2O$)

(ab) 100 g Ammonium chloride

(ac) 2 ml concentrated Hydrochloric acid.

Method of Preparation: Dissolve 50 g of hydrated Magnesium chloride and 100 g of Ammonium chloride in 500 ml of water. Add slight excess of Ammonia solution. Allow standing overnight and filter if precipitate is present. Acidity with dilute HCl and add further 2 ml of concentrated HCl and dilute to 1000 ml.

(b) Aqua Regia: 3 parts of concentrated Hydrochloric acid and 1 part of concentrated Nitric acid.

(c) Citric Acid Solution 20 %.

Procedure:

- On a small watch glass place 0.15 to 0.20 g of sample on dry basis and weigh accurately (M1). Transfer as much of the Phosphorus as possible by tapping into a tall 400 ml unlipped beaker covered with a watch glass. Reweigh the watch glass (M2). Find the exact mass of sample taken (M1-M2). Cover the Phosphorus in the beaker with 20 ml of cold distilled water followed by 30 ml of aqua-regia. If necessary initiate the reaction by warming but once the reaction started, allow it to proceed quietly of its own accord. Any relatively large particles of Phosphorus should be crushed with suitable glass rod and the beaker should be left for least 30 minutes on a boiling water bath to complete reaction. Care must be taken to see that all the Phosphorus is in solution before proceeding further.
- Cool the contents of the beaker. If the insoluble residue appears, filter through a No. 42 Whatman filter paper and wash the funnel and filter paper thoroughly with hot water. To the solution add 5 g of Citric acid (i.e. 25 ml of a 20% solution) and neutralize with strong Ammonia solution.
- Add 50 ml of Magnesia mixture and 20 drops of phenolphthalein solution. Heat the solution to boiling point and while it is still boiling, very slowly run in dilute

Ammonia solution (i.e. vol ammonia solution per 9 vol distilled water approximately 1.5 N) with constant stirring until a crystalline. Precipitate appears.

- Cool the mixture. Add concentrated Ammonia approximately to one fifth the volume of the solution, stir and leave aside overnight or at least for 4 hours. Wash the precipitate thrice by decantation with dilute Ammonia transferring it to a silica Gooch crucible containing a layer of asbestos and which has been previously ignited to constant mass (M3) at bright red heat. Wash the precipitate free from chloride with dilute Ammonia solution and finally moisten it with several drops of saturated solution of Ammonium nitrate in dilute Ammonia solution.
- Dry the crucible in an oven a 100 °C to 140 °C and then ignite gently at first (e.g. in an open nickel crucible heated over a suitably controlled Bunsen flame) until all fumes of Ammonia have been displaced. Finally ignite to constant mass (M4) at bright red heat (i.e. 900 °C to 1000 °C).

Calculation:

$$\text{Phosphorus, \% by mass} = \frac{(M_4 - M_3) \times 0.2786 \times 100}{(M_1 - M_2)}$$

Appendix-'B'

5) DETERMINATION OF WHITE PHOSPHORUS (Ref. JSS:6810-56:2014):

Procedure- Weigh accurately about 10 g of sample in a measuring cylinder; add 20 ml of carbon disulphide. Shake well allow it to settle for 2 hours. Place a few drops of the clear supernatant liquid upon a piece of the copper sulphate solution (made by soaking filter paper in 20 % copper sulphate solution and drying in the boiling water oven. Absence of any brown stain indicates the absence of white phosphorus.

Appendix-'C'

6) DETERMINATION OF ACIDITY AS H_2SO_4 (Ref. JSG 0112:2015)

Apparatus

a) No. 15 IS Sieve.

b) Stoppered glass cylinder.

c) Volumetric flask 250 ml capacity.

Reagents:

(a) 0.1 N Sodium Hydroxide Solution.

(b) 0.1 N Hydrochloric Acid.

(c) Phenolphthalein Indicator.

(d) Methyl orange indicator.

Procedure:

- Shake 10 g of the material passing No.15 IS sieve (if in the form of lumps or coarse powder, crush the same to the required size) with 200 ml of freshly boiled and cooled distilled water in a stoppered glass cylinder for about 10 minutes. Filter the liquid into a 250 ml volumetric flask. Wash the residue thoroughly with distilled water and make up the volume up to the mark. Take exactly 100 ml of extract by pipette and titrate with 0.1 Normal Sodium Hydroxide solution or Hydrochloric Acid using appropriate indicator (as specified in the relevant specification).
- Carry out a blank determination on the distilled water and apply the necessary correction.

Calculation

1 ml of N/10 NaOH= 0.0049 g of H_2SO_4

1 ml of N/10 HCl= 0.0053 g of Na_2CO_3

$$\text{Acidity as } H_2SO_4, \text{ \% by mass} = \frac{(V_1 - V_2) \times f \times 0.0049 \times 100 \times 250}{M \times V}$$

Where,

V_1 = Volume of 0.1 N NaOH consumed for sample, ml.

V_2 = Volume of 0.1 N NaOH consumed for blank, ml.

V = Volume of the extract taken (say 50 ml or 100 ml).

M = Mass of the sample taken.

f = Factor of 0.1 N NaOH.

Appendix-'D'

7) DETERMINATION OF MOISTURE(Ref. JSG 0112:2015)

Apparatus:

a) Oven heated and adjusted to the specified temperature.

b) Flat bottomed glass dish, approximately 60 mm diameter and 30 mm deep having a ground glass cover or Aluminum dish approximately 60 mm in diameter and 30 mm deep, with a fitting cover.

c) Desiccators, with anhydrous Calcium Chloride ($CaCl_2$) as desiccant.

d) Oven maintained at 105°C -5 °C

Procedure

- Heat the dish in the oven at the specified temperature for 30 minutes. Cool it in desiccators and weigh (M_1). Place 5 g of the sample unless stipulated otherwise, in the relevant specification in the dish, replace the cover and weigh accurately (M_2). Uncover the dish and heat the sample in the oven till constant, mass in obtained (unless stipulated otherwise in the relevant specification). Cover the dish with the lid and cool it in desiccators at room temperature and weigh (M_3).
- Express the loss in mass as a percentage on the original sample and record it as either content or volatile matter or both.

Calculation:

$$\text{Percentage of either Moisture content or volatile matter or} = \frac{(M_2 - M_3)}{(M_2 - M_1)} \times 100$$

Where,

M_1- Mass of the empty dish in gm.

M_2- Mass of dish + sample taken (before heating) in gm.

M_3- Mass of the dish + sample (after heating) in gm.

Appendix-'E'

8) TEST FOR COPPER AND IRON

Apparatus:

Atomic Absorption Spectrometer.

Note: The manufacturer's instructions shall be followed for all instrumental analysis.

Reagents:

Conc. Nitric Acid- conforming to IS: 264

Conc. Sulphuric Acid- conforming to IS: 266

Nitro Phenol Solution- Dissolve 0.2 g in hot water and dilute to 100 ml. IS: 265.

Standard Solution of Copper – Prepare standard solution of copper by diluting appropriately the 1000 ppm solution of Merck standard of copper.

Standard Solution of Iron – Prepare standard solution of iron by diluting appropriately the 1000 ppm solution of Merck standard of iron.

Procedure:

Weigh accurately 1.00 g of the material in a 250 ml beaker. Add 50 ml of water. Add 10 ml of conc. HNO3 and rapidly boil down to 3 ml on hot plate. At stage, rapid evolution of nitrous acid fumes appears. Remove the beaker from hot plate and add 10 ml of conc. Sulphuric acid. Heat to fumes and continuously evaporate to near dryness. Cool and dissolve using 6 N hydrochloric acid and dilute to 100 ml in a volumetric flask with 6 N hydrochloric acid.

Determine the copper and iron content by Atomic Absorption Spectrometer using wave length 324.8 nm for copper and 248 nm for iron. The element content, expressed as ppm in given by the formula:

$$\frac{C \text{ X } V}{\text{M}}$$

Where,

C- concentration of the element in test solution, in mg/lit;

V- volume in ml; and

M- mass of the test portion, in g.

Appendix-'F'

9) DETERMINATION OF PARTICLE SIZE (SIEVE TEST):

Weigh accurately 100 g sample. Transfer the material to 63 µm IS test sieve. Sieve the material gently, taking care to avoid dust cloud formation. Transfer the remaining material with aid of soft camel hairbrush to a previously tarred paper and note the weight accurately. Determine percent of mass passing through 63 µm test sieve.

Appendix-'G'

10) DETERMINATION OF STABILIZER CONTENT:

Reagents:

(a) 5% HCl solution
(b) 0.0.1 M EDTA

Procedure:

- Weigh accurately about 5 g (W) of the sample into a beaker.
- Add 50 ml 5% HCl solution and boil for 5 minutes.
- Filter through Whatman filter paper No.42, further wash with 20 ml 5% HCl solution and then with water.
- Collect the filtrate and washing into a 500 ml volumetric flask and make up the volume to the mark with distilled water.
- Stopper the flask and mix the solution well.
- Transfer 100 ml of this solution in to a 250 ml conical flask.
- Add few drop of Methyl Red and neutralize by 1.0N NaOH solution, till yellow color.
- Add drop by drop 1N H_2SO_4 till slight pink color is obtained.
- Add 5 ml Ammonia buffer solution and add 3-4 drops of Erichrome Black-T indicator.
- Titrate against 0.01 M EDTA solution till color changes to blue.
- Note the burette reading (V ml).

Calculation:

$$\text{Stabilizer as } Mg(OH)_2,\ (\%W/W) = \frac{BR \times M \times 5.83}{\text{Sample weight}} \times \frac{500}{100}$$

Where,

BR: Burette reading.
M: The actual molarity of EDTA (~ 0.01 M) when standardized with analytical grade zinc.