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Draft Indian Standard

2-CHLOROANILINE - SPECIFICATION

(Second Revision of IS 4334)

(ICS 71.080.99)

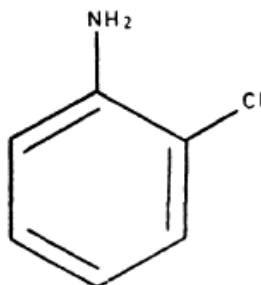
Dye Intermediates Sectional Committee,
PCD 26

Last date for comments
28 January 2023

FOREWORD

(Formal clauses to be added later)

2-Chloroaniline (C₆H₈NCl) is widely used as a diazo component in dyestuffs of the azo series. It is also used in the manufacture of other intermediates and dyestuffs. It has the following structural formula:



2-Chloroaniline
Molecular mass 127.57
CAS NO. 95-51-2

This standard was first published in 1967. The Committee responsible for the preparation of this standard decided to revise it in order to stipulate the requirement of maximum limits of impurities such as aniline, 4-chloroaniline, 3-chloroaniline and others. In the *first* revision, requirements of distillation range was revised and thin-layer chromatographic test method was incorporated for estimation of impurities. In this (*second*) revision, Gas chromatography method for determination of assay and impurities has been incorporated. A new characteristic i.e. colour, its determination and requirement has been added. Characteristics such as crystallization point, distillation range and solubility in hydrochloric acid are deleted.

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 : 2023. 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

1.1 This standard prescribes the requirements and methods of sampling and tests for 2-chloroaniline.

2 REFERENCES

The following Indian Standards contain provisions which through reference in the text, constitute provisions of this Standard. At the time of publication the additions 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 recent editions of the standards indicated below:

<i>IS No.</i>	<i>Title</i>
1070 : 2023	Reagent grade water — Specification (<i>fourth revision</i>)
2552 : 1989	Steel drums (galvanized and ungalvanized) – Specification (<i>third revision</i>)
5299 : 2001	Methods of sampling and tests for dye intermediates (<i>first revision</i>)

3 REQUIREMENTS

3.1 Description

The material shall be in the form of colourless to pale yellow liquid free from visible impurities.

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 Requirement for 2-Chloroaniline
(Clauses 3.2 and D-6)

SI No.	Characteristic	Requirement	Method of Test. Ref to Annex
(1)	(2)	(3)	(4)
i)	Assay by GC ¹⁾ , percent area, <i>Min</i>	99.5	A
	<i>Or</i>		
	Assay by titration, percent by mass, <i>Min</i>	99	B
ii)	Aniline Content by GC, percent area, <i>Max</i>	0.20	A
	<i>Or</i>		
	Aniline Content by thin layer chromatography, by mass, <i>Max</i>	0.5	F
iii)	<i>p</i> -Chloro aniline content by GC, percent area, <i>Max</i>	0.20	A
	<i>Or</i>		
	<i>p</i> -Chloro aniline content by thin layer chromatography, by mass, <i>Max</i>	0.5	F

iv)	Total unknown impurity content by GC percent area, <i>Max</i>	0.30	A
	<i>Or</i>		
	Total unknown impurity content by thin layer chromatography, by mass, <i>Max</i>	0.5	F
v)	Moisture Content By Karl Fischer, <i>Max</i>	0.20	C
vi)	Hazen Value(Pt-Co) ² , <i>Max</i>	100	D

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

²For determination of Hazen value (pt-co), IS 8768 as alternate method.

4 PACKING AND MARKING

4.1 Packing

Unless otherwise agreed to, the material shall be packed in suitable steel drums (*see* IS 2552) or in tanker/ISO tanks.

4.2 Marking

4.2.1 Each bag shall bear legibly and indelibly the following information:

- Name of the material;
- Name of the manufacturer and his recognized trade-mark, if any;
- Batch number;
- Gross, net and tare mass;
- Month and year of manufacture;
- Shelf life of the material; and
- Any other statutory requirements

4.2.2 Each container shall, in addition, bear the minimum cautionary notice worded as under:

“AVOID CONTACT WITH SKIN, DO NOT HEAT TO DECOMPOSITION”

4.2.3 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 Representative samples of the material shall be drawn as prescribed in Annex E.

6. TEST

6.1 Tests shall be conducted according to the methods prescribed in col 4 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, Sl. No. (i), (ii), (iii), (iv) and Clause 5.1)

DETERMINATION OF 2-CHLORO ANILINE ASSAY, ANILINE CONTENT, *p*-CHLORO ANILINE CONTENT, TOTAL UNKNOWN IMPURITY CONTENT BY GAS CHROMATOGRAPHY USING FLAME IONIZATION DETECTOR

A-1 APPARATUS

A-1.1 Analytical Balance

A-1.2 Syringe

A-1.3 Gas chromatography with FID Detector

A-1.3.1 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 Pressure	:	125 kpa
Injection Mode	:	Split (1:20)
Purge Flow	:	3.0 ml/min
Make up Pressure /Flow	:	50 kpa
Hydrogen Pressure/ Flow	:	50 kpa
Zero Air Pressure/Flow	:	50 kpa
Oven temp.	:	Initial Temp — 100 °C, Hold Time — 3.0 min Program Rate — 10 °C/min Final Temp — 230 °C Final Time — 14 min
Injector temp	:	275 °C
Detector temp	:	275 °C
Type of Detector	:	Flame Ionization detector (FID)
Run time	:	30 min.
Injection volume	:	0.2 μl

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, H₂, N₂) 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-2 PROCEDURE

Take a 0.2 µl sample in a micro syringe and confirm there are no air bubbles in the syringe. Inject the sample by Auto sampler / manual, allow the run to complete run time. Assay determination of 2-chloro aniline shall be carried by Gas chromatography instrument through area percent calculation.

A-3 PEAK TIME

2-CHLORO ANILINE	:	11.80 min
ANILINE	:	8.6 min
<i>p</i> -CHLORO ANILINE	:	13.5 min

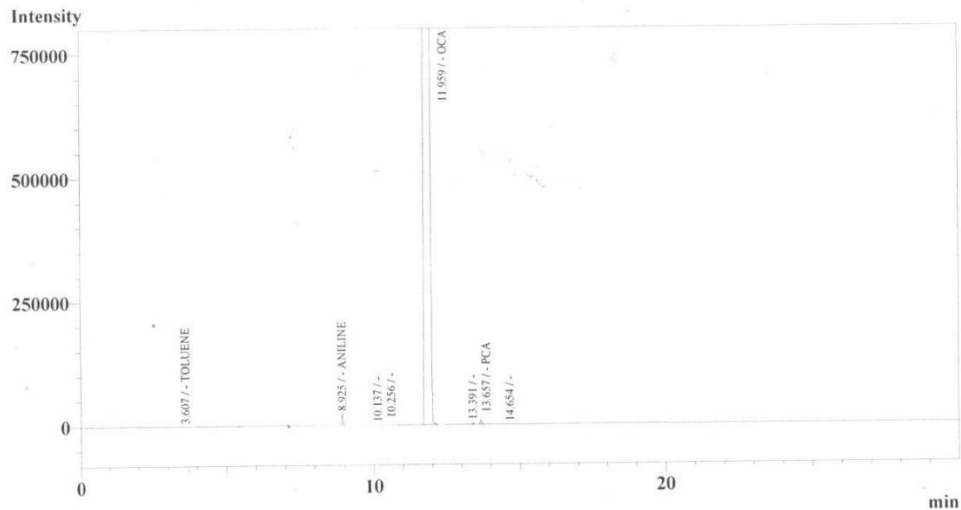


FIG 1 A TYPICAL CHROMATOGRAM

A-4 CALCULATION

A-4.1 Calculate the peak area of individual constituent pertaining to 2-chloroaniline 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 2-chloroaniline.

$$\text{Assay, percent by area} = \frac{\text{peak area 2-chloroaniline in the sample}}{\text{Sum Areas of all peaks in the chromatogram}} \times 100$$

A-4.2 Similarly, contents of aniline and *p*-chloro aniline shall be calculated.

A-4.3 Total unknown impurity content = Assay – concentration (aniline+ *p*-chloro aniline)

ANNEX B
(Table 1, Sl. No.(i))

DETERMINATION ASSAY OF 2-CHLORO ANILINE BY DIRECT TITRATION

B-1 OUTLINE OF THE METHOD

2-chloroaniline is estimated by direct titration with standard sodium nitrite solution using starch iodide paper as indicator.

B-2 REAGENTS

B-2.1 Sodium Nitrite Solution — Approximately 0.2 N, freshly standardized

B-2.2 Starch Iodide Papers

B-2.3 Concentrated Hydrochloric Acid — Conforming to IS 265

B-3 PROCEDURE

Accurately weigh by difference from a weighing bottle about 10 g of the material and transfer to a beaker containing 400 ml of water at about 60 °C and 50ml of hydrochloric acid and stir to dissolve completely, warming further, if necessary. Cool to 20 °C. Make upto to 1000 ml in a volumetric flask.

Transfer by means of a pipette 100 ml of the above solution into a beaker containing 200 g of crushed ice and 200 ml water with 5g of potassium bromide and 20 ml concentrated hydrochloric acid. While stirring mechanically, titrate with sodium nitrite solution maintaining a temperature between 0 °C to 10 °C as rapidly as possible to a distinct blue ring test on a starch iodide paper. The end point is taken when the test persist for 5 minutes without further addition of nitrite.

B-4 CALCULATION

$$\text{Assay, percent by mass} = \frac{127.57 \times V \times N}{M}$$

where

V = volume of sodium nitrite solution used, in ml;

N = normality of sodium nitrite solution, and

M = mass of the material used in the test, in g

ANNEX C
(Table 1, Sl. no. (v))

DETERMINATION OF MOISTURE CONTENT BY KARL FISCHER

C-1 REAGENTS

C-1.1 Karl Fischer reagent

C-1.2 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 dried methanol in titration vessel to dip the platinum electrode and start stirrer. Neutralize initial moisture in methanol. Weigh testing sample as per the below weight table and keep it ready for testing. For liquid samples, use a 20 ml Plastic Disposable Syringe for weight. 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 to 25 seconds to allow the sample to get dissolved into the methanol. Press the START button.

Sl. No.	Product Name	Sample weight
1	2-Chloroaniline	20g to 25 g

As soon as the titration is over, note down the reading.

C-4 Calculation

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

$$\text{Moisture Content, in percent} = \frac{KFR \times \text{Factor (mg/ml)} \times 100}{\text{Sample weight (g)} \times 1000}$$

Or

$$\text{Moisture Content in ppm} = \frac{KFR \times \text{Factor} \times 1000}{\text{Sample weight (g)}}$$

ANNEX D

(Table 1, Sl.no. (vi))

DETERMINATION OF HAGEN VALUE OF 2-CHLORO ANILINE

D- 1 REAGENTS

D-1.1 Methanol, AR Grade

D-2 APPARATUS

D-2.1 Tintometer

D-2.2 Optical Glass Cell, 50 mm

D-2.3 Analytical Balance

D-3 PROCEDURE

Set the instrument as per manufacturers instrument manual. For zeroing, place the demineralized water sample (Pt-co standard value- 0) into the clean 50 mm optical glass cell. Ensure that there are no air bubbles and the cell end windows are dry. Now, put the cell on the right hand side of the cell compartment and close the instrument lid. Press the READ button. Once zeroing of the instrument is done, the instrument is ready to carry out Pt-Co sample color

measurement. Now, rinse the cell with sample for 2-3 times. Then fill the cell with a sample upto around 75%. Now, put the sample cell in the compartment and press READ button and note the reading of Pt-Co unit. After analysis, clean the cell with methanol and distilled water.

ANNEX E

(Clause 4.1)

SAMPLING OF 2-CHLOROANILINE

E-1 GENERAL REQUIREMENTS

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

E-1.2 Samples shall be taken at a place protected from damp air, dust and soot.

E-1.3 Sampling instrument shall be clean and dry.

E-1.4 Precautions shall be taken to protect the samples, the material being sampled, the sampling instrument and the containers for samples from adventitious contamination.

E-1.5 To draw a representative sample, the contents of each container selected for sampling, shall be mixed as thoroughly as possible, by suitable means.

E-1.6 The samples shall be placed in a clean, dry and air-tight glass stoppered containers on which the material has no action.

E-1.7 The sample containers shall be of such a size that they are almost completely filled by the sample.

E-1.8 Each sample container shall be sealed air-tight after filling and marked with full details of sampling, the date of sampling, year of manufacture, and other important particulars of the consignment.

E-1.9 Samples shall be stored in a cool and dry place.

E-2. SAMPLING INSTRUMENT

E-2.1 The following forms of sampling instruments may be used :

- a) Sampling bottle or can for taking samples from various depths in large tanks, and
- b) Sampling tube.

E-2.2 Sampling Bottle or Can — It consists of a weighed bottle or metal container with removable stopper or top, to which is attached a light chain (*see* Fig. 2). The bottle or can is fastened to a suitable pole. For taking a sample, it is lowered in the tank to the required depth, and the stopper or top is removed by means of the chain for filling the container.

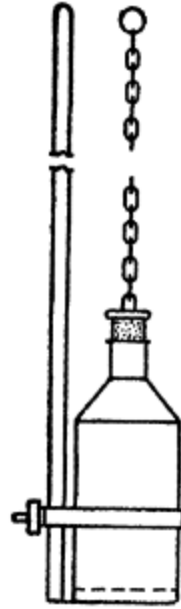


FIG. 2 SAMPLING BOTTLE OR CAN

E-2.3 Sampling Tube — It is made of metal or thick glass and is about 20 mm to 40 mm in diameter and 400 mm to 800 mm in length (*see* Fig. 3). The upper and lower ends are conical and reach 5 mm to 10 mm diameter at the narrow ends. Handling is facilitated by two rings at the upper end. For taking a sample, the apparatus is first closed at the top with the thumb or a stopper and lowered until the desired depth is reached. It is then opened for a short time to admit the material and finally closed and withdrawn.

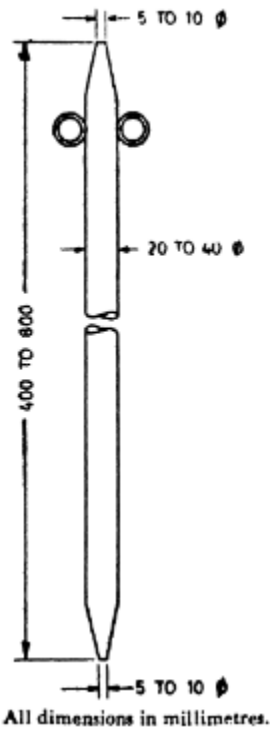


FIG. 3 SAMPLING TUBE

E-2.3.1 For small containers, the size of the sampling tube may be altered suitably.

E-3. SCALE OF SAMPLING

E-3.1 Lot — In any consignment all the containers of the same size and drawn from the same batch of manufacture, shall constitute a lot. If a consignment is known to consist of different batches of manufacture or of different sizes of containers, the containers belonging to the same batch and size shall be grouped together and each such group shall constitute a separate lot.

E-3.2 Test shall be conducted on each lot separately for ascertaining its conformity to the requirements of this specification. The number of containers to be chosen at random from the lot for this purpose shall depend on the size of the lot and shall be in accordance with col 1 and 2 of Table 2.

E-3.3 The containers shall be chosen at random from the lot with the help of a suitable random number table. In case no such table is available, the following procedure is recommended for use:

Starting from any container from the lot, count them as 1, 2,... up to r and so on, in one order, where r is the integral part of N/n (N being the number of containers in the lot and n being the number of containers to be selected) . Every r th container, thus counted shall be withdrawn to give samples for test.

TABLE 2 SCALE OF SAMPLING
(Clause E-3.2)

Lot Size (N) (1)	No. or Containers to be Selected (n) (2)
Up to 15	2
16 to 25	3
26 to 50	4
51 and above	5

E-4. PREPARATION OF TEST SAMPLES

E-4.1 From each of the containers selected as in **E-3.2**, a small representative portion of the material from different parts of the container shall be drawn with the help of a suitable sampling instrument (*see E-2*).

E-4.2 Out of these portions a small but equal quantity of material shall be taken and mixed thoroughly to form a composite sample. The composite test 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.

E-4.3 The remaining portion of the material from each of the container (*see E-4.2*) shall be divided into three equal parts each forming an individual sample. One set of individual samples representing the containers sampled shall be marked for the purchaser, another for the supplier and the third to be used as a referee sample.

E-4.4 All the individual and composite samples shall be transferred to separate containers and shall be sealed and marked with full identification particulars given under **E-1.8**.

E-4.5 The referee test samples consisting of a composite sample and a test of n individual samples, shall bear the seal of both the purchaser and the supplier. These shall be kept at a place agreed to between the purchaser and the supplier to be used in case of any dispute between the two.

E-5 NUMBER OF TESTS

E-5.1 Tests for the determination of moisture content and purity shall be conducted on each of the individual samples (*see E-4.3*).

E-5.2 Test for the determination of all other characteristics given in 3.2 and Table 1 shall be conducted on the composite sample (*see E-4.2*).

E-6 CRITERIA FOR CONFORMITY

E-6.1 For Individual Samples — The lot shall be declared as conforming to the requirements of assay and moisture content, if each of the individual test results satisfy the relevant requirements given in Table 1.

E-6.2 For Composite Samples — For declaring the conformity of a lot to the requirements of all other characteristics tested on the composite sample (*see E-4.2*), the test results for each of characteristics shall satisfy the relevant requirements given in 3.2 and Table 1.

ANNEX F

(Table 1, Sl. No.(ii),(iii),(iv))

DETERMINATION OF IMPURITIES

F-1 General – The assay and impurities in 2-chloroaniline is determined by ascending thin layer chromatographic method.

F-1.1 Apparatus

F-1.1.1 *Micropipette*

F-1.1.2 *Developing Chamber*

F-1.1.3 *Thin-layer Chromatographic Glass Plates* – 20 × 20 cm.

F-1.1.4 *Chromatographic Sprayer*

F-1.1.5 *Adjustable Thin Plate Applicator*

F-1.1.6 *Weighing Bottle*

F-1.1.7 *Oven*

F-1.2 Reagents

F-1.2.1 *Silica Gel G Neutral*

F-1.2.2 *Developing Solvent* – Benzene : Chloroform (95 : 5) (v/v).

F-1.2.3 *Sample Solution* – 1 percent solution in methanol.

F-1.2.4 *Reference Solutions:*

- a) 0.005 percent solution of 100 percent aniline in methanol;
- b) 0.005 percent solution of 100 percent 3-chloroaniline in methanol; and
- c) 0.005 percent solution of 100 percent 4-chloroaniline in methanol.

F-1.2.5 *Spray Reagent* – N-1-Naphthylethylenediamine dihydrochloride (1 percent in water).

F-1.3 Procedure

F-1.3.1 *Preparation of Chromatographic Plates* – Mix about 50 g of neutral silica gel G with 85 to 90 ml of water for three minutes to form an uniform slurry. Then by means of the applicator, coat the plate with this slurry to get silica gel G layer of thickness not exceeding 0.25 mm. Activate it in the oven maintained at 110°C for 90 minutes. By

means of a needle mark a thin line widthwise on all plates at about 3 cm from the upper edge. Also remove a band of about 5 mm width silica gel G from either of the lateral sides of each plate.

F-1.3.2 Chromatographic Separation – Pipette 10 µl of the sample solution (**F-1.2.3**) and 10 µl of reference solutions (**F-1.2.4**) and apply in the form of a uniform spot on the plate, at a distance of 3 cm from the bottom edge. After complete evaporation of the solvent, place the plate in the chromatographic chamber and allow the developing solvent (**F-1.2.2**) to run up to 14 cm at room temperature. Take out the plate and dry completely. Keep the plate for 2 minutes in a chamber containing nitrous acid fumes (prepared by mixing sodium nitrite and hydrochloric acid). Blow out the excess nitrous fumes from the plate and spray with the spraying reagent (**F-1.2.5**). The material and the constituent impurities are identified by their respective characteristic colours as under:

<i>Substance</i>	<i>Zone</i>	<i>R_f value</i>	<i>Colour</i>
Aniline	I	0.31	Bluish-violet
4-Chloroaniline	II	0.38	Blue
3-Chloroaniline	III	0.47	Red
2-Chloroaniline	IV	0.67	Brownish-red

F-1.4 Reporting — Report impurity as that which is nearest intensity to the reference samples. In case, the colour intensity does not come in the range of the standard spots of impurity, repeat the whole procedure under suitable concentrations of various impurities.

ANNEX G (Foreword)

Pictograms, signal word, hazard statement and precautionary statement

Pictogram(s) :



Signal Word :

ACUTE TOXICITY HEALTH HAZARD ENVIROMENTAL
HAZARD

Hazard Statement :

Toxic: If swallowed.
Toxic in contact with skin.
Causes serious eye irritation
Inhalation
Long term or repeated exposure may cause damage to organs
Very toxic to aquatic life with long lasting effects

Precautionary Statement :

Precaution

Do not breathe dust / fume / gas/ mist / vapours / spray
Wash skin thoroughly after handling
When using this product do not eat, drink or smoke
Use only outdoors or in a well ventilated place
Avoid release to the environment
Wear protective gloves / eye protection / face protection.

Response

IF SWALLOWED: Immediately call a POISON CENTER or doctor

If on skin: Wash with plenty of soap and water

If inhaled: Remove victim to fresh air and rest and keep breathing comfortable posture

If EYES: Rinse cautiously with water for several minutes as wearing contact lenses and can be easily removed, continue cleaning.

If you feel unwell, shall medical advice / attention

The leak: Collect spillage.

In case of fire: Use water spray, alcohol-resistant foam, carbon dioxide fire extinguishing

Storage

Store in a well ventilated place Keep container tightly closed

Storage shall be locked out

Disposal

Dispose of waste and packaging materials in accordance with national and local regulations
