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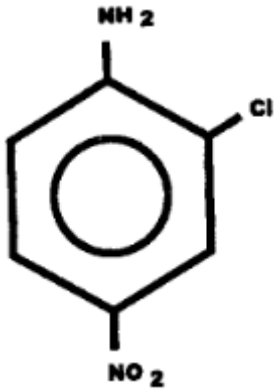
Draft Indian Standard
ORTHO-CHLORO PARA-NITRO ANILINE — SPECIFICATION
(*First Revision* of IS 15132)
(ICS 71.080.30)

Dye Intermediates Sectional Committee, PCD 26	Last date for Comments 29th April 2024

FOREWORD
(*Formal clauses to be added later*)

Ortho-chloro para-nitro aniline is an important intermediate used in the manufacture of azo dyes. It is represented by the following formula:



ORTHO-CHLORO PARA-NITRO ANILINE
Molecular mass: 172.5
CAS no.: 121-87-9

This standard was originally published in 2002. In this (*first*) revision, determination of ortho-chloro para-nitro aniline content (assay) and impurities content that are 3,4-Dichloronitrobenzene, para-chloro ortho-nitro aniline by Gas chromatography have been added. The characteristics of moisture and volatile matter and matter insoluble in methanol have been modified to moisture content and matter insoluble in acetone respectively.

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 G, 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 ortho-chloro para-nitro aniline.

2 REFERENCES

The following Indian 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 given below:

IS No	*Title*
1070:2023	Reagent grade water — Specification *(fourth revision)*
5299:2001	Methods for sampling and tests for dye intermediates *(first revision)*

3 REQUIREMENTS

3.1 Description

The material shall be in the form of dry yellow powder, free from lumps and extraneous substances powder.

3.2 The materials shall also comply with the requirements given in Table 1, when tested according to the methods prescribed in col 4 and col 5 of Table 1.

TABLE 1 REQUIREMENTS FOR ORTHO-CHLORO PARA-NITRO ANILINE
(*Clauses* 3.2, 5.3 *and* 6.1)

Sl No.	**Characteristic**	**Requirement**	**Method of tests, Ref to**	
			Annex	**IS**
(1)	**(2)**	**(3)**	**(4)**	**(5)**
i)	Assay by GC[1)], percent area, *Min*	99.00	A	—
	Or			
ii)	Assay (diazo), percent by mass, *Min*	98.50	B	—
iii)	3,4-Dichloronitrobenzene Content by GC, percent area, *Max*	0.20	A	—
iv)	Para-chloro ortho-nitro aniline by GC, percent area, *Max*	0.20		—
v)	Other impurities by GC, percent area, *Max*	0.50		—
vi)	Moisture Content by Karl Fischer, percent by mass, *Max*	0.50	C	IS 2362

vii)	2,6-Dichloro-4-Nitro aniline, percent by mass, *Max*	0.2	D	—
viii)	4- Nitroaniline, percent by mass (on dry basis), *Max*	0.2		—
ix)	Melting point, ° C, *Min*	105 to 107	E	9 of IS 5299
x)	Acetone Insoluble, percent by mass, *Max*	0.20	F	—

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

4 PACKING AND MARKING

4.1 Packing

The material shall be packed in HDPE /jumbo bags lined with suitable polyethylene film or as agreed to between the purchaser and the supplier.

4.2 Marking

4.2.1 Each bag shall be securely closed and 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;
h) The minimum cautionary notice worded as under:

‘**DANGER! HAZARDOUS SOLID AND VAPOURS RAPIDLY ABSORBED THROUGH SKIN**’.

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 Tests for assay and impurities shall be conducted on each of the individual samples.

5.2.2 Test for the remaining characteristics that are moisture content, melting point and acetone insoluble content 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 requirements of all tests mentioned in **5.2.1**, if each of the individual test results satisfies the relevant requirements given in Table 1.

5.3.2 *For Composite Sample*

For declaring the conformity of the lot to the requirements of the characteristics tested on the composite sample (*see* **5.2.2**), the test result for each of the characteristics shall satisfy the relevant requirement given in Table 1.

6. TESTS

6.1 Tests shall be conducted according to the methods prescribed in col 4 and 5 of Table 1.

6.2 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, *S1. No.* (i), (iii), (iv) *and* (v)]
DETERMINATION OF ASSAY OF ORTHO-CHLORO PARA-NITRO ANILINE BY GAS CHROMATOGRAPHY

A-1 GENERAL

Determine ortho-chloro para-nitro aniline content (assay), 3, 4-dichloronitrobenzene, para-chloro-ortho-nitro aniline content and other impurities content by gas chromatography using flame ionization detector.

A-2 APPARATUS

A-2.1 Analytical Balance

A-2.2 Micro syringe

A-2.3 Volumetric flask — 10ml

A-2.4 Pipette

A-2.5 Gas Chromatograph — any gas chromatograph equipped with a flame ionization detector (FID) may be used with following accessories and typical operating conditions:

A-2.5.1 *Column* — (14 percent cyanopropyl-phenyl)-methylpolysiloxane with length 30 m, inner diameter 0.25 mm and film thickness 1.0 µm or equivalent.

A-2.5.2 *Gas Chromatography Parameters* :

Carrier Gas	: Nitrogen
Injector Temperature	: 275°C
Carrier Gas Pressure	: 110 kpa (16psi)

Column Oven programme

Rate (°C/min)	Temperature (°C)	Hold time (min)
--	120	0
10	240	13

Hydrogen flow : 30 ml/min

Zero air flow : 350 ml/min

Purge Flow : 3.0 ml/min

Make up gas (N_2) flow : 25 ml/min

Split Ratio : 1:40

Detector Type : Flame Ionization Detector (FID)

Detector Temperature : 300 °C

Injection Volume : 1.0 µl

Total run time : 25 min

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.

A-3 REAGENTS

A-3.1 Acetone

A-4 PROCEDURE

Weigh accurately about 1 g of ortho-chloro para-nitro aniline into a 10 ml volumetric flask and dissolved in acetone and make up volume upto mark using acetone and mix well. Take a 1.0 µl sample in a micro syringe and confirm there are no air bubbles. Inject the sample and allow the run to complete run time.

A-5 PEAK TIME

Ortho-chloro para-nitro aniline :20.80 min

3, 4-dichloronitrobenzene :10.38 min

Para-chloro ortho-nitro aniline :16.14 min

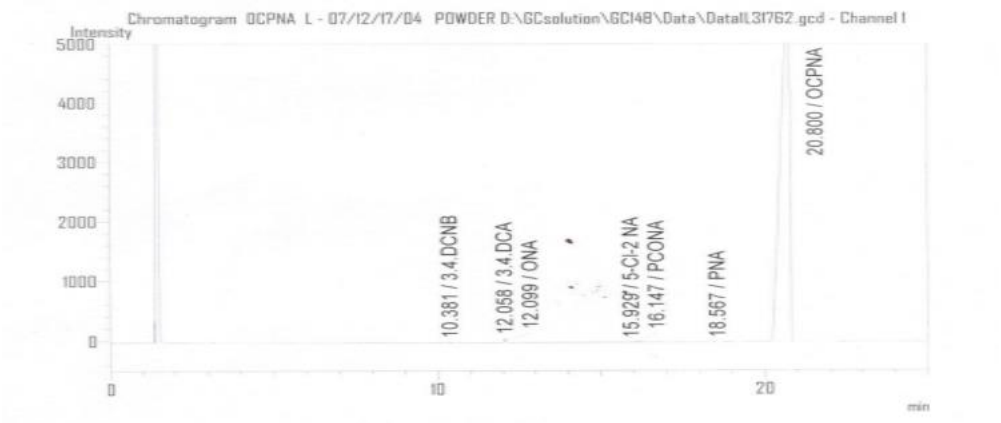


FIG.1 A TYPICAL CHROMATOGRAM

A-6 CALCULATION

A-6.1 Calculate the peak area of individual constituent pertaining to ortho-chloro para-nitro aniline 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 ortho-chloro para-nitro aniline.

$$\text{Assay, percent by area} = \frac{\text{ortho−chloro para−nitro aniline peak area inthe sample}}{Sum\ area\ of\ all\ the\ peaks\ in\ the\ chromatogram} \times 100$$

A-6.2 Similarly, 3, 4-dichloronitrobenzene and para-chloro ortho- nitro aniline content shall be calculated.
A-6.3 Determination of other impurities content shall be calculated as:

Other impurities, percent by area =

$$100 - (Assay + 3{,}4\ dichloronitrobenzene\ content + para - chloro\ ortho - nitro\ aniline\ content)$$

ANNEX B
[*Table* 1, *S1. No.* (ii)]
DETERMINATION OF ASSAY (DIAZO) OF ORTHO-CHLORO PARA-NITRO ANILINE

B-1 APPARATUS

B-1.1 Beaker — 1000 ml

B-1.2 Calibrated Burette — 50 ml

B-1.3 Glass Rod

B-1.4 Electric Stirrer

B-1.5 Analytical balance

B-2 REAGENTS

B-2.1 Sulphuric acid — 98 percent, Analytical Reagent Grade

B-2.2 Hydrochloric acid — 30 percent w/w, Analytical Reagent Grade

B-2.3 Potassium bromide — Analytical Reagent Grade

B-2.4 Sodium nitrite solution — 0.2 N

B-2.5 Ice

B-2.6 Starch iodide paper

B-3 PROCEDURE

Weight accurately about 1 g to 1.5 g of ortho-chloro para-nitro aniline and transfer to a 1liter beaker with the help of water. Add 400 ml of Distilled water to dissolve it then add 50 ml of sulphuric acid and then cool to room temperature. Add 30 ml hydrochloric acid to it using measuring cylinder and 1.0 g potassium bromide and ice pieces. Temperature should be maintained 0-5 ^{o}C. Then titrate against 0.2 N sodium nitrate solution. Observe the end point as a faint blue ring just appears on Starch Iodide paper. Endpoint should be constant for 5 minutes.

B-4 CALCULATION

$$\text{Assay (by diazo), percent by mass} = \frac{V \times N \times 172.5 \times 100}{M \times 1000}$$

where,

V = volume of standard sodium nitrite solution used in the titration, ml;
N = normality of sodium nitrite solution; and
M = mass of the material taken for the test, g

ANNEX C

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

DETERMINATION OF ORTHO-CHLORO PARA-NITRO ANILINE MOISTURE CONTENT BY KARL FISCHER

C-1 APPARATUS

C-1.1 Karl Fischer Instrument with Detection Limit

C-1.2 Micro syringe

C-1.3 Digital Balance

C-2 REAGENT

C-2.1 Karl Fischer reagent

C-2.2 Methanol Dried

C-3 PROCEDURE

Add approximately 60 ml methanol in titration vessel and stir with magnetic stirrer. Now, add Karl Fischer reagent to complete neutralization of methanol. After that, weigh 0.5 g to 1.0 g of ortho-chloro para-nitro aniline(sample) in titration vessel and dissolve it in methanol. If they are not soluble in methanol then heat the solution. Now, instrument automatically starts addition of Karl Fischer reagent in the titration vessel to titrate moisture content present in sample. Instrument will stop adding Karl Fischer reagent automatically once it reaches the electrometric endpoint. Note down the burette reading.

C-4 CALCULATION

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

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*. (vii) *and* (viii)]

DETERMINATION OF 2,6-DICHLORO-4-NITRO ANILINE AND 4- NITROANILINE CONTENTS

D-1 For details of TLC test method, reference may be made to IS 5299

D-2 APPARATUS

D-2.1 Aluminium foils pre-coated with silica gel

D-2.2 Calibrated syringe

D-2.3 Hair drier

D-2.4 Development chamber

D-2.5 UV cabinet

D-2.6 Iodine chamber

D-3 CHEMICALS

D-3.1 4-Nitroaniline standard sample

D-3.2 3, 4 Dichloro nitro-benzene standard sample (3,4 DCNB)

D-3.3 2, 6 Dichloro-4-nitroaniline standard sample

D-3.4 4-nitroaniline

D-3.5 Toluene

D-3.6 Chloroform

D-3.7 Ammonia solution — Specific gravity 0.91, 25 percent m/m.

D-4 PREPARATION OF STOCK SOLUTIONS

D-3.1 Weigh exactly 0.1 g of standard 3,4 DCNB. Make the volume to 100 ml using chloroform. Strength of this solution is 1 ml = 1 mg of DCNB (Use this as a stock solution).

D-3.2 Take 5 ml of above stock solution and dilute it to 100 ml with chloroform and use for spotting.

D-3.3 Similarly, prepare standard sample solutions of 2,6 Dichloro-4-nitroaniline and 4-nitroaniline.

D-3.4 Then prepare sample solution of 100 ml in chloroform from 0.1 g sample. If insoluble matter is present, filter it and use.

D-4 SPOTTING, DEVELOPING AND ANALYSIS

D-4.1 Spot 2, 4,6,8,10 ml of stock solution. These spots are corresponding to 0.1 percent, 0.2 percent, 0.3 percent, 0.4 percent and 0.5 percent of standard DCNB respectively. Spot 10 ml of sample solution also. Dry the spots with hair drier.

D-4.2 Develop the plate in toluene solvent saturated with ammonia. Dry the plate and observe the plate in UV cabinet at 254 nm.

D-4.3 Compare the intensity of DCNB spots of standard DCNB solutions with the spots at same Rf value produced by the sample.

D-4.4 DCNB can be quantitatively determined up to 0.5 percent in sample by comparing the colour intensities. For 0.5 percent to 2 percent DCNB content spot 2,4,6,8 ml of standard DCNB along with 2 ml of sample solution. Repeat the process. The standard DCNB spots corresponds to 0.5 percent, 1 percent, 1.5 percent and 2 percent DCNB respectively.

D-4.5 Similarly, determine the percentage of 2, 6 dichloro-4-nitroaniline and 4-nitroaniline present.

ANNEX E
[*Table* 1, *s1. no.* (ix)]
DETERMINATION OF MELTING POINT OF ORTHO-CHLORO PARA-NITRO ANILINE

D-1 Apparatus

D-1.1 One end sealed capillary tube

D-1.2 Melting point apparatus

D-1.3 Thermometer

NOTE— The thermometer shall bear a calibration certificate from any institution authorized to issue certificate traceable to international or national measurement standards.

D-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. Now, start heating slowly 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
[*Table* 1, *s1. no.* (x)]
DETERMINATION OF ORTHO-CHLORO PARA-NITRO ANILINE CONTENT INSOLUBLE IN ACETONE

E-1 APPARATUS

E-1.1 Filtration Assembly

E-1.2 Whatman Filter paper — 42 micron

E-1.3 Measuring cylinder

E-1.4 Vacuum Pump

E-1.5 Weighing Balance — least count of 0.0001 gm

E-2 REAGENT

E-2.1 Acetone

E-3 PROCEDURE

Dissolve 5.0 g of the ortho-chloro para-nitro aniline (sample) in approximately 100 ml acetone. Record weight of filter paper (V_1). Turn vacuum on and filter above solution. Wash the filter paper with 50 of acetone to dissolve the sample. Remove filter paper from filter assembly and dry at 80 °C for 1 h. Weigh the filter paper and record weight as final weight of paper (V_2).

NOTE —Alternatively, methanol may be used as a solvent in place of acetone.

E-4 CALCULATION

$$\text{Insoluble} = \frac{V_2 - V_1}{V} \times 100$$

where

V_2 = final weight of filter paper
V_1 = initial weight of filter paper

V = weight of sample

ANNEX G
(*Foreword*)

Pictograms, signal word, hazard statement and precautionary statement:

Pictogram(s)		
Signal Word	Warning	Environmental hazard
Hazard Statement	H301 Harmful if swallowed. H411 Toxic to aquatic life with long lasting effects. H333 May be harmful if inhaled.	
Precautionary Statement	**Prevention** P264 Wash all exposed external body areas thoroughly after handling. P270 Do not eat, drink ok or smoke when using this product. P273 Avoid release to the environment. **Response** P304+P312 IF INHALED: Call a POISON CENTER/doctor/physician/first aider/if you feel unwell. P391 Collect spillage. P301+P312 IF SWALLOWED: Call a POISON CENTER/doctor/physician/first aider/if you feel unwell. P330 Rinse mouth. **Disposal** P501 Dispose of contents/ container in accordance with local regulations.	