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Draft Indian Standard

3-BROMOBENZANTHRONE, TECHNICAL – SPECIFICATION

(Second Revision of IS 6961)

(ICS 71.080.99)

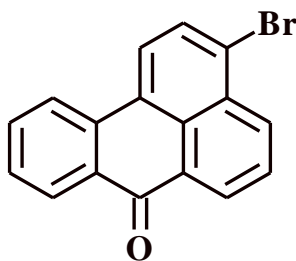
Dye Intermediates Sectional Committee,
PCD 26

Last date for Comments
25th December 2023

FOREWORD

(Formal Clause to be added later)

3-Bromobenzanthrone is an important intermediate used in the manufacture of vat dyes. It has the following structural formula:



3-Bromobenzanthrone
(Molecular Mass 309.2)
(CAS No.: 81-96-9)

This standard was first published in 1973 and subsequently revised in 1984. The first revision was taken up to incorporate stipulated quantity of components namely, benzanthrone and 3, 9-dibromobenzanthrone, their chromatographic separation and estimation using by spectrophotometer. The moisture content was also modified. In this (*second*) revision, High-performance liquid chromatography method for determination of 3-Bromobenzanthrone and its impurities such as benzanthrone and 3, 9-dibromobenzanthrone 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 given in Annex C, 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

1.1 This standard prescribes the requirements, the method of sampling and test for 3-bromobenzanthrone, technical.

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 possibilities 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>)
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 yellow powder and shall be 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 col 4 and col 5 of Table 1.

Table 1 Requirements for 3-Bromobenzanthrone, Technical
(*Clause 3.2, 5.3.1, 5.3.2 and 6.1*)

SI No.	Characteristic	Requirement	Method of Test, Ref to	
			Annex	Clause of IS 5299
(1)	(2)	(3)	(4)	(5)
i)	Assay by HPLC ¹⁾ , percent by area, <i>Min</i> <i>Or</i>	95.0	A	—
ii)	Assay by Chromatographic method, percent by mass, <i>Min</i>	88.0	B	—
iii)	Moisture content, percent by mass, <i>Max</i>	1.0	—	10.3
iv)	Sulphated ash, percent by mass, <i>Max</i>	1.0	—	12.2
v)	Impurities (by HPLC)			
	a) Benzanthrone, percent by area, <i>Max</i>	2.0		
	b) 3,9-Dibromobenzanthrone, percent by area, <i>Max</i>	2.0	A	—
	<i>Or</i>			

vi)	Impurities (by Chromatographically)			
	a) Benzanthrone, percent by mass, <i>Max</i>	4		B
	b) 3,9-Dibromobenzanthrone, percent by mass, <i>Max</i>	4		
vii)	Melting point, °C, <i>Min</i>	163	—	9

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 suitably packed in steel drums lined with polyethylene bags or as agreed to between the purchaser and the supplier.

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 and its impurities shall be conducted on each of the individual samples.

5.2.2 Test for the determination of remaining characteristics, namely, description moisture content and sulphated ash 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 purity if each of the individual test results satisfies the relevant requirement given in Table 1.

5.3.2 For Composite Sample

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

6 TEST METHODS

6.1 Tests shall be carried out as prescribed in col 4 and col 5 of Table 1.

6.2 Quality of Reagents

Unless specified otherwise, 'pure chemicals' and distilled water (*see* IS 1070) shall be used 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) and (v, a) and (v, b)]

DETERMINATION OF 3-BROMOBENZANTHRONE CONTENT (ASSAY), 3, 9-DIBROMOBENZANTHRONE AND BENZANTHRONE (IMPURITIES) BY HPLC

A-1 GENERAL

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.

A-2 APPARATUS

A-2.1 HPLC – quaternary gradient liquid chromatography system with UV-visible detector capable of being operated under conditions suitable for resolving the individual constituents into distinct peak may be used.

A-2.1.1 Column — C18 column of 100 Å with length 250 m, internal diameter 4.6 mm and particle size 5 µm or equivalent.

A-2.2 Volumetric Flask — class A grade

A-3 REAGENTS

A-3.1 3-Bromobenzanthrone — known purity

A-3.2 Benzanthrone — known purity

A-3.3 3,9-Dibromobenzanthrone — known purity

A-3.4 Acetonitrile — HPLC grade

A-3.5 Tetrahydrofuran (THF) — HPLC grade

A-3.6 Water — HPLC grade

A-4 STANDARD SOLUTION PREPARATION

A-4.1 Benzanthrone

Weigh accurately 20.0 mg of benzanthrone into 50 ml volumetric flask. Add 2 ml tetrahydrofuran (THF) to it and dissolve. Make the volume up to the mark with acetonitrile.

A-4.2 3,9-Dibromobenzanthrone

Weigh accurately 20.0 mg of 3,9-Dibromobenzanthrone into 50 ml volumetric flask. Add 2 ml tetrahydrofuran (THF) to it and dissolve. Make the volume up to the mark with acetonitrile.

A-5 SAMPLE SOLUTION PREPARATION

Weigh accurately 50.0 mg sample into 50 ml volumetric flask. Add 2 ml tetrahydrofuran (THF) to it and dissolve. Make the volume up to the mark with acetonitrile.

A-6 FLOW RATE — 1.2 ml/min

A-7 MOBILE PHASE — Acetonitrile: Water, 85: 15 (v/v)

A-8 COLUMN OVEN TEMPERATURE — Ambient temperature.

A-9 INJECTION VOLUME — 20 µl.

A-10 RUN TIME — 25 min.

A-11 WAVELENGTH — 210 nm.

A-12 PEAK TIME

Benzanthrone:	5.1 min
3-Bromobenzanthrone:	8.3 min
3, 9-Dibromobenzanthrone:	13.5 min

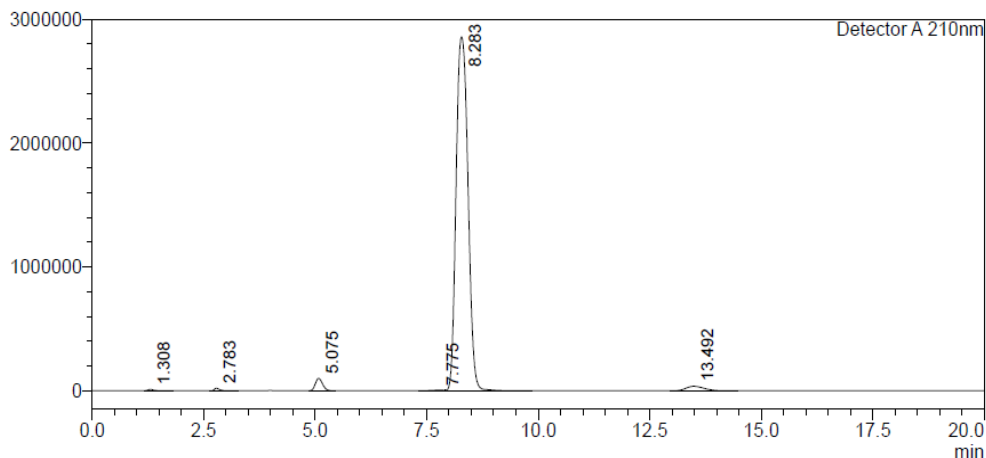


FIG 1 TYPICAL CHROMATOGRAPH

TABLE 2 TYPICAL PEAK TABLE

Components	Retention time	Area	Area percent
	1.31	75310	0.14
	2.78	150645	0.27
Benzanthrone	5.08	1102145	1.99
	7.78	81360	0.15
3-Bromobenzanthrone	8.28	52989740	95.67
3,9-Dibromobenzanthrone	13.49	987352	1.78
Total		55386552	100.00

A-13 CALCULATION

A-13.1 Calculate the peak area of individual constituent pertaining to 3-bromobenzanthrone on the chromatogram of the material. The concentration of the constituent may be obtained on the basis of peak area on chromatogram obtained with known amount of pure 3-bromobenzanthrone.

$$\text{3-Bromobenzanthrone, percent by area} = \frac{\text{3-Bromobenzanthrone Peak area in sample}}{\text{Sum Areas of all peaks in the chromatogram}} \times 100$$

A-13.2 Similarly, contents of benzanthrone and 3,9-dibromobenzanthrone shall be calculated.

ANNEX B

[Table 1, Sl No. (ii), (vi, a) and (vi, b)]

**DETERMINATION OF 3-BROMOBENZANTHRONE,
 3,9-DIBROMOBENZANTHRONE AND BENZANTHRONE**

B-1.0 Outline of the Method - The purity of the sample is estimated by employing the chromatographic method. 3-Bromobenzanthrone, 3,9-dibromobenzanthrone and benzanthrone are separated chromatographically and determined quantitatively by spectrophotometer.

B-1.1 Reagents

B-1.1.1 Toluene – Dry for 24 hours over anhydrous calcium chloride filter and distil. Collect the portion boiling at 110°C. The optical density shall not exceed 0.005 at 395, 400 and 385 μm .

B-1.1.2 Alumina-Column chromatography grade which is neutral and shall pass through 160-micron IS Sieve. To get material of desired activity treat alumina anhydrous neutral as follows:

Spread out the alumina evenly on stainless steel tray in a thin layer, add 1 percent of water slowly from a burette covering the whole of the tray as evenly as possible. Mix the alumina by hand initially and then transfer to a kilner jar and mix by rolling mechanically for at least 1 hour. Then retest for activity. If still too active repeat the procedure adding more water in the increment of 0.25 percent.

B-1.2 Preparation of Sample

B-1.2.1 Dissolve about 0.5 g of the sample in minimum amount of toluene. Transfer the solution gradually to the chromatographic column. Elute further by toluene. Collect the first band of 3-9-dibromobenzanthrone. Concentrate the solution of 3-9-dibromobenzanthrone by evaporation until crystallization occurs on cooling to room temperature. Filter off the crystals and dry to constant mass in a vacuum oven at 70 to 80°C. To check the purity of material dissolve about 0.01 g in minimum quantity of toluene and pass the solution through a chromatographic column. Set up as described above. Elute as necessary with toluene, collect the bands carefully and determine the optical density at 400 μm .

B-1.2.2 Make up a solution of crystals in solvent. Determine its optical density in the same way.

B-1.2.3 A difference in optical density of more than 0.003 indicates the impurities present in the purified 3-9-dibromobenzanthrone. In that case repeat the chromatographic purification until this check test is satisfied.

B-1.3 Preparation of Column

B-1.3.1 Set up vertically a glass tube, length 40 cm and about 1.5 cm internal diameter joined with 50 ml thistle funnel at the upper end fitted with stop cock at the lower end. Place a cotton wool plug in the tube and press to the bottom of the tube by means of a glass rod, flattered at the end. Place a disc of filter paper. Cut to the approximate internal diameter of chromatographic tube on top of the cotton wool.

B-1.3.2 Prepare a slurry of about 50 g alumina deactivated with 1 percent water in toluene and transfer it into the tube, wash down the side of the tube and pack the column by light tapping. Place disc of filter paper first and then a cotton wool plug at the top surface of the alumina. Always keep enough solvent in the column so that it remains wet and at least 2cm of solvent layer shall always persist over the top of alumina. On no account allow the alumina to run dry. In the event of this happening re-slurry the alumina and repack.

B-1.4 Procedure

B-1.4.1 Weigh accurately about 60 mg of sample in 100-ml dry conical flask. Add about 50 ml of toluene and reflux for 10 to 15 minutes. Cool and transfer the solution to a 100-ml volumetric flask. Wash the conical flask well with toluene and transfer the washings to the flask. Dilute the solution to 100 ml mark.

B-1.4.2 Drain the excess solvent from the column so that the top remains just wet. Carefully transfer 100 ml of the sample solution with the help of a burette to the top of a chromatographic column. Add the solution to the column dropwise and at the same time drain the solvent from the column at same rate without allowing the top of the column to go dry. Fill the upper part of the tube with solvent and allow the chromatogram to develop keeping a good head of solvent about the alumina throughout.

B-1.4.3 Three bands will be separated out in column. Collect the first fraction when the band is about 1.5 cm from the lower tip of tube. This is a band of 3,9-dibromobenzanthrone. When the band is eluted dilute it to 100 ml exactly. Then

collect the second band of 3-bromobenzanthrone, in 250-ml volumetric measuring flask. After complete elution of same band dilute it to 250 ml mark with toluene.

B-1.4.4 Same way collect the third band which is of benzanthrone in 100-ml volumetric measuring flask with the completion of elution dilute it to 100 ml mark with toluene.

B-1.4.5 Adjust the wavelength of maximum absorption to the predetermined value and then adjust the instrument in such a manner that the transmittance through the blank becomes 100 percent after inserting the cell with black solution.

Replace the cell with the solution of the sample and read the optical density.

B-1.4.6 Determine the optical density of the following:

- | | |
|-------------------------------|-------------------|
| a) 3,9-Dibromobenzanthrone at | 400 μm |
| b) 3-Bromobenzanthrone at | 395 μm |
| c) Benzanthrone at | 385 μm |

B-1.5 Calculation

B-1.5.1 The assay of above fractions are calculated as follows:

$$\text{3,9-Dibromobenzanthrone} = \frac{\text{Optical density}}{\text{mass in g} \times 0.2218}$$



$$\text{3-Bromobenzanthrone} = \frac{\text{Optical density} \times 2.5}{\text{mass in g} \times 0.4003}$$

$$\text{Benzanthrone} = \frac{\text{Optical density}}{\text{mass in g} \times 0.4701}$$

NOTE – Optical density of pure compound 1 mg per 100 ml will be affected to a certain extent by factors such as band width of the region (this depends upon the resolving power of the instrument) and accurate selection of wavelength. Therefore, it is necessary to determine and verify from time to time the constants of the instrument that is being used.

ANNEX C
(Foreword)

Pictograms, signal word, hazard statement and precautionary statement

Pictogram(s)	:	 
Signal Word	:	Danger Health Hazard
Hazard Statement	:	Harmful if swallowed. Toxic if inhaled. May cause allergy or asthma symptoms or breathing difficulties if inhaled
Precautionary Statement	:	Avoid breathing dust / fumes / gas / mist / vapour / spray. Wear protective gloves. [In case of inadequate ventilation] wear respiratory protection. If experiencing respiratory symptoms: Call a POISON CENTER / doctor. Store locked up. Dispose of contents /container in accordance with local / regional / national / international regulations.
