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भारतीय मानक
बैंजीन — विशिष्टि
(चौथा पुनरीक्षण)

Indian Standard
BENZENE — SPECIFICATION
(*Fourth Revision*)

ICS 71.080.15

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BUREAU OF INDIAN STANDARDS
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Price Group 11

Petroleum, Lubricants and Their Related Products Sectional Committee, PCD 3

FOREWORD

This Indian Standard (Fourth Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Petroleum, Lubricants and Their Related Products Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

Benzene is derived by suitable fractionation and refining by washing with acid or hydrotreating of crude benzole recovered from the gas produced during carbonization of coal in coke ovens and retorts or recovered as by-product in petroleum refining or petrochemical operations.

Earlier benzene was essentially a coal base product being made available as by-product from coke ovens of steel plants. The requirements and methods of test were also stipulated on the basis of the publications by National Benzole and Allied Products Association (NBA) and the Standardization of Tar Products Test Committee (STPTC), UK in order to suit the prevailing quality of the product. However, cognizance was taken of the fact that consequent upon exploration of oil fields in the recent past specially the Bombay High, substantial quantities of indigenous crude was being made available, which has completely changed the scenario. On a quantum basis there is a distinct shift in production of various aromatic hydrocarbons from coal base to petroleum base as a result of which benzene is currently being made available in abundance. The Committee, therefore, decided to update the standard in accordance with the latest developments in the field, both in production and usage and in the light of the experience gained in the past.

This standard was first published in 1955. In view of the growing demand for benzene for organic synthesis it was considered necessary to include the material for this end use also. It was also felt that pure and ordinary grades of the material should be brought under a composite standard on the subject. The standard was, therefore, revised in 1965 amalgamating with IS 535 : 1955 'Specification for benzene, pure, nitration grade'. In the second revision, the method of test for total sulphur was replaced by Raney nickel method, as the latter was found more convenient and reliable. Various changes covered under Amendment No. 1 issued in March 1973 were also incorporated in the third revision.

In the third revision in 1992, keeping in view various end uses and the source of crude base, benzene was classified into three types. In view of stringent quality of benzene required for the manufacture of caprolactam, it was decided to incorporate additional requirement of aliphatic and aromatic impurities and bromine index.

In the present revision, Type C has been deleted in order to align with the International practices. Additional requirements like purity of benzene by GC method including percent of toluene, non-aromatic hydrocarbons 1,4 dioxane, carbon disulphide, N-formylmorphine as nitrogen, residue on evaporation and *n*-heptane have been included, in addition to making the requirements of other characteristics more stringent. Requirements like copper corrosion and neutrality have been deleted.

'IS 1840 : 1961 Benzene, reagent grade' has been withdrawn, as it was observed by the technical committee, that this standard would cover the requirements of reagent grade benzene.

In the formulation of this standard, considerable assistance has been drawn from the following standards published by International Organization for Standardization (ISO) and American Society for Testing and Materials, USA:

ASTM D 835 : 1995	Standard specification for refined benzene — 485 (<i>withdrawn</i>)
ASTM D 848 : 1997	Standard test method for acid wash color of industrial aromatic hydrocarbons
ASTM D 850 : 1999	Standard test method for distillation of industrial aromatic hydrocarbons and related materials
ASTM D 852 : 1997	Standard test method for solidification point of benzene
ASTM D 853 : 1997	Standard test method for hydrogen sulfide and sulfur dioxide content (qualitative) of industrial aromatic hydrocarbons

(Continued on third cover)

Indian Standard

BENZENE — SPECIFICATION

(Fourth Revision)

1 SCOPE

This standard prescribes the requirements and the methods of sampling and tests for benzene.

2 REFERENCES

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 agreements based on this 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>
82 : 1973	Method of sampling and test for thinners and solvents for paints (<i>first revision</i>)
1070 : 1992	Reagent grade water (<i>third revision</i>)
1260 (Part 1) : 1973	Pictorial marking for handling and labelling of goods: Part 1 Dangerous goods (<i>first revision</i>)
1446 : 2002	Classification of dangerous goods (<i>second revision</i>)
4644 : 1968	Code of safety for benzene, toluene and xylene
4905 : 1968	Methods for random sampling
5165 : 1969	Interchangeable conical ground-glass joints

3 TERMINOLOGY

For the purpose of this standard, the definitions given in IS 82 and the following shall apply.

3.1 Bromine Index — The number of milligrams of bromine consumed by 100 g of sample under given conditions.

3.2 Solidification Point — An empirical constant defined as the temperature at which the liquid phase of a substance is in approximate equilibrium with a relatively small portion of the solid phase.

4 TYPES

There shall be two types of material, namely:

- a) Type A — Suitable for manufacture of caprolactam; and
- b) Type B — Suitable for manufacture of other products

5 REQUIREMENTS

5.1 Description

The material shall be a clear liquid, free of sediments and haze when observed at 18° to 26°C.

5.2 The material shall comply with the requirements as given in Table 1.

6 PACKING, MARKING AND STORAGE

6.1 Packing and Storage

6.1.1 The material shall be packed as agreed to between the purchaser and the supplier.

6.1.2 All the containers in which the material is packed shall be dry, clean, and free from substances soluble in benzene and leak proof.

6.1.3 The containers shall be securely closed, protected from light, and shall be stored in a cool place.

6.1.4 The containers for storage and transport of the material, since classified as flammable and dangerous goods, shall, in addition comply with the requirements of the latest issue of Red Tariff and the requirements as laid down from time to time by the Chief Controller of Explosives, Government of India, for packing, storage and transit of flammable liquids and the Board of Trade Regulations as applicable thereon for transport by steamers.

6.1.5 Necessary safeguards against the risk arising from the storage and handling of large volumes of flammable liquids (*see* IS 1446) shall be provided and all due precautions shall be taken [*see* IS 1260 (Part 1)] at all times to prevent accidents by fire or explosion.

6.1.6 Except when they are opened for the purpose of cleaning and rendering them free from benzene vapour, all empty tanks or other containers shall be kept securely closed unless they have been thoroughly cleaned and freed from benzene vapour.

6.2 Marking

6.2.1 Each container shall be securely closed and marked legibly and indelibly with the following information:

- a) Name and type of the material,
- b) Indication of the source of manufacture,
- c) Net mass of the material in the container,

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- d) Batch number or code number, and
e) Date of manufacture.

6.2.2 Each container shall have the caution label 'FLAMMABLE' together with the corresponding symbol for labelling of dangerous goods as given in IS 1260 (Part 1).

6.2.3 BIS Certification Marking

The containers may also be marked with the BIS Certification Mark.

6.2.3.1 The use of the Standard Mark is governed by the provisions of *Bureau of Indian Standards Act, 1986* and the Rules and Regulations made thereunder. The details of conditions under which the licence for the use of the Standard Mark may be granted to manufacturers or producers may be obtained from the Bureau of Indian Standards.

7 HANDLING

Benzene is highly toxic and therefore it shall be handled

carefully (*see* IS 4644). Exposure of benzene in atmosphere should be monitored regularly. Persons exposed to benzene shall be periodically checked according to State Factory Rules and Local State Regulations.

8 SAMPLING

Representative samples of the material shall be prepared as prescribed in Annex M.

9 TEST METHODS

9.1 Tests shall be conducted according to the methods referred to in col 5 of Table 1.

9.2 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.

Table 1 Requirements for Benzene
(Clauses 5.2, 9.1 and M-6.1.1)

SI No.	Characteristic	Requirement		Methods of Test, Ref to Annex
		Type A	Type B	
(1)	(2)	(3)	(4)	(5)
i)	Benzene, percent by mass, <i>Min</i>	99.90	99.80	A
ii)	Colour, Pt-Co scale, <i>Max</i>	10	10	B
iii)	Relative density, 15.56/15.56°C	0.882 0 to 0.886 0	0.882 0 to 0.886 0	C
	or			
	Density 20°C, ml	0.878 0 to 0.882 0	0.878 0 to 0.882 0	C
iv)	Sulphur, mg/kg, <i>Max</i>	1	As agreed to between the purchaser and the supplier	D
v)	Distillation range including the temperature 80.1°C at 101.3 kPa (760 mm Hg) pressure, °C, <i>Max</i>	1.0	1.0	E
vi)	Non-aromatic hydrocarbons, percent by mass, <i>Max</i>	0.10	0.10	A
vii)	Toluene, percent by mass, <i>Max</i>	0.01	0.05	A
viii)	Bromine index, <i>Max</i>	10	20	F
ix)	Solidification point, anhydrous basis, °C, <i>Min</i>	5.45	5.35	G
x)	Thiophene, mg/kg, <i>Max</i>	0.6	1	H
xi)	Acid wash colour, <i>Max</i>	Pass with 1	Pass with 1	J
xii)	N-formylmorphine as nitrogen	As agreed to between the purchaser and the supplier	As agreed to between the purchaser and the supplier	K
xiii)	1,4 Dioxane	do	—	A
xiv)	Carbon disulphide	do	As agreed to between the purchaser and the supplier	L
xv)	Residue on evaporation, mg/100 ml, <i>Max</i>	do	do	Clause 8 of IS 82
xvi)	<i>n</i> -heptane, higher aliphatic and acyclic compounds (cyclohexane and methyl hexane), mg/kg, <i>Max</i>	do	do	A

NOTE — If purity by GC method [SI No.(i)] is carried out, distillation test and solidification point test are optional.

ANNEX A

[Table 1, Sl No. (i), (vi), (vii), (xiii) and (xvi)]

DETERMINATION OF PURITY OF BENZENE BY GC

A-1 OUTLINE OF THE METHOD

A-1.1 A known amount of an internal standard is added to the specimen. A small volume of this mixture is injected into a gas chromatograph equipped with a flame ionization detector (FID) and a capillary column.

A-1.2 The peak area of each impurity and the internal standard is measured by an electronic integrator. The concentration of each impurity is calculated from the ratio of the peak area of the internal standard versus the peak area of the impurity. Purity is calculated by subtracting the sum of the impurities found from 100.00 mass, percent. Results are reported in mass, percent.

A-2 INTERFERENCES

A-2.1 Benzene is typically resolved from naturally occurring components with boiling points less than 138°C. Naturally occurring components include non-aromatic hydrocarbons, toluene, C₈ aromatics and 1,4-dioxane. An adequate separation of known impurities from benzene should be evaluated for the column selected.

A-2.2 The internal standard chosen shall be sufficiently resolved from any impurity and the benzene peak.

A-3 APPARATUS

A-3.1 Gas Chromatograph — Any chromatograph having a flame ionization detector that can be operated at the conditions given in Table 2 may be used. The system should have sufficient sensitivity to obtain a minimum peak height response for a 0.000 5 mass, percent impurity twice the height of the signal background noise.

A-3.2 Electronic Integrator — Computer based capable of handling internal standard calculations and peak grouping is recommended.

A-3.3 Column — Fused silica capillary column with crosslinked polyethylene glycol stationary phase is recommended. Alternate stationary phases may be used if they produce at least the same aromatic separation and elute C₉ non-aromatic impurities before benzene.

A-3.4 Microsyringes, 10 and 100 µl capacity.

A-4 REAGENTS AND MATERIALS

A-4.1 Carrier Gas, chromatographic grade helium is recommended.

Table 2 Typical Instrumental Parameters

(Clauses A-3.1 and A-5.1)

Sl No.	Characteristic	Requirement
(1)	(2)	(3)
i)	Detector	Flame ionization
ii)	Column:	Fused silica
	a) Length, m	50
	b) Inside diameter, mm	0.32
	c) Stationary phase	Crosslinked polyethylene glycol
	d) Film thickness, µm	0.25
iii)	Temperatures:	
	a) Injector, °C	200
	b) Detector, °C	250
	c) Column, °C	70 isothermal
iv)	Carrier gas	Helium
v)	Linear velocity, cm/s	22
vi)	Split ratio	200 : 1
vii)	Sample size, µl	0.5
viii)	Recorder	Electronic integration required

A-4.2 High Purity Benzene, 99.99 percent by mass, minimum, prepared by multiple step recrystallization of commercially available benzene of not less than 99 percent purity.

A-4.3 Internal Standard, *n*-Nonane, (*n*C₉) with a purity of 99 percent by mass, minimum is recommended. Other compounds may be acceptable provided they can be obtained in high purity and meet the requirements of A-2.2.

A-4.4 Pure compounds for calibration should include toluene, benzene, ethyl benzene, cyclohexane and 1,4-dioxane of a purity not less than 99 percent. If the purity of the calibration compounds is less than 99 percent, the concentration and identification of impurities must be known so that the composition of the final weighed blends can be adjusted for the presence of the impurities.

A-5 PREPARATION OF APPARATUS

A-5.1 Follow manufacturer's instructions for mounting the column into the chromatograph and adjusting the instrument to the conditions described in Table 2. Allow sufficient time for the equipment to reach equilibrium.

A-6 CALIBRATION

A-6.1 Prepare a synthetic mixture of high purity benzene and representative impurities by direct

weighing. Weigh each impurity to the nearest 0.1 mg. Table 3 contains a typical calibration blend. Cyclohexane is used for the non-aromatic portion and ethyl benzene for the C₈ aromatic portion.

Table 3 Typical Calibration Blend, G

Sl No. (1)	Compound (2)	Weight, Percent (3)
i)	Benzene	99.000 0
ii)	Toluene	0.050 0
iii)	Cyclohexane	0.050 0
iv)	Ethyl benzene	0.050 0
v)	1,4 Dioxane	0.020 0

A-6.2 Using the exact mass for each impurity, calculate the percent by mass, concentration of the calibration blend.

A-6.3 Into a 50-ml volumetric flask, add 50 ml of *n*C₉ to 49.95 ml of the calibration blend and mix well. Using a density of 0.874 g/ml for the calibration blend and a density of 0.718 g/ml for the *n*C₉, the resulting *n*C₉ concentration will be 0.082 5 percent by mass.

A-6.4 Inject 0.5 µl of the blend with internal standard into the chromatograph and integrate the area under each peak, excluding benzene.

A-6.5 Calculate the relative response factors (*RRF*) as follows:

$$RRF_i = (A_s)(C_i)/(C_s)(A_i)$$

where

RRF_i = impurity, *i*;

A_s = peak area of internal standard;

A_i = peak area of impurity, *i*;

C_i = percent by mass, impurity, *i*, from **A-6.2**; and

C_s = concentration of internal standard, percent by mass from **A-6.3**.

A-7 PROCEDURE

A-7.1 Into a 50-ml volumetric flask, add 50 µl of *n*C₉ internal standard and dilute to the mark with specimen. Mix well.

A-7.2 Inject 0.5 µl of mixture into the chromatograph.

A-7.3 Integrate the area under all peaks except for benzene. Sum the non-aromatic fraction up to *n*C₉ for reporting as a single component (see Fig. 1 for a typical chromatogram).

A-8 CALCULATION

A-8.1 Calculate the amounts of each individual impurity as required. Sum the areas of all the non-aromatic peaks.

A-8.2 Calculate the mass, percent concentration of each impurity as follows:

$$C_i = (A_i)(RRF_i)(C_s)(A_s)$$

A-8.3 Calculate the benzene purity as follows:

$$\text{Benzene, percent by mass} = 100.00 - C_i$$

where

C_i = total concentration of all impurities, percent by mass.

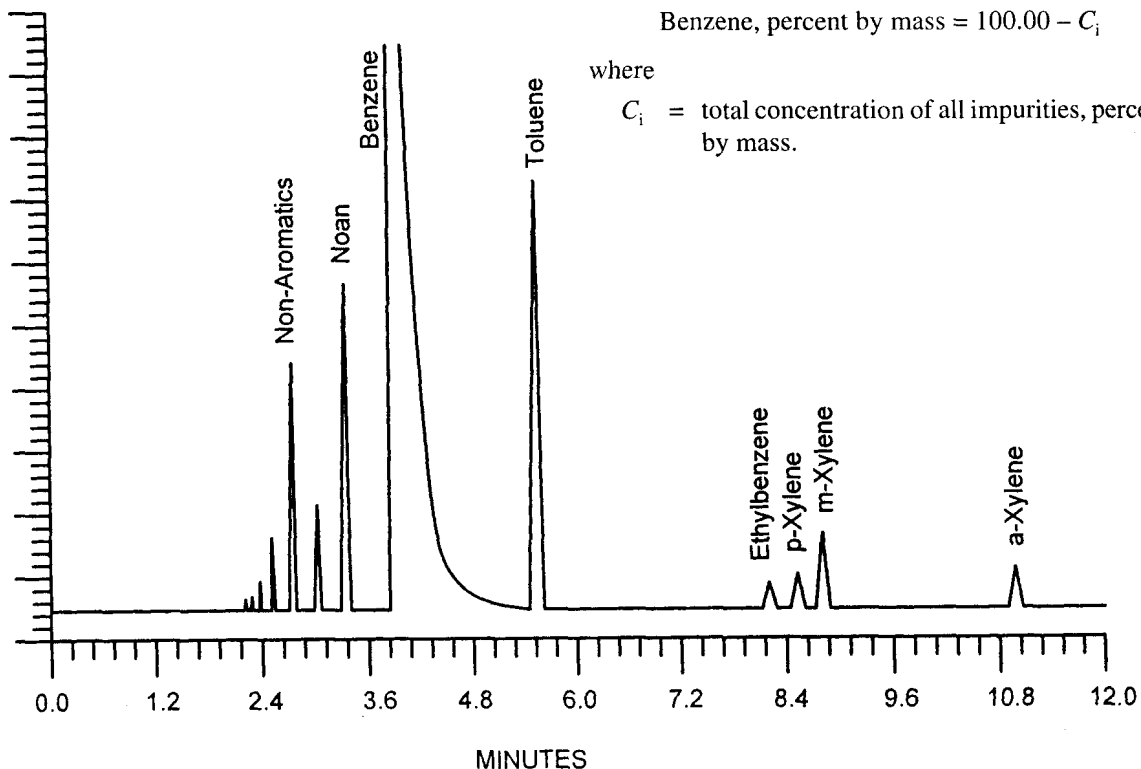


FIG. 1 TYPICAL CHROMATOGRAM

ANNEX B

[Table 1, Sl No. (ii)]

DETERMINATION OF COLOUR (PLATINUM-COBALT SCALE)

B-1 OUTLINE OF THE METHOD

Visual comparison of the colour of a sample with that of colour standard, and expression of the result in terms of Hazen (platinum-cobalt) colour units. For routine control purposes an instrument such as a comparator, colorimeter or spectrophotometer may be used, provided that it has first been established that the results so obtained are identical with those obtained by visual comparison.

B-2 DEFINITION

B-2.1 Hazen Colour Unit — The colour of a solution containing 1 mg of platinum per litre in the form of chloroplatinic acid, in the presence of 2 mg of cobalt (II) chloride hexahydrate per litre.

B-3 CHEMICALS

B-3.1 Cobalt (II) Chloride Hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$)

B-3.2 Hydrochloric Acid — approximately 1.19 g/ml. About 38 percent (*m/m*) solution, or approximately 12 N solution.

B-3.3 Chloroplatinic Acid — Dissolve 1.00 g platinum in a sufficient quantity of *aqua regia* in a glass or porcelain dish by heating on a boiling water bath. When the metal has dissolved, evaporate the solution to dryness. Add 4 ml of the hydrochloric acid solution (B-3.2) and again evaporate to dryness. Repeat this operation twice more. In this way 2.10 g of chloroplatinic acid (H_2PtCl_6) are obtained.

or

B-3.4 Potassium Chloroplatinate (K_2PtCl_6)

B-4 APPARATUS

B-4.1 Two Colorimetric Tubes, flat based if possible, with a graduation mark at least 100 mm above the base and matched especially with respect to colour of glass and height of graduation mark above the base. Suitable tubes are available commercially as 50 ml or 100 ml Nessler cylinders.

For the measurement of low colorations (less than 50 Hazen units), the height of the graduation mark above the base must be greater than for the measurement of deeper colours and must be sufficient that, on looking through this greater depth of liquid, a clear distinction between the standard Hazen matching solution can be observed.

B-5 PREPARATION OF STANDARD COLORIMETRIC SOLUTIONS

B-5.1 Standard Colorimetric Solution, 500 Hazen Units — Dissolve 2.00 g of the cobalt chloride (*see B-3.1*), and the equivalent of 1.00 g of platinum, that is either 2.10 g of the chloroplatinic acid (*see B-3.3*), or 2.49 g of the potassium chloroplatinate (*see B-3.4*), in water in a 2 000-ml one-mark volumetric flask, add 200 ml of the hydrochloric acid solution (*see B-3.2*), dilute to the mark and mix. This solution has a colour of 500 Hazen colour units.

B-5.2 Standard Hazen Matching Solution (Diluted Solution) — Into two series of ten 500-ml and fourteen 250-ml one-mark volumetric flasks, place the volumes of standard colorimetric solution (*see B-5.1*) shown in Table 4, dilute to the mark and mix.

B-5.3 Storage

Store these solutions (*see B-5.1* and *B-5.2*) in the dark in stoppered glass bottles. Under these conditions the colour standard solution (*see B-5.1*) is stable for at least one year. The standard Hazen matching solution (*see B-5.2*), although stable for at least one month shall preferably be prepared fresh.

B-6 PROCEDURE

B-6.1 First check visually that the sample has colour characteristics close to those of the standard Hazen matching solution (*see B-5.2*). If not, follow the instructions given in **B-7.2**.

B-6.2 Pour into one of the colorimetric tubes (*see B-4.1*) a quantity of the sample sufficient to fill it to the graduation mark. Similarly pour the standard Hazen matching solution (*see B-5.2*) which appears to have a similar colour into the other tube to the mark.

B-6.3 Compare the colour of the sample with that of the standard, by looking down the tubes from top to bottom against a white background strongly illuminated by daylight or by an electric 'daylight' lamp, taking care to avoid any side illumination.

B-6.4 Repeat, if necessary, with other standard Hazen matching solutions until the closest match is obtained.

NOTES

1 Instruments are available which permit visual comparison of a liquid of a given depth, with a moving tinted glass disc corresponding to the different standard Hazen matching solutions. The use of such instruments, whose standards are

Table 4 Standard Hazen Matching Solutions

(Clause B-5.2)

500-ml Volumetric Flasks		250-ml Volumetric Flasks	
Volume of Standard Colorimetric Solution (see B-5.1)	Corresponding Colour Hazen units	Volume of Standard Colorimetric Solution (see B-5.1)	Corresponding Colour Hazen units
ml	Hazen units	ml	Hazen units
0	0	30	60
5	5	35	70
10	10	40	80
15	15	45	90
20	20	50	100
25	25	62.5	125
30	30	75	150
35	35	87.5	175
40	40	100	200
50	50	125	250
—	—	150	300
—	—	175	350
—	—	200	400
—	—	225	450

very stable, is permissible provided that it has been established that using these tinted glass discs give the same results as do the corresponding standard Hazen matching solutions.

2 For routine control purposes, a colorimeter or spectrophotometer may be used, the instrument being standardized by means of the standard colorimetric solutions (see B-5.1 and B-5.2), provided that it has been confirmed that the use of that instrument gives the same results as does visual comparison.

B-7 EXPRESSION OF RESULTS

B-7.1 Express the colour of the sample as the number

of Hazen colour units corresponding to the standard Hazen matching solution having the closest match to the sample.

B-7.2 If the colour of the sample does not correspond with that of any of the standard Hazen matching solutions (brownish-yellow), give, if possible, an estimate of the colour and a description of the observed colour.

ANNEX C

[Table 1, Sl No. (iii)]

DETERMINATION OF DENSITY OR RELATIVE DENSITY

C-1 OUTLINE OF THE METHOD

A small volume (approximately 0.7 ml) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

C-2 APPARATUS

C-2.1 Digital Density Analyzer — A digital analyzer consisting of a U-shaped, oscillating sample tube and a system for electronic excitation, frequency counting,

and display. The analyzer must accommodate the accurate measurement of the sample temperature during measurement or must control the sample temperature as described in C-2.2. The instrument shall be capable of meeting the precision requirements described in this test method.

C-2.2 Circulating Constant — Temperature bath (Optional) capable of maintaining the temperature of the circulating liquid constant to $\pm 0.05^\circ\text{C}$ in the desired range. Temperature control can be maintained as part of the density analyzer instrument package.

C-2.3 Syringes, at least 2 ml in volume with a tip or

an adapter tip that will fit the opening of the oscillating tube.

C-2.4 Flow-Through or Pressure Adapter, for use as an alternative means of introducing the sample into the density analyzer either by a pump or by vacuum.

C-2.5 Thermometer, calibrated and graduated to 0.1°C, and a thermometer holder that can be attached to the instrument for setting and observing the test temperature. In calibrating the thermometer, the ice point and bore connections should be estimated to the nearest 0.05°C.

C-3 REAGENTS AND MATERIALS

C-3.1 Water, redistilled, freshly boiled and cooled reagent water (*see* IS 1070) for use as a primary calibration standard.

C-3.2 Petroleum Naphtha, for flushing viscous petroleum samples from the sample tube.

Warning — EXTREMELY FLAMMABLE.

C-3.3 Acetone, for flushing and drying the sample tube.

Warning — EXTREMELY FLAMMABLE.

C-3.4 Dry Air, for blowing the oscillator tube.

C-4 PREPARATION OF APPARATUS

Set up the density analyzer and constant temperature bath following the manufacturer’s instructions. Adjust the bath or internal temperature control so that the desired test temperature is established and maintained in the sample compartment of the analyzer. Calibrate the instrument at the same temperature at which the density of the sample is to be measured.

Caution — Precise setting and control of the test temperature in the sample tube is extremely important. An error of 0.1°C can result in a change in density of one in the fourth decimal.

C-5 CALIBRATION OF APPARATUS

C-5.1 Calibrate the instrument when first set up and whenever the test temperature is changed. Thereafter, conduct calibration checks at weekly intervals during routine operation.

C-5.2 Initial calibration, or calibration after a change in test temperature, necessitates calculation of the values of the constants *A* and *B* from the periods of oscillation (*T*) observed when the sample cell contains air and redistilled, freshly boiled and cooled reagent water. Other calibrating materials such as *n*-nonane, *n*-tridecane, cyclohexane, and *n*-hexadecane (for high temperature applications) can also be used as appropriate.

C-5.2.1 While monitoring the oscillator period, *T*, flush the sample tube with petroleum naphtha, followed with

an acetone flush and dry with dry air. Contaminated or humid air can affect the calibration. When these conditions exist in the laboratory, pass the air used for calibration through a suitable purification and drying train. In addition, the inlet and outlet ports for the U-tube must be plugged during measurement of the calibration air to prevent ingress of moist air.

C-5.2.2 Allow the dry air in the U-tube to come to thermal equilibrium with the test temperature and record the *T*-value for air.

C-5.2.3 Introduce a small volume (about 0.7 ml) of redistilled, freshly boiled and cooled reagent water into the sample tube from the bottom opening using a suitable syringe. The test portion must be homogeneous and free of even the smallest air or gas bubbles. The sample tube does not have to be completely full as long as the liquid meniscus is beyond the suspension point. Allow the display to reach a steady reading and record the *T*-value for water.

C-5.2.4 Calculate the density of air at the temperature of test using the following equation:

$$d_a, \text{ g/ml} = 0.001\ 293 [273.15/T] [P/760] \dots\dots\dots (1)$$

where

- T* = temperature, K and
- P* = barometric pressure, torr.

C-5.2.5 Determine the density of water at the temperature of test by reference to Table 5.

C-5.2.6 Using the observed *T*-values and the reference values for water and air, calculate the values of the constants *A* and *B* using the following equations:

$$A = [T_w^2 - T_a^2] / [d_w - d_a] \dots\dots\dots (2)$$

$$B = T_a^2 - (A \times d_a) \dots\dots\dots (3)$$

where

- T_w* = observed period of oscillation for cell containing water,
- T_a* = observed period of oscillation for cell containing air,
- d_w* = density of water at test temperature, and
- d_a* = density of air at test temperature.

Alternatively, use the *T* and *d* values for the other reference liquid, if one is used.

C-5.2.7 If the instrument is equipped to calculate density from the constants *A* and *B* and the observed *T*-value from the sample, then enter the constants in the instrument memory in accordance with the manufacturer’s instructions.

C-5.2.8 Check the calibration and adjust, if needed by performing the routine calibration check described in C-5.3.

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C-5.2.9 To calibrate the instrument to display relative density, that is, the density of the sample at a given temperature referred to the density of water at the same temperature, follow sections **C-5.2.1** through **C-5.2.7**. Substitute 1.000 for d_w in performing the calculations described in **C-5.2.6**.

C-5.3 Weekly calibration adjustments to constants *A* and *B* can be made if required, without repeating the calculation procedure.

NOTE — The need for a change in calibration is generally attributable to deposits in the sample tube that are not removed by the routine flushing procedure. Although this condition can be compensated for by adjusting *A* and *B*, it is good practice to clean the tube with warm chromic acid solution (**Warning** — Causes severe burns). A recognized carcinogen, whenever a major adjustment is required. Chromic acid solution is the most effective cleaning agent; however, surfactant cleaning fluids have also been used successfully.

C-5.3.1 Flush and dry the sample tube as described in **C-5.2.1** and allow the display to reach a steady reading. If the display does not exhibit the correct density for air at the temperature of test, repeat the cleaning procedure or adjust the value of constant *B* commencing with the last decimal place until the correct density is displayed.

C-5.3.2 If adjustment to constant *B* was necessary in **C-5.3.1** then continue the recalibration by introducing redistilled, freshly boiled and cooled reagent water into the sample tube as described in **C-5.2.3** and allow the display to reach a steady reading. If the instrument has been calibrated to display the density, adjust the reading to the correct value for water at the test temperature (see Table 5) by changing the value of constant *A*, commencing with the last decimal place. If the instrument has been calibrated to display the relative density, adjust the reading to the value 1.000 0.

NOTE — In applying this weekly calibration procedure, it can be found that more than one value each for *A* and *B*, differing in the fourth decimal place, will yield the correct density reading for the density of air and water. The setting chosen would then be dependent upon whether it was approached from

a higher or lower value. The setting selected by this method could have the effect of altering the fourth place of the reading obtained for a sample.

C-5.4 Some analyzer models are designed to display the measured period of oscillation only (*T*-values) and their calibration requires the determination of an instrument constant *K*, which must be used to calculate the density or relative density from the observed data.

C-5.4.1 Flush and dry the sample tube as described in **C-5.2.1** and allow the display to reach a steady reading. Record the *T*-value for air.

C-5.4.2 Introduce redistilled, freshly boiled and cooled reagent water into the sample tube as described in **C-5.2.3**, allow the display to reach a steady reading and record the *T*-value for water.

C-5.4.3 Using the observed *T*-values and the reference values for water and air (see **C-5.2.4** and **C-5.2.5**), calculate the instrument constant *K* using the following equations:

For density:

$$K_1 = [d_w - d_a] / [T_w^2 - T_a^2] \dots\dots\dots (4)$$

For relative density:

$$K_2 = [1.000 0 - d_a] / [T_w^2 - T_a^2] \dots\dots\dots (5)$$

where

- T_w = observed period of oscillation for cell containing water,
- T_a = observed period of oscillation for cell containing air,
- d_w = density of water at test temperature, and
- d_a = density of air at test temperature.

C-6 PROCEDURE

C-6.1 Introduce a small amount (about 0.7 ml) of sample into the clean, dry sample tube of the instrument using a suitable syringe.

Table 5 Density of Water
(Clauses C-5.2.5 and C-5.3.2)

Temperature °C	Density g/ml	Temperature °C	Density g/ml	Temperature °C	Density g/ml
0.0	0.999 840	21.0	0.997 991	40.0	0.992 212
3.0	0.999 964	22.0	0.99 769	45.0	0.990 208
4.0	0.999 972	23.0	0.997 537	50.0	0.988 030
5.0	0.999 964	24.0	0.997 295	55.0	0.985 688
10.0	0.999 699	25.0	0.997 043	60.0	0.983 191
15.0	0.999 099	26.0	0.996 782	70.0	0.980 546
15.56	0.999 012	27.0	0.996 511	75.0	0.977 759
16.0	0.998 943	28.0	0.996 231	80.0	0.974 837
17.0	0.998 774	29.0	0.995 943	85.0	0.971 785
18.0	0.998 595	30.0	0.995 645	90.0	0.968 606
19.0	0.998 404	35.0	0.994 029	100.0	0.965 305
20.0	0.998 203	37.78	0.993 042		

C-6.2 The sample can also be introduced by siphoning. Plug the external TFE-fluorocarbon capillary tube into the lower entry port of the sample tube. Immerse the other end of the capillary in the sample and apply suction to the upper entry port using a syringe or vacuum line until the sample tube is properly filled.

C-6.3 Turn on the illumination light and examine the sample tube carefully. Make sure that no bubbles are trapped in the tube, and that it is filled to just beyond the suspension point on the right hand side. The sample must be homogeneous and free of even the smallest bubbles.

NOTE — If the sample is too dark in color to determine the absence of bubbles with certainty, the density cannot be measured within the stated precision limits.

C-6.4 Turn the illumination light off immediately after sample introduction, because the heat generated can affect the measurement temperature.

C-6.5 After the instrument displays a steady reading to four significant figures for density and five for T -values, indicating that temperature equilibrium has been reached, record the density or T -value.

C-7 CALCULATION

C-7.1 Calculating Density Analyzers

The recorded value is the final result, expressed either

as density, in g/ml or g/m^3 , or as relative density.

NOTE — $\text{kg/m}^3 = 1\,000 \times \text{g/ml}$.

C-7.2 Non-calculating Density Analyzers

Using the observed T -value for the sample and the T -value for water and appropriate instrument constants determined as in C-5.4.3, calculate the density or relative density using Equations 6 and 7. Carry out all calculations to six significant figures and round the final results to four.

For density:

$$\text{density, g/ml (kg/dm}^3\text{) at } t = d_w + K_1 (T_s^2 - T_w^2) \dots (6)$$

For relative density:

$$\text{relative density, } t/t = 1 + K_2 (T_s^2 - T_w^2) \dots (7)$$

where

T_w = observed period of oscillation for cell containing water;

T_s = observed period of oscillation for cell containing sample;

d_w = density of water at test temperature;

K_1 = instrument constant for density;

K_2 = instrument constant for relative density, and

t = temperature of test, in $^{\circ}\text{C}$.

ANNEX D

[Table 1, Sl No. (iv)]

DETERMINATION OF TOTAL SULPHUR CONTENT

D-0 OUTLINE OF THE METHOD

The sample is reacted with Raney nickel. The hydrogen sulphide liberated from the nickel sulphide thus formed is absorbed and titrated with mercuric acetate. Certain oxygenated sulphur compounds are not completely determined and some olefins interfere with the test.

NOTE — Stringent precautions shall be taken to avoid sulphur contamination from atmosphere, apparatus, and reagents or other sources. Care should be taken not to allow sodium hydroxide reagent or apparatus 'wet' with this reagent to be exposed to laboratory atmosphere.

D-1 APPARATUS

D-1.1 Reduction Apparatus — The reduction apparatus shall be of the shape, dimensions and assembly as shown in Fig. 2. The cone and delivery tube is connected to a supply of nitrogen via a Dreschel

bottle and the luted venting device. Rubber tubing shall not be used for nitrogen supply connection; PVC or other sulphur-free plastics tubing is suitable. The 100 ml flask is heated electrically by means of a mantle. The apparatus consists of the following.

D-1.1.1 Reduction Flask — 100-ml round-bottomed flask with two short upright necks having respectively 10/19 and 14/23 ground-glass sockets (see IS 5165). The flask is also fitted with a 10/19 ground-glass socket inclined to centre-bottom.

D-1.1.2 Glass Delivery Tube (Year to be Given in N.R.) — A 10/19 (see IS 5165) cone and stem with the end drawn out to a 1-mm hole, of such a length that the tip is within 5 mm of the centre of the bottom of the flask when the cone is in position in the inclined socket.

D-1.1.3 Tap Funnel, capacity 20 ml with 10/19 (see IS 5165) cone and socket.

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D-1.1.4 Adaptor, right-angle connection with 10/19 cone.

D-1.1.5 Condenser, a Liebig condenser, effective length 150 mm, with a 14/23 cone and socket.

D-1.1.6 Absorber — A delivery tube of 6 ± 0.5 mm outer diameter bent at 110° and containing a small expansion chamber in the upright section. The lower end of the tube has a 1-mm hole, and fits into a covered $200 \text{ mm} \times 32 \text{ mm}$ outer diameter boiling tube. The upper end of the delivery tube is bent at an angle of 70° and fitted with a 14/23 cone at a distance of approximately 135 mm from the longer arm.

D-1.1.7 Gas Washing Bottle, Dreschel bottle having a dip-tube of about 6 mm outer diameter.

D-1.1.8 Microburette, capacity 10 ml arranged so that the liquid in the absorber can be titrated.

D-1.2 Flask, a 500-ml stoppered conical flask, marked at the 400-ml level with the cone and stopper lubricated with silicone grease.

D-1.3 Measuring Cylinder, 10 ml capacity.

D-1.4 Pipette (not to be operated by mouth).

D-1.5 Thermometer, any suitable thermometer including the interval 75° to 80°C .

D-2 REAGENTS

D-2.1 Acetone

D-2.2 Propan-2-ol

D-2.3 Nitrogen

D-2.4 Raney Nickel, 50 percent nickel, 50 percent aluminium.

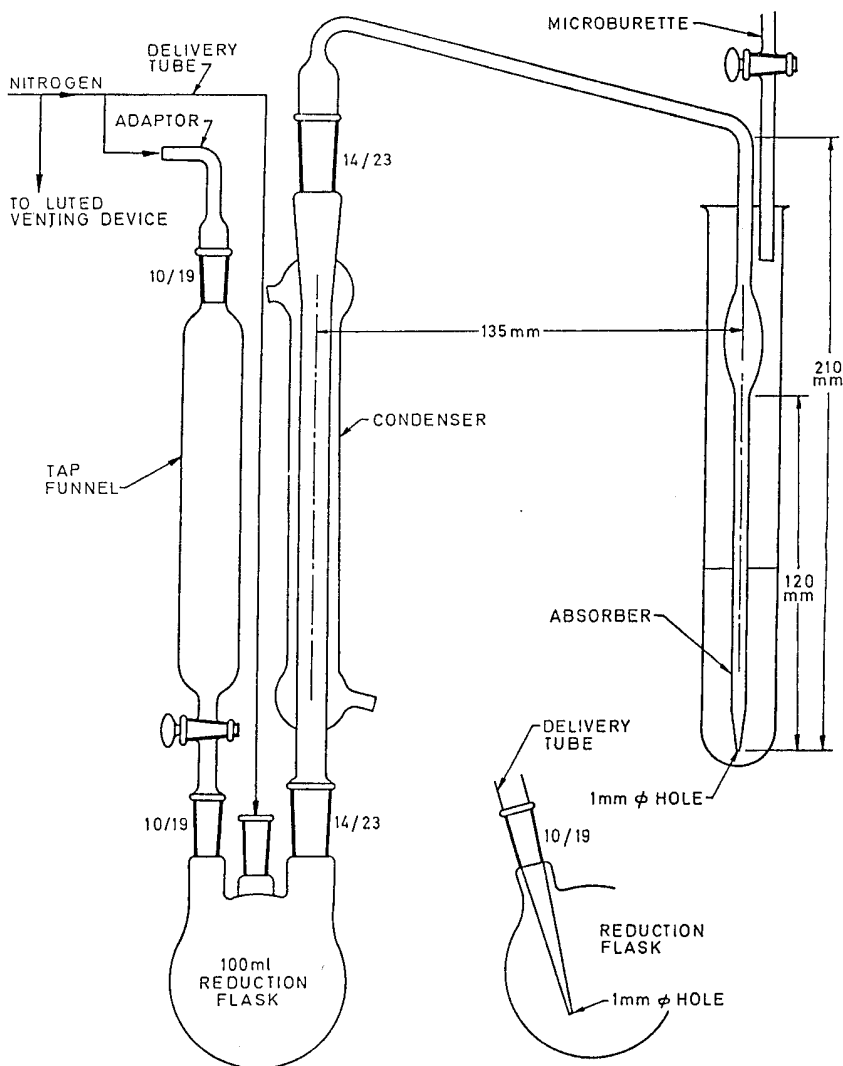


FIG. 2 REDUCTION APPARATUS

D-2.5 Sodium Hydroxide Solutions, 2.5 N and 1 N — Clean the conical flask with nitric acid/potassium dichromate mixture [prepared by dissolving 5 g of potassium dichromate in 5 ml of water and adding 100 ml of concentrated (15 N) nitric acid, stirring continuously]; rinse thoroughly with water. Fill with water to the 400-ml mark and add the mass of sodium hydroxide pellets appropriate for preparation of the 2.5 N or 1 N solution. Swirl gently until dissolution is complete and allow to cool.

D-2.6 Hydrochloric Acid, 5 N

D-2.7 Potassium Hydroxide, 40 g/l solution in ethandiol.

D-2.8 Mercuric Acetate Solution — Dissolve 0.675 g of mercuric oxide, previously dried at 100°C, in 50 ml of water containing 2 ml of glacial (17 M) acetic acid. Dilute to 1 000 ml with water and mix well. Dilute 50 ml of the solution thus prepared to 250 ml with water and mix well. One millilitre of the diluted solution is equivalent to 0.02 mg of sulphur.

D-2.9 Dithizone Indicator Solution, 1 g/l in acetone, prepared fresh daily, or every 3 days if stored in a refrigerator.

NOTE — When experience has been gained with the concentration of indicator required, a few grains of the solid indicator may be added to the absorber. In this way any instability of indicator solution is overcome.

D-3 PROCEDURE

D-3.1 Clean the apparatus thoroughly with a mixture of nitric acid and potassium dichromate. Rinse thoroughly with water and acetone and dry in an oven which has not been contaminated with sulphur or sulphur containing materials in previous use. The apparatus is self scouring and, when in constant use, shall not be cleaned between determinations, except for rinsing the flask, delivery tube, absorber and thermometer with water. When not in constant use, it shall be cleaned between determinations with water and acetone.

NOTE — For activating nickel perfectly, the weighed Raney nickel is kept in caustic solution for at least four hours.

D-3.2 Weigh accurately about 0.5 g of Raney nickel and put it in the reduction flask using a cone made from glazed paper, and add 10 ml of sodium hydroxide solution (2.5 N) from the measuring cylinder.

NOTE — Incrustations around the stoppers and necks of sodium hydroxide bottles contain sufficient quantities of sulphur to affect test results. Such incrustations should be removed without allowing material to fall into the bottle. Before using solution from the bottle, pour a little to waste. Replace the stopper promptly.

Care shall be taken at this stage because there is a vigorous reaction.

When the reaction has subsided, swirl the liquid in the flask to bring the nickel adhering to the sides of the flask to the bottom. Set the flask aside for 10 min and then decant off the supernatant liquid. Wash down both necks of the flask with 10 to 15 ml of water. Swirl the water vigorously to disturb the nickel residue, but avoid entrainment of air and, with minimum delay for settling, decant off the water as completely as possible without too much attention to removing the last drop. Repeat the water wash three times more, and follow with a wash with 10 ml of propan-2-ol. Decant most of the propan-2-ol leaving enough to cover the catalyst, and add a further 10 ml of propan-2-ol.

D-3.3 Assemble the apparatus except for the tap funnel, lightly greasing all the joints with silicone grease. Add 50 ml of a mixture of equal parts of sodium hydroxide solution (1 N) and acetone to the boiling tube and add 5 drops of the dithizone indicator solution.

D-3.3.1 Calculate the appropriate size of sample as follows:

$$\frac{100 \text{ ml}}{\text{Specified or expected sulphur content (mg/kg)}}$$

(with a maximum of 50 ml) and pipette this volume into the flask through the 10/19 socket.

D-3.4 Complete the assembly of the apparatus. Measure 10 ml of the hydrochloric acid solution into the tap funnel. Pass nitrogen at the rate of 2 or 3 bubbles/second as shown in the Dreschel bottle containing the ethane-di-ol potassium hydroxide solution. Note the burette reading and titrate the contents of the absorber with the mercuric acetate solution to a pale pink colour.

D-3.4.1 Heat the flask at such a rate that the contents boil gently in about 10 min. Maintain the heating for a further period of 30 min at such a rate that small bubbles rise copiously from the nickel and gentle refluxing occurs.

D-3.4.2 Increase the input to the heating mantle slightly and allow the hydrochloric acid solution to drip slowly (10 ml in 5 to 10 min) into the flask. Vigorous generation of hydrogen will occur, but little or no hydrogen sulphide will be evolved until about half the hydrochloric acid has entered the flask. Titrate the absorbing solution to a pink colour. As hydrogen sulphide is evolved and absorbed and the colour of the absorbing solution reverts to yellow, titrate in more mercuric acetate solution in order to restore the pink colour. After the addition of the acid, open the tap of the funnel occasionally to sweep forward any hydrogen sulphide that may have collected below it. When the evolution of hydrogen sulphide has almost ceased, increase the nitrogen flow rate to about 5 bubbles/

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second in the bottle to improve the transfer of hydrogen sulphide to the absorber.

D-3.4.3 When the evolution of hydrogen sulphide has apparently ceased, turn off the nitrogen temporarily and cool the flask by reducing the heat input and by blowing a little air on to it or by applying a damp cloth. The reduction in pressure will cause the absorbing solution to rise up the delivery tube. Restore the nitrogen flow before the absorbing solution reaches the bend above the cone. Repeat this operation at about 2 min intervals until no more hydrogen sulphide is washed down. If any liquid enters the cone, the test shall be abandoned.

D-3.4.4 Boil the contents of the flask vigorously and continue the titration to the end point.

D-3.4.5 Carry out a blank test on the reagents omitting the sample. Once a day is normally sufficient but the blank shall always be re-determined, if there is any

change in the reagents, apparatus or laboratory atmosphere which could conceivably affect the blank value. This value should not exceed 0.6 ml.

D-4 CALCULATION

$$\text{Total sulphur content, mg/kg} = \frac{20 (V_1 - V_2)}{V \times D}$$

where

V_1 = volume of mercuric acetate solution used for the sample titration, in ml;

V_2 = volume of mercuric acetate solution used for the blank test, in ml;

V = volume of sample taken for the test, in ml; and

D = density of the sample at the temperature at which it was measured, in g/ml.

ANNEX E

[Table 1, Sl No. (v)]

DETERMINATION OF DISTILLATION RANGE**E-1 OUTLINE OF THE METHOD**

The distillation is carried out via a carefully controlled distillation wherein temperature readings are noted for the first drop of distillate and at the dry point.

E-2 APPARATUS

E-2.1 Flask — A standard 200-ml side-tube, heat-resistant glass distillation flask conforming to the following dimensions (*see* Fig. 3):

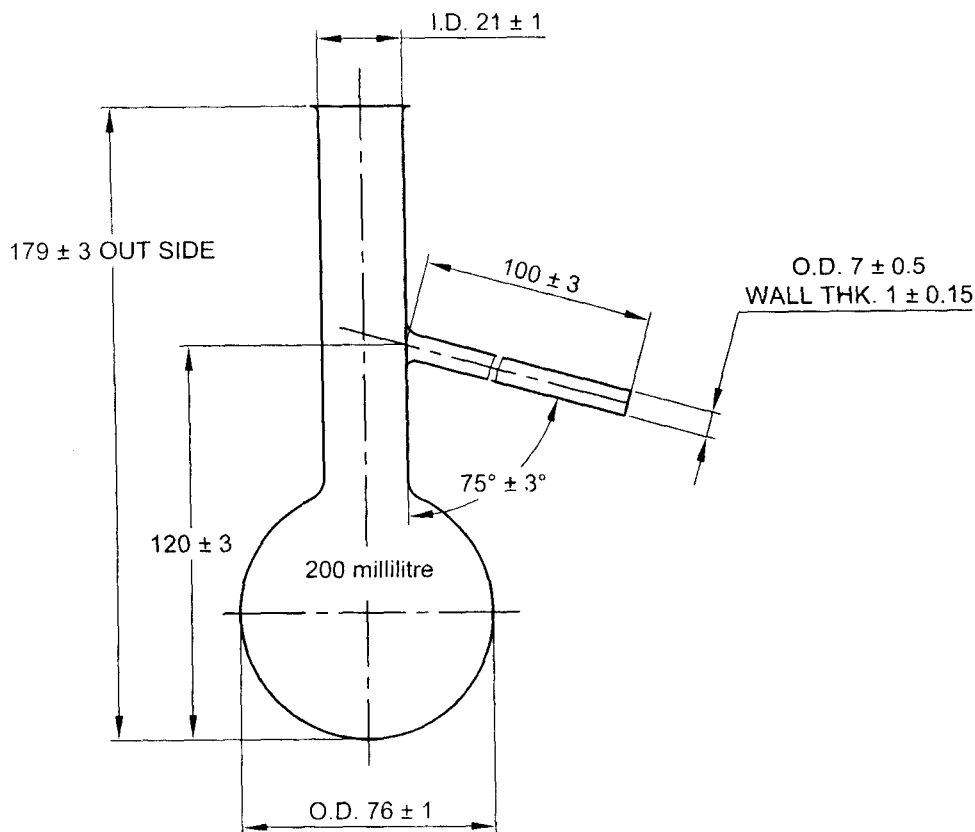
Diameter of bulb, outside, mm	: 76 ± 1.5
Diameter of neck, inside, mm	: 21 ± 1
Height of flask, outside, mm	: 179 ± 3
Vertical distance from bottom of bulb outside to bottom of vapour-tube opening in neck, mm	: 120 ± 3
Length of side tube, mm	: 100 ± 3
Diameter of side tube, outside, mm	: 7 ± 0.5
Angle of wide tube with vertical axis of bulb and neck	: 75 ± 3

E-2.2 Thermometer — A suitable thermometer having 0.2°C subdivisions and covering the entire range may be used.

E-2.3 Condenser — The condenser tube may consist

of a straight glass tube 600 to 610 mm in length and 12 mm in inside diameter, of standard wall thickness (about 1.25 mm) with the exit end cut off square and ground flat. It shall be set in a cooling trough so that at least 380 mm of the tube is in contact with the water. Clearance between the condenser tube and any parallel side of the trough shall be not less than 19 mm. The water in the cooling trough shall be maintained at 10° to 20°C. This may be done by adding ice to the water or by circulating chilled water through the trough. The trough shall be so mounted that the condenser tube is set at an angle of 75° with the vertical.

E-2.4 Receiver — A graduate of the cylindrical type, of uniform diameter, with a pressed or moulded base and a lipped top. The cylinder shall be graduated to contain 100 ml, and the graduated portion shall be neither less than 178 mm nor more than 203 mm in length. It shall be graduated in single millilitres and each fifth mark shall be distinguished by a longer line. It shall be numbered from the bottom up at intervals of 10 ml. The overall height of the graduate shall not be less than 248 mm nor more than 260 mm. The graduations shall not be in error by more than 1 ml at any point on the scale. The bottom 1 ml graduation may be omitted.



All dimensions in millimetres.

FIG. 3 DISTILLATION FLASK

E-2.5 Support for Flask — A sheet of 3 to 6 mm hard insulation board 152 mm² with a circular hole in the center, supported on a circular metal shield enclosing the Bunsen burner, and approximately 50 mm higher than the top of the burner. The hole shall be 25 mm in diameter.

E-2.6 Heater — An electric heater or a Bunsen burner, fully adjustable and capable of giving sufficient heat to distill the product at the required rate is used. When a Bunsen burner is used, the burner shall be adjusted so as to produce an entirely blue flame. In case of dispute concerning results obtained with gas heat versus electric heat, gas heat shall be accepted as the standard.

Caution — Superheating of the flask can cause erroneous results and is more likely to occur with electric heaters than with Bunsen Burners as heat sources.

E-3 ASSEMBLY OF THE APPARATUS

E-3.1 Assemble the apparatus as shown in Fig. 4. Mount the flask on the insulation board of appropriate dimensions, with the side tube extending through a tightly fitting cork stopper about 50 mm into the condenser tube.

E-3.2 Support the distillation thermometer in the neck of the flask by means of a cork stopper with the thermometer vertical and centered in the neck of the flask and in such a position that the top of the bulb (or top of contraction bulb, if present) is level with the lowest point of juncture between the side tube and the neck of the flask (see Fig. 5).

E-3.3 Place the burner directly under the centre of the hole in the insulation board.

E-4 PROCEDURE

E-4.1 Carefully measure a 100-ml specimen of the material to be tested in the 100-ml graduated cylinder at room temperature and transfer to the distillation flask, draining the cylinder at least 15 s. This is preferably done before mounting the flask in position, in order to prevent liquid from entering the side arm. Connect the flask to condenser and apparatus, assembled as described in E-3. Do not rinse out the graduated cylinder used to measure the sample for distillation, but place under the lower end of the condenser tube to receive the distillate. Heat the flask slowly, especially after ebullition has begun, so as to allow the mercury column of the thermometer to become fully expanded

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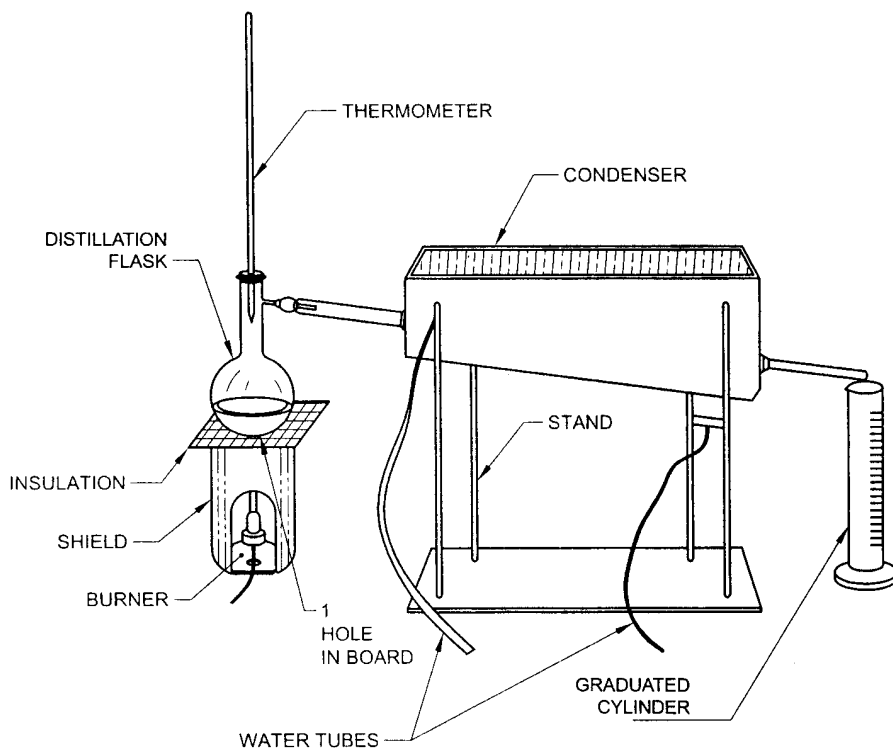


FIG. 4 APPARATUS ASSEMBLY FOR DISTILLATION FLASK

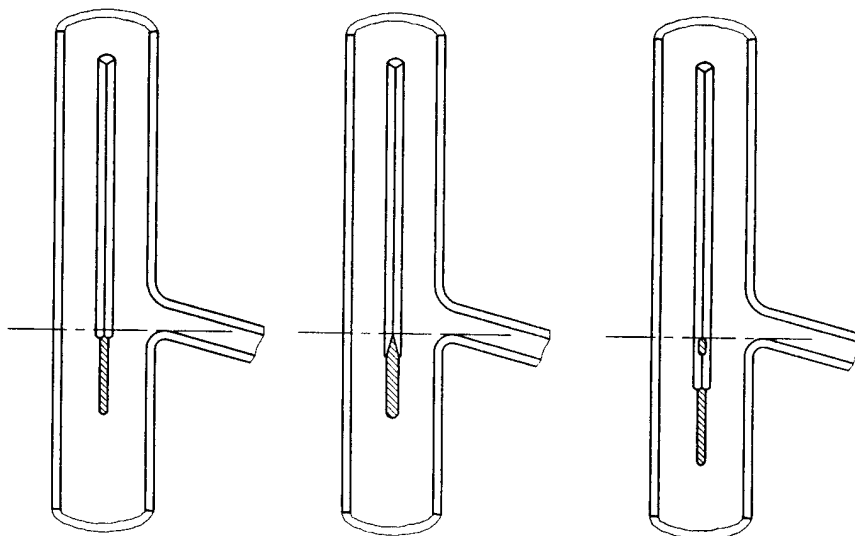


FIG. 5 POSITION OF THERMOMETER IN DISTILLATION FLASK

before the first drop distils over. Regulate the rate of heating so that the ring of condensing vapour on the wall of the flask reaches the lower edge of the side arm in not less than 90 s, and preferably approximately 120 s, from the start of the rise of the vapour ring. The total time from the start of the heating until the first drop falls into the receiver should be not less than 5 min or more than 10 min. Avoid major changes in

heating rate. Even operation is best gained through experience with the method. When distillation starts, adjust the receiver to allow condensation to flow down its inner wall to prevent loss of spattering; then adjust the heater to continue the distillation at the rate of 5 to 7 ml/min (about 2 drops/s). Maintain this rate, and continue the distillation to dryness. The total yield of distillate shall not be less than 97 percent.

E-4.2 Take the temperature reading when the first drop of distillate falls into the receiving cylinder and report as the initial boiling point (IBP). Take a final reading when the liquid just disappears from the flask, and report this reading as the dry point temperature.

E-4.3 Observe and record the following additional data at the time and place of the distillation test:

- a) Correction for inaccuracy of the thermometer, and
- b) Barometer reading and temperature of the barometer. The observed barometric pressure shall be corrected by reference to standard tables and reported in terms of millimetres of mercury at 0°C.

E-5 TEMPERATURE CORRECTIONS

E-5.1 Inaccuracy of Thermometer

This correction shall be obtained by calibration of the

thermometer used in the test and applied to the observed thermometer reading.

E-5.2 Variation from Standard Barometric Pressure

This correction shall be applied to the observed temperature after correcting for accuracy of the thermometer and is determined by the following equation:

$$C = [0.0427 + \{0.000025 \times (760 - P)\}] \times (760 - P)$$

where

- C = the correction, in °C; and
- P = the measured barometric pressure, in millilitres of mercury, corrected to 0°C.

E-5.3 Combined Corrections

If the overall distillation range of the sample does not exceed 2°C, a combined correction for thermometer inaccuracy and barometric pressure may be made on the basis of the difference between the observed 50 percent boiling point and the true boiling point at 760 mm of benzene, that is, 80.1°C.

ANNEX F

[Table 1, Sl No. (viii)]

DETERMINATION OF BROMINE INDEX

F-1 OUTLINE OF THE METHOD

The specimen is added to a solvent and titrated with electrolytically generated bromine at room temperature. The end point is determined by a dead stop method. The time of titration is proportional to the bromine added to the specimen.

F-2 APPARATUS

F-2.1 Amperometric — Coulometric Apparatus

It is an automatic apparatus, suitable for bromine index titrations with variable generator current and timer. A typical circuit diagram of suitable equipment is shown in Fig. 6.

F-2.2 Syringe, 2 ml with needle and rubber cap seal.

F-2.3 Stirrer, magnetic.

F-3 REAGENTS

F-3.1 Electrolyte — To make 1 litre, mix 600 ml of

glacial acetic acid, 260 ml of absolute methanol, and 140 ml of potassium bromide solution (119 g/l). Dissolve 2 g of mercuric acetate in this mixture.

F-3.2 Potassium Bromide Solution (119 g/l) — Dissolve 119 g of potassium bromide (KBr) in water and dilute to one litre.

F-4 PROCEDURE

F-4.1 Place 50 ml of electrolyte in a clean, dry titration cell, insert the electrodes, and begin stirring. Apply the generation current in accordance with Table 6.

Table 6 Specimen Size and Generation Current

Sl No.	Estimated Bromine Index	Specimen Weight g	Generation Current mA
(1)	(2)	(3)	(4)
i)	0-20	1.000	1.0
ii)	20-200	0.600	5.0
iii)	200-2 000	0.060	5.0

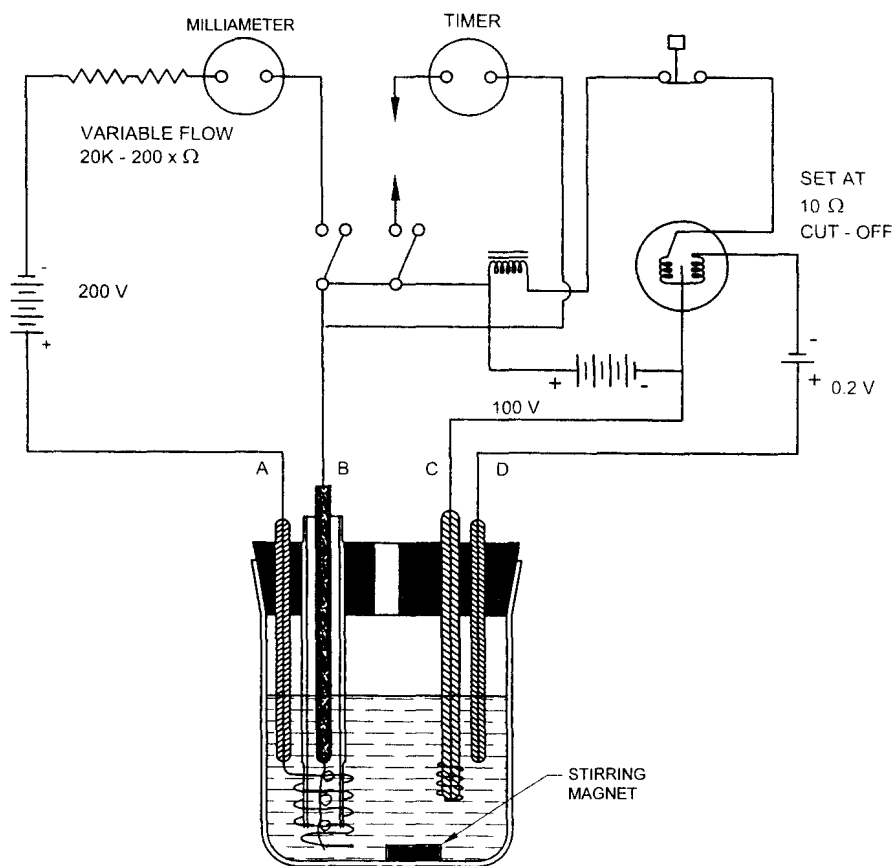


FIG. 6 AUTOMATIC AMPEROMETRIC — COULOMETRIC TITRATOR CIRCUIT

F-4.2 Before introducing the specimen and immediately before each determination, bring the coulometer to equilibrium.

F-4.3 Draw into the syringe the amount of sample prescribed in Table 6 corresponding to the estimated bromine index. Wipe the needle with a clean cloth, attach a rubber cap seal to the needle, and weigh on the analytical balance. Remove the seal, add the specimen to the electrolyte, and set the timer to zero. Replace the seal, reweigh the syringe, and calculate the specimen weight.

F-4.4 Begin titration of the specimen. As the titration proceeds, keep the generation current at the selected value. The generation of bromine will continue as long as it is consumed by the sample. At the end point an incremental increase in bromine concentration causes the titrator and timer to stop automatically. Forty seconds after the titrator has shut off, continue the

titration. If the titrator cuts off immediately, the end point has been reached and the titration may be considered complete. Otherwise, it may be necessary to continue the titration in steps, waiting about 40 s between steps, until the titration time increment is 4 s or less. Note the total titration time and generation current.

F-5 CALCULATION

Calculate the bromine index, *B*, as follows:

$$B = \frac{TI \times 79.9}{965 M}$$

where

- T* = titration time, in s;
- I* = generation current, in mA; and
- M* = mass of sample, in g.

ANNEX G

[Table 1, Sl No. (ix)]

DETERMINATION OF SOLIDIFICATION POINT

G-1 OUTLINE OF THE METHOD

Solidification point is measured by noting the maximum temperature reached during a controlled cooling cycle after the appearance of a solid phase.

G-2 APPARATUS

G-2.1 Benzene Container, air jacketed.

G-2.1.1 Inner Container, a test tube 15 mm in outside diameter and 125 mm in length.

G-2.1.2 Air Jacket, a standard test tube 25 mm in outside diameter and 150 mm in length.

G-2.1.3 Insulation, with dry absorbent cotton or glass wool.

G-2.2 Benzene Container (Thick Walled), a glass test tube 18 mm in outside diameter, 14 mm in inside diameter and 150 mm in length.

G-2.3 Ice Bath, a one litre beaker or similar suitable container having an effective depth of at least 127 mm and filled with chipped or shaved ice.

G-2.4 Stirrer, consisting of a 1-mm wire (copper or stainless steel) or a 2-mm glass rod with one end bent into a circular form at right angles to the shaft so that it will move freely in the annular space between the thermometer stem and the wall of the smaller test tube.

G-2.5 Temperature Measurement Device, either device described below has been found satisfactory.

G-2.5.1 Thermometer, Benzene freezing point thermometer having a range from 4.0 to 6.0°C and least count of 0.01°C and conforming to the following requirements:

Name	—	Solidification Point of Benzene
Reference Fig. No.	—	10
Range, °C	—	4 to 6
a) Immersion	—	Total
Graduations, °C:		
Subdivisions	—	0.02
Long lines at each	—	0.1
Numbers at each	—	0.02
Scale error, <i>Max</i>	—	0.04
Expansion chamber:		
Permit heating to	—	50°C
a) Total length, mm	—	210 to 220
b) Stem OD, mm	—	6.0 to 7.0
c) Bulb length, mm	—	25 to 35

d) Bulb OD, mm — 6.0 to > stem

Scale location:

Bottom of the bulb to line at — 4°C

a) Distance, mm — 110 to 115

b) Length of graduated portion, mm — 45 to 75

G-2.5.2 Thermistor — Type CSP, with accuracy of 0.01°C with a nominal resistance at 2 500 Ω at 25°C. The thermistor shall be equipped with an ohmmeter capable of reading resistance to the nearest 0.1 Ω.

G-2.6 Stirring Apparatus (Optional) — The apparatus may be an acceptable replacement for manually stirring the benzene solution.

G-3 PREPARATION OF APPARATUS

G-3.1 Fit the benzene container with a two-hole cork stopper. Through one hole insert the temperature measurement device. The thermometer should be inserted up to the 4.0°C mark. The thermistor should be inserted so as to contact the benzene solution. Through the other hole insert shaft of the stirrer.

G-3.2 If using the benzene container (air jacketed), place a 3.2-mm layer of dry absorbent cotton or glass wool in the bottom of the larger test tube and insert the inner container up to the lip into a cork stopper or annular ring of cork that just fits into the mouth of the air jacket.

G-4 PROCEDURE

G-4.1 Saturate the sample of benzene with water by placing 7 to 8 ml of the sample in the benzene container, add one drop of water, and shake the tube and contents vigorously.

G-4.2 Place the cork stopper onto the benzene container and onto the stirring apparatus, if available.

G-4.3 When using the benzene container (air jacket), the operator may cool the smaller test tube and contents rapidly to about 6°C in the ice bath, while stirring. Wipe dry the outside of the smaller test tube and insert it into the larger test tube. Place the assembled test tubes in the ice bath.

G-4.4 Stir the benzene continuously and observe the thermometer reading closely. The temperature will fall to a minimum, then rise to a maximum, remain constant at this maximum for approximately 15 s, and then fall again (*see Note 1*). The minimum temperature is due to super-cooling before

solidification starts and shall not be more than 0.7°C below the maximum. Record the maximum constant temperature observed to the nearest 0.01°C and designate it as 'wet' (*see* Note 2).

NOTES

1 If distinct minimum and maximum points are not evident, or if the temperature does not remain constant at the maximum for at least 15 s, the determination shall be repeated.

2 The precision can be increased to $\pm 0.01^\circ\text{C}$ by using a magnifying glass that ensures a reading perpendicular to the stem of the thermometer. In such cases it may be necessary to correct for stem exposure, that under ordinary conditions this correction will be less than 0.01°C.

G-5 EXPRESSION OF RESULTS

Results shall be reported on the anhydrous basis. Since the determination is actually made on water-saturated benzene, the solidification point shall be corrected to the anhydrous basis by adding 0.09°C to the observed maximum temperature following the minimum corrections for the accuracy of the thermometer shall be made.

G-6 PRECISION

Duplicate determinations on the same sample shall not differ by more than 0.02°C (*see* G-4.4, Note 2).

ANNEX H

[Table 1, Sl No. (x)]

DETERMINATION OF THIOPHENE

H-1 OUTLINE OF THE METHOD

Thiophene is reacted with isatin, under prescribed conditions, to form a coloured compound. The compound is extracted into sulphuric acid, and the intensity of the colour is measured spectrophotometrically. Thiophene concentration is obtained by correlation with known concentration of samples.

H-2 APPARATUS

H-2.1 Separatory Funnels, 50, 250, 500, and 1 000 ml, glass-stoppered.

H-2.2 Spectrophotometer — Any spectrophotometer may be used that is capable of repeatability of 0.005 absorbance units in the range from 0.1 to 1.4 absorbance and repeatability of wavelength of 1 nm in the region from 400 to 700 nm.

H-2.3 Absorption Cells, 1 cm, matched, glass or silica.

H-2.4 Analytical Balance

H-2.5 Pipettes, 1, 2, 5 and 10 ml.

H-2.6 Graduated Cylinders, 250 and 1 000 ml.

H-2.7 Volumetric Flasks, glass-stoppered, 50, 100, 250 and 1 000 ml.

H-2.8 Filter Paper, medium filter (Whatman 1) and rapid hardened (Whatman 54).

H-3 REAGENTS

H-3.1 Cadmium Chloride Solution (20 g/l) — Dissolve 20 g of anhydrous cadmium chloride (CdCl_2) or 25 g of cadmium chloride hydrate ($\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$) in 200 ml of water and dilute to one litre.

H-3.2 Sulphuric Acid (sp gr 1.84), concentrated.

H-3.3 Benzene, Thiophene, free.

H-3.3.1 Wash 700 ml of benzene in a 1 000-ml separatory funnel with successive 100-ml portions of concentrated sulphuric acid (H_2SO_4) to which has been added 5 ml of isatin solution, until the H_2SO_4 layer is light yellow or colourless. Wash the benzene with 100 ml of water and then twice with 100 ml of cadmium chloride solution (CdCl_2). Finally, wash with another 100-ml portion of water. Filter the benzene through medium filter paper into a storage bottle and tightly stopper.

H-3.3.2 Prepare 1 400 ml of thiophene-free benzene. Measure the absorbance of this material by the procedure outlined in **H-5.2** and **H-6.2**. The absorbance should be not greater than 0.01.

H-3.4 Ferric Sulphate-Sulphuric Acid Solution — Add 0.2 g of ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) together with 38 ml of water to a 1-litre volumetric flask. Swirl to dissolve. Cautiously add about 100 ml of H_2SO_4

and swirl. Allow time for the heat of reaction to subside and dilute to volume with H_2SO_4 .

Caution — Protective clothing and goggles should be worn whenever H_2SO_4 is used.

H-3.5 Isatin-Chloroform-Benzene Solution — Add 0.5 g of isatin to 200 ml of chloroform. Heat, in a fume hood, to a temperature just below the boiling point (61°C) of chloroform and maintain for 5 min with stirring. Filter into a 250-ml volumetric flask through hardened rapid filter paper. Wash the filter paper with two 20-ml portions of thiophene-free benzene (see **H-3.3**) eluting the washings into the volumetric flask. Dilute to volume with thiophene-free benzene.

H-3.6 Thiophene

H-4 PREPARATION OF REAGENT BLANKS AND SAMPLE BLANK

H-4.1 Reagent Blank 1 — To a 50-ml separatory funnel pipette 5 ml of isatin solution and 10 ml of ferric sulphate-sulphuric acid solution. Stopper and shake for 2 min \pm 15 s. The shaking is accomplished by wrist action in a rocking motion through a 180° arc roughly once each second. Allow the two phases to separate and draw off the lower H_2SO_4 layer into a 50-ml volumetric flask. Add 10 ml of H_2SO_4 to the separatory funnel, stopper, and shake for 30 ± 5 s. Again draw off the lower H_2SO_4 layer into the 50-ml volumetric flask containing the first extract. Dilute to volume with H_2SO_4 and mix. This blank is stable for 8 h and need not be repeated with each analysis during this period.

H-4.2 Reagent Blank 2 — Into a 50-ml volumetric flask, pipette 10 ml of ferric sulphate-sulphuric acid solution and dilute to volume with H_2SO_4 . Stopper and mix. This blank is stable for 8 h and need not be repeated with each analysis during this period.

H-4.3 Sample Blank — Take a 100-ml portion of the CdCl_2 washed and filtered benzene sample (prepared in accordance with the procedure in **H-6.1**). Transfer to a 250-ml separatory funnel. Add 10 ml of ferric sulphate-sulphuric acid solution, stopper, and shake for 2 min \pm 15 s. Allow the two phases to separate and draw off the lower H_2SO_4 layer into a 50-ml volumetric flask. Add 10 ml of H_2SO_4 to the separatory funnel and shake for 30 ± 5 s. Again draw off the lower H_2SO_4 layer into the 50-ml volumetric flask containing the first extract. Dilute to volume and mix. Repeat with each specimen.

H-5 PREPARATION OF CALIBRATION CURVES

H-5.1 Add approximately 0.2 g of thiophene, weighed to the nearest 0.000 2 g to a 100-ml volumetric flask containing about 50 ml of thiophene-free benzene.

Dilute to volume with thiophene-free benzene and mix. This is Solution 1. Pipette 1 ml of Solution 1 into a 100-ml volumetric flask, dilute to volume with thiophene-free benzene, stopper, and mix. This is Solution 2 and will contain approximately 20 mg of thiophene per millilitre.

H-5.2 Pipette 0, 1, 2, 5, 7, and 10 ml of Solution 2 into 100-ml volumetric flasks and dilute to volume with thiophene-free benzene. Transfer to 500-ml separatory funnels and follow the procedure in **H-6.2** and **H-6.3** for each concentration. Plot absorbance *versus* concentration, in microgram per millilitre.

H-5.3 Prepare Solution 3 containing approximately 40 μg of thiophene per millilitre by pipetting 2 ml of Solution 1 into a 100-ml volumetric flask and diluting to volume with thiophene-free benzene. Follow the procedure in **H-5.2** to obtain the calibration curve for 50-ml specimens.

H-6 PROCEDURE

H-6.1 To a 500-ml separatory funnel, add 250 ml of sample and 40 ml of cadmium chloride solution. Stopper and shake for approximately 30 s. Allow to settle and discard the aqueous layer. Filter the benzene layer through medium filter paper into a 250-ml graduated cylinder. Part of the filtered benzene is to be used for the sample blank. Proceed with preparation of the sample blank as described in **H-4.3**. From the remaining filtered benzene, transfer 100 ml to 250-ml separatory funnel.

H-6.2 To the separatory funnel add 5 ml of isatin solution and 10 ml of ferric sulphate-sulphuric acid solution. Stopper and shake for 2 min \pm 15 s. Allow the phases to separate and draw off the lower H_2SO_4 layer into a 50-ml volumetric flask. Add 10 ml of H_2SO_4 to the separatory funnel, stopper, and shake for 30 ± 5 s. Again draw off the lower H_2SO_4 layer into the 50-ml volumetric flask containing the first extract. Dilute to volume with H_2SO_4 and mix.

H-6.3 Measure the absorbance of this material at 589 nm in a 1 cm cell *versus* Reagent Blank 1 (see **H-4.1**) in a matched 1-cm cell. Instrument conditions should be identical with those employed during calibration.

H-6.4 Determine the concentration of thiophene from the calibration curve (see **H-5**). If the absorbance is greater than 1.5, repeat the procedure using a 50-ml specimen instead of 100 ml. If the 50-ml specimen still gives absorbance above 1.5, then the specimen must be diluted with thiophene-free benzene before proceeding.

H-6.5 Determine the absorbance of the sample blank (see **H-4.3**) at 589 nm using Reagent Blank 2 (see **H-4.2**) as reference. Determine the apparent concentration of thiophene in the sample blank.

H-7 CALCULATION

Calculate the thiophene content of the sample in milligrams per kilogram as follows:

$$\text{Thiophene, mg/kg} = (A - B) F/d$$

where

A = thiophene for sample determined from

appropriate calibration curve (see Table 7), $\mu\text{g/ml}$;

B = apparent thiophene determined for sample blank from appropriate calibration curve (see Table 7), $\mu\text{g/ml}$;

F = dilution factor of sample; and

d = density of benzene at the temperature of the sample.

Table 7 Calculation Factors

Sl No.	Designation of Equation of H-7	Cell Solutions	
		Solution of Sample (3)	Solution of Reference (4)
i)	A	$\text{H}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$; isatin after contact with sample (see H-6.2)	Reagent blank 1 (see H-4.1) ®
ii)	B	Sample blank (see H-4.3)	Reagent blank 2 (see H-4.2)

ANNEX J

[Table 1, Sl No. (xi)]

DETERMINATION OF ACID WASH COLOUR

J-1 OUTLINE OF THE METHOD

A mixture of the aromatic hydrocarbon and sulphuric acid is vigorously shaken and the colour of the acid layer is compared with that of colour standards prepared from CoCl_2 and FeCl_3 .

J-2 APPARATUS

J-2.1 Containers for Colour Standards — Clear and unblemished, clean, French square, flint glass, flat-bottom, glass-stoppered, 1-oz capacity bottles holding 31 to 33 ml when filled to the neck. The bottles shall be numbered consecutively from 0 to 14.

J-2.2 Test Containers — Containers exactly like described in J-2.1 except that each French square bottle shall be marked by etching to show when the bottle contains the volume of 7 and 28 ml, respectively. Coloured crayons and similar markers shall not be used for marking the bottles.

J-3 REAGENTS

J-3.1 Hydrochloric Acid (1 + 39), mix 25 ml of hydrochloric acid (31 percent by mass, HCl) with 975 ml of water.

J-4 PREPARATION OF REFERENCE COLOUR STANDARDS

J-4.1 Stock Solutions

Prepare the following basic reagent solutions for use in preparing the reference colour standard.

J-4.1.1 Solution A — Dissolve 59.50 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in HCl and make up to one litre in a volumetric flask with HCl.

J-4.1.2 Solution B — Dissolve 45.054 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in HCl and make up to one litre in a volumetric flask with HCl.

J-4.1.3 Solution C — Mix 3 ½ volumes of Solution A with 36 ½ volumes of Solution B and dilute with 90 volumes of water.

J-4.1.4 Solution D — Mix 3 ½ volumes of Solution A with 36 ½ volumes of Solution B.

J-4.1.5 Solution E — Prepare an aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_4$ saturated at 21°C.

J-4.1.6 Solution F — Prepare an aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ saturated at 21°C and dilute with an equal volume of water.

J-4.2 Prepare reference colour standard solutions having the following compositions and numbered from 0 to 14:

- No. 0 – Distilled water.
- No. 1 – 1 volume of Solution C plus 1 volume of water.
- No. 2 – 5 ½ volumes of Solution C plus 2 volumes of water.
- No. 3 – Solution C.
- No. 4 – 1 volume of Solution D plus 1 volume of water.
- No. 5 – 5 ½ volumes of Solution D plus 2 volumes of water.
- No. 6 – Solution D.
- No. 7 – 5 volumes of Solution E plus 2 volumes of water.
- No. 8 – Solution E.
- No. 9 – 7 volumes of Solution E plus ½ volume of Solution F.
- No. 10 – 6 ½ volumes of Solution E plus 1 volume of Solution F.
- No. 11 – 5 ½ volumes of Solution E plus 2 volumes of Solution F.
- No. 12 – 1 volume of Solution E plus 1 volume of Solution F.
- No. 13 – 2 volumes of Solution E plus 5 volumes of Solution F.
- No. 14 – Solution F.

J-4.3 Rinse the No. 0 container (see J-2.1) and its glass stopper three times with water, fill with water, and stopper. Rinse the No. 1 container and its stopper three times with reference colour standard solution No. 1 (see J-4.2), fill with this solution, and stopper. In this way, prepare the set of containers of colour standards from 0 to 14 having the compositions shown for the corresponding colour solution standards in J-4.2. When filling the French square bottles, leave 6 mm of vapour space below the neck of the bottle. Seal each container with paraffin to prevent loss by evaporation or seepage.

J-5 PROCEDURE

J-5.1 Rinse a test container (see J-2.1) twice with acid of the strength specified in Table 8 for the type of sample to be tested (see Note 1). Drain the rinsings and fill with the acid up to the 7-ml mark. Add sufficient sample to bring the total volume to the 28-ml mark (see Note 2). Insert the stopper, hold a finger over the stopper, and give vigorous shakes with a stroke of 13 to 25 cm, shaking for a total of 150 cycles over a period of 40 to 50 s, that is at a rate of 3 to 3.75 cycles/s.

NOTES

1 Concentrated sulphuric acid will cause severe burns on

contact with the skin. As a precaution the test container should be wrapped in a towel or enclosed in a plastic bag during the shaking period.

2 If the room temperature is above 29°C, maintain the acid, sample, and reference colour standards at a temperature between 25°C and 29°C through the test, and insulate the test container in some convenient way, such as wrapping with a cloth, during the shaking period.

J-5.2 Allow the container to stand protected from direct sunlight, for the period of time shown in Table 8. Without further delay invert the container gently once or twice to obtain a uniform colour in the acid layer, and compare the colour of the acid layer with that of the standards (see J-4.3). Make the comparison against a white background or against daylight, using transmitted light (see Note). When testing samples in Group 1 (see Table 8), observe the colour of the oil layer as well as that of the acid layer.

NOTE — Agreement of results may be improved by using a colour comparator of a suitable type for observing the colour of the acid layer in comparison with the reference standard colour solution.

J-5.3 Designate the colour of the acid layer by the number of the nearest matching standard, following the number with a plus or minus sign if the sample is darker or lighter, respectively, than the standard. Disregard any difference in hue and determine only whether the colour of the acid layer is darker or lighter than the colour of the reference standard to which the sample most nearly corresponds. If the hue of the acid colour is different from the hue of the reference colour standard, record the colour number followed by (X). Thus 'No. 4 – (X)' means that the acid wash test colour is slightly lighter than No. 4 colour standard and that the hue of the No. 4 colour standard is not the same as the hue of the acid layer.

J-6 INTERPRETATION OF RESULTS

J-6.1 Report sample (see Table 8) as passing the test only when the oil layer shows no change in colour and when the acid layer is not darker than the specified colour standard.

Table 8 Acid Strength and Standing Times

(Clauses J-5.1, J-5.2 and J-6.1)

Sample	Acid Strength Percent	Standing Time min
(1)	(2)	(3)
Benzene, Toluene, Xylene (except Xylene, industrial grade), Any other most highly refined products	96	15

J-6.2 A cloudiness of haze in the oil layer should not be interpreted as a change in colour.

ANNEX K

[Table 1, Sl No. (xii)]

DETERMINATION OF N-FORMYLMORPHINE AS NITROGEN

K-1 OUTLINE OF THE METHOD

The sample of liquid petroleum hydrocarbon is injected into a stream of inert gas (helium or argon). The sample is vaporized and carried to a high temperature zone where oxygen is introduced and organic and bound nitrogen is converted to nitric oxide (NO). The NO contacts ozone and is converted to excited nitrogen oxide (NO₂). The light emitted as the excited NO₂ decays is detected by a photomultiplier tube and the resulting signal is a measure of the nitrogen contained in the sample.

K-2 APPARATUS

K-2.1 Furnace, Electric — Electric furnace held at a temperature sufficient to volatilize and pyrolyze the entire sample and oxidize the organically bound nitrogen to NO. Furnace temperature(s) for petroleum substances shall be as recommended by the manufacturer.

K-2.2 Combustion Tube, fabricated from quartz is required. The inlet end of the tube holds a septum for syringe entry of the sample and has a side arm for introduction of oxygen (O₂) and inert gas. The construction is such that the inert gas sweeps the inlet zone transporting the entire volatilized sample into a high temperature oxidation zone. The oxidation section shall be large enough (Fig. 7 and Fig. 8) to ensure complete oxidation of the sample. Fig. 7 and Fig. 8 depict conventional pyrolysis tubes. Other configurations are acceptable, if precision is not degraded.

K-2.3 Drier Tube — The reaction products include

water vapour that must be eliminated prior to measurement by the detector. This can be accomplished with a magnesium perchlorate Mg(ClO₄)₂ scrubber or a membrane drying tube (permeation drier), or both.

K-2.4 Chemiluminescent Detector, capable of measuring light emitted from the reaction between NO and ozone.

K-2.5 Totalizer, having variable attenuation, and capable of measuring, amplifying and integrating the current from the chemiluminescent detector. The amplified or integrated output signal shall be applied to a digital display and to strip chart recorder, if desired.

K-2.6 Microlitre Syringe, of 5, 10, 25, 50, or 250 µl capacity capable of accurately delivering microlitre quantities is required. The needle should be long enough to reach the hottest portion of inlet section furnace when injecting the sample.

K-2.7 Recorder (Optional)

K-2.8 Constant Rate Injector System (Optional), capable of delivering a sample at a precisely controlled rate and may have independent signal processing and data display capabilities (optional).

K-2.9 Boat Inlet System (Optional), to facilitate analysis of samples that would react with the syringe or syringe needle. Pyrolysis tube for boat inlet use may require specific construction permitting insertion of a boat fully into the inlet furnace section.

K-2.10 Outlet End of Pyrolysis Tube (Optional) — It may be constructed to hold a removable quartz insert tube.

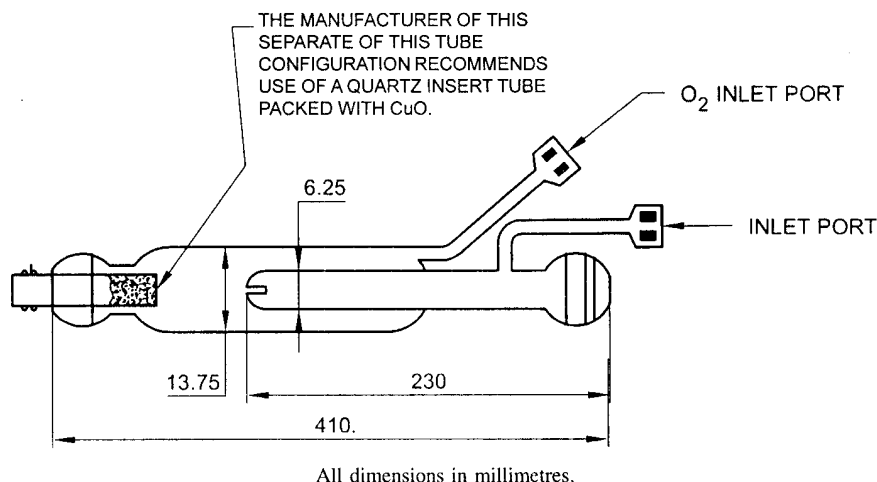
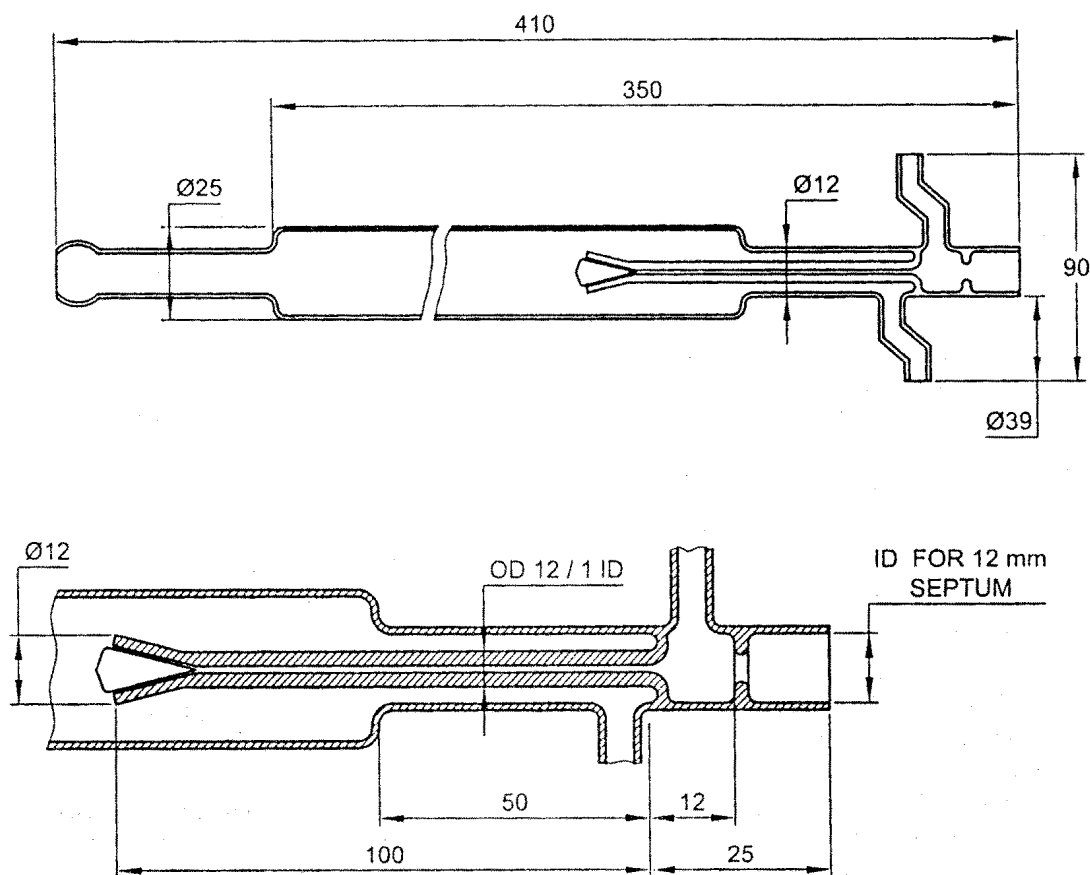


FIG. 7 QUARTZ PYROLYSIS TUBE



BURNER TIP AND SEPTUM DETAIL

All dimensions in millimetres.

FIG. 8 QUARTZ PYROLYSIS TUBE

K-2.11 Quartz Insert Tube (Optional) — It may be packed with cupric oxide (CuO) which may aid in completing oxidation. This is inserted into the exit end of the pyrolysis tube in one manufacturer's configuration.

K-3 REAGENTS

K-3.1 Magnesium Perchlorate $Mg(ClO_4)_2$, for drying products of combustion (if permeation drier is not used).

Warning — STRONG OXIDIZER, IRRITANT.

K-3.2 Inert Gas, argon or helium only, ultra-high purity grade (UHP).

K-3.3 Oxygen, ultra-high purity grade (UHP).

Warning — VIGOROUSLY ACCELERATES COMBUSTION.

K-3.4 Solvent, toluene, isooctane, cetane, or other solvent similar to compound present in the sample to be analyzed.

Warning — FLAMMABLE SOLVENTS.

K-3.5 Nitrogen Stock Solution, 1 000 mg N/ml — Prepare a stock solution by accurately weighing 1.195 g of carbazole or 0.565 g of pyridine into a tarred 100-ml volumetric flask. Acetone may be first used to dissolve carbazole. Dilute to volume with selected solvent. This stock may be further diluted to desired nitrogen concentrations.

NOTES

- 1 Pyridine should be used with low boiling solvents.
- 2 Carbazole should be used with high boiling solvents.
- 3 Working standards should be remixed on a regular basis depending upon frequency of use and age. Typically, standards have a useful life of about 3 months.

K-3.6 Cupric Oxide Wire, as recommended by instrument manufacturer.

K-3.7 Quartz Wool

K-3.8 Pyridine

Warning — FLAMMABLE, IRRITANT.

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Warning — FLAMMABLE.

K-4 PREPARATION OF APPARATUS

K-4.1 Assemble apparatus in accordance with manufacturer's instructions.

K-4.2 Adjust the gas flows and the pyrolysis temperature to the desired operation conditions. The inlet temperature will depend upon which inlet method is used (see **K-2.2** and **K-2.9**).

K-5 CALIBRATION AND STANDARDIZATION

K-5.1 Prepare a series of calibration standards using a stock solution covering the range of operation and consisting of nitrogen type and matrix similar to samples to be analyzed.

K-5.2 Volumetric measurement of the injected sample can be obtained by filling the syringe to the 80 percent level, retracting the plunger so that the lower liquid meniscus falls on the 10 percent scale mark, and recording volume of liquid in the syringe. After the sample has been injected, again retract the plunger so that the lower liquid meniscus falls on the 10 percent scale mark, and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of sample injected.

K-5.3 Alternatively, the sample injection device may be weighed before and after injection to determine the amount of sample injected. This test method provides greater precision than the volume delivery method, provided a balance with a precision of ± 0.01 mg is used.

K-5.4 Insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at a uniform rate of 0.2 to 1.0 $\mu\text{l/s}$. Rate of injection is dependent on such factors as viscosity, hydrocarbon type and nitrogen concentration. Each user must adopt a method whereby a consistent and uniform injection rate is ensured.

K-5.5 For the method blank, rinse the syringe thoroughly with the solvent blank. Then inject the same amount of solvent blank as utilized with standards and obtain the reading. Measure the blank a second time and average the results. The solvent blank should contain less than 1 mg/kg of nitrogen.

K-5.6 If the system features a totalizer with calibration adjust, repeat the measurement of each calibration standard three times. The average of the three results shall be adjusted with the calibration setting to this average. System performance shall be checked with suitable calibration standard each day and when changing concentration ranges.

K-5.7 For those detectors not equipped with a calibration adjust, construct a standard curve as follows:

Repeat the determination of each calibration standard and the blank three times to determine the average net response for each standard. Construct a curve plotting of milligrams of nitrogen injected *versus* detector response (integration count). The response curve should be linear and shall be checked at least once per week.

K-6 PROCEDURE

K-6.1 Sample sizes ranging from 3 to 40 μl are acceptable. It is advisable that the size of injected sample shall be similar to the size of injected standard.

K-6.2 Flush the microlitre syringe several times with the unknown sample. Determine the sample size as described in **K-5.4**.

K-6.3 Experience dictates the best sensitivity setting and sample size. Typical sample sizes have been given in Table 9.

Table 9 Typical Sample Sizes

Sl No. (1)	Nitrogen mg/kg (2)	Sample Size μl (3)
i)	≤ 1	Up to 40
ii)	10	Up to 8
iii)	100	Up to 8
iv)	> 100	Dilute sample to most convenient level

K-7 CALCULATION

K-7.1 For analyzers equipped with a calibration adjust, calculate the nitrogen content of the sample parts per million (mg/kg) by mass as follows:

$$\text{Nitrogen, mg/kg} = (I - B) \times K / (V \times D)$$

$$\text{Nitrogen, mg/kg} = (I - B) \times K / M$$

where

D = density of sample, in g/ml;

K = dilution factor;

V = volume of sample, in ml;

M = mass of sample, in mg;

I = visual display readings of sample, in mg N;
and

B = average of visual display readings of blank,
in mg N.

K-7.2 For analyzers not equipped with calibration adjust, calculate the milligrams per kilograms by mass nitrogen as follows:

$$\text{Nitrogen, mg/kg} = I \times S \times K / (V \times D)$$

where

D = density of sample, in g/ml;

S = slope of standard curve, in mg N/count;

V = volume of sample, in μl ;

I = detector response, integration counts; and

K = dilution factor (when applicable).

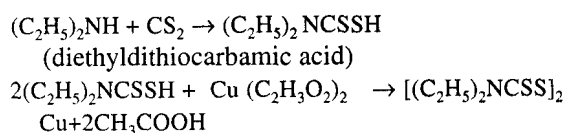
ANNEX L

[Table 1, Sl No. (xiv)]

DETERMINATION OF CARBON DISULPHIDE

L-1 OUTLINE OF THE METHOD

Under specified conditions diethylamine-cupric acetate reagent reacts with carbon disulfide to produce the yellow-orange color of cupric diethyl-dithiocarbamate. The intensity of the color produced is measured by means of a spectrophotometer.



L-2 APPARATUS

L-2.1 Spectrophotometer, suitable for measurements at 430 nm with a band width not greater than 35 nm.

L-2.2 Cells, 5 cm, chemically resistant glass.

L-2.3 Weighing Bulbs, either as prepared in the laboratory or commercially supplied.

L-2.4 Mohr Pipette, 5 ml equipped with suction bulb.

L-3 REAGENTS AND MATERIALS

L-3.1 Benzene (Carbon Disulphide-Free) — To a 2 l separatory funnel add 1 000 ml of benzene and 200 ml of alcoholic sodium hydroxide (NaOH) and shake well. Allow to stand for 1 h, shaking at 15 min intervals. Draw off and discard the lower layer. Wash 4 times using 300 ml of water each time, and drawing off and discarding the water (lower) layer after each washing. Filter the treated benzene through dry filter paper into a 1-litre glass stoppered bottle. Check the treated benzene for the presence of carbon disulphide as described in L-5. If carbon disulfide is present, repeat the benzene purification given above. Carbon disulfide-free benzene will not undergo further diminution in absorbance at 430 nm when it has been thus retreated.

L-3.2 Carbon Disulfide (CS_2)

L-3.3 Cupric Acetate in Methanol — Add 1.0 + 0.001 g of cupric acetate monohydrate, powdered,

neutral crystals to a 1 000-ml glass-stoppered volumetric flask containing approximately 600 ml of methanol. Shake to dissolve. Dilute the contents to volume with methanol and mix thoroughly. This reagent should be prepared fresh, each month, or sooner if appreciable amounts of copper salts separate from the solution.

L-3.4 Diethylamine—Cupric Acetate Reagent —

Using a Mohr pipette, add 2.5 ml of diethylamine to approximately 50 ml of carbon disulfide-free benzene contained in a 100-ml glass-stoppered volumetric flask. Using a graduated cylinder, add 20 ml of cupric acetate solution and dilute to volume with carbon disulfide-free benzene. Invert to mix.

NOTES

1 The mouth should not be used for pipetting any solutions, especially where diethylamine or benzene are present.

2 This reagent is unstable and a fresh supply must be prepared daily.

L-3.5 Sodium Hydroxide, Alcoholic Solution (40 g/l)

— Weigh 40 ± 1 g of sodium hydroxide (NaOH) pellets and transfer to a 300-ml Erlenmeyer flask containing 50 ml of water. Swirl to dissolve, cool to room temperature, and then transfer to a 1 000-ml volumetric flask. Dilute to volume with methanol (95 percent), and mix by shaking. Allow to stand overnight. Filter the clear solution into a one litre bottle.

L-4 CALIBRATION AND STANDARDIZATION

Prepare a calibration curve or table showing concentration *versus* absorbance by making solutions in the range of 1.0 to 4 mg/kg of carbon disulphide in carbon disulphide-free benzene, and then developing the colour. Read the absorbance using the method to be used in the test. The solutions can be prepared by weighing the carbon disulphide in a weighing bulb, breaking it under carbon disulphide-free benzene, and diluting to the proper concentrations with the same grade benzene. The dilution can be made by weighing or, more conveniently, by volume that can be reduced

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to weight by multiplying the volume added by the density of the benzene used.

L-5 PROCEDURE

L-5.1 Filter a portion of the sample through dry filter paper to remove any water that might be present.

L-5.2 Pipette 30 ml of the filtered sample to a glass-stoppered 50-ml volumetric flask.

L-5.3 Pipette 3.0 ml of the diethylamine-cupric acetate reagent into the flask (final volume, 33 ml).

L-5.4 Insert the stopper and mix well.

L-5.5 Allow to stand 30 ± 10 min.

L-5.6 Read the absorbance at 430 nm in 5-cm glass cells using the filtered sample as a reference material.

NOTE — If the absorbance is >1.0 , dilute an aliquot of the material obtained in **L-5.1** with carbon disulphide-free benzene

and repeat **L-5.2** through **L-5.6**. Dilution factors must be taken into consideration when calculating the final results.

L-5.7 Obtain a reagent blank, using the procedure described in **L-5.2** to **L-5.6**, substituting carbon disulfide-free benzene for the sample. Subtracting this value from the absorbance value of the sample obtained in **L-5.6**.

L-6 CALCULATIONS AND INTERPRETATION OF RESULTS

Determine the concentration by referring to concentration *versus* absorbance curve or table prepared in accordance with **L-4** for each spectrophotometer.

L-7 REPORT

Report the milligrams per kilogram of carbon disulphide corresponding to the absorbance read after a factor for any sample dilution has been applied.

ANNEX M

(Clause 8)

SAMPLING OF BENZENE**M-1 GENERAL REQUIREMENTS OF SAMPLING**

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

- a) Samples shall not be taken in an exposed place;
- b) The sampling instrument shall be clean and dry and shall be made of low or reduced spark generating material;
- c) The samples, the material being sampled, the sampling instrument and the containers for samples shall be protected from adventitious contamination;
- d) To draw a representative sample, the contents of each container selected for sampling shall be mixed as thoroughly as possible by shaking or stirring or both, or by rolling, so as to bring all portions into uniform distribution;
- e) The sample containers shall be of such a size that they are almost, but not completely, filled by the sample;
- f) The samples shall be placed in suitable, clean, dry and air-tight glass containers preferably of amber or blue colour;

- g) The sample container shall be sealed air-tight with a suitable stopper after filling and marked with full details of sampling, such as the type of benzene, the date of sampling, the year of manufacture of material, the batch number, the name of the sampler etc. Particular care shall be taken to ensure that sealing methods do not contaminate the sample; and
- h) Samples shall be stored in such a manner that the temperature of the material does not vary unduly from the normal temperature.

M-1.2 Additional Precautions

The following additional precautions shall be observed:

- a) Rubber stoppers or composition corks shall not be used for closing the sample bottles;
- b) Sealing wax or other plastic material, if used, shall be applied in such a way that it does not contaminate the sample when the bottles are opened; and
- c) Each sample container shall be protected by covers of oil-proof paper, metal foil, viscose or other suitable impervious material over the stopper to keep away moisture and dust from the mouth of the bottle and to protect it while being handled.

M-2 SAMPLING INSTRUMENT

M-2.1 The following forms of sampling instrument may be used:

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

M-2.1.1 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. 9). 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.

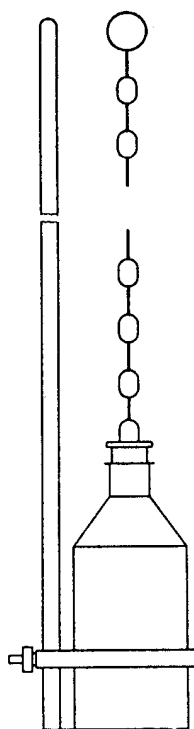
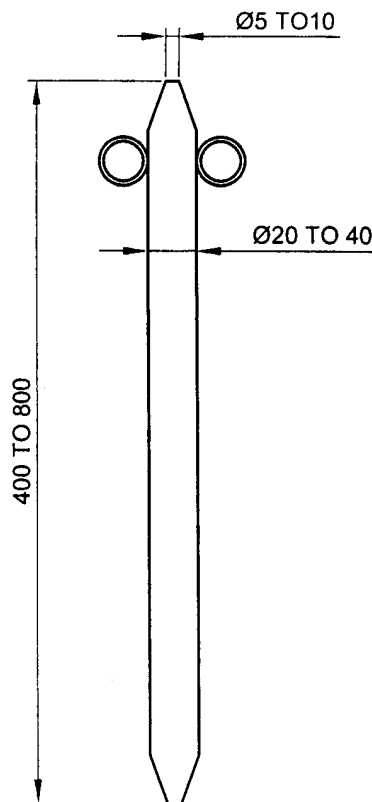


FIG. 9 SAMPLING BOTTLE OR CAN

M-2.1.2 Sampling Tube

M-2.1.2.1 It is made of metal or thick glass and is about 20 to 40 mm in diameter and 400 to 800 mm in length (see Fig. 10). The upper and lower ends are conical and reach 5 to 10 mm internal 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.

M-2.1.2.2 For small containers, the size of the sampling tube may be altered suitably.



All dimensions in millimetres.

FIG. 10 SAMPLING TUBE

M-3 SCALE OF SAMPLING

M-3.1 Lot

In a single 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 containers of different sizes or of different batches of manufacture, then the containers belonging to the same size and batch of manufacture shall be grouped together and each such group shall constitute a separate lot. In case the consignment is in large tanks or vessels, the tanks or vessels belonging to the same batch of manufacture shall constitute a lot.

For ascertaining the conformity of the lot to the requirements of the specification, tests shall be carried out for each lot separately.

M-3.2 Sampling from Containers

M-3.2.1 The number of containers *n* to be selected for sampling shall depend on the size *N* of the lot and shall be in accordance with Table 10.

M-3.2.2 The containers shall be selected at random. In order to ensure the randomness of selection, random sampling procedure given in IS 4905 may be adopted.

M-3.3 Sampling from Tanks or Vessels — Each of

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Table 10 Scale of Sampling for Containers
(Clause M-3.2.1)

Sl No.	Lot Size (n)	No. of Containers to be Selected (N)
(1)	(2)	(3)
i)	Up to 100	5
ii)	101 to 200	6
iii)	201 to 300	7
iv)	301 to 400	8
v)	401 to 500	9
vi)	501 and above	10

NOTE — In the case of very small lots where the selection of the five containers may be uneconomical, all the containers shall be selected.

the tanks/vessels in the lot shall be sampled separately for determining the conformity of the lot to the requirements of the specification.

M-4 PREPARATION OF THE TEST SAMPLES

M-4.1 Test Samples from Containers

To ensure that the sample taken from each container is fairly representative, the contents shall be mixed thoroughly, when possible, by shaking or stirring or rolling. Draw small samples of the material from various depths with the help of the sampling tube (see Fig. 10). The approximate quantity of the material to be drawn from a container shall be nearly equal to thrice the quantity required for testing purposes as indicated in M-5.1.

M-4.1.1 Out of the material drawn from individual containers, a small but equal quantity of material shall be taken and thoroughly mixed to form a composite sample, sufficient for carrying out triplicate determinations for all the characteristics specified under M-5. The composite sample shall be divided into three equal parts, one for the purchaser, another for the supplier and the third for the referee.

M-4.1.2 The remaining portion of the material from each container shall be divided into 3 equal parts, each forming an individual sample. One set of individual samples representing the containers n selected shall be for the purchaser, another for the supplier and the third for the referee.

M-4.1.3 All the individual and composite samples shall be transferred to separate sample containers. These containers shall then be sealed air-tight with stoppers and labelled with full identification particulars given in M-1.1(g).

M-4.1.4 The referee test sample, consisting of a composite sample and a set of n individual samples, shall bear the seals of both the purchaser and the supplier. They shall be kept at a place agreed to between the purchaser and the supplier, to be used in case of any dispute.

M-4.2 Test Samples from Tanks/Vessels

M-4.2.1 For drawing a sample from a tank/vessel, lower the closed sampling bottle or can (see M-2.1) slowly to the required depth, open and fill it at that depth. Three samples shall be obtained at levels of one-tenth of the depth of the liquid from the top surface (top sample), one half of the depth (middle sample) and nine-tenths of the depth of the liquid from the top surface (lower sample). All the three samples thus obtained from a tank/vessel shall be mixed together in a clean dry container, and shall be divided into three parts, one for the purchaser, another for the supplier and the third for the referee. Each of the tanks/vessels in the lot shall be sampled in the above manner and separate samples obtained for each of the tanks/vessels. The approximate quantity of the material to be drawn from a tank/vessel shall nearly be equal to thrice the quantity required for carrying out tests for all the requirements prescribed in M-5.

M-4.2.2 All the samples thus obtained from the tanks/vessels in the lot shall be transferred to separate sample containers. These containers shall then be sealed air-tight with stoppers and labelled with full identification particulars given in M-1.1(g).

M-4.2.3 The referee test samples consisting of the samples from the tanks/vessels in the lot, shall bear the seals of both the purchaser and the supplier. They shall be kept at a place agreed to between the purchaser and the supplier, to be used in case of any dispute.

M-5 NUMBER OF TESTS

M-5.1 For Samples from Containers

M-5.1.1 Tests for the determination of distillation range, residue on evaporation, solidification point, aromatic impurities, non-aromatic hydrocarbons and aliphatic impurities shall be conducted on each of the individual samples separately (see M-4.1.2).

M-5.1.2 Tests for the determination of all other characteristics given in Table 1 shall be conducted on the composite samples separately (see M-4.1.1).

M-5.2 For Samples from Tanks/Vessels — Tests for the determination of all the characteristics given in Table 1 shall be conducted on the samples from different tanks or vessels separately.

M-6 CRITERIA FOR CONFORMITY

M-6.1 For Containers

M-6.1.1 For Distillation Range

M-6.1.1.1 For individual samples

The lot shall be declared as conforming to the requirements of the distillation range if test results for

each of the individual samples tested in respect of distillation range satisfy the requirements as given in Table 1, Sl No. (v).

M-6.1.1.2 For residue on evaporation, solidification point, aromatic impurities and aliphatic impurities which have been tested on the individual samples, the mean (X) and the range (R) of test results, shall be computed (the range is defined as the difference between the maximum and the minimum values of test results):

- a) The lot shall be declared as conforming to the requirements of residue on evaporation, aromatic impurities and aliphatic impurities if the value of the expression $(X + 0.6 R)$ as calculated from relevant test results are less than or equal to the respective values for each of the requirement given in Table 1.

- b) The lot shall be declared as conforming to the requirements of solidification point if the value of the expression $(X - 0.6 R)$ as calculated from relevant test results is equal to or more than the respective values given in Table 1.

M-6.1.1.3 For composite samples

In respect of all other characteristics, the lot shall be considered as conforming, if the composite sample satisfies each one of these requirements.

M-6.2 For Tanks/Vessels

The lot shall be declared as conforming to the specified requirements for various characteristics, if each of the test results satisfies the relevant requirements specified in the standard individually.

(Continued from second cover)

ASTM D 1492 : 1996	Standard test method for bromine index of aromatic hydrocarbons by coulometric titration
ASTM D 1685 : 1995	Standard test method for traces of thiophene in benzene by spectrophotometry
ASTM D 2359 : 1998	Standard specification for refined benzene - 535
ASTM D 4045 : 1996	Standard test method for sulfur in petroleum products by hydrogenolysis and rateometric colorimetry
ASTM D 4052 : 1996	Standard test method for density and relative density of liquids by digital density meter
ASTM D 4492 : 1996	Standard test method for analysis of benzene by gas chromatography
ASTM D 4629 : 1996	Standard test method for trace nitrogen in liquid petroleum hydrocarbons by syringe/inlet oxidative combustion and chemiluminescence detection
ASTM D4734 : 1998	Standard specification for refined benzene-545
ISO 2211 : 1973	Liquid chemical products — Measurement of colour in hazen units (Platinum-Cobalt scale)

ASTM D 1353 is also available for determining the characteristic, Residue on Evaporation and in case of dispute clause 8 of IS 82, as given in Table 1 shall be the referee test method.

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 : 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

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