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BUREAU OF INDIAN STANDARDS

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Draft Indian Standard

4-CHLORO-2-NITROANILINE — SPECIFICATION

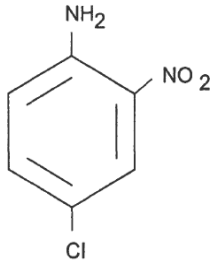
(*Second Revision of* IS 7643)
(ICS 71.080.99)

Dye Intermediates Sectional Committee, PCD 26	Last date for comment 28 January 2023

FOREWORD

(*Formal clauses to be added later*)

4-Chloro-2-nitroaniline ($C_6H_5O_2N_2Cl$) is an important dye intermediate, used in the manufacture of dyestuff and pigments. It is also used as a diazo component in azoic dyeing in which case it is called Fast Red 3 GL Base. It is represented by the following structural formula:



4-Chloro-2-Nitroaniline
Molecular Mass 172.6
CAS no. 89-63-4

This standard was first published in 1975 and subsequently revised in 2003. In *first* revision, thin layer chromatography was included as the method of test to keep pace with the ongoing trends in the industry. In this (second) revision, 4-chloro-2-nitroaniline has been divided into two grades i.e dry material and wet material. Requirement for determination of 4-chloro-2-nitroaniline content and impurities such as 2,5-dichloroaniline , 2,5-dichloronitrobenzene, 2-Chloro-4-nitroaniline and other impurities by GC method has been incorporated. Further, three new characteristics such as moisture content by KF, acetone Insoluble and diazo purity has been 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 mentioned at Annex F, which are derived from GHS guidelines. At the time of publication, the latest edition of GHS guidelines were 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 methods of sampling and test for 4-Chloro-2-Nitroaniline in two grades.

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*
1070 : 2023	Reagent grade water — Specification *(fourth revision)*
2552 : 1989	Steel drums (galvanized and ungalvanized) *(third revision)*
5299 : 2001	Methods for sampling and tests for dye intermediates *(first revision)*

3 GRADES

3.1 There shall be two grades of the material, namely:

a) Dry material
b) Wet material

4 REQUIREMENTS

4.1 Description

The material shall be in the form of Orange to Bright Orange powder, free from lumps and extraneous substances for dry material and Orange to Bright Orange wet cake, free from lumps and extraneous substances for wet material.

4.2 The material shall also comply with the requirements as given in Table 1, when tested according to the methods prescribed in col 5 and 6 of Table 1.

Table 1 Requirements for 4-Chloro-2-Nitroaniline
(*Clauses* 4.2, 6.3.1, 6.3.2 *and* 7.1)

Sl No.	**Characteristic**	**Requirement**		**Method of Test, Ref to**	
		Dry	Wet	**Annex**	**IS**
(1)	(2)	(3)	(4)	(5)	(6)
i)	Assay by diazo, percent by mass, on dry basis, *Min*	98.50	80	A	—
	Or				
	Assay by GC[1)], percent area, *Min*	99.0	99.0	B	—
ii)	Impurities by GC method				

	a) 2,5 Dichloroaniline Content, percent area, *Max*	0.20	0.20	B	
	b) 2,5 Dichloronitrobenzene, percent area, *Max*	0.20	0.20		
	c) 2-chloro-4-nitroaniline, percent area, *Max*	0.50	0.20		
	d) Other impurities, percent area, *Max*	0.50	0.50		
iii)	2-chloro-4- nitroaniline by TLC, percent by mass, *Max*	0.20	0.20	C	—
iv)	Moisture content by KF, percent by mass, *Max*	0.50	20	D	IS 2362
v)	Matter insoluble in acetone, percent by mass, *Max*	0.20	—	E	—
vi)	Melting point[2)]	115 °C to117 °C	115 °C to 117 °C	F	—

[1)] In case of dispute, determination of assay by GC shall be the referee method
[2)] Melting point is optional requirement

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

4.2.1 Each container shall bear 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, impurities, moisture content and melting point shall be conducted on each of the individual samples.

5.2.2 Tests for the determination of all other characteristics like description, 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, impurities, moisture content and melting point, 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 5 and 6 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 (Diazo) OF 4-CHLORO 2-NITRO ANILINE

A-1 APPARATUS

A-1.1 Beaker — 1 000 ml

A-1.2 Calibrated Burette — 50 ml

A-1.3 Glass Rod

A-1.4 Electric Stirrer

A-1.5 Analytical Balance

A-2 REAGENTS

A-2.1 Sulphuric acid — purity 98 percent

A-2.2 Hydrochloride acid — purity 30 percent w/w

A-2.3 Potassium bromide (AR Grade)

A-2.3 Standardize Sodium Nitrite solution — 0.2 N

A-2.4 Ice

A-2.5 Starch Iodide Paper

A-3 PROCEDURE

Take 1g to 1.5 g of sample on butter paper. Transfer it in one liter beaker. Add 50 ml pure Sulphuric acid (98 percent). Stir with a glass rod and dissolve it. Add 400 ml distilled water under stirring then cool to room temperature. Then transfer the solution into a one-liter beaker. Add 30 ml Hydrochloride acid (30 percent w/w) and 1.0 g Potassium bromide and ice pieces. Temperature should be maintained 0 °C to 5 °C. Then titrate against 0.2 N sodium nitrite solution. Observe the end point as a faint blue ring just appears on Starch Iodide paper. Endpoint should be constant for 5 min.

A-4 CALCULATION

$$\text{Assay, percent by mass} = \frac{V \times N \times 172.5}{weight\ of\ sample \times 1000} \times 100$$

where

V = volume of Sodium nitrite solution, in ml
N = normality of sodium nitrite solution, and
W = mass of the sample, in g

ANNEX B

(Table 1, *S1No.* (ii))

DETERMINATION OF 4-CHLORO - 2-NITRO ANILINE ASSAY, 2, 5 DICHLOROANILINE CONTENTS, 2,5 DICHLORONITROBENZENE CONTENTS , 2-CHLORO-4-NITROANILINE CONTENTS BY GAS CHROMATOGRAPHY USING FLAME IONIZATION DETECTOR

B-1 GENERAL

4-Chloro-2-Nitroaniline and impurities like 2,5 Dichloroaniline, 2,5 Dichloronitrobenzene, 2-chloro-4-nitroaniline and other impurities are determined using gas chromatography (GC).

B-2 APPARATUS

B-2.1 Analytical Balance

B-2.2 Syringe

B-2.3 Volumetric Flask — 10 ml

B-2.4 Gas chromatograph with FID Detector

B-2.4.1 Gas Chromatography Parameters

Column Details	DB 1701 or Equivalent Film Thickness : 1.0 µm Column Dimension : Length 30 m, Internal Diameter 0.25 mm, Temperature Limit : -20°C to 280°C
Carrier Gas	Nitrogen
Carrier Gas Pressure	110 kpa (16psi)
Injection Mode	Split (1:40)
Purge Flow	3.0 ml/min
Make up pressure/flow	25ml/min
Hydrogen pressure/flow	30 ml /min
Zero air pressure/flow	350ml/min
Oven parameters	Initial Temperature — 120 °C Hold time — 0.0 min Program rate — 10 °C/min Final Temperature — 240 °C Final Time — 13 min
Total run time	25 min
Injector Temperature	280 °C
Detector Temperature	300 °C
Injection Volume	1.0 µl from sample preparation

NOTE — The above gas chromatographic (GC) conditions are suggestive. However, any GC method having difference in detector, column packing material and type (like packed/capillary, diameter, length, film thickness etc.), calibration technique (internal standard, external standard, area normalization, percent area etc.), carrier gas (He, H_2, N_2) may be used with applicable GC operating parameters, provided standardization and calibration of the components is established after setting GC parameters for the resolution and accuracy level as specified in this standard.

B-3 REAGENTS

B-3.1 Acetone

B-3.2 4-chloro- 2- nitroaniline, Reference standard

B-4 SAMPLE PREPARATION

Weigh accurately about 1 g of 4-chloro-2-nitroaniline into a 10 ml volumetric flask and dissolved in acetone and make up volume upto mark the mark using acetone. Mix well.

B-5 PROCEDURE

Take 1.0 µl sample in a micro syringe and confirm that there are no air bubbles in the syringe. Inject the sample by Auto Sampler / manual. Allow the instrument to complete run time.

B-6 PEAK TIME

4-Chloro-2-Nitroaniline : 16.6 minutes

2, 5 Dichloroaniline : 10.4 min

2, 5 Dichloronitrobenzene: 10.6 min

2-chloro-4-nitroaniline : 20.0 min

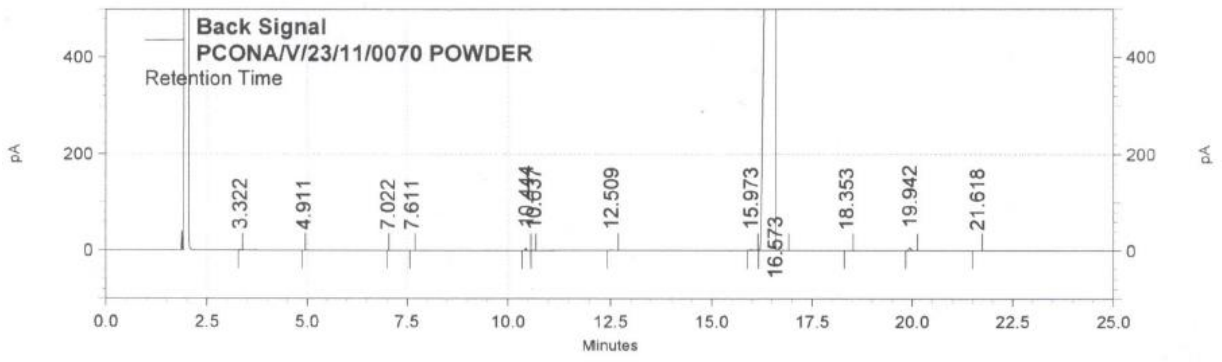


FIG 1 A TYPICAL CHROMATOGRAM

A-6 CALCULATION

A-6.1 Calculate the peak area of individual constituent pertaining to 4-chloro-2-nitroaniline on the chromatogram of the material. The concentration of the constituent may be obtained on the basis of peak area on chromatogram obtained with standard 4-chloro-2-orthonitroaniline.

$$\text{Assay, percent by area} = \frac{\text{para chloro orthonitroaniline peak area in the sample}}{\text{Sum Areas of all peaks in the chromatogram}} \times 100$$

A-6.2 Similarly, contents of like 2,5 Dichloroaniline, 2,5 Dichloronitrobenzene and 2-chloro-4- nitroaniline shall be calculated.

A-6.3 Other impurities content , percent by area = Assay – concentration **(** 2,5 Dichloroaniline + 2,5 Dichloronitrobenzene + 2-chloro-4- nitroaniline)

ANNEX C
(*Table* 1, *S1No.* (iii))
2-CHLORO-4-NITROANILINE BY THIN LAYER CHROMATOGRAPHIC METHOD

C-1 GENERAL

Impurities are determined by thin layer chromatography. Reference may be made to IS 5299 for details of TLC test method to be followed. However, necessary details of test conditions are given below for guidance only:

a) Product name	:4-Chloro-2-Nitroaniline or Red 3 GL
b) Sample solution (on 100 percent basis	:5 percent in acetone
c) Application / volume for spotting	:10 µl (for sample) :2 µl and 4 µl (for impurities)
d) Standard	:Reference standard
e) Test substance for impurities	:2-Chloro-4-Nitroaniline
f) Plate type	:Silica gel G
g) Eluent	:Benzene : Ethyl Acetate

	90 : 10 (Saturated -Double run)
h) Elution time	:1h
j) Temperature	:25 ± 5°C
k) Detection spray	:[1)] $SnCl_2$ solution + PDAB solution
m) Evaluation	:Semi quantitative
n) Approximate Rf Value –Main band	:4-Chloro-2-Nitroaniline : Rf 0.6
— Impurities	:2-Chloro-4-Nitroaniline : Rf 0.3

[1)]$Sncl_2$ solution : 10 percent solution in (1:1) water + 5 NHCI
PDAB solution : *p*-Dimethylamino benzaldehyde 1 percent solution in (1: 0.5:0.5) Methanol : Water: 5N HCI.

ANNEX C

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

DETERMINATION OF 4-CHLORO 2-NITRO ANILINE MOISTURE CONTENT BY KARL FISCHER

C-1 REAGENT

C-1.2 Karl Fischer Reagent

C-1.3 Methanol Dried

C-2 APPARATUS

C-2.1 Karl Fischer Instrument with Detection Limit

C-2.2 Micro syringe

C-2.3 Digital Balance

C-3 PROCEDURE

Take about 60 ml of dry methanol in titration vessel to dip the platinum electrode and start stirrer. Neutralize initial moisture in methanol. Weigh 0.5 g to 1.0 g testing sample and keep it ready for testing. Stop the stirrer and remove the large rubber stopper of the beaker and add a weighed quantity of sample right into the methanol in the beaker. Care should be taken not to lose any part of sample on the wall of the beaker or on the electrode. The stopper is removed for minimum time to avoid atmospheric moisture to get into the beaker. Immediately after adding the sample, start the stirrer. Wait for about 20 s to 25 s to allow the sample to get dissolved into the methanol. Press the START button.

C-4 CALCULATION

The calculation of moisture content can be calculated by using the following formula.

$$\text{Moisture content, percent w/w} = \frac{V \times F \times 100}{W \times 1000}$$

where

V = volume of karl fischer reagent consumed, in ml:
F = karl fischer reagent factor, in mg/ml and;
W = weight of sample taken, in g

ANNEX D
(*Table* 1, *Sl No.* (v))
DETERMINATION OF MATTER INSOLUBLE IN ACETONE

D-1 APPARATUS AND REAGENT

D-1.1Filtration Assembly

D-1.2 Whatman Filter paper 42 micron (diameter 70mm)

D-1.3 Measuring cylinder

D-1.4 Vacuum Pump

D-1.5 Weighing Balance

D-1.6 Acetone

D-2 PROCEDURE

Weigh filter paper using a balance with 0.0001 g precision. Record weight at initial weight of filter paper (W_1). Connect assembly to vacuum pump. Dissolve 5.0 g of the sample in approx.100 ml acetone and dissolve the sample. Record weight of sample (S). Turn vacuum on and filter above solution. Wash the filter paper with 50 ml Acetone to dissolve the sample. Remove filter paper from filter assembly and dry at 80 ºC for 1 h. Weigh the filter paper and record weight as final weight of paper (W_2).

D-3 CALCULATION

$$\text{Insoluble in Acetone, percent by mass} = \frac{W_2 - W_1}{S} \times 100$$

where

W_2 = final weight of filter paper with residue, in g
W_1 = initial weight of filter paper, in g and
S = mass of the sample, in g

ANNEX E
(*Table* 1, *Sl No.* (v))

DETERMINATION OF MELTING POINT OF 4-CHLORO 2-NITRO ANILINE

E-1 APPARATUS

E-1.1 One end sealed capillary tube

E-1.2 Melting point Apparatus

E-2 PROCEDURE

Grind the sample into powder form & fill it in a one end sealed glass capillary tube. Keep this capillary tube in a melting point apparatus, start slowly heating and observe the temperature in a calibrated thermometer/temperature controller. When substance in the capillary tube starts melting, note down the temperature and when the substance is completely melted, note down the temperature.

ANNEX F
(*Foreword*)

Pictograms, signal word, hazard statement and precautionary statement

Pictogram(s) :	  
Signal Word :	**WARNING HEALTH HAZARD ENVIRONMENTAL HAZARD**
Hazard Statement :	Harmful if inhaled, swallowed or absorbed through skin. Avoid breathing dust or vapour. Avoid contact with eyes, skin and clothing. Use with adequate ventilation. Wash thoroughly after handling.
Precautionary Statement :	In case of contact, immediately flush eyes or skin with plenty of water atleast 15 minutes while removing contaminated clothing and shoes. Call a physician. If inhaled, remove to fresh air, if not breathing, give artificial respiration. Preferably mouth to mouth. If breathing is difficult, get oxygen. If swallowed, give two glasses of water. Call for medical help. Never give anything by mouth to an unconcious person.