KENYA STANDARD

DKS 2470:2013

HEXANE FOR INDUSTRIAL USE - SPECIFICATION

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REVISION OF KENYA STANDARDS

In order to keep abreast of progress in industry, Kenya Standards shall be regularly reviewed. Suggestions for improvements to published standards, addressed to the Managing Director, Kenya Bureau of Standards, are welcome.

KENYA STANDARD **DKS 2470: 2013**

HEXANE FOR INDUSTRIAL USE - SPECIFICATION

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Preface

This Kenya Standard was prepared by the Technical Committee on Industrial solvents and chemicals under the authority of Kenya Bureau of Standards.

Hexane is a hydrocarbon which is a colourless liquid at room temperature.

It is mainly used as a non-polar solvent. Other uses include preparation of adhesives, coatings, printing inks, as raw materials in chemical synthesis operations and as solvent in various kinds of extraction operations.

This Kenya Standard addresses the requirements of industrial hexane, test methods and packaging and marking requirements

During the preparation of this standard, reference was made to the following publications and acknowledgement is made for its assistance with thanks:

- D 1836-07: - Standard Specification for Commercial Hexanes
- D611-12:- Standard Test Methods for Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents.
- D2710-09: Standard Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration.
- D3120-08: Standard Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry.
- D1133-10: Standard Test Method for Kauri-Butanol Value of Hydrocarbon Solvents1
- D4367-02 Standard Test Method for Benzene in Hydrocarbon Solvents by Gas Chromatography
- IS 3470:2002 Hexane, Food Grade - Specification

KENYA STANDARD

HEXANE FOR INDUSTRIAL USE - SPECIFICATION

1. SCOPE

This Kenya Standard specifies requirements and methods of test for hexane for industrial use. It has a chemical formula of C_6H_{14}.
Nb This standard does not cover food grade hexane

2. REQUIREMENTS

Hexane shall satisfy the requirements specified in the Table below:

Table 1: Requirements for Hexane

SL.NO	Characteristics	Requirements	Method of test
1	Appearance	Clear and free from suspended matter	Visual
2	Colour, Lovibond scale, Hazen Units	10 maximum	Annex A
3	Specific Gravity, at 20^{o}C	0.6594	KS 666
4	Distillation range at 1013 mbar, ºC IBP D.P	 63 71	KS 666
5	Refractive Index at 20^{o}C	1.375-1.384	KS 666
6	Residue on evaporation,mg/100ml,	1 max	KS 914
7	Odor	Non-residual	KS 914
8	Aniline point	57^{0}C min	Annex B
	Benzene content, weight%,	0.1	Annex C
	Bromine index,	100 max	Annex D
9	Kauri-butanol value,	33 max	Annex E
	Sulfur, ppm,	5	Annex F
10	Reaction of non volatile residue (Neutrality test)	Neutral to methyl orange	Annex G

4. MARKING AND PACKING

Hexane shall be packaged in suitable and serviceable containers and marked indelibly with the following information:

(a) Name of the product
(b) Manufacturer's name and/or registered trade mark; and address
(c) Country of origin
(d) Net weight;
(e) Batch Number
(f) The words 'inflammable' and its Standard Symbol;
(g) Precautionary measures i.e. may cause irritation to the eyes, respiratory system and skin.

ANNEX A

DETERMINATION OF COLOUR IN HAZEN UNITS (LOVIBOND SCALE)

A.1 PRINCIPLE

Visual comparison of the colour of a sample with that colour of standards, and expression of the result in terms of hazen

Note: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.

A.2 REAGENTS

Distilled water, or water of equivalent purity, shall be used in the test.

A.3 APPARATUS

Ordinary laboratory apparatus and the Lovibond comparator

A.3.1 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, clear distinction between the standard Hazen matching solutions can be observed.

NOTE: 1. For routine control purposes, a colorimetric or spectrophotometer may be used, the instrument being standardized by means of the standard colorimetric solutions provided that it has been confirmed that the use of that instrument gives the same results as does visual comparison.

A.4 Expression of Results

Express the colour of the sample as the number of Hazen colour units

A.5 TEST REPORT

The test report shall include the following particulars:

(a) the reference of the method used

(b) the result, expressed in Hazen colour units

(c) any unusual features noted during the determination

(d) any operation not included in this standard or regarded as optional.

Annex B
Determination of Aniline Point

B.1 The test method covers the determination of aniline point. Aniline point is the minimum equilibrium solution temperature for equal volumes of aniline and sample.
The aniline point is useful as an aid in the characterization of pure hydrocarbons and in the analysis of hydrocarbon mixtures. In homologous series the aniline points increase with increasing molecular weight.

B.2 Apparatus

B.2.1 Heating and Cooling Bath—A suitable air bath, a nonvolatile, transparent liquid bath, or an infrared lamp (250 to 375 W), provided with means for controlling the rate of heating.
Water should not be used as either a heating or cooling medium since aniline is hygroscopic and moist aniline will give erroneous test results.

B.2.2 Thermometers, or other temperature sensing devices, such as thermocouples or platinum resistance thermometers that cover the temperamental range of interest and can provide equivalent or better accuracy and precision.
B.2.3 Pipette, or equivalent volume dispensing devices, capable of delivering volumes with capacities of 10 ± 0.04 mL and 5 ± 0.02 mL, for use in the test.

B.2.4 Balance—A laboratory balance sensitive to 0.01 g, suitable for weighing the tube and sample when the sample cannot be pipetted conveniently.

B.2.5 Safety Goggles.

B.2.6 Plastic Gloves, impervious to aniline.

B.3 Reagents

B.3.1 Aniline (**Warning**—Aniline should not be pipetted directly by mouth because of its extreme toxicity. Aniline is also toxic by absorption through the skin even in very small quantities, and should be handled with great caution.) The aniline shall be sufficiently pure.

B.3.2 Calcium Sulfate, anhydrous.

B.3.3 The apparatus shown in Fig. B-1 shall consist of the following
B.3.3.1 *Test Tube,* approximately 25 mm in diameter and 150 mm in length, made of heat-resistant glass.
B.3.3.2 *Jacket,* approximately 37 to 42 mm in diameter and 175 mm in length, made of heat-resistant glass.
B.3.3.3 *Stirrer,* manually operated, metal, approximately 2 mm in diameter metal wire as shown in Fig.B-1
B.3.3.4 A concentric ring shall be at the bottom, having a diameter of approximately 19 mm. The length of the stirrer to a right-angle bend shall be approximately 200 mm. The right-angle bend shall be approximately 55 mm long. A glass sleeve approximately 65 mm in length of 3-mm inside diameter shall be used as a guide for the stirrer or any suitable mechanical device for operating the stirrer

B.4 Procedure

B.4.1 Specified volumes of aniline and sample, are placed in a tube and mixed mechanically. The mixture is heated at a controlled rate until

the two phases become miscible. The mixture is then cooled at a controlled rate and the temperature at which two phases separate is recorded as the aniline point or mixed aniline point.

B.4.2 Dry the sample by shaking vigorously for 3 to 5 min with about 10 volume % of a suitable drying agent such as anhydrous calcium sulfate (or anhydrous sodium sulfate).
Remove any suspended drying agent by use of a centrifuge or by filtration.
Clean and dry the apparatus. Deliver 10 mL of aniline and 10 mL of the dried sample into the test tube fitted with stirrer and thermometer. If the material is too viscous for volumetric transfer, weigh to the

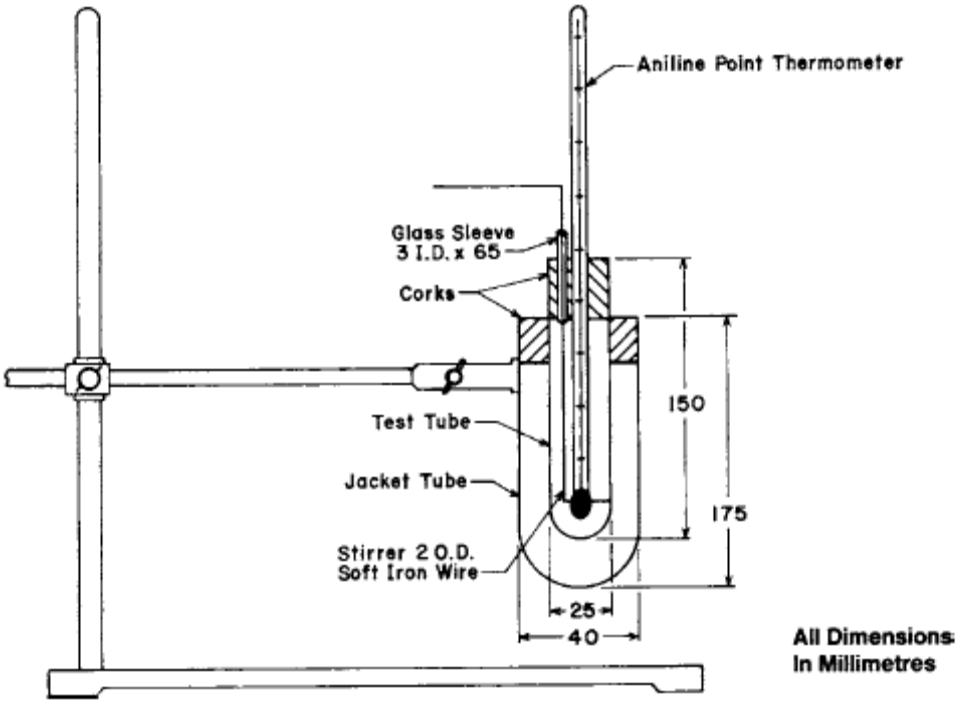


Fig. B-1 Aniline Point Apparatus

nearest 0.01 g a quantity of the sample corresponding to 10 mL at room temperature. Center the thermometer in the test tube so that the immersion mark is at the liquid level, making sure that the thermometer bulb does not touch the side of the tube. Center the test tube in the jacket tube. Stir the mixture rapidly using a 50-mm stroke, avoiding the introduction of air bubbles.

B.4.3 If the aniline-sample mixture is not miscible at room temperature, apply heat directly to the jacket tube so that the temperature rises at a rate of 1 to 3°C min by removing or reducing the heat source until complete miscibility is obtained. Continue stirring and allow the mixture to cool at a rate of 0.5 to 1.0°C min. Continue cooling to a temperature of 1 to 2°C below the first appearance of turbidity, and record as the aniline point the temperature at which the mixture suddenly becomes cloudy throughout. This temperature,

and not the temperature of separation of small amounts of material, is the minimum equilibrium solution temperature.

The true aniline point is characterized by a turbidity that is so cloudy as to obscure the thermometer bulb in reflected light.

B.4.4 If the aniline-sample mixture is completely miscible at room temperature, substitute a non-aqueous cooling bath for the heating source, allow to cool at the rate specified in B.4.3 and determine the aniline point as described.

B.4.5 Repeat the observation of aniline point temperature by heating and cooling repeatedly until a report as directed in Section B.5 can be made.

B.5 **Report**

If the range of three successive observations of the aniline point temperature is not greater than 0.1°C report the average temperature of these observations, corrected for thermometer calibration errors, to the nearest 0.05°C as the aniline point.

Annex C
Determination of Benzene

C.1 Summary

This method is for determination by gas chromatography of benzene at levels from 0.01 to 1 volume % in hydrocarbon solvents.

An internal standard, methyl ethyl ketone (MEK), is added to the material and then introduced into a gas chromatograph equipped with two columns connected in series. The specimen passes first through a column packed with the nonpolar phase, methyl silicone, which separates the components by boiling point. After octane has eluted, the flow through the nonpolar column is reversed, flushing out the components heavier than octane. The octane and lighter components then pass through a column with the highly polar phase, 1,2,3-tris(2-cyanoethoxy)propane, that separates the aromatic and nonaromatic compounds. The eluted components are detected by a conventional detector and recorded on a strip chart. The peak areas are measured and the concentration of each component is calculated by reference to the internal standard.

C.2 Significance and Use

C.2.1 Benzene is classed as a toxic and carcinogenic material. A knowledge of the concentration of this compound may be an aid in evaluating the possible health hazards to persons handling and using hydrocarbon solvents, but this test method is not intended to evaluate such hazards.

C.3 Apparatus

C.3.1 Chromatograph—Any gas chromatographic instrument that has a backflush system and flame ionization detector and that can be operated at the conditions given in Table 2. The detector-recorder combination must produce a 4-mm deflection for a 1-µL specimen containing 0.05 volume % MEK when operated at maximum sensitivity.

C.3.2 Columns, one 0.8-m (2.5-ft) length of 3.2-mm (⅛-in.) outside diameter stainless steel tubing and one 4.6-m (15-ft) length of 3.2-mm (⅛-in.) outsider diameter stainless steel tubing.

C.3.2 Recorder, Strip Chart—Potentiometer with with a full-scale deflection of 1 mV, a full-scale response time of 2 s or less, and a maximum noise level of 60.3 % of full scale.

C.3.3 Microsyringe, 5-µL capacity.

C.3.4 Pipets, measuring 1 and 2 mL, graduated in 0.01 mL; 5, 10, and 20-mL capacity.
C.3.5 Flasks, volumetric, 25 and 100-mL capacity.
C.3.6 Vibrator, electric.
C.3.7 Vacuum Source.
C.3.8 Evaporator, vacuum, rotary.
C.3.9 Flask, boiling, round-bottom, short-neck, joint, 500-mL capacity. Suitable for use with the evaporator
C.3.10 Lamp, infrared.
C.3.11 Burets, automatic, with integral reservoir, 25-mL capacity.

TABLE 2 Instrument Conditions Found Satisfactory for Measuring Low Concentrations of Benzene in Hydrocarbon Solvents

Detector	flame ionization
Columns	two, stainless steel
Length, m	(A) 0.8; (B) 4.6
Outside diameter, mm	3.2
Stationary phases	(A) methyl silicone, 10 weight % (B) TCEP, 25 weight %
Support	(A) acid-washed calcined diatomite, 60 to 80-mesh (B) acid-washed pink diatomaceous earth, 80 to 100-mesh
Reference column	any column or restriction may be used
Temperature, °C	
Injection port	150
Column, isothermal	100
Detector block	150
Carrier gas	helium
Flow rate, mL/min	approximately 30
Recorder range, mV	0 to 1
Chart speed, mm/min	10
Specimen size, µL	1.0
Time to backflush, min	approximately 2
Total cycle time, min	approximately 30

C.4 . Reagents and Materials

C.4.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
C.4.2 Acetone.
C.4.3 Chloroform.
C.4.4 Diatomaceous Earth4—Acid-washed, 60 to 80 mesh and 80 to 100 mesh.
C.4.5 Helium, 99.99 % pure.
C.4.6 Methanol.
C.4.7 Methylene Chloride.
C.4.8 Methyl Ethyl Ketone (MEK), 99.9 mol %.
C.4.9 Methyl Silicone.4
C.4.10, 1,2,3-Tris(2-Cyanoethoxy) Propane (TCEP).4
C.4.11 Calibration Standards.
C.4.11.1 Benzene, 99^{+} mol %.
C.4.11.2. Isooctane, 99^{+} mol %.
C.4.11.3.n-Nonane, 99^{+} mol %.

C.5 Preparation of Columns

C.5.1 Column Packing Preparation—Prepare the two packing materials, one containing 10 % methyl silicone and the other 25 % TCEP, as follows:
Weigh 45 g of the acid-washed calcined diatomite support 60 to 80 mesh, into a 500-mL flask . Dissolve 5 g of the methyl silicone in approximately 50 mL of chloroform. (**Warning**—Chloroform is a toxic material and

inhalation must be avoided.) Pour the methyl silicone–chloroform solution into the flask containing the support. Attach the flask to the evaporator connect the vacuum, and start the motor. Turn on the infrared lamp and allow the packing to
mix thoroughly until dry.
Weigh 75 g of acid-washed pink diatomaceous earth, 80 to 100 mesh, into a 500-mL flask. Dissolve 25 g of TCEP in 200 mL of methanol and pour into the flask containing the support. Attach the flask to the evaporator, connect the vacuum, and start the motor. Turn on the infrared lamp and allow the packing to mix thoroughly until dry, but do not heat the packing above 180°C.

C.5.2 Column Preparation
Clean the stainless steel tubing as follows: Attach a metal funnel to one end of the steel tubing. Hold or mount the stainless steel tubing in an upright position and place a beaker under the outlet end of the tubing. Pour about 50 mL of methylene chloride into the funnel and allow it to drain through the steel tubing into the beaker. Repeat the washing with 50 mL of acetone. Remove the funnel and connect the steel tubing to an air line, by means of vinyl tubing. Remove all solvent from the steel tubing by blowing filtered, oil-free air through or applying a vacuum.

Pack the 0.8-m (2.5-ft) tubing (Column A) with the methyl silicone packing and the 4.6-m (15-ft) tubing (Column B) with the TCEP packing as follows:
Preform Columns A and B separately to fit the chromatographic instrument. Close one end of each tubing with a small, glass wool plug and connect this end to a vacuum source by means of a glass-wool packed tube. To the other end connect a small polyethylene funnel by means of a short length of vinyl tubing. Start the vacuum and pour the appropriate packing into the funnel until the column is full. While filling each column, vibrate the column with the electric vibrator to settle the packing. Remove the funnel and shut off the vacuum source. Remove the top 6 mm (1⁄4 in.) of packing and insert a glass wool plug in this end of the column.

C.6 . Preparation of Chromatographic Apparatus and Establishment of Conditions

C.6.1 Column Conditioning—Join Columns A and B as shown in Fig.C-1. Connect the inlet of Column A to the injection port of the chromatograph. Pass helium gas through the column at approximately 40 mL/min. Condition the columns in accordance with the following time-temperature schedule.

Temperature, °C	Time, h
50	½
100	½
150	1
170	3

Connect the outlet of Column B to the detector port. Adjust the operating conditions to those listed in Table 2, but do not turn on the detector circuits. Check the system for leaks. Adjust the flow rate as follows:
Set the value in the *forward flow* mode (Fig. C-2(*a*)) and adjust Flow Controller A to give the required flow rate (Table 2). Measure the flow rate at the detector vent, specimen side. Set the valve in the *backflush position* (Fig. C-2(*b*)) and measure the flow rate at the detector vent, specimen side. If the rate has changed, adjust Flow Controller B to obtain the required flow rate to within ±1 mL/min.

Turn on the detector circuit. Change the valve from *forward flow* to the *backflush* position several times and observe the baseline. There should be no baseline shift or drift after the initial peak resulting from the pressure surge with the valve change. If there is a baseline shift, slightly increase or decrease flow with Controller B to balance the baseline. (A persistent drift indicates leaks somewhere in the system.)
Determine time before backflushing, which varies for each column system and must be determined experimentally as follows:
Prepare a mixture of 5 volume % *iso*octane in *n*-nonane. Using the injection technique described in 11.3 and with the system in the *forward flow* mode, inject 1 µL of the *iso*octane–*n*-nonane mixture. Allow the chromatogram to run until the *n*-nonane has eluted and the recorder pen has returned to baseline. Measure the time in seconds from the injection until the recorder pen returns to baseline between the *iso*octane and *n*-nonane peaks. At this point all of the *iso*octane but essentially none of the *n*-nonane should have eluted. One half of the measured time approximates the time to backflush and should be from 30 to 120 s.

Repeat the run, including the injection, but switching the system to the *backflush* mode at the determined backflush time. This should result in a chromatogram of *iso*octane with little or no *n*-nonane evident. If necessary, make additional runs, adjusting the time to backflush until a chromatogram of all the *iso*octane and little or none of the *n*-nonane is obtained. This established backflush time, including the *actual valve operations, must be used* in all subsequent calibrations and analyses.

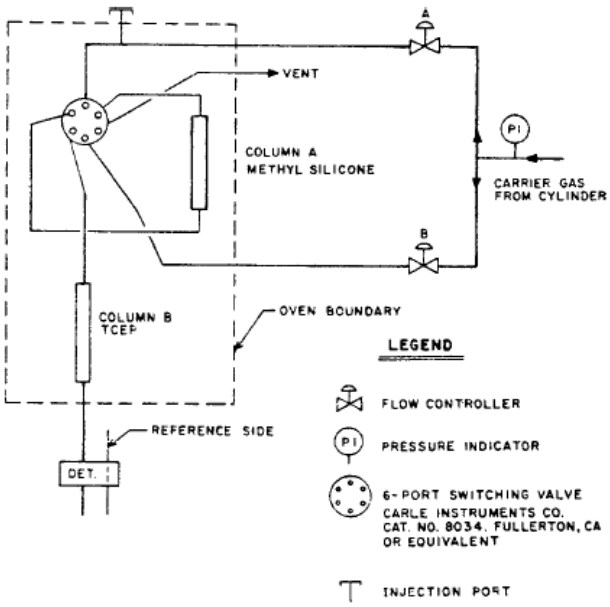


FIG. C-1 Tubing Assembly and Instrumentation

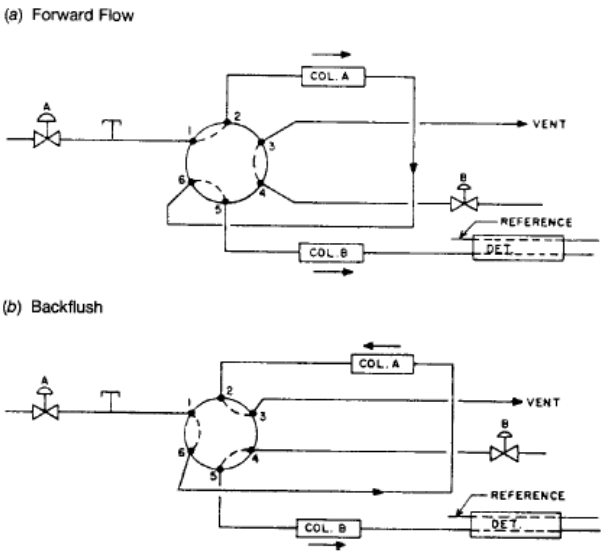


FIG. C-2 Flow Switching System

C.7 Calibration and Standardization

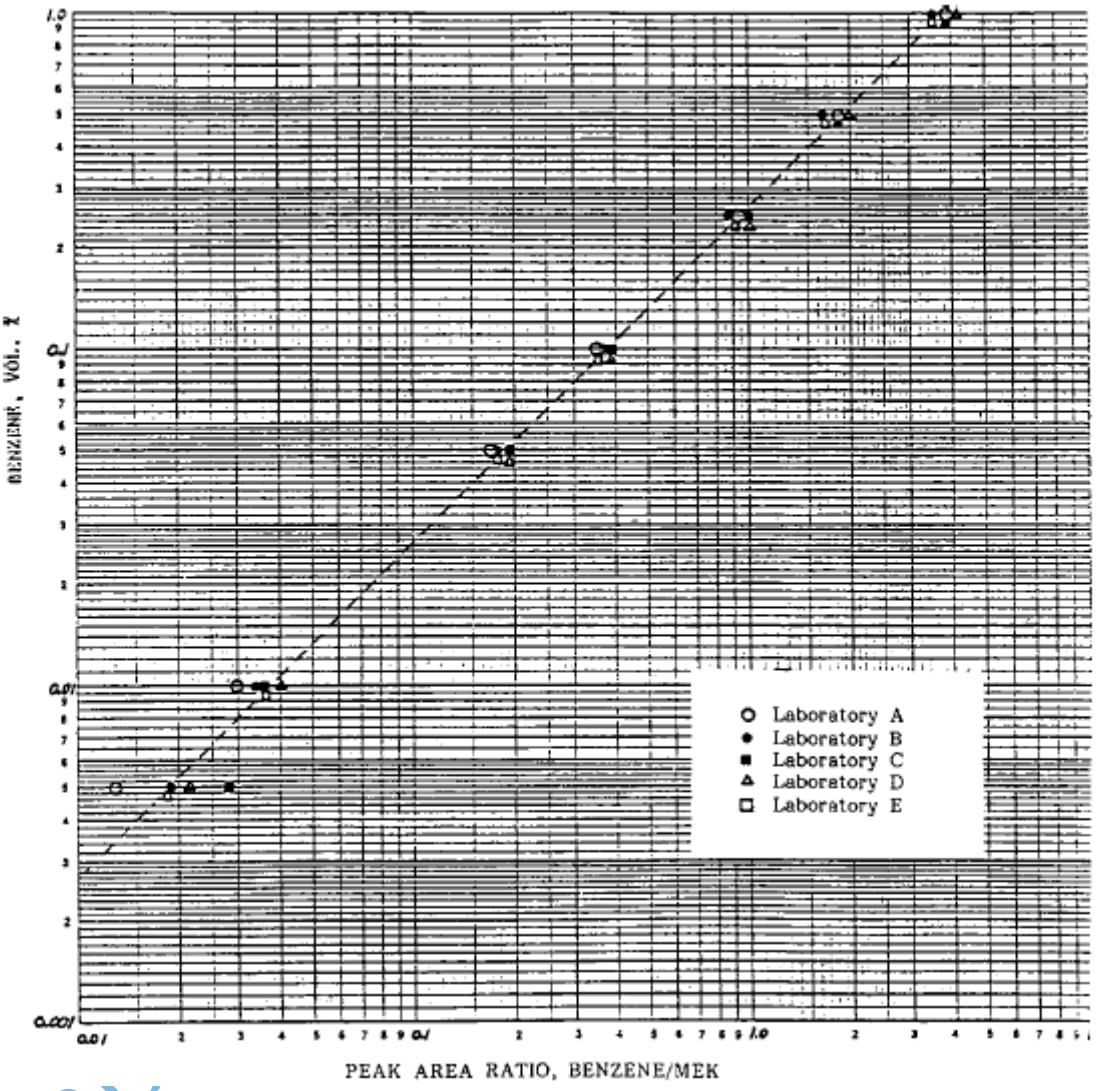
C.7.1 *Standard Solutions*—Prepare seven standard solutions covering the range of 0 to 1 volume % benzene as follows: For each standard, measure the volume of benzene listed below into a 100-mL volumetric flask. Dilute to volume with *iso*octane, with all components and glassware at normal room temperature, and mix thoroughly.

Benzene	
Volume %	mL
1	1
0.5	0.5
0.25	0.25
0.10	0.10
0.05	0.05
0.01	0.01
0.005	0.005

C.7.2 *Calibration Solutions*—Accurately measure 0.5 mL of MEK into a 100-mL volumetric flask, fill to the mark with the first standard solution and mix thoroughly. Repeat with each of the other standard solutions.

C.7.3 *Chromatographic Analysis*—Using the conditions established in C.6.1 chromatograph each of the calibration solutions after injecting them as follows: Flush the 5-µL microsyringe at least three times with the calibration solution and then fill with about 3 µL, avoiding inclusion of air bubbles in the syringe. Slowly eject the material until 1.0 µL remains in the syringe. Wipe the needle with a tissue and draw back the plunger to admit 1 µL of air into the syringe. Insert the needle of the syringe into the septum cap of the chromatograph and push through the septum until the barrel of the syringe is resting against the septum cap; then rapidly push the plunger to the hilt and immediately withdraw the needle from the injection port. This injection technique is necessary to obtain sharp symmetrical peaks.

C.7.4 *Calibration*—Measure the areas of the benzene and of MEK peaks by conventional means . Calculate the ratio of the benzene peak area to the MEK peak area. Plot the concentration of benzene versus the ratio as in Fig. C-3. The calibration must be done to ensure that the entire chromatographic system is operating properly and that the concentration of any one component has not exceeded the linear response range of any part of the system—column, detector, integrator, and other components. The calibration plot should be linear . Determine the retention times for each component for future identification.



NOTE—Determine for each analytical system.
FIG. C-3 Typical Calibration Curve for Benzene

C.8 Procedure

C.8.1 *Test Solution*—Accurately measure 0.5 mL of MEK into a 100-mL volumetric flask. Fill to the mark with the material under test and mix well. Chromatograph a specimen from the test solution using the conditions established in C.6.1 and the injection technique.

Note that the valves must be turned to the *backflush* mode at the established backflush time so that undesirable components do not enter Column B. Identify on the chromatogram the benzene and the internal standard MEK peaks from the retention times of the standards.The order of elution is nonaromatic hydrocarbons, benzene, MEK, and toluene when using the specified columns, as shown in Fig. C-4. Measure the areas under the benzene peak and under
the MEK peak by conventional methods.

C.9 Calculation

Calculate the ratio of peak area of benzene to the peak area of MEK. Read from the calibration curve the volume % of benzene corresponding to the calculated peak ratio. If the results are desired on a weight basis, convert to weight % as follows:

Benzene, weight% (*V*/*D*) 0.8844

where:
V = benzene, volume %, and
D = relative density of sample at 15.6/15.6°C (60/60°F).

Report the following information: benzene content in volume or weight % to the nearest 0.005 %. Two results, each the mean of duplicates, obtained by the same operator on different days should be considered suspect if they differ by more than 0.027 % absolute.

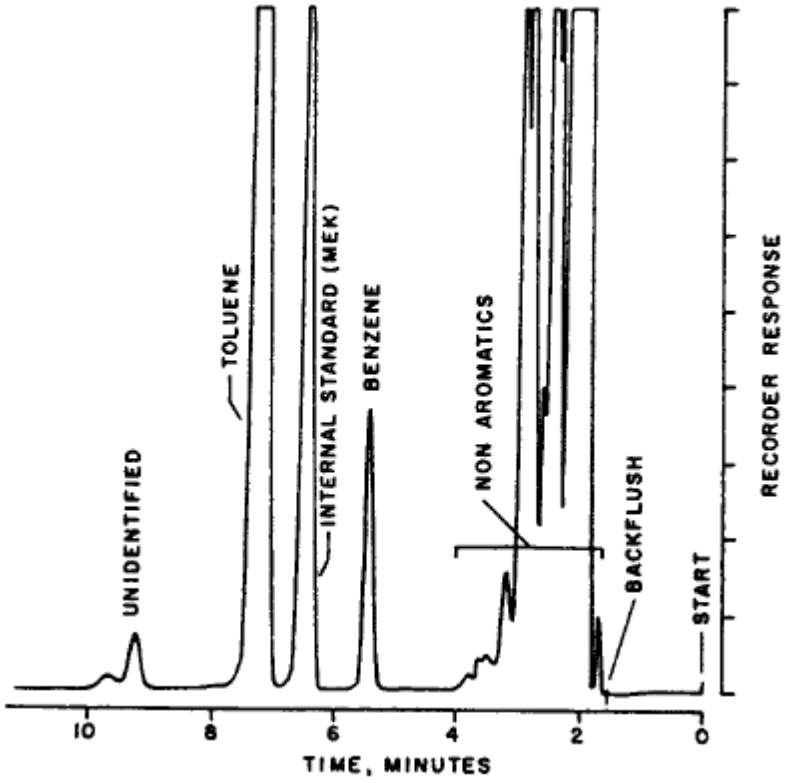


FIG. C-4 Typical Chromatogram

Annex D
Test Method for Bromine Index

D.1 Summary and Application

This test method covers the determination of the amount of bromine-reactive material in petroleum hydrocarbons and is
thus a measure of trace amounts of unsaturates in these materials. bromine index is the number of milligrams of bromine that will react with 100 g of sample under the conditions of the test.

A known mass of the sample dissolved in a specified solvent is titrated with standard bromide-bromate solution. The end point is indicated by a dead stop electrometric titration apparatus when the presence of free bromine causes a sudden change in the electrical conductivity of the system.

D.2 Apparatus

D.2.1 *Electrometric End Point Titration Apparatus*—Any apparatus designed to perform titrations to pre-set end points may be used in conjunction with a high-resistance polarizing current supply capable of

maintaining approximately 0.8 V across two platinum electrodes and with a sensitivity such that a voltage change of approximately 50 mV at these electrodes is sufficient to indicate the end point. Other types of commercially available electric titrimeters, including certain pH meters, have also been found to be suitable.
D.2.2 Titration Vessel—A jacketed glass vessel of approximately150-mL capacity of such a form that can be conveniently maintained at 0 to 5°C (32 to 41°F). A pair of platinum electrodes spaced not more than 5 mm apart shall be mounted to extend well below the liquid level. Stirring shall be by a mechanical or electromagnetic stirrer and shall be rapid, but not so vigorous as to draw air bubbles down to the electrodes.

D.2.3 *Burets,* 10 and 50-mL capacity.

D.2.4 *Iodine Number Flasks,* glass-stoppered, 500-mL capacity.

D.3 Reagents

Only analytical grade reagents and distilled water shall be used
D.3.1 *Preparation and Standardization :*
D.3.2 *Bromide-Bromate Standard Solution* (*0.05 N*)—Dissolve 5.1 g of potassium bromide (KBr) and 1.4 g potassium bromate (KBrO3) in water and dilute to 1 L. Standardize to four significant figures as follows: Place 50 mL of glacial acetic acid (**Warning** —Poison. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled) and 1 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) (**Warning**—Poison. Corrosive. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled.) in a 500-mL iodine number flask. Chill the solution in an ice bath for approximately 10 min, and with constant swirling of the flask, add from a 50-mL buret 40 to 45 mL of bromide-bromate solution, estimated to the nearest 0.01 mL, at a rate such that the addition takes between 90 and 120 s. Stopper the flask immediately, shake the contents, place it again in the ice bath, and add 5 mL of potassium iodide (KI) solution in the lip of the flask. After 5 min, remove the flask from the ice bath and allow the KI solution to flow into the flask by slowly removing the stopper. Shake vigorously, add 100 mL of water in such a manner as to rinse the stopper, lip, and walls of the flask, and titrate promptly with the standard sodium thiosulfate (Na2S2O3) solution. Near the end of the titration, add 1 mL of starch indicator solution and titrate slowly to the disappearance of the blue color. Calculate the normality of the bromidebromate solution as follows:

*N*1 = *A*2*N*2/*A*1
where:
*N*1 = normality of the bromide-bromate solution,
*A*1 = millilitres of the bromide-bromate solution,
*N*2 = normality of the Na2S2O3 solution, and
*A*2 = millilitres of the Na2S2O3 solution required for titration of the bromide-bromate solution.

D.3.3 *Potassium Iodide Solution (150 g/L)*—Dissolve 150 g of KI in water and dilute to 1 L.
D.3.4 *Sodium Thiosulfate, Standard Solution* (0.05*N)*— Dissolve 12.5 g of sodium thiosulfate pentahydrate (Na2S2O3·5H2O) in water and add 0.01 g of sodium carbonate (Na2CO3) to stabilize the solution. Dilute to 1 L and mix thoroughly by shaking. Standardize by any accepted procedure that determines the normality with an error not greater than ±0.0002. Restandardize at intervals frequent enough to detect changes of 0.0005 in normality.

D.3.5 *Starch Indicator Solution*—Mix 5 g of soluble starch with approximately 3 to 5 mL of water. If desired, add about 0.65 g salicylic acid as preservative. Add the slurry to 500 mL of boiling water and continue boiling for 5 to 10 min. Allow to cool and decant the supernatant liquid into glass bottles and seal well. Starch solutions (some preserved with salicylic acid) are also commercially available and may be substituted.

D.3.6 *Sulfuric Acid* (*1+5*)—Carefully add 1 volume of concentrated sulfuric acid (H2SO4, sp gr 1.84) to 5 volumes of water and thoroughly mix. (**Warning** —Poison. Corrosive. Strong oxidizer. Contact with organic material may cause fire. May be fatal if swallowed.)

D.3.7 *Titration Solvent*—Prepare 1 L of titration solvent by mixing the following volumes of materials: 714 mL of glacial acetic acid, 134 mL of 1,1,1-trichloroethane or dichloromethane, 134 mL of methanol, and 18 mL of H2SO4 (1+5)
D.3.8 *Solvents:*

- *Acetic Acid,* glacial. (**Warning**—Poison. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.)
- *Methanol* (**Warning**—Flammable. Vapor harmful. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.)
- *1,1,1-Trichloroethane* (**Warning**—Harmful if inhaled. High concentrations may cause unconsciousness or death. Contact may cause skin irritation and dermatitis.)
- *Dichloromethane* (**Warning**—Harmful if inhaled. High concentrations may cause unconsciousness or death. Contact may cause skin irritation and dermatitis.)

D.4 Procedure

D.4.1 Switch on the titrimeter and allow the electrical circuits to stabilize in accordance with the manufacturer's instructions. Cool the titration vessel to 0 to 5°C by circulating a suitable coolant through the jacketed titration vessel. Introduce 110 mL of titration solvent into the titration vessel and pipet in a quantity of sample as indicated in Table D-1. Switch on the stirrer and adjust to a rapid stirring rate, but avoid any tendency for air bubbles to be drawn down into the solution. Allow the contents to cool to 0 to 5°C and maintain at this temperature throughout the titration.
(**Warning**—Hydrocarbon samples, particularly those boiling below 205°C are flammable.)

Frequently the order of magnitude of the bromine index of a sample is unknown. In this case, a trial test is recommended using an 8 to 10-g sample in order to obtain the approximate magnitude of the bromine index. This exploratory test should be followed with another determination using the appropriate sample size as indicated in Table D-1. The sample mass can be determined by obtaining the density of the sample and calculating the mass of a measured volume. Set the end point potential. With each instrument, the manufacturer's instructions should be followed for end point setting and to achieve the sensitivity in the platinum electrode circuit. Depending on the titrator apparatus, add the bromidebromate solution manually or by microprocessor control in small increments from the buret. The end point of the titration is achieved when the potential reaches the pre-set value and persists for more than 30 s.

D.4.2 Blanks—Make duplicate blank titrations on each batch of titration solvent and reagents. Less than 1.0 mL of bromidebromate solution should be required.

D.5 . Calculation

Calculate the bromine index as follows:

$$\text{Bromine index} = [(A - B)N \times 7990]/W$$

where:
A = millilitres of bromide-bromate solution required for titration of the sample,
B = millilitres of bromide-bromate solution required for titration of the blank,
N = normality of bromide-bromate solution, and
W = grams of sample.

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed 14 in only one case in twenty.

Annex E
Determination of Kauri-Butanol value

E.1 Summary:

kauri-butanol value, n—of a solvent, the volume in millilitres at 25°C of the solvent, corrected to a defined standard, required to produce a defined degree of turbidity when added to 20 g of a standard solution of kauri resin innormal butyl alcohol.
The kauri resin solution is standardized against toluene, which has an assigned value of 105, and a mixture of 75 % *n*-heptane and 25 % toluene on a volume basis, which has an assigned value of 40. The kauri-butanol value is used as a measure of solvent power of hydrocarbon solvents. High kauri-butanol values indicate relatively strong solvency.

E.2 Apparatus

E.2.1 *Water Bath,* capable of being maintained at 25 6 5°C. Alternatively, a temperature controlled environment maintained at 25 6 5°C may be used.

E.2.2 *Volumetric Flask,* 200-mL capacity.

E.2.3 *Erlenmeyer Flask,* 250-mL capacity.

E.2.4 *Sample Dispensing Device,* Buret, of at least 50-mL capacity, or equivalent, that is capable of accurately determining the volume dispensed to the nearest 0.1 mL.

E.2.5 *Print Specimen*—A sheet of white paper having on it black 10 or 12 point print, No. 31 Bruce old style type.

E.3 Reagents

E.3.1Kauri-Butanol Solution4—Place in a 3-L flask 400 g of clean, pale, bold kauri resin of Grade XXXX, XXX, or XX ground to pea-size or smaller. Add, while agitating vigorously, 2000 g of n-butyl alcohol, Shake on a mechanical shaker until the resin goes into solution, warming to about 55°C, if necessary to aid solution. If a mechanical shaker is not available, fit the flask with a reflux condenser and heat on a steam bath until all of the kauri resin is dissolved. Permit the solution to stand 48 h and then clarify by filtering through a Büchner funnel with suction, using double filter paper and changing as frequently as necessary.

E.3.2 Standard Toluene

E.3.3 Heptane-Toluene *Blend* consisting of 25 ± 0.1 % toluene and 75 ± 0.1 % *n*-heptane on a volume basis, for use as a low-solvency standard. The heptane shall be spectroscopic, HPLC, or knock test grade.

E.4 Standardization

E.4..1 Weigh out 20 ± 0.10 g of kauri-butanol solution in a 250-mL Erlenmeyer flask. Check that the temperature of the KB solution in the flask is 25 ± 5°C. If not, place the Erlenmeyer flask and its contents in a water bath or temperature controlled environment maintained at 25 ± 5°C and allow to equilibrate for at least 30 min. If the flask was placed in a water bath, remove the flask from the water bath. Titrate the contents of the flask with the standard toluene. Swirl the contents of the flask during titration, periodically stopping to observe the clarity of the print beneath the flask. Gradually reduce the successive amounts of toluene added as the end point is approached. The end point is reached when the sharp outlines of 10-point print placed directly beneath the Erlenmeyer flask and observed through the liquid are first perceived to be obscured or blurred. The point where the print becomes illegible is past the end point. Check the temperature in the flask immediately after the end point has been reached, and if over 30°C or under 20°C, repeat the titration.

E.4..2 The volume of toluene used, in millilitres, represents the actual titer for the particular kauri-butanol solution at hand. This value should lie reasonably close to 105 mL, but not over 110 nor under 100 mL. If these limits are exceeded, adjust the concentration of the kauri-butanol solution to bring the total volume of toluene within them. Designate the final value using toluene as *A*.

E.4.3 Weigh out 20 ± 0.10 g of the kauri-butanol solution in a 250-mL Erlenmeyer flask and place in the water bath. Titrate with the heptane-toluene blend in the same manner . Designate the volume, in millilitres, of the blend used in this titration as *B*.

NB Freshly prepared kauri-butanol solution may change in standardization from day to day. It is, therefore, desirable to permit the solution to age before initial standardization and, in any case, the standardization should be rechecked on successive days until the toluene
factor and blend factor remain constant.

E.5 Procedure

E.5.1 Weigh 20 ±0.10 g of the adjusted kauri-butanol solution into a 250-mL Erlenmeyer flask. Check that the temperature of the KB solution in the flask is 25 ±5°C. If not, place the Erlenmeyer flask and its contents in a water bath or temperature controlled environment maintained at 25 ± 5°C and allow to equilibrate for at least 30 min. If the flask was placed in a water bath, remove the flask from the water bath.
Fill the sample dispensing device with the solvent being tested. Titrate the contents of the flask with the solvent. Swirl the contents of the flask during the titration, periodically stopping to observe the clarity of the print beneath the flask. Gradually reduce the successive amounts of solvent added as the end point is approached. The end point is reached when the sharp outlines of 10-point print (see E.2.5) placed directly beneath the Erlenmeyer flask and observed through the liquid are first perceived to be obscured or blurred. The point where the print becomes illegible is past the end point. Check the temperature in the flask immediately after the end point has been reached and if over 30°C or under 20°C, repeat the titration. Designate the volume of solvent, in millilitres, to produce turbidity as *C*.

E.6 . Calculation

E.6..1 Calculate the kauri-butanol value, *V*, as follows:

$$V = [65(C - B)/(A - B)] + 40$$

where:
A = toluene required to titrate 20 g of kauri-butanol solution mL,

B = heptane-toluene blend required to titrate 20 g of kauributanol solution mL, and

C = solvent under test required to titrate 20 g of kauributanol solution mL.

Report the calculated kauri-butanol value to the nearest 0.5 KB unit.

Annex F
Determination of Sulphur

F.1 Summary of Test Method

F.1.1 A liquid sample is introduced into a pyrolysis tube maintained at a temperature between 900-1200°C, having a flowing stream of gas containing 50-80% oxygen and 20-50% inert gas (for example, argon, helium, etc.) Oxidative pyrolysis converts the sulfur to sulfur dioxide, which then flows into a titration cell where it reacts with triiodide ion present in the electrolyte. The triiodide ion consumed is coulometrically replaced and the total current (i × t) required to replace it is a measure of the sulfur present in the sample. The reaction occurring in the titration cell as sulfur dioxide enters is:

$$I_3^- + SO_2 + H_2O \rightarrow SO_3 + 3I^- + 2H^+$$

The triiodide ion consumed in the above reaction is generated coulometrically thus:

$$3I^- \rightarrow I_3^- + 2e^-$$

These microequivalents of triiodide ion (iodine) are equal to the number of microequivalents of titratable SO2 ionentering the titration cell.

F.2 Apparatus

F.2.1 The configuration of the pyrolysis tube and furnace may be constructed as is desirable as long as the operating parameters are met. Fig. F-1 is typical of apparatus currently in use.

F.2.2 A typical assembly and oxidative gas flow through a coulometric apparatus for the determination of trace sulfur is shown in Fig. F-2.

F.2.3 *Furnace*—Maintained at a temperature sufficient to completely pyrolyze the organic matrix, 900-1200°C, and completely oxidize the organically bound sulfur to SO2. Independently controlled inlet and outlet temperature zones are optional. An electrical furnace has been found suitable to use.

F.2.4 *Pyrolysis Tube*— Fabricated from quartz and constructed so the sample is vaporized in a heated zone before the furnace and swept into the oxidation zone by an inert carrier gas, where the vaporized sample mixes with oxygen and is pyrolyzed. The inlet shall be constructed large enough to accommodate a sample boat completely into the oxidation zone of the pyrolysis tube or allow the direct injection of the sample into the heated zone before the furnace. The pyrolysis tube shall have side arms for the introduction of oxygen and inert carrier gas.

F.2.5 *Titration Cell*— Consisting of a sensor/reference pair of electrodes to detect changes in triiodide ion concentration, a generator anode-cathode pair of electrodes to maintain a constant triiodide ion concentration, an inlet for gaseous sample from the pyrolysis tube, and an outlet to vent the exit gases from the titration cell. The reference electrode can be either an Ag/AgCl double junction reference electrode or a platinum wire in a saturated triiodide half-cell. The sensor electrode and both the anode and cathode electrodes of the generator are made of platinum. The titration cell shall require mixing, which can be accomplished with a magnetic stir bar, stream of gas, or other suitable means. Other sensor and reference electrodes may be used if they meet the performance criteria of this test method.

NOTE —Take care not to use excessive stirring and possibly damage the electrodes with the stir bar. The creation of a slight vortex is adequate.

F.2.6 *Microcoulometer*— The apparatus' microcoulometer, with variable attenuation and gain control, shall be capable ofmeasuring the potential of the sensing-reference electrode pair and compare this potential to a bias potential. By amplifying this potential difference and applying the difference to a working-auxiliary pair of electrodes (the generator), a titrant is generated. The microcoulometer integrates the amount of current used, calculates the equivalent mass of sulfur titrated and calculates the concentration of sulfur in the sample.

F.2.7 *Strip Chart Recorder (Optional)* —To monitor and plot the mV potential of the titration cell during the analysis.
F.2.8 *Flow Control*—The apparatus shall be equipped with flow controllers capable of maintaining a constant supply of
oxygen and inert carrier gas.

F.2.9 *Dryer Tube*—The oxidation of samples produces water vapor which, if allowed to condense between the exit of the
pyrolysis tube and the titration cell, will absorb the SO2 formed and result in low recovery. Steps shall be taken to prevent such an occurrence. This is easily accomplished by placing a phosphoric acid dehydration tube between the titration cell and exit of the pyrolysis tube. Other approaches, such as heating tape or permeation tubes, can be used if precision and accuracy are not degraded.

F.2.10 *Sampling Syringes*—Microlitre syringes able to accurately deliver 5 to 80 mL of sample are required. The volume
injected should not exceed 80% of a syringe's capacity.

F.2.11 *Sample Inlet System*—Either type of sample inlet system described can be used.

F.2.11.1 *Boat Inlet System*—The inlet of the pyrolysis tube is sealed to the boat inlet system. The system provides a cooled area before the furnace for the sample boat prior to quantitative introduction of sample into the boat and is purged with the inert carrier gas. The boat driving mechanism then fully inserts the boat into the oxidation zone of the furnace. The drive mechanism shall advance and retract the sample boat into and out of the oxidation zone of the furnace at a controlled and repeatable rate

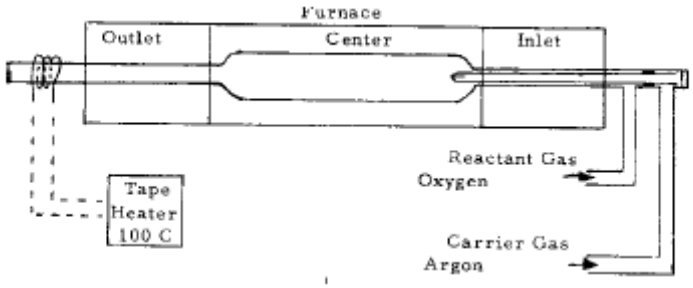


FIG. F-1 Typical Pyrolysis Tube

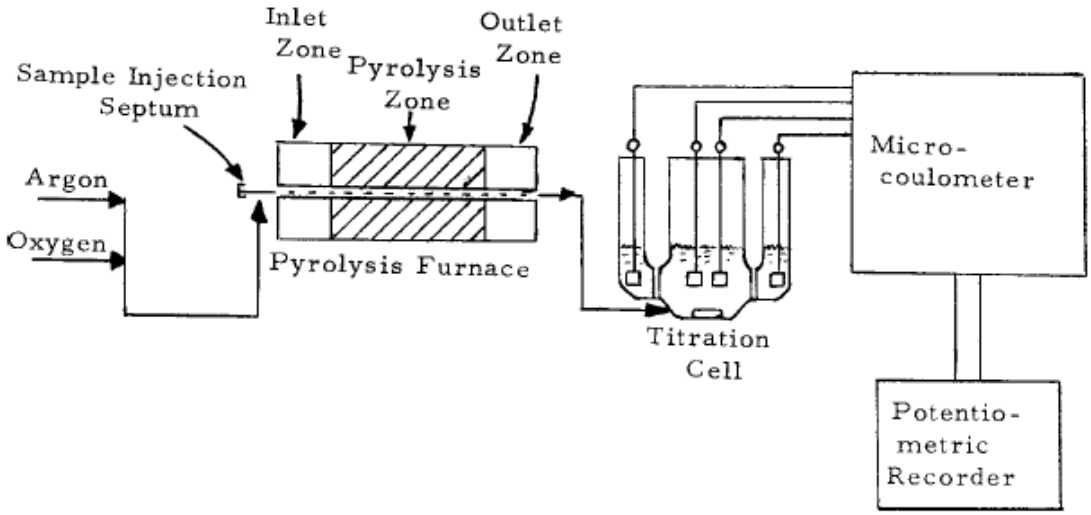


FIG. F-2 Flow Diagram for Typical Coulometric Apparatus for Trace Sulfur Determination

F.2.11.2 *Boat Inlet Cooler (Optional)*—Sample volatility and injection volume may require an apparatus capable of cooling the sample boat prior to sample introduction. Thermoelectric coolers (peltier) or recirculating refrigerated liquid devices are strongly recommended. Switching sample boats between each analysis may prove effective, provided sample size is not too large.

F.2.11.3 *Sample Boats*—Quartz or other suitable material which will not react with the sample or sulfur compounds being analyzed and able to withstand the temperatures extremes of the test method.

F.2.11.4 *Syringe Inlet System*—The system shall deliver a quantitative amount of sample from a microlitre syringe into a heated area before the oxidation zone of the pyrolysis tube at a controlled and repeatable rate. There the sample is volatilized and the inert carrier gas stream purging the heated area transports the volatilized sample into the oxidation zone of the pyrolysis furnace. An adjustable drive mechanism capable of injecting the sample from a microlitre syringe at a constant rate between 0.5 to 1.0 mL/s is required

NOTE: Take care not to introduce the sample too fast into the oxidation zone of the furnace and overload the combustion capacity of the pyrolysis tube. Program the sample inlet system to deliver the sample at a sufficiently controlled and repeatable rate to prevent any incomplete combustion by-products (coke or soot) from forming at the exit of the pyrolysis tube.

F.2.12 *Balance*—With a weighing precision of 60.01 mg.

F.3 Reagents and Materials

F.3.1 *Quartz Wool*—Grade fine.

F.3.2 *Acetic Acid* (CH3COOH) —Glacial acetic acid with specific gravity = 1.05. (**Warning—** Poison. Corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.)

F.3.3 *Phosphoric Acid (85 % w/w)*—Orthophosphoric acid (H3PO4). (**Warning—**Poison. Corrosive. May be fatal if swallowed. Causes severe burns.)

F.3.4 *Inert Gas*—Argon or helium, high purity grade (HP),5 used as carrier gas. (**Warning—**Compressed gas under high
pressure. Gas reduces oxygen available for breathing.)

F.3.5 *Oxygen*—High purity grade (HP),5 used as the reactant gas. (**Warning—**Oxygen vigorously accelerates combustion.)

F.3.6 *Gas Regulators*—Two-stage gas regulators shall be used for the oxygen and inert carrier gas.

F.3.7 *Cell Electrolyte Solution*—Dissolve 0.5 g of potassium iodide (KI) and 0.6 g of sodium azide (NaN3) in approximately 500 mL of high-purity water, add 6 mL of glacial acetic acid (CH3COOH), and dilute to 1000 mL or follow the manufacturer's specifications.
Take care to store bulk quantities of the electrolyte in a dark place. It is recommended to prepare fresh electrolyte at least every three months.

F.3.8 Sodium Azide (NaN3), fine granular. (**Warning—** Toxic. Causes eye and skin irritation. Explosive.)

F.3.9 Potassium Iodide (KI), fine granular.

F.3.10 *Potassium Nitrate* (KNO3), fine granular. Used for the 1M Ag/AgCl double junction reference electrode.
F.3.11 *Iodine* (I), 20 mesh or less, for saturated reference electrode.

F.3.12 *Toluene, Xylenes, Isooctane*—Reagent grade. (Other solvents similar to those occurring in the samples being analyzed are acceptable.)Asolvent blank correction is required due to the inherent sulfur present in the solvents used for standard preparation and sample dilution. (**Warning—** Flammable solvents. Harmful if inhaled. Vapors may cause flash fire.)

F.3.13 *Dibenzothiophene*—FW 184.26, 17.399 % (mass/ mass) S

F.3.14 *n-Butyl Sulfide*—FW 146.29, 21.92 % (mass/mass) S

F.3.15 *Thionaphthene (Benzothiophene)*—FW 134.20, 23.90% (mass/mass) S

F.3.16 *Sulfur, Standard Solution* (approximately 1000 mg-S/ mL)—Prepare a stock solution by accurately weighing approximately 0.5748 g of dibenzothiophene or 0.4652 g of n-butyl sulfide or 0.4184 g of thionaphathene into a tared 100 mL, type A volumetric flask. Dilute to volume with a selected solvent. This stock can then be further diluted to prepare sulfur working and calibration standards as outlined in Tables F-1 to F-3

F.3.17. *Potassium Chloride* (KCl), fine granular. Used for the 1M Ag/AgCl double junction reference electrode.

$$\mu g - S/mL = \frac{A \times B \times C \times 10^6}{100\ mL}$$

where:

A = grams of standard.
B = weight of fraction sulfur (S) in standard.
C = weight of fraction standard purity.

F.3.18 *Sulfur, Standard Working Solution* —Prepare the working standards using standard type A volumetric pipet as outlined in Table F-1.

Working and calibration standards prepared on a regular basis recommended, depending upon frequency of use and age. Stock solutions typically have a useful life of about 3 months.Calibration standards can be prepared and diluted on a mass/mass basis, when calculation results are adjusted to accommodate them. Stock, working and calibration standards from commercial sources can be used if checked for accuracy and can meet the performance criteria of this test method.

F.4 Hazards

F.4.1 High temperature is employed in this test method. Extra care shall be exercised when using flammable materials near the furnace.To preserve volatile components which are in some samples, do not uncover samples any longer than necessary. Samples should be analyzed as soon as possible after collection from bulk supplies to prevent loss of sulfur, or contamination due to exposure or contact with sample container.

F.5 Preparation of Apparatus

F.5.1 Carefully insert the quartz pyrolysis tube into the furnace, and connect the oxygen and inert carrier gas lines. Connect the boat drive system or syringe drive system to the pyrolysis tube. Perform a leak check according to the manufacturer's instructions. Assemble the titration cell, and add all required solutions, including cell electrolyte, according to the manufacturer's instructions. Connect the titration cell to the apparatus according to the manufacturer's instructions. Adjust the flow of gases and set the furnace temperatures and instrumental parameters according to the manufacturer's instructions.

TABLE F-1 Recommended Preparation of Working Standards

Working Standard Concentration, µg-S/mL	Stock Standard Concentration, µg-S/mL	Volume Stock Standard, mL	Total Volume Working Standard, mL
500	1000	25	50
50	1000	5	100
10	500[A]	2	100

[A] Working standard.

TABLE F-2 Recommended Calibration Standards versus Desired Calibration Range

Calibration Range, mg-S/kg	Calibration Standards Concentration		
	Concentration 1, mg-S/mL	Concentration 2, mg-S/mL	Concentration 3, mg-S/mL
Trace–2.5	0.2	1.0	2.5
0.5–50	0.2	5	50
1.0–250	0.5	10	250
2.5–500	1.0	25	500
5.0–1000	2.5	50	1000

TABLE F-3 Recommended Preparation of Calibration Standards

Concentration Working Standard, µg-S/mL	Volume of Working Standard, mL	Total Volume Calibration Standard, mL	Concentration Calibration Standard, µg-S/mL
10	2	100	0.2
10	5	100	0.5
50	2	100	1.0
50	5	100	2.5
50	10	100	5.0
500	5	100	25
500	10	100	50
1000[A]	25	100	250
500	. . .	. . .	500
1000[A]	. . .	. . .	1000[A]

[A] Standard stock solution.

If using a boat inlet system, pre-bake the sample boats used for the analysis per the manufacturer's instructions.

F.6. Calibration and Standardization

F.6.1 Following the manufacturer's recommended procedures, set the operational parameters of the apparatus for internal calibration. If the apparatus is not so equipped, analyze the solvent blank and calibration standards, record their values as µg or ng of sulfur, and manually generate a calibration curve.

F.6.2 *Calibration Standards*—Select the desired calibration range from Table F-2. Prepare the appropriate calibration standards for the range selected as outlined in Table F-3. The calibration standards concentrations are calculated based on the formula below:

$$\text{Calibration Standard Concentration: } \mu g - S/mL = \frac{A \times B}{100\ mL}$$

where:
A = µg-S/mL of working or stock solution.
B = mL of working or stock solution.

NOTE —A calibration curve with three standards is recommended. It is recommended to use standards covering the range of sulfur concentrations expected in the samples being analyzed.

F.6.3 Select the appropriate syringe based on the recommended sample size in Table F-4 for the concentration of standards used to calibrate the apparatus.

TABLE F-4 Recommended Sample Size for Expected Sample Concentrations

Sample Concentrations, mg-S/kg	Injected Volume, µL	Mass Sulfur, µg-S
Trace–5.0	80	Trace–0.25
0.5–50	60	0.03–1.5
1.0–250	30	0.03–5.0
2.5–500	20	0.05–5.0
5.0–1000	10	0.05–10

F.6.4 Flush the microlitre syringe several times with the sample prior to analysis. If bubbles are present in the liquid column, flush the syringe and withdraw a new sample. 11.5 The sample size can be determined volumetrically or by mass with a syringe. The sample size should be 80% or less of the syringe's capacity.

F.6.5 Volumetric Measurement—Obtain the volume of injected material by filling the syringe to the selected level,retracting the plunger so the lower meniscus falls on the 10% scale mark, and recording the volume of liquid in the syringe. After the sample has been injected, retract the plunger again so the lower liquid meniscus falls on the 10% scale mark, and record the volume of liquid in the syringe. The difference between the two readings is the volume of sample injected.

F.6.6 Mass Measurement—The sample syringe may be weighed before and after the injection to determine the amount of sample injected. This technique provides greater precision than the volume delivery method, provided a balance with a precision of 60.01 mg is used. Once the appropriate sample size has been measured into the microlitre syringe, promptly and quantitatively deliver the sample into the apparatus. Again, there are two alternative techniques available.

F.6.7 Boat Inlet System—Add the sample by slowly discharging quantitatively the contents of the syringe into a sample boat containing quartz wool, being careful to include the last drop from the tip of the syringe needle. Remove the syringe and immediately start the analysis. The apparatus' baseline should remain stable until the boat approaches the furnace and volatilization of sample begins. The program of the inlet system should keep the boat completely in the oxidation zone of the furnace a time (residence time) sufficient to totally oxidize the sample before withdrawing the sample boat out of the furnace. Allow at least 2 min for cooling before the next sample injection after the boat has reached the fully retracted position. Reduce the boat drive introduction rate, sample size or both if coke or soot is observed on the exit end of the

pyrolysis tube. Increase the residence time for the boat in the oxidation zone of the furnace if coke or soot is observed on the boat after the analysis is finished.

F.6.8 Syringe Inlet System—For direct injection, carefully insert the syringe needle into the inlet of the combustion tube and attach the syringe to the driving mechanism. Allow time for the sample residues to be volatilized from the needle (needle blank). Once the baseline has been reestablished, immediately start the analysis. Remove the syringe once the sample has been syringe once the sample has been completely injected and the analysis is finished. Reduce the sample size, rate of injection, or both, for the direct injection the test sample into the furnace if coke or soot is observed on the exit end of the pyrolysis tube. Calibrate the instrument using one of the following two techniques:

F.6.9 Automatic Internal Calibration—Measure the calibration standards and solvent blank using one of the procedures described in F.6.3–F.6.8. Analyze the solvent blank and each standard a minimum of three times. Calibrate the apparatus per the manufacturer's instructions. Use either a first or second order linear regression and use this calibration curve to determine the amount of sulfur in the unknown sample. The system's performance shall be checked each day of use.

F.6.9 Manual Calibration Curve—Measure the solvent blank and calibration standards using one of the procedures described in F.6.3–F.6.8. Analyze the solvent blank and each calibration standard a minimum of three times and record their absolute values in either µg or ng sulfur. Subtract the averaged blank value from each calibration standard and construct a curve plotting the mass of sulfur measured for each calibrationstandard (*y*-axis) verses the theoretical mass of sulfur injected. Perform a first or second order linear regression and use the calibration curve to determine the amount of sulfur in the unknown sample. The system's performance shall be checked each day of use.
If the fraction of sulfur converted to SO2 (recovery factors) drops below 75% of the standard solutions, prepare fresh standards to check if the standards have been altered. Procedural details should be reviewed if a low recovery factors persist.

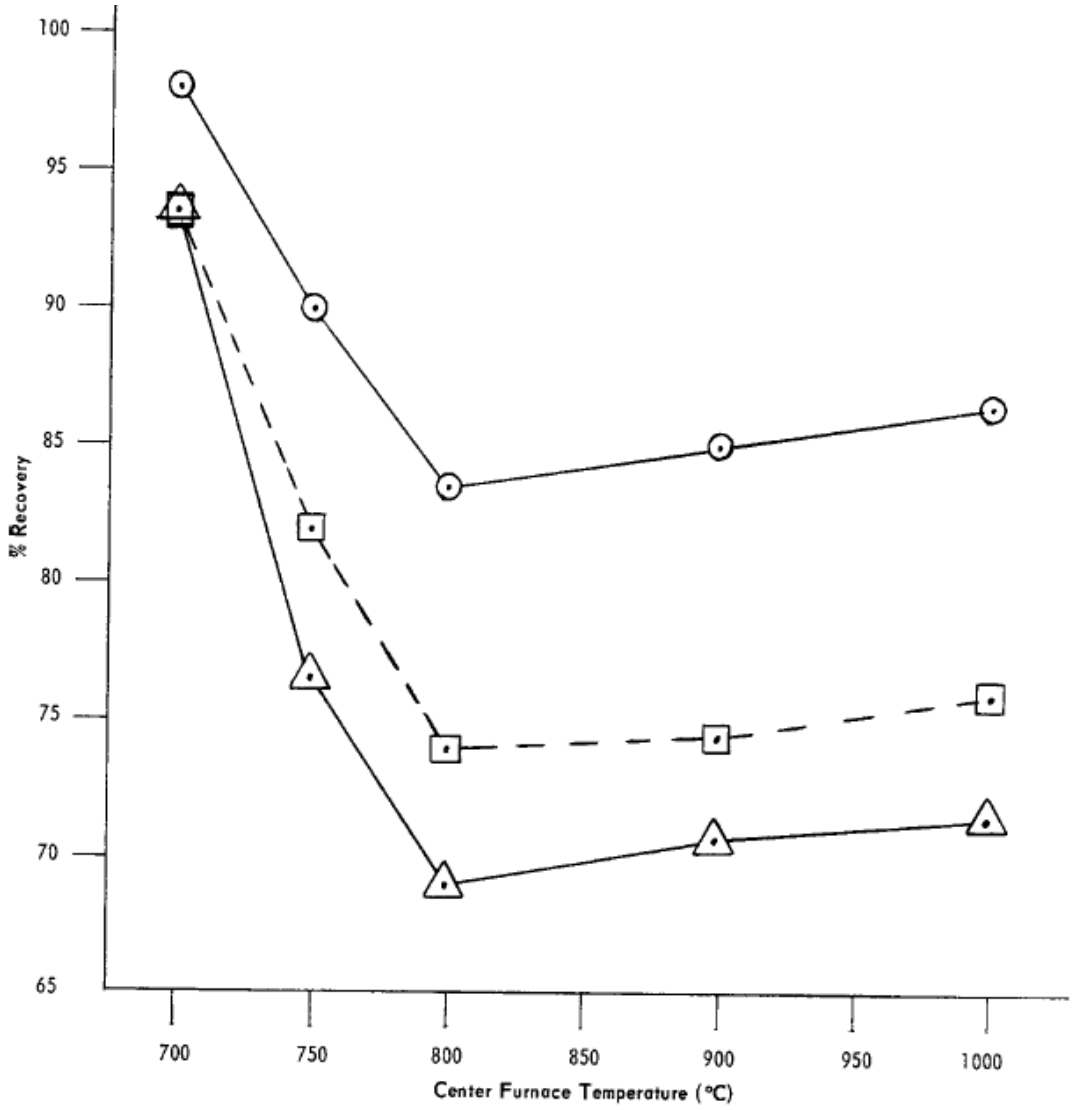
F.6.10 Cleaning and Recalibration—Clean any coked or sooted parts per the manufacturer's instructions. Assemble and leak check the apparatus per the manufacturer's instructions after any cleaning or adjustment. Repeat instrument calibration prior to reanalysis of test samples.

F.7 Procedure

F.7.1 Obtain a test sample using the procedure described in Section 9. The sulfur concentration in the test sample shall be less than the concentration of the highest standard and greater than the concentration of the lowest standard used in the calibration. If required, a dilution should be performed on either a weight or volume basis.

F.7.2 Gravimetric Dilution, (mass/mass)—Record the mass of the test sample and the total mass of the sample and solvent.

F.7.3 Volumetric Dilution, (mass/volume)—Record the mass of the test sample and the total volume of the test sample and solvent. Flush the sampling syringe several times with the unknown sample. Determine the sulfur concentration using one of the procedures described in F.6.3–F.6.8. Inspect the combustion tube and other flow path components to verify complete oxidation of the test sample.



Oxidative sulfur system: Thiophene in cyclohexane (10 ppm S) using 0.06% azide electrolyte

	Flow rate (cc/min)		
Legend	Oxygen	Argon	O_2/Ar ratio
⊙——⊙	40	160	1:4
□- - -□	100	100	1:1
△——△	160	40	4:1

FIG. F-3 Percent Recovery versus Temperature (°C)

F.7.4 Boat Inlet Systems—Reduce the boat drive introduction rate, sample size, or both, if coke or soot is observed on the exit end of the pyrolysis tube. Increase the residence time for the boat in the oxidation zone of the furnace if coke or soot is observed on the boat after the analysis is finished.

F.7.5 Syringe Inlet Systems—Reduce the sample size, rate of injection, or both, for the direct injection the test sample into the furnace if coke or soot is observed on the exit end of the pyrolysis tube.

F.7.6 Cleaning and Recalibration—Clean any coked or sooted parts per the manufacturer's instructions. Assemble andleak check the apparatus per the manufacturer's instructions after any cleaning or adjustment. Repeat instrument calibration prior to reanalysis of test samples.

F.7.8 To obtain one result measure each test sample solution three times and calculate the average value. If the sample size is determined by volume, density values needed for calculations are to be measured at the temperature at which the sample was tested. If the sample size was determined by weight, density values are not required.

F.8 Calculation

F.8.1 Calculate the sulfur concentration in the test sample in mg/kg (ppm) as follows:

$$\text{Sulfur, mg/kg (ppm)} = \frac{C \times 1000}{M \times K} \text{ or}$$

$$\text{Sulfur, mg/kg (ppm)} = \frac{C \times 1000}{V \times D}$$

where:

C = sulfur found in test sample (either directly from the instrument or calculated manually from the calibration curve), µg.

K = gravimetric dilution factor, mass of test sample/mass of test sample and solvent, g/g.

M = mass of test sample solution injected, either directly measured or calculated from measured volume injected and density, V × D, mg.

V = volume of test sample solution injected, either measured directly or calculated from measured mass injected and density, M/D, µL.

D = density of sample, g/mL. 1000 = Factor to convert µg/mg to mg/kg (ppm).

Annex G
Neutrality Test (Reaction of Non-Volatile Residue)

G.1 **Reagent**
Methyl orange shall be used as an indicator.

G.2 **Procedure**
Dissolve 0.01g of methyl orange in 100ml of water.
To a conical flask containing the non-volatile residue as in KS 914, add 100ml of distilled water and shake the contents thoroughly. Transfer the clean aqueous layer to a clean test tube by means of a pipette. Add one drop of methyl orange solution.
The residue shall be taken to have passed the test if no pink or red colour is formed.