

**BRITISH STANDARD**

This Standard is confirmed.  
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*February 1998*

**BS 2000 :  
Part 346 : 1996**

**Methods of test for**

# **Petroleum and its products**

**Part 346. Determination of polycyclic  
aromatics in unused lubricating base oils and  
asphaltene free petroleum fractions - Dimethyl  
sulphoxide extraction refractive index method**

**(Identical with IP 346/96)**

Confirmed  
January 2010

**BSi**  
British Standards

## National foreword

This British Standard was published under the authority of the Materials and Chemicals Sector Board and comes into effect on 29 February 1996.

BS 2000 comprises a series of test methods for petroleum and its products that are published by the Institute of Petroleum (IP) and have been accorded the status of a British Standard. Each method should be read in conjunction with the preliminary pages of 'IP Standard methods for analysis and testing of petroleum and related products' which gives details of the BSI/IP agreement for publication of the series, provides general information on safety precautions, sampling and other matters, and lists the methods published as Parts of BS 2000.

The numbering of the Parts of BS 2000 follows that of the corresponding methods published in 'IP Standard methods for analysis and testing of petroleum and related products'. Under the terms of the agreement between BSI and the Institute of Petroleum, BS 2000 : Part 346 will be published by the IP (in 'Standard methods for analysis and testing of petroleum and related products' and as a separate publication). BS 2000 : Part 346 : 1996 is thus identical with IP 346/96.

**Compliance with a British Standard does not of itself confer immunity from legal obligations.**

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The following BSI references  
relate to the work of this  
standard:  
Committee reference PTI/13

# Determination of polycyclic aromatics in unused lubricating base oils and asphaltene free petroleum fractions – Dimethyl sulphoxide extraction refractive index method

This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations.

## 1 Scope

1.1 This method specifies the determination of polycyclic aromatics (PCA) over the concentration range 1–15 mass % in unused additive free lubricating base oils having an atmospheric boiling point of 300°C minimum at 5% recovered sample. This method may apply to PCA concentrations outside this range and to other asphaltene-free petroleum fractions, but the precision has not been determined.

## 2 Definition

2.1 Polycyclic aromatics are aromatic hydrocarbons, and related sulphur and nitrogen compounds, containing three or more fused aromatic rings. These rings may have short alkyl or cycloalkyl groups as substituents.

## 3 Principle

3.1 A weighed sample of the oil under test or, if necessary, of the topped oil sample is diluted with cyclohexane and extracted twice with dimethyl sulphoxide at a temperature of  $23 \pm 2^\circ\text{C}$ . The extracts are combined, diluted with an aqueous salt solution, and re-extracted twice with cyclohexane. After washing and drying the cyclohexane extract, the solvent is removed. The PCA residue is weighed and its refractive index is determined to give a measure of the degree of aromaticity.

## 4 Apparatus

4.1 *Drain tray* – Made of a solvent-resistant material.

4.2 *Drying oven* – For glassware.

4.3 *Funnels* – Diameter about 60 mm.

4.4 *Refractometer* – Abbe type, range 1.30–1.71, capable of being operated at 25°C and 80°C.

4.5 *Rotating evaporator* – Equipped with a water or oil bath. The evaporator should be connectable to

atmospheric pressure, water pump vacuum and oil pump vacuum.

4.6 *Flasks* – Round bottomed, of 50 ml, 250 ml and 1000 ml capacity, with ground-glass joints and fitted with hooks for use with safety retaining springs.

4.7 *Vigreux distillation column* – 500 mm.

4.8 *Reflux head*.

4.8.1 Quickfit 'Shell type' vapour divider.

4.8.2. Kontes/Martin type liquid divider.

4.9 *Reflux ratio controller quickfit timer*.

4.10 *Solenoid*.

4.11 *Vacuum measuring gauge*.

4.12 *Separating funnels* – Spherical, of 250 ml and 1000 ml capacity, equipped with ground-glass stoppers and locked, self-lubricating, PTFE stopcocks.

4.13 *McLeod gauge*.

4.14 *Bubble counter*.

4.15 *Heating bath* – Water for temperatures up to 80°C. Oil for temperatures up to 110°C.

## 5 Reagents and materials

5.1 *Cotton wool* – Medicinal quality, oil-free.

5.2 *Cyclohexane* – Analytical reagent grade.

5.3 *Dimethyl sulphoxide (DMSO)* – Analytical reagent grade, clear and completely colourless, purity 99.5% m/m minimum, water content 0.1% maximum. DMSO should be stored in a well-closed, dark-coloured glass bottle with a PTFE screw-cap.

Because of its very hygroscopic nature, excessive exposure to the air should be avoided. Also avoid contact with metals (e.g. copper) which react with DMSO in the presence of air.

**5.4 DMSO, Pre-equilibrated with cyclohexane** – Prepare by shaking in a separating funnel, at 21°C minimum, 900 ml of DMSO and 70 ml of cyclohexane. Allow to separate until the lower layer is completely clear. Draw off and store the lower layer in a well-closed, dark-coloured glass bottle with a PTFE screw-cap.

**5.5 Folded filter papers** – 125 mm diameter.

**5.6 Glass beads** – Diameter 2–3 mm for use as anti-bumping material.

**5.7 Glass wool** – Oil-free.

**5.8 Pentane.**

**5.9 Nitrogen** – Compressed and chemically pure, containing less than 10 ml oxygen per m<sup>3</sup>.

**5.10 Sodium chloride** – Analytical reagent grade.

**5.11 Sodium chloride solution, 4% m/m aqueous** – Dissolve 80 g of sodium chloride in 2 kg of demineralized water.

**5.12 Sodium sulphate** – Anhydrous, analytical reagent grade.

**5.13 Toluene** – Analytical reagent grade.

**CAUTION** — To safeguard the analyst against skin contact, wear gloves impermeable to oil and solvents. It is mandatory also to wear a laboratory coat and safety spectacles. Operate in a well-ventilated hood above a drain tray, preferably in a secluded part of the laboratory used solely for this work. Before removing gloves rinse their outer surface with pentane to remove adhering oil.

During the operation of the test observe adequate measures of personal and laboratory hygiene. For instance, avoid spillage, leakage of the sample or its extract, or breakage of the glass equipment.

Collect all cyclohexane solutions, and PCA extracts after determination of their weight and refractive index, for disposal in a specially reserved container.

When full, arrange safe disposal of its contents. Safely dispose of aqueous DMSO solutions.

## 6 Sampling

**6.1** Samples shall be drawn in accordance with the procedures set out in Petroleum Measurement Manual, Part VI, Sampling, Section 1, Manual Methods, or ISO 3170/BS 3195, Part 1, Petroleum Liquids – Manual Sampling.

**6.2** Samples shall not be taken and stored in plastic containers since volatile material may diffuse through the walls.

## 7 Sample preparation

**7.1** Determine the true boiling range distribution of the oil sample. If the oil sample:

- contains not more than 5% of components boiling below 300°C at 100 kPa, continue the test without preliminary preparation of the sample;
- contains between 5% and 95% of components boiling below 300°C at 100 kPa, top the sample by laboratory fractionation (Section 7.2) and continue the test using the distillation residue;
- contains more than 95% of components boiling below 300°C at 100 kPa report accordingly and add 'The content of PCA extract was not determined'.

**7.2 Procedure for laboratory vacuum fractionation:**

**7.2.1** Place 250 g of sample in a 1000 ml round-bottomed flask equipped with a dip tube for nitrogen purging. Connect the flask to a 500 mm Vigreux column with reflux head, ratio controller and suitable receiver. Connect assembly to a vacuum system equipped with a vacuum measuring device (McLeod gauge).

**7.2.2** Before heating, purge contents of the bottom flask with about 15 l/h of chemically pure nitrogen for 10 min to remove dissolved oxygen.

**7.2.3** Reduce the nitrogen flow rate and evacuate the fractionation assembly, to a pressure of 2 kPa. Maintain a very moderate nitrogen flow (corresponding to a passage of about one bubble per second through a bubble counter) to prevent a boiling lag. Commence heating the bottom flask. When boiling starts and the condensate reaches the column, adjust the heating of the bottom flask in such a way that the load of the column is evenly distributed over its length so as just to avoid flooding at any place in the column.

**7.2.4** Set the reflux ratio at 1:1 (i.e. 2 s closed and 2 s open) and start to collect the distillate.

**7.2.5** When a top temperature of 280°C at 100 kPa is attained, adjust the reflux ratio to 2:1 (4 s closed and 2 s open) and continue collecting the distillate, until a top temperature of 310°C at 100 kPa is reached.

NOTE 1 — Calculate the top temperature (°C) at 100 kPa from the observed temperature at reduced pressure at the top of the column by means of the nomogram for temperature-pressure conversion for petroleum hydrocarbons, according to J. B. Maxwell and L. S. Bonnell, *Ind. Eng. Chem.* **49**, 1187–1196 (1957).

**7.2.6** Set the system at total reflux, switch off the heating of the bottom flask and column and allow the contents of the bottom flask to cool under vacuum to 50–70°C. Increase the nitrogen purging rate, until

atmospheric pressure is reached. Then connect the system to the atmosphere and disconnect the flask containing the residue.

**7.2.7** Weigh the distillate fraction and the residue to the nearest gramme.

NOTE 2 — The loss, i.e. the difference in mass between initial sample (Section 7.2.1) and the sum of the masses of distillate fraction and residue (Section 7.2.7), should not exceed 5 g.

**7.3** If necessary, check that the distillation residue does not contain more than 5% components boiling below 300°C at 100 kPa.

**7.4** Homogenize a representative sample of the oil to be tested. If the sample is viscous and/or waxy, heat to 90°C maximum while stirring. If the heated sample contains any solid material, filter before use.

**7.5** Determine the kinematic viscosity of the oil sample at 100°C by Method IP 71 (see Note 3 in 9.11).

## 8 Apparatus preparation

**8.1** To avoid contamination of the sample with foreign matter during the determination, do not use grease for lubricating taps and joints. Use instead taps and sleeves made of PTFE.

**8.2** Before use, immerse the separating funnels overnight at ambient temperature in a 1.5% m/m aqueous solution of a concentrated cleaning agent for glass laboratory equipment to remove grease and sticky deposits. Wash the cleaned equipment thoroughly, first with tap water, then with demineralized water. Dry in an oven at 70–80°C.

**8.3** Before use, clean the rotating evaporator by distilling about 200 ml of toluene.

## 9 Procedure

**9.1** To the nearest mg weigh into a 50 ml beaker between 3.85 g and 4.15 g of the oil sample, slightly heated if required.

**9.2** Measure 45 ml of cyclohexane in a measuring cylinder and introduce approximately 10 ml of this volume into a 250 ml separating funnel. Using the remaining volume of cyclohexane transfer the contents of the beaker quantitatively to the same separating funnel.

**9.3** Mix the contents by swirling or shaking the separating funnel and add 100 ml of DMSO pre-equilibrated with cyclohexane. Extract at a temperature of  $23 \pm 2^\circ\text{C}$  by shaking vigorously for exactly 1 min (approximately 100 shakes). Allow the layers to separate completely, for a period of at least 20 min. Draw off the lower layer of DMSO extract through a funnel containing a plug of cotton wool into a 1 l separating funnel (Note 1). The DMSO extract thus collected should be completely clear.

NOTE 1 — The plug of cotton wool retains tiny dirt particles which after settling, particularly with highly aromatic oil samples, can collect at the boundary of the two layers.

**9.4** Repeat the extraction of the upper cyclohexane layer with a fresh 100 ml portion of pre-equilibrated DMSO. After complete separation, draw off the lower layer of DMSO extract through the same plug of cotton wool into the same 1 l separating funnel. Wash the cotton wool with 10 ml of pre-equilibrated DMSO and collect the wash liquid in the 1 l separating funnel. Safely dispose of the plug of cotton wool.

**9.5** Add 40 ml of cyclohexane and 400 ml aqueous sodium chloride solution to the 1 l separating funnel containing the combined DMSO extract layers. Shake vigorously for 2 min and allow the two layers to separate completely.

**CAUTION** — The heat of reaction can cause pressure build-up during the procedure (9.5). Therefore ensure that the separating funnel is vented away from the face, into the fume-hood, 2–4 times in the first minute of shaking.

**9.6** Draw off the lower DMSO/water/salt layer into a second 1 l separating funnel. Draw off the upper layer of cyclohexane solution into a 250 ml separating funnel. Rinse the first 1 l separating funnel successively with two portions of 25 ml of cyclohexane and add the washings to the 250 ml separating funnel. Rinse the first 1 l separating funnel with 12 ml of demineralized water and add the wash liquid to the second 1 l separating funnel.

**9.7** Add 40 ml of cyclohexane to the second 1 l separating funnel and shake vigorously for 2 min. After complete separation, draw off and discard the lower layer. Combine the upper layer with the contents of the 250 ml separating funnel. Rinse the second 1 l separating funnel successively with two portions of 5 ml of cyclohexane and add the wash liquid to the 250 ml separating funnel.

**9.8** Wash the combined cyclohexane layers with two portions of 25 ml of the warm aqueous sodium chloride solution (at a temperature of approximately 70°C). Discard the lower aqueous sodium chloride layer. Dry the washed cyclohexane solution by passing it through a funnel containing a folded filter paper and 5 g of anhydrous sodium sulphate. Collect the clear filtrate in a 250 ml round-bottomed flask containing some glass beads. Wash the filter and drying agent with two portions of 8 ml of cyclohexane and collect the wash liquid in the same round-bottomed flask.

NOTE 2 — Filtration can be run continuously and unattended by ensuring that the funnel exit is close to the surface of the drying agent and that the stopper is tightly fitted. With this arrangement a constant head is maintained until filtration is complete.

**9.9** Connect the round-bottomed flask to the rotating evaporator, using safety springs. Adjust the contact thermometer of the heating bath at 80°C and

carefully evaporate the solvent at a pressure of  $1.5 \pm 0.5$  kPa. Apply vacuum gradually to ensure a regular evaporation. When the round-bottomed flask still contains 15 to 17 ml of cyclohexane solution, slowly switch to atmospheric pressure and raise the round-bottomed flask from the heating bath.

**9.10** Add some glass beads to a 50 ml round-bottomed flask and weigh to the nearest 0.1 mg. Transfer the contents of the 250 ml round-bottomed flask quantitatively into the 50 ml flask through a funnel containing a plug of glass wool placed so as to retain the glass beads. Rinse the 250 ml flask successively with three 5 ml portions of cyclohexane and collect the wash liquid in the 50 ml flask.

**9.11** Attach the 50 ml round-bottomed flask to the rotating evaporator, using safety springs. Continue the evaporation of the solvent at a bath temperature of  $80^\circ\text{C}$  and at a pressure of  $1.5 \pm 0.5$  kPa for 1 h (Note 3).

**NOTE 3** — If the original oil sample is very viscous (i.e. kinematic viscosity at  $100^\circ\text{C}$  above  $1.5 \times 10^{-5}$  m<sup>2</sup>/s) its PCA extract tends to retain traces of solvent. In this case start with a heating bath temperature of  $80^\circ\text{C}$  and a pressure of  $1.5 \pm 0.5$  kPa for 15 min, then at  $105$ – $110^\circ\text{C}$  at oil pump vacuum (approximately 0.2 kPa) for a further 1 h.

**9.12** Raise the flask from the heating bath and allow it to cool for 5 min. Release the vacuum, disconnect the flask and clean its outside, if necessary by rinsing with pentane. Wipe the outside with a clean, dry cloth and allow to cool at ambient temperature for 30 min. Weigh the flask to the nearest 0.1 mg. Determine the refractive index of the PCA extract at a temperature of  $25^\circ\text{C}$ , or  $80^\circ\text{C}$  for very viscous or solid extracts.

## 10 Calculation

**10.1** Calculate the content of PCA extract of the original sample by means of the following equation:

$$\text{Content of PCA extract, \% mass} = \frac{100 (C - B)}{A (1 + D/R)}$$

where  $A$  = mass of oil sample, topped if necessary, used in the DMSO extraction,

$B$  = tare mass of the 50 ml round-bottomed flask, including the glass beads,

$C$  = mass of the 50 ml round-bottom flask + glass beads + PCA extract,

$D$  = mass of distillate fraction obtained by topping the oil sample,

$R$  = mass of distillate residue obtained by topping the oil sample.

**10.2** If the original sample was not topped prior to the extraction, use the equation

$$\text{Content of PCA extract, \% mass} = \frac{100 (C - B)}{A}$$

**10.3** Calculate the refractive index of the PCA extract at  $25^\circ\text{C}$  from that measured at  $80^\circ\text{C}$  by means of the equation

$$n_D^{25} = n_D^{80} + 0.0222$$

## 11 Expression of results

**11.1** Report the content of PCA extract, IP 346 to the nearest 0.1% m/m on the original sample, and the refractive index of the PCA extract to the nearest 0.001.

**11.2** If the content of PCA extract is less than 0.05% m/m report 'Content of PCA extract, IP 346, less than 0.1% m/m'.

## 12 Precision

The precision of this method is as follows:

	PCA extract	Refractive index
Repeatability	$0.112 x^{0.7}$	0.004
Reproducibility	$0.228 x^{0.7}$	0.028

where  $x$  is the average of the two PCA extract results. Precision values for typical values of  $x$  are given in Table 1.

These precision values as defined in IP 367/ISO 4259 have been obtained by statistical examination of inter-laboratory results, and were first published in 1980.

**NOTE** — The types of samples used in the inter-laboratory study were lubricating base oils with 95% of components boiling above  $300^\circ\text{C}$ . There were four such samples tested by 11 laboratories, the PCA extract results covered the ranges 1.5% to 14.5% and the refractive index results covered the range 1.574 to 1.674.

Table 1

PCA extract x% mass	Repeatability	Reproducibility
1	0.1	0.2
3	0.2	0.5
5	0.3	0.7
7	0.4	0.9
9	0.5	1.0
11	0.6	1.2
13	0.6	1.3
15	0.7	1.5



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