THE INSTITUTE
OF PETROLEUM

STANDARD METHODS

FOR ANALYSIS AND TESTING OF PETROLEUM AND RELATED PRODUCTS AND BRITISH STANDARD 2000 PARTS

2001

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FOR ANALYSIS AND TESTING OF PETROLEUM AND RELATED PRODUCTS AND BRITISH STANDARD 2000 PARTS 2001

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SAFETY PRECAUTIONS

The methods in this book do not purport to address all of the safety problems associated with their use. It is the responsibility of the user of these methods to establish appropriate safety and health practises and determine the applicability of regulatory limitations.

In addition manufacturers guidelines and recommendations for the use of chemicals and equipment shall be consulted.

Notice to Users

It has been assumed by the compilers that all users of this book will, if not themselves fully trained, at least be under the supervision of a responsible trained person who will be familiar with all normal laboratory practice, and engineering practice as appropriate, and safety precautions, and that all such precautions will be observed. It is the responsibility of users to ensure that the requirements of the Health and Safety at Work etc. Act, 1974 are fully complied with.

It has also been assumed that reagents of adequate purity will be used, along with apparatus and equipment of correct specification, properly maintained. Specification for reagents, apparatus and equipment are given in manufacturers' catalogues and various standards, specifications, etc.

There are numerous handbooks on first aid, and on laboratory safety such as that issued by the Royal Society of Chemistry. Refer also to the current issue of "Guidance Note EH40 Occupational Exposure Limits" issued by the Health and Safety Executive in the UK (or the latest publication of "Documentation of Threshold Limit Values for Substances in Workroom Air" published by the American Conference of Governmental Industrial Hygienists).

Where the compilers considered that a special hazard exists, attention has been drawn to this in the text. It cannot be too strongly emphasized that prompt first aid, decontamination, or administration of the correct antidote can save life, but that incorrect treatment can make matters worse.

It is emphasized that both supervisors and operators should be familiar with emergency procedures before starting an operation involving any degree of hazard. Should any accident involving chemical contamination of the skin, ingestion or inhalation be such that medical attention is necessary, a doctor consulted should be made fully aware of the chemical composition of the contaminant and given any other relevant information which would assist him in deciding what specific treatment should be given. Such information might be obtained from technical data sheets from the supplier or from the label on the chemical container.

CONTENTS

IP 342/2000 ISO 3012 : 1999 ASTM D3227-96 BS 2000 : Part 342 : 2000

Petroleum products — Determination of thiol (mercaptan) sulfur in light and middle distillate fuels — Potentiometric method

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a method for the determination of thiol (mercaptan) sulfur in light distillates, such as gasolines and naphtha fractions, and middle distillate fuels, such as kerosines and gas oils, in the range of 0,000 3 % (*m/m*) to 0,010 0 % (*m/m*) (3 mg/kg to 100 mg/kg). Organic sulfur compounds such as sulfides, disulfides and thiophene do not interfere. Elemental sulfur does not interfere at contents less than 0,000 5 % (*m/m*). Hydrogen sulfide interferes, if not removed as described in 8.2.

NOTE For the purposes of this International Standard, the term "% (*m/m*)" is used to represent the mass fraction of a material.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 3170:1988, *Petroleum liquids — Manual sampling.*

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling.*

[SO 3675:1998, *Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 12185:1996, *Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method.*

3 Principle

A hydrogen sulfide-free sample is dissolved in an alcoholic sodium acetate titration solvent and the solution obtained is titrated potentiometrically with silver nitrate standard alcoholic solution, using as an indicator the potential between a glass reference electrode and a silver/silver sulfide indicating electrode. Under these conditions, the mercaptan sulfur is precipitated as silver mercaptide, and the end-point of the titration is shown by an inflection point in the curve of titrated volume versus cell potential.

4 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade. All references to water shall be understood to mean water conforming to grade 3 of ISO 3696.

4.1 Propan-2-ol, of 99 % minimum purity.

It is important that all propan-2-ol used in this analysis is free from peroxides. Either ensure that the alcohol is free from peroxides by analysis, or pass it through a column of activated alumina to remove peroxides that may have formed during storage.

4.2 Cadmium sulfate acid solution

For referee analysis, dissolve 150 g ± 1 g of cadmium sulfate ($3CdSO_4 \cdot 8H_2O$) in water, add 10 ml of approximately 16 % (*m/m*) sulfuric acid and dilute to 1 litre with water.

For routine analysis, use sodium hydrogen carbonate (4.2.1).

WARNING — Cadmium sulfate is toxic, and shall be disposed of as environmental toxic waste.

4.2.1 Sodium hydrogen carbonate solution

Dissolve 50 g ± 1 g of sodium hydrogen carbonate ($NaHCO_3$) in water, and make up to 1 litre. Since sodium sulfide is colourless, the removal of hydrogen sulfide shall be confirmed by the use of lead acetate paper (4.2.2).

4.2.2 Lead acetate paper

Soak strips of filter paper in a 5 % (*m/m*) solution of lead acetate [$(CH_3COO)_2Pb \cdot 3H_2O$] in water, and allow to dry in a closed container.

4.3 Potassium iodide solution

Dissolve 17,0 g ± 0,5 g of potassium iodide (KI), weighed to the nearest 0,01 g, in 100 ml of water and dilute to 1 000 ml in a volumetric flask with propan-2-ol (4.1). Calculate the concentration in moles per litre.

4.4 Silver nitrate solutions

4.4.1 Preparation of 0,1 mol/l solution

Dissolve 17,0 g ± 0,5 g of silver nitrate ($AgNO_3$) in 100 ml of water and dilute to 1 litre with propan-2-ol (4.1). Store in a dark bottle and standardize at intervals frequent enough to detect a change of 0,000 5 mol/l or greater.

4.4.2 Standardization

Add 6 drops of concentrated nitric acid [HNO_3 = 35 % (*m/m*)] to 100 ml of water in a 300 ml tall-form beaker and boil for 5 min. Cool to ambient temperature and pipette 5 ml of potassium iodide solution (4.3) into the beaker. Titrate with the silver nitrate solution, choosing the end-point at the inflection of the titration curve.

4.4.3 Preparation of 0,01 mol/l solution

Prepare daily by the dilution of 100 ml of 0,1 mol/l solution (4.4.1) to 1 000 ml with propan-2-ol (4.1) in a volumetric flask.

NOTE Commercial standard volumetric solutions are suitable.

4.5 Sodium sulfide solution

Prepare daily by dissolving 10 g of sodium sulfide (Na_2S) in water and diluting to 1 litre.

NOTE Anhydrous sodium sulfide is not widely available, and is expensive. An aqueous solution of hydrated sodium sulfide ($Na_2S \cdot 9H_2O$) at 30,5 g/l is satisfactory.

4.6 Titration solvents

Mercaptans of low molecular mass, as usually found in light distillates, are readily lost from the titration solution if an acidic titration solvent is used. For the determination of mercaptans of higher molecular mass, as found in middle distillates, the acidic titration solvent is used to achieve more rapid equilibrium between successive additions of the titrant.

4.6.1 Alkaline titration solvent

Dissolve 2,7 g of sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$) or 1,6 g of anhydrous sodium acetate (CH_3COONa) in 25 ml of oxygen-free water, and pour into 975 ml of propan-2-ol (4.1). Remove dissolved oxygen by purging the solution with a rapid stream of nitrogen for 10 min each day prior to use. Keep the solvent protected from the atmosphere.

4.6.2 Acidic titration solvent

Dissolve 2,7 g of sodium acetate trihydrate or 1,6 g of anhydrous sodium acetate in 20 ml of oxygen-free water, and pour into 975 ml of propan-2-ol (4.1) and add 4,6 ml of glacial acetic acid. Remove dissolved oxygen by purging the solution with a rapid stream of nitrogen for 10 min each day prior to use. Keep the solvent protected from the atmosphere.

5 Apparatus

Any automatic titration system that meets the precision requirements of this International Standard, and is capable of selecting the end-points specified in clause 8, is suitable. Subclauses 5.1 to 5.4 describe a manual system.

5.1 Titration burette, conforming to the requirements of ISO 385-1, of 10 ml capacity, graduated in 0,05 ml intervals, and with a tip that extends approximately 120 mm below the stopcock.

5.2 Cell system, consisting of a reference electrode and an indicating electrode.

The reference electrode shall be a sturdy, pencil-type glass electrode, having a shielded lead connected to earth (ground). The indicating electrode shall be made from a silver wire, 2 mm in diameter or larger, mounted in an insulated support.

NOTE A silver billet electrode is also suitable as an indicating electrode.

5.3 Electronic voltmeter, operating on an input of less than 9×10^{-12} A, and having a sensitivity of ± 2 mV over a range of at least ± 1 V.

The voltmeter shall be electrostatically shielded, and the shield shall be connected to earth (ground).

5.4 Titration stand, preferably built as an integral part of the meter housing and provided with supports for the electrodes and electrical stirrer, all connected to earth (ground).

No permanent change in the meter reading shall be noticeable upon connecting or disconnecting the stirrer motor.

5.5 Abrasive paper or cloth, having an average particle size of 18 µm (800 grit).

6 Samples and sampling

6.1 Unless otherwise specified, samples shall be obtained by the procedures given in ISO 3170 or ISO 3171.

6.2 Samples of light distillates shall be kept cold (< 4 °C) to avoid loss of volatile components containing thiols. When analyzing light distillates with high thiol content, the titration solvent, and preferably the titration burette and pipette for measuring the test portion, shall also be cooled to a similar temperature, and the analysis shall be carried out as soon as possible after removal from the cooling chamber.

NOTE Light naphtha fractions of high thiol content (> 100 mg/kg) boiling below 85 °C have been shown to be very sensitive to the titration temperature.

7 Preparation of apparatus

7.1 Glass electrodes

After each manual titration, or batch of titrations in the case of automatic titration systems, wipe the electrode with a soft clean tissue and rinse with water. Clean the electrode at frequent intervals (at least once per week) by stirring in strong oxidizing acid solution for 5 s to 10 s. When not in use, keep the lower half of the electrode immersed in water.

NOTE Chromosulfuric acid was historically the reference strong oxidizing acid cleaning solution, but users are recommended to use a non chromium-containing alternative to obtain equivalent cleanliness.

7.2 Silver/silver sulfide electrode

7.2.1 Prior to use, prepare a fresh silver sulfide coating on the electrode by the method given in 7.2.2 to 7.2.6.

7.2.2 Burnish with an abrasive paper or cloth (5.5) until a clean, polished surface shows.

7.2.3 Place the electrode in the operating position and immerse it in 100 ml of titration solvent (4.6) containing 8 ml of sodium sulfide solution (4.5).

7.2.4 Add slowly from a burette, while stirring, 10 ml of 0,1 mol/l silver nitrate solution (4.4.1) over a period of 10 min to 15 min.

7.2.5 Remove the electrode from the solution, wash with water, and wipe with a soft, clean tissue.

7.2.6 Between manual titrations, or batches of titrations in the case of automatic titration systems, store the electrode for at least 5 min in 100 ml of titration solvent (4.6) containing 0,5 ml of 0,1 mol/l silver nitrate solution (4.4.1).

8 Procedure

8.1 Determination of density

If the sample is to be measured volumetrically, determine the density in accordance with ISO 3675 or ISO 12185 at the temperature at which the test portion will be taken.

NOTE The density may be calculated from determined density at a reference temperature by use of the Petroleum Measurement Tables (ISO 91-1 or ISO 91-2).

8.2 Removal of hydrogen sulfide

Test the sample qualitatively for hydrogen sulfide by shaking 5 ml of the sample with 5 ml of the cadmium sulfate acid solution (4.2), or by immersion of a small strip of lead acetate paper (4.2.2). If no precipitate appears with the cadmium sulfate acid solution, or the colour of the lead acetate paper does not change to brown or black, proceed as described in 8.3. If a yellow precipitate appears with cadmium sulfate, or the lead acetate paper changes colour, remove the hydrogen sulfide as described in 8.2.1 or 8.2.2.

8.2.1 *Cadmium sulfate acid solution method*

8.2.1.1 Place a quantity of the sample (three to four times that required for the analysis) in a separating funnel containing a volume of the cadmium sulfate acid solution (4.2) equal to one-half that of the sample, and shake vigorously.

8.2.1.2 Draw off and discard the aqueous phase containing the yellow precipitate. Repeat the extraction with a fresh portion of cadmium sulfate acid solution, discarding the aqueous phase. Wash the sample with three 25 ml to 30 ml portions of water, discarding the aqueous phase after each washing.

8.2.1.3 Filter the washed sample through a qualitative filter paper, and test a small portion of the washed and filtered sample with an approximately equal volume of the cadmium sulfate acid solution.

8.2.1.4 If no further precipitate is formed, proceed as described in 8.3.

8.2.1.5 If a precipitate appears, repeat the extraction and filtration described in 8.2.1.1 to 8.2.1.3 until all of the hydrogen sulfide has been removed.

8.2.2 Sodium hydrogen carbonate solution method

8.2.2.1 Place a quantity of the sample (three to four times that required for analysis) in a separating funnel containing a volume of the sodium hydrogen carbonate solution (4.2.1) equal to one-half that of the sample, and shake vigorously.

8.2.2.2 Draw off and discard the aqueous phase, and check for the existence of hydrogen sulfide in the sample phase with lead acetate paper as described in 8.2.

8.2.2.3 If hydrogen sulfide is still present in the sample phase, repeat the washing with successive portions of sodium hydrogen carbonate solution until no hydrogen sulfide is detected.

8.2.2.4 Wash the sample phase with 30 ml to 50 ml of water, shaking vigorously, and discard the aqueous phase.

8.3 Analysis of sample

8.3.1 Either measure with a pipette, or weigh, 20 ml to 50 ml of the original or treated sample into a 300 ml beaker containing 100 ml of the appropriate titration solvent (4.6). Place the beaker on the titration stand (5.4) or on the autosampler carousel of an automatic titration system. Adjust the position of the titration stand so that the electrodes are about half-immersed. Fill the burette (5.1) with 0,01 mol/l silver nitrate solution (4.4.3), and position it in the titration assembly so that the tip extends approximately 25 mm below the surface of the liquid in the beaker. Adjust the speed of the stirrer to give vigorous stirring without spattering.

NOTE 1 Samples with a thiol content above 0,010 0 % (*m/m*) (100 mg/kg) may be analyzed by an appropriate reduction in test portion mass, ensuring that the minimum volume of titration solvent plus test portion exceeds 120 ml. If additional titration solvent is used to maintain this requirement, a similar volume should be used for the blank titration (8.4). No precision has been determined for thiol contents above 0,010 0 % (*m/m*) (100 mg/kg).

NOTE 2 If an automatic titration system is used, appropriate modifications to 8.3.1 to 8.3.4, in line with the manufacturer's instructions, may be made.

8.3.2 Record the initial burette and cell-potential readings. Add suitable small portions of the silver nitrate solution and, after waiting until a constant potential has been established, record the burette and voltmeter readings.

NOTE 1 The usual voltmeter readings for mercaptan presence are in the range −250 mV to −350 mV.

NOTE 2 If potential readings obtained with freshly prepared electrodes are erratic, it is possible that the electrodes are not properly conditioned. This difficulty usually disappears in succeeding titrations.

NOTE 3 A cell potential is considered constant if it changes by less than 6 mV/min.

NOTE 4 With certain instruments, the algebraic sign of the potential may appear reversed.

8.3.3 When the change of potential is small for each increment of silver nitrate solution, add volumes as large as 0,5 ml. When the change of potential becomes greater than 6 mV per 0,1 ml, use 0,05 ml increments of silver nitrate solution. Near the end-point of the titration, 5 min or 10 min may elapse before a constant potential is obtained. Nevertheless, it is important that the duration of the titration be as short as possible in order to avoid oxidation of the sulfur compounds by atmospheric oxygen. Once started, a titration shall never be interrupted and resumed later.

8.3.4 Continue the titration until the meter reading change of the cell potential per 0,1 ml of silver nitrate solution has become relatively constant (see note 1 in 8.3.1). Remove the titrated solution, rinse the electrodes well with propan-2-ol (4.1), and wipe them with a clean, dry tissue. If an automatic titration system is used, rinse the electrodes well with propan-2-ol, allow the excess to drain off the electrodes, and then proceed with the next sample. Between successive determinations (or batches of determinations in the case of an automatic titration system) on the same day, store electrodes as described in 7.1 and 7.2.5.

8.4 Blank determination

Carry out the procedures described in 8.3.1 to 8.3.4 on 100 ml (see note 1 in 8.3.1) of the appropriate titration solvent, omitting the test portion addition. Record the volume of 0,01 mol/l silver nitrate solution used to reach the end-point.

9 Interpretation of results

9.1 Treatment of data

Plot the cumulative volumes of 0,01 mol/l silver nitrate solution (4.4.3) added against the corresponding cell potentials. Select the end-point at the most positive value of the steepest portion of each "break" in the titration curve, as shown in Figure 1. The shape of the titration curve may change with different instruments. However, the above interpretation of end-point shall be followed.

9.2 Thiols (mercaptans) only

If mercaptans alone are present in the sample, the titration produces a curve of the first type shown in Figure 1, having a plateau in the vicinity of −300 mV to −350 mV and an end-point at approximately +300 mV.

9.3 Mercaptans and elemental sulfur

9.3.1 When elemental sulfur and mercaptans are both present in the sample, a chemical interaction occurs which, in the titration solvent used, precipitates silver sulfide during the titration.

9.3.2 When mercaptans are present in excess, the end of the silver sulfide precipitation occurs at approximately −500 mV, and is followed by the precipitation of the silver mercaptide at the +300 mV end-point. This situation is shown by the middle curve of Figure 1. Since all of the silver sulfide originates from an original amount of mercaptan, the total titration to the mercaptide end-point shall be used to calculate the amount of mercaptan sulfur.

9.3.3 When elemental sulfur is present in excess, the end of the silver sulfide precipitation

is taken in the same region (+300 mV) as in the case of silver mercaptide, and the elemental sulfur is calculated as mercaptan sulfur.

10 Calculation

Calculate the thiol (mercaptan) sulfur content of the sample, w_S, as a percentage by mass [% (*m/m*)], using the following equation.

$$w_S = \frac{(V_1 - V_0) \times c \times 3{,}206}{m}$$

where

V_1 is the volume, in millilitres, of titrant required to titrate the sample to the end-point;

V_0 is the volume, in millilitres, of titrant required to titrate the blank to the end-point;

c is the concentration of the silver nitrate solution, in moles per litre;

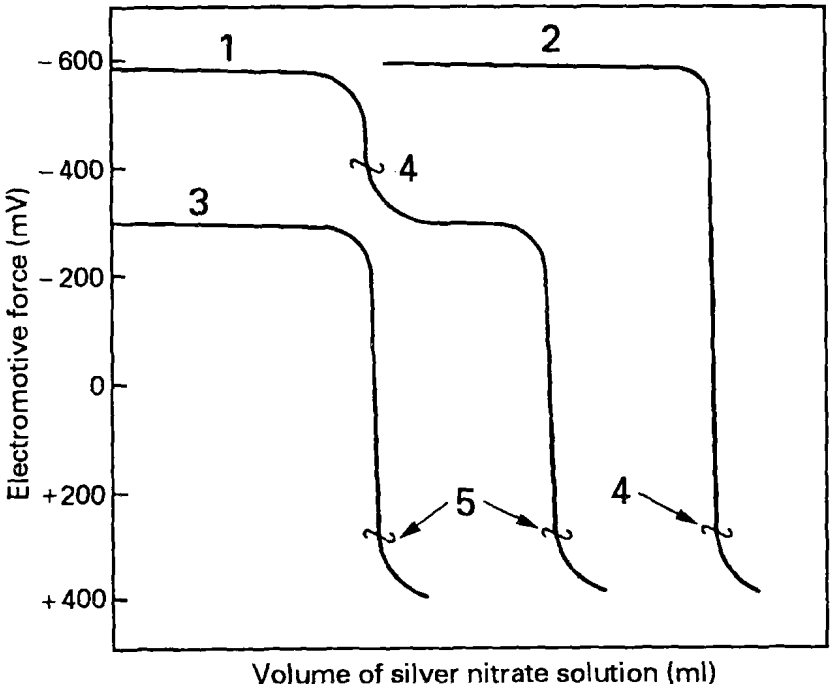
m is the mass, in grams, of the test portion;

3,206 is 100 times the relative millimolar mass of sulfur in mercaptan.

NOTE If measured volumetrically, the mass of test portion mass is equal to the volume times the density at the temperature of measurement (see 8.1).

11 Expression of results

Report the result to the nearest 0,000 1 % (*m/m*) or to the nearest 1 mg/kg.



Key

1 Elemental sulfur + excess mercaptans
2 Mercaptans + excess sulfur
3 Mercaptans alone
4 Silver sulfide
5 Silver mercaptide

Figure 1 — Examples of potentiometric titration curves

12 Precision

12.1 General

The precision, as determined by statistical examination of interlaboratory test results, is given in 12.2 and 12.3, and is illustrated in Figure 2.

12.2 Repeatability

The difference between two 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 the following value in only one case in twenty.

$$r = 0{,}000\ 07 + 0{,}027\ \bar{X}$$

where $\bar{X}$ is the average of the values being compared.

12.3 Reproducibility

The difference between two single and independent test results obtained by different operators working in different laboratories on identical test material would in the long run, in the normal and correct operation of the test method, exceed the following value in only one case in twenty.

$$R = 0{,}000\ 31 + 0{,}042\ \bar{X}$$

where $\bar{X}$ is the average of the values being compared.

13 Test report

The test report shall contain at least the following information:

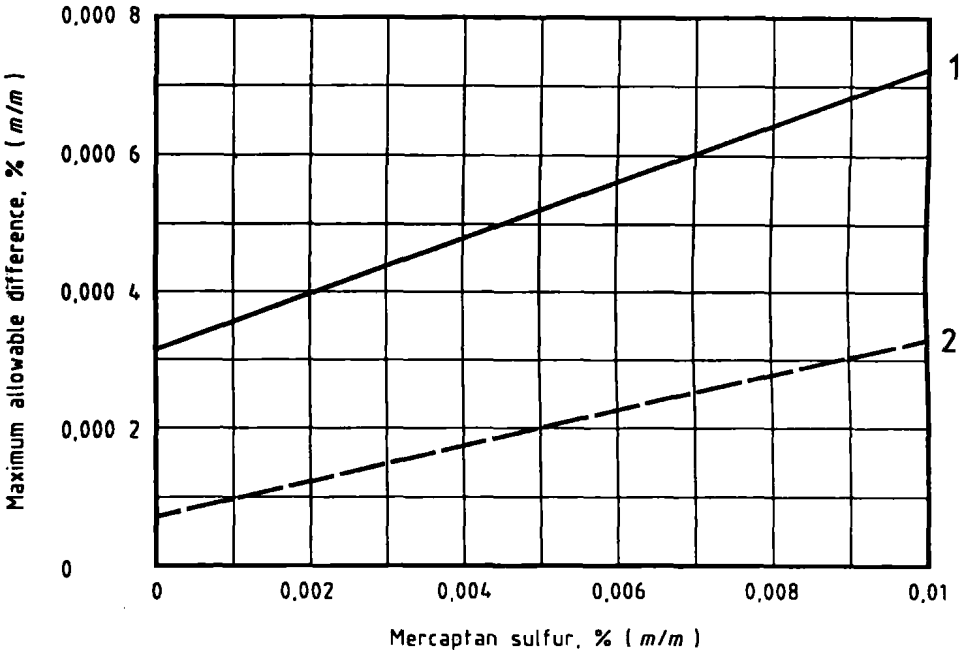
a) a reference to this International Standard;

b) the type and complete identification of the product tested;

c) the result of the test (see clause 11);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.



Key

1 Reproducibility
2 Repeatability

Figure 2 — Precision curves

Bibliography

[1] ISO 91-1:1992, *Petroleum measurement tables — Part 1: Tables based on reference temperatures of 15 °C and 60 °F.*

[2] ISO 91-2:1991, Petroleum measurement tables — Part 2: Tables based on a reference temperature of 20 °C.

Determination of 2,4-dimethyl-6-tertiary-butyl phenol content of aviation turbine fuel – High performance liquid chromatography method

1. SCOPE

1.1. This method is intended for the direct quantitative determination of commercial 2,4-dimethyl,6-tertiary butyl phenol (24M6B) in aviation turbine fuels, over the concentration range 5–40 mg/litre.

2. SUMMARY OF METHOD

2.1. A suitable sample volume is introduced to a high-efficiency liquid chromatograph equipped with a suitable adsorption column, pump, ultra-violet absorption detector monitoring at 280 nm, and strip chart recorder or data system. The concentration of 24M6B in the sample is obtained by comparing its peak height or area with that produced by a standard solution of 24M6B, of similar concentration, chromatographed under identical experimental conditions.

3. APPARATUS

3.1. Any liquid chromatograph capable of meeting the required operating conditions, fitted with an ultra-violet detector monitoring at 280 nm. The detector must have sufficient sensitivity to obtain a peak height of at least twice the noise level of 1 mg/litre of 24M6B under the specified operating conditions. A sample introduction system is required so that up to 10 µl of sample can be admitted to the column. The sample volume must be reproducible such that successive runs agree to within 3 mm or 3% (whichever is the greater) of the measured 24M6B peak height or area.

4. MATERIALS[1]

4.1. *Stationary Phase* – see Appendix A1, Table A1.

4.2. *Mobile Phase* – solvents of spectroscopic quality – see Table A1.

4.3. *Commercial Grade 2,4-Dimethyl-6-tertiary butyl phenol* – normally 85% approximately.

5. PREPARATION OF APPARATUS

5.1. Set up the chromatograph with a combination of column and mobile phase selected as described in Appendix A1.

5.2. Set the detector wavelength to 280 nm.

5.3. Adjust the recorder chart speed to 60 mm/min.

5.4. Prepare a synthetic blend containing approximately 20 mg/litre of 24M6B in mobile phase.

5.5. When operating conditions are steady, as indicated by a stable baseline, inject 10 µl of the synthetic blend and measure the retention time of 24M6B. Adjust the concentration of the more polar component of the mobile phase so that the inhibitor emerges as a separate peak (see Fig. 1).

5.6. Adjust the detector sensitivity so that the height of the 24M6B peak corresponds to at least 50% full-scale deflection.

NOTE 1: Alternatively a computer data system or integrater may be used to collect peak height, peak area and peak retention time data.

6. CALIBRATION

6.1. Accurately prepare a series of standard solutions of 24M6B in mobile phase to cover the range 3 to 40 mg/litre.

6.2. Using the experimental conditions established in Section 5, inject 10-µl portions of each of the standard solutions.

6.3. Measure the height or area of each peak. Check that a plot of peak height or area against concentration of 24M6B is linear. Departure from linearity could indicate that either the mobile phase

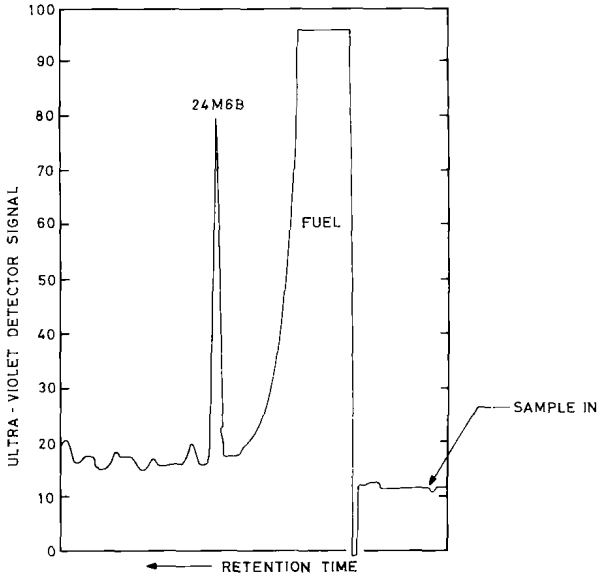


Fig. 1. Typical chromatogram of blend containing 24M6B.

[1] A list of suppliers may be obtained on application to the Institute of Petroleum.

flow rate is inconstant, the detector is unstable, or that the column has not reached equilibrium.

7. PROCEDURE

7.1. Using the same conditions as used for Calibration (Section 6), inject 10 µl of sample. Measure the height of the peak attributed to 24M6B.

8. CALCULATION

8.1. Calculate the concentration of 24M6B from the following expression:

$$\text{24M6B (mg/litre)} = \frac{\text{Peak height of 24M6B in sample}}{\text{Peak height of 24M6B in standard}} \times \text{Concentration of standard solution}$$

8.2. Alternatively use the computer data system to plot a linear calibration curve and use this to calculate the concentration of 24M6B in the sample.

$$y = mP + c$$

Where:

y is mg/l 24M6B
m is the slope of the calibration curve
P is the peak height or area of the 24M6B standard
c is the intercept.

9. REPORTING

9.1. Report the results as mg/litre of commercial 2,4-dimethyl,6-tertiary butyl phenol, to the nearest 0.5 mg/litre, IP 343.

10. PRECISION

10.1. The precision of this method is as follows:

$$\text{Repeatability } 0.584\sqrt{x}$$
$$\text{Reproducibility } 1.467\sqrt{x}$$

where x is the average of the two results in mg/litre. Precision values for typical values of x are given in Table 1. These values (as defined in Appendix E) have been obtained by statistical examination of inter-laboratory results, and were first published in 1980.

TABLE 1. Precision data for typical values (mg/litre)

x	Repeatability	Reproducibility
5	1.31	3.28
10	1.85	4.64
15	2.26	5.68
20	2.61	6.56
25	2.92	7.34
30	3.20	8.04
35	3.46	8.68
40	3.70	9.28

x is the average of the two determinations.

NOTE 2: The types of samples used in the inter-laboratory study were production samples of an aviation turbine fuel to which known amounts of 24M6B had been added.

APPENDIX A1

COLUMNS AND CONDITIONS

A1.1. The columns and conditions given in Table A1 have been used successfully for this analysis in co-operative work. Columns and conditions other than those listed may be used provided they are capable of meeting the sensitivity, separation and precision requirements of the method.

TABLE A1. Experimental conditions used in establishment of precision data

Stationary phase	Partisil	Spherisorb	Partisil	Partisil	Partisil
Nominal particle size, μm	5	5	10	5	5
Column length, mm	250	200	250	200	200
Column diameter, mm	4.6	4.6	4.6	5.0	5.0
Mobile phase, v/v	20% dichloromethane 80% cyclohexane	100% cyclohexane	1% ethyl acetate 99% *n*-heptane	1% acetonitrile* 99% *n*-hexane	20% dichloromethane 80% *n*-hexane
Flow rate, ml/min	1.0	6.0	1.0	1.0	1.0
Inlet pressure, bar	55	138	28	21	21
Efficiency, plates/m (for 24M6B)	32,000	9,300	23,700	50,000	50,000
Retention time, min	7	5.8	10.5	7.5	7.0

Stationary phase	Cyano-Sil-X	Partisil	Partisil PAC	LiChrosorb SI 60	LiChrosorb SI 60	LiChrosorb D10L
Nominal particle size, μm	13	10	10	5	5	10
Column length, mm	500	250	250	250	150	125
Column diameter, mm	2.6	4.6	4.6	4.6	5.0	5.0
Mobile phase, v/v	0.03% isopropanol 99.7% iso-octane	20% dichloromethane 80% *n*-hexane	20% dichloromethane 80% *n*-hexane	0.5% acetonitrile* 99.5% *n*-heptane	10% dichloromethane 90% iso-octane	0.1% ethanol 99.9% iso-octane
Flow rate, ml/min	1.5	2.0	3.0	1.1	1.0	1.1
Inlet pressure, bar	28	28	41	—	—	—
Efficiency, plates/m (for 24M6B)	1,700	22,000	20,000	28,000	51,300	22,500
Retention time, min	8.0	6.0	4.5	10	2.5	5.5

* Because of the toxic properties of acetonitrile this mobile phase is the least recommended.