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BUREAU OF INDIAN STANDARDS

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Draft Indian Standard

NITRODIAZO ACID — SPECIFICATION

(*Second Revision* of IS 8634)

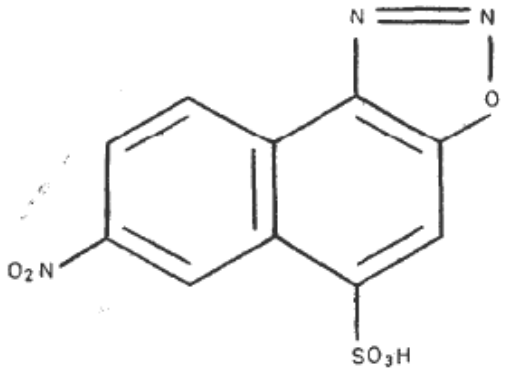
(ICS 71.080.99)

Dye Intermediates Sectional Committee, PCD 26	Last date for comments: 28 October 2023

FOREWORD

(*Formal Clause to be added later*)

Nitrodiazo acid ($C_{10}H_5N_3O_6S$), chemically described as 1-diazo-2-naphthol-6-nitro-4-sulphonic acid, is an important intermediate used in the manufacture of wool dyestuffs. It is obtained by nitration of diazo acid (1-diazo-2-naphthol-4-sulphonic acid). It is represented by the following structural formula:



NITRODIAZO ACID
(Molecular Mass 295.2)
CAS No. 5366-84-7

This standard was originally published in 1977 and subsequently revised in 1987. In order to update the standard in accordance with the quality of the material being produced and also to introduce High-performance liquid chromatographic method for the determination of assay, the standard has been revised. A new characteristic 1,2,4-diazo acid and its test method for determination is incorporated.

The bags in which the material is stored or transported may also be labelled with pictograms, signal word, hazard statement, and precautionary statement as given in Annex E, which are derived from GHS guidelines. At the time of publication, the latest edition of GHS guidelines was referred and are subject to revision and parties to agreement, are encouraged to investigate the possibility of applying the most recent labels as indicated.

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 the methods of sampling and tests method for Nitrodiazo acid.

2 REFERENCE

The following standards contain provisions which through reference in the 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 agreement, based on the standard are encouraged to investigate the possibility of applying the most editions of the standards indicated below:

IS No.	*Title*
1070: 2023	Reagent grade water — Specification (*fourth revision*)
2552: 1989	Steel drums (galvanized and ungalvanized) — Specification (*third revision*)
5299: 2001	Methods of sampling and tests for dye intermediates *(first revision)*
5762: 1970	Methods for determination of melting point and melting range

3 REQUIREMENTS

3.1 Description

The material shall be yellowish to reddish brown powder or wet cake. The material darkens on prolonged storage.

3.2 The material shall also comply with the requirements given in Table 1, when tested according to the methods prescribed in col 4 of Table 1.

Table 1 Requirements for Nitrodiazo Acid
(*Clauses* 3.2, 5.4.1, 5.4.2 *and* 6.1)

Sl. No.	**Characteristic**	**Requirement**	**Method of Test, Ref to Annex**
(1)	(2)	(3)	(4)
i)	Assay, percent by mass, *Min*	55	A
	Or		
	Assay by HPLC[1)], percent area, *Min*	90	B
ii)	1,2,4-diazoacid by HPLC, percent area *Max*	10	B
iii)	Free acidity (*as* H_2SO_4), percent by mass, *Max*	15	C
iv)	Solubility in sodium hydroxide solution	To pass the test	D

[1)]In case of disputes, determination of assay by HPLC shall be the referee method.

4 PACKING AND MARKING

4.1 Packing

The material shall be packed in steel drums (*see* IS 2552) lined with suitable polyethylene film or as agreed to between the purchaser and the supplier. Each container shall be securely closed.

4.2 Marking

Each container shall be legibly and indelibly the following information:

a) Name of the material;
b) Name of the manufacturer and his recognized trade-mark, if any;
c) Batch number;
d) Gross, net and tare mass;
e) Month and year of manufacture;
f) Shelf life of the material; and
g) Any other statutory requirements

4.2.2 *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.

5 SAMPLING

5.1 The method of drawing representative samples of the material shall be as prescribed in **4** of IS 5299.

5.2 Number of Tests

5.2.1 Test for assay shall be conducted on each of the individual samples.

5.2.2 Tests for the determination of all other characteristics given under Table 1, shall be conducted on the composite sample.

5.3 Criteria for Conformity

5.3.1 *For Individual Samples*

The lot shall be declared as conforming to the requirement of assay if each of the individual test results satisfies the relevant requirement given in Table 1.

5.3.2 *For Composite Samples*

For declaring the conformity of a lot to the requirements of all other characteristics tested on the composite sample, the test results for each of the characteristics shall satisfy the relevant/ requirements given in Table 1.

6 TESTS

6.1 Tests shall be carried out according to the methods prescribed in col 4 of Table 1.

6.2 Quality of Reagents

Unless specified otherwise, 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 ASSAY FOR NITRODIAZO ACID

A-1 OUTLINE OF THE METHOD

The material is coupled with alkaline solution of resorcinol and resulting monoazo dye is reduced by standard titanium trichloride solution.

A-2 APPARATUS

A-2.1 Titanous Chloride Bottle

A-2.2 Reduction Flask — 250 ml capacity, detachable from lid with ground glass joint. The lid is provided with five ground glass sockets. The central hole is for feeding titanium trichloride solution covered with kerosine while other holes are for burette, thermometer, reflux-condenser and carbon dioxide bubbling.

A-2.3 Graduated Flasks

A.3 REAGENTS

A-3.1 Resorcinol Solution 10 percent (*m/v*) — Dissolve 10 g of the pure substance in 40 ml of 10 percent (*m/v*) sodium hydroxide solution and water and dilute the solution to 100 ml with water in a volumetric flask.

A-3.2 Sodium Hydroxide Solution 10 percent — Dissolve 50 g of sodium hydroxide pellets in water and dilute to 500 ml in a volumetric flask.

A-3.3 Dilute Acetic Acid Solution of 1: 1

A-3.4 Ammonium Thiocyanate Solution — 20 percent (*m/v*).

A-3.5 Sodium Potassium Tartrate Solution — 15 percent (*m/v*).

A-3.6 Standard Titanous Chloride Solution (0.1 N)

Prepare a 15 percent (*m/v*) solution of titanous chloride. Take 200 ml of this solution and filter through a thick pad of glass wool. Add 100 ml of concentrated hydrochloric acid and mix by passing a current of an inert gas, such as carbon dioxide or nitrogen for some time. Finally add 700 ml of boiled water and mix by passing inert gas. Store the reagent in a bottle under carbon dioxide supplied by Kipp's apparatus. Paint the bottle with black paint to protect the solution from sunlight. It is advantageous, though not necessary, to allow the reagent to stand for 10 days before it is used.

A-3.7 Standard Ferric Ammonium Sulphate Solution (0.1 N)

For preparing one liter of this solution, dissolve 58.821g of pure ferrous ammonium sulphate $Fe[(NH_4)_2SO_4]_2.6H_2O$ in 300 ml of water and add 40 ml of concentrated sulphuric acid. Shake well. Weigh exactly 4.74 g of potassium permanganate, dissolve in 200 ml of warm water and slowly add to ferrous ammonium sulphate solution with stirring. Potassium permanganate solution should be just enough to oxidize ferrous salt. Add the last few millilitres in small portions. Cool the solution and dilute to 1000 ml with water. Standardize the solution against a standard solution of potassium dichromate.

A-4 PROCEDURE

A-4.1 Weigh accurately about 100 g of wet cake of nitrodiazo acid. Dissolve in water and dilute to 1 000 ml in a measuring flask. Pipette out 100 ml of the solution and couple this with 50 ml (*m/v*) resorcinol solution with 70 ml of sodium hydroxide solution at 15 °C to 20 °C. Allow to stand for about one and a half hours. Finally dilute accurately to 1 000 ml.

A-4.2 Take a 10 ml aliquot portion of the solution prepared as in **A-4.1** into a 250 ml reduction flask, adjust the pH to 4 by dilute acetic acid. Add 50 ml of sodium potassium tartrate solution. Pass carbon dioxide gas in the storage bottle containing titanous chloride solution. Immediately draw 25 ml titanous chloride solution through an automatic dispenser, burette or by pipette and add it to the reduction flask. Heat the flask in a boiling water-bath, while bubbling carbon dioxide through the solution. Titrate the excess titanous chloride against standard ferric ammonium sulphate solution at 15 °C to 20 °C with 5 ml of ammonium thiocyanate solution added near the end point as an indicator. The end point is marked by an orange colour. Call this as reading A.

A-4.3 Determine blank reading following the procedure given in **A-4.2** with 25 ml of water, containing the same amounts of titanous chloride, hydrochloric acid and ammonium thiocyanate indicator solution. Call this as reading B.

A-5 CALCULATION

$$\text{Assay, percent by mass} = \frac{(B-A)\times N\times 295.2\times 10}{M}$$

where

B = Volume in ml of ferric ammonium sulphate titre reading with blank,

A = Volume in ml of ferric ammonium sulphate titre reading with sample,

N = Normality of ferric ammonium sulphate solution, and

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

ANNEX B

[*Table* I, *SI No.* (i), (ii)]

ASSAY OF NITRODIAZO ACID AND 1,2,4 DIAZO ACID BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

B-1 OUTLINE OF METHOD

High-performance liquid chromatography or High-pressure liquid chromatography (HPLC) is a chromatographic method that is used to separate a mixture of compounds in analytical chemistry and biochemistry so as to identify, quantify or purify the individual components of the mixture.

B-2 OBJECTIVE

To determine and active content of Nitrodiazo acid and 1,2,4-diazo acid content by High-performance liquid Chromatography.

B-3 APPARATUS

Binary Gradient Liquid chromatography system with UV detector capable of being operated under conditions suitable for resolving the individual constituents into distinct peak may be used.

B-4 COLUMN — C18 100 Å, 250 × 4.6 mm, 5 µm or equivalent.

B-5 REAGENTS

B-5.1 Acetonitrile, HPLC grade

B-5.2 Water, HPLC grade

B-5.3 Tetra n-butylammonium hydrogen sulphate

B-5.4 Nitrodiazo acid, Reference Standard

B-6 STANDARD PREPARATION

Weigh accurately 0.0500 g (50 mg) reference standard Nitrodiazo acid in 100 ml volumetric flask dissolve it in Water : Acetonitrile (2:8) and make up to the mark with Water : Acetonitrile (2:8).

B-7 SAMPLE PREPARATION

Weigh accurately 0.500 g (50 mg) sample in 100 ml volumetric flask dissolve it in Water: Acetonitrile (2:8) and make up to the mark with Water: Acetonitrile (2:8)

B-8 BUFFER PREPARATION

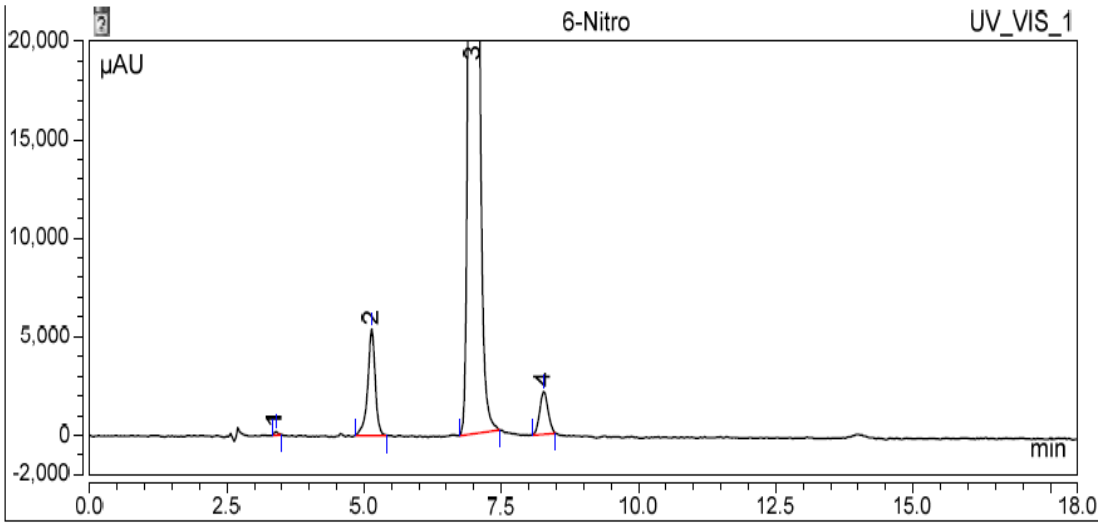
Take 2 g Tetra-n-butylammonium hydrogen Sulphate in 1000ml volumetric flask. Add 200 ml HPLC grade water and complete dissolve it and make total volume with HPLC grade water. Sonicate and filter though the 0.20 µm Membrane filter.

B-9 FLOW RATE: 0.80 ml/min

B-10 MOBILE PHASE

Time	Acetonitrile	Buffer
0.01	40	60
18.00	STOP	

B-11 COLUMN OVEN TEMPERATURE	Ambient	
B-12 INJECTION VOLUME	2µl	
B-13 RUN TIME	18 minute	
B-14 WAVE LENGTH	254 nm	
B-15 PEAK TIME	1,2,4-Diazoacid	5.12 minute
	Nitrodiazo Acid	7.15 minute



B-16 CALCULATION

Calculate the peak area of individual constituent pertaining to Nitrodiazo acid the chromatogram of the material. The concentration of the constituent may be obtained as per below calculation.

Percent of Nitrodiazo acid = $\frac{A}{Total\ Area} \times 100$

where,

A — area of Nitrodiazo acid peak

B-16.2 Similarly, 1,2,4 diazoacid acid content shall be calculated.

ANNEX C
[*Table* 1, *Sl.No.* (iii)]
DETERMINATION OF FREE ACIDITY

C-1 REAGENTS

C-1.1 Concentrated Hydrochloric Acid

C-1.2 Barium Chloride Solution — 10 percent (*m/v*)

C-2 PROCEDURE

Weigh accurately 10 g of the sample in a 250 ml beaker, dissolve in about 150 ml of water. Filter the solution into 500 ml measuring flask and adjust to the mark. Pipette out 50 ml aliquot sample into 250 ml beaker and add 50 ml of water. Add about 0.5 ml of hydrochloric acid. Warm the solution and then add 15 ml of barium chloride solution. Filter through ashless Whatman filter paper. Wash the precipitate with hot water till it is free from chloride. Dry in an oven, incinerate and weigh the white residue to constant mass.

C-3 CALCULATION

Free acidity (as H_2SO_4), percent by mass = $\frac{m \times 98 \times 500 \times 100}{233.4 \times 50M}$

where

m = mass of the precipitate, in g; and

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

ANNEX D
[*Table* 1, *Sl.No.* (iv)]
DETERMINATION OF SOLUBILITY IN SODIUM HYDROXIDE SOLUTION

D-1 REAGENT

D-1.1 Sodium Hydroxide Solution — Dissolve 10 g of caustic soda pellets in water contained in 100-ml measuring flask and make up to the mark.

D-2 PROCEDURE

Weigh about 15 g (on 100 percent assay) of the material and dissolve in 100 ml of sodium hydroxide solution. The sample shall be taken to have passed the test if a clear solution is obtained which, on filtration, does not leave any residue.

ANNEX E
(*Forward*)

Pictograms, signal word, hazard statement and precautionary statement

Pictogram(s) :		
Signal Word :	Flammable	Corrosive
Hazard Statement :	H242	Heating may cause a fire
	H314	Causes severe skin burns and eye dam age.
Precautionary Statement :	P210	Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking
	P262	Do not get in eyes, on skin, or on clothing
	P351	Rinse cautiously with water for several minutes
	P353	Rinse skin with water/shower
	P281	Use personal protective equipment as required.
	P313	Get medical advice/attention