

British Standard Methods of test for

Petroleum and its products

Part 284. Saponifiable and unsaponifiable matter in oils, fats and waxes

(Identical with IP 284/86)

Méthodes d'essai des produits pétroliers

Partie 284. Matières saponifiables et non saponifiables — huiles, graisses et cires

Verfahren zur Prüfung von Erdöl und Erdölprodukten

Teil 284. Verseifbare und nicht verseifbare Stoffe

Oil, Fats, Waxes
WITHDRAWN

Foreword

BS 2000 comprises a series of test methods for petroleum and its products that have been published previously by the Institute of Petroleum (IP) and have been accorded the status of British Standards. Each method should be read in conjunction with BS 2000 : Part 0 'General introduction', 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 scheduled for publication as Parts of BS 2000. When BS 2000 : Part 0 was first published in 1982, it included a list of more than 60 methods intended for publication in the first group of Parts of BS 2000; it is envisaged that Part 0 will be revised from time to time to take account of the publication of additional methods.

The numbering of the other Parts follows that of the corresponding methods published in 'IP Standards for petroleum and its products, Part 1 Methods for analysis and testing', which in 1987 was retitled 'IP Standard methods for analysis and testing of petroleum and related products. BS 2000 : Part 284 is thus identical with IP 284/86. The previous edition of this Part was identical with IP 284/72(79). In the present revision the changes include the following.

- (a) The hot plate mentioned in previous editions in 3.2 has been superseded by a steam bath.
- (b) Clause 4 on reagents has been modified and renumbered.
- (c) Safety precautions limiting the apparatus used when handling diethylether have been revised.
- (d) Note 1 has been amended to accommodate removal of very volatile hydrocarbons.
- (e) Clause 6 on procedure has been altered to overcome slow separation due to high soap concentration.
- (f) A new note 3 emphasises the importance placed on the requirement of unsaponifiable matter being subjected to further examination.
- (g) Figure 1 has three minor alterations.

During the preparation of this revision a number of modifications to the text of the IP method to be incorporated in the 1988 IP Book were notified by the IP. Of these, typographical corrections have been made to the text of this Part of BS 2000 and other changes have been accommodated by marginal notes.

It is intended to issue further revisions when necessary in line with changes that may be made in subsequent editions of this IP method.

This Part of BS 2000 supersedes BS 2000 : Part 284 : 1982 which is withdrawn.

Caution. Attention is drawn to the safety precautions mentioned in Part 0 of this British Standard and to the safety precautions described in clause 5.

NOTE. The titles of the publications referred to in this Part of BS 2000 are listed on the inside back cover.

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

Method (identical with IP 286/86)**1. SCOPE**

1.1. This method may be used to determine the unsaponifiable and saponifiable matter in blends of mineral and fatty oils. It is also suitable for essentially fatty materials.

1.2. The method is not suitable in the following cases:

1.2.1. If the sample contains products saponifiable with difficulty, such as certain waxes, resins, or esters of higher fatty acids which form sparingly soluble potassium salts.

1.2.2. If the sample contains unsaponifiable constituents of high melting point and low solubility in ether.

1.2.3. If the sample contains highly polymerized fatty oils which form emulsions that can be separated only with difficulty. In this case the procedure may become very cumbersome, if not impossible.

1.3. If free acids are present these will be included in the saponifiable matter.

1.4. The fatty acids and unsaponifiable matter isolated may be examined for identification if this is desired.

2. SUMMARY OF METHOD

2.1. The weighed sample is saponified with alkali solution, and the unsaponifiable matter is separated and weighed. The fatty acids are liberated, separated, and weighed.

3. APPARATUS

3.1. *Flask and Condenser* – a flask, 250 ml capacity, alkali resistant, and chemically clean, to which is attached an adequate water condenser. The straight type condenser shall be fitted to the flask with a ground-glass joint: the mushroom-type shall fit loosely to permit venting of the flask.

3.2. *Steam Bath (or suitable electrically heated mantle)* – as an alternative a conventional rotary evaporator may be used.

3.3. *Oven* – explosion proof, capable of temperature control up to 100°C.

NOTE to 3.1. A flask and a condenser complying respectively with BS 6352 and BS 5922 are suitable.

NOTE to 3.2. Delete the alternative use of rotary evaporator.

CAUTION: See Section 5.1.

3.4. *Two Separating Funnels* – 500 ml.

3.5. *Beaker* – 600 ml.

3.6. *Two Flasks* – 250 ml.

3.7. *Two Stoppered Flasks* – 500 ml.

3.8. *Rotary Evaporator or other distillation apparatus.*

3.9. *Filter Funnels, Filter pack.*

NOTE to 3.4. Separating funnels complying with BS 2021 are suitable.

NOTE to 3.6. Flasks complying with BS 2734 are suitable.

NOTE to 3.7. Flasks complying with BS 6352 are suitable.

4. REAGENTS

4.1. *Alcoholic potassium hydroxide, IM Solution* – Dissolve 56 g of potassium hydroxide in 50 ml of deionised water and make up to 1 litre with alcohol purified as described in 4.2.

4.2. *Alcohol* – absolute alcohol, 95% ethanol or IMS 74 op which has been purified in the following manner:

Dissolve 1.5 g of silver nitrate in about 3 ml of water, add to 1 litre of alcohol in a glass-stoppered bottle, and mix thoroughly. Dissolve 3 g of potassium hydroxide in 10 to 15 ml of warm alcohol. After cooling, add slowly to the alcoholic silver nitrate solution, stirring slightly. Allow the precipitated silver oxide to settle, syphon off the clear supernatant solution, and distil on a steam bath.

4.3. *Diethyl Ether* – weight per ml 0.714–0.716 g at 20°C.

4.4. *Hydrochloric Acid* – approx. 3N.

4.5. *Methyl Orange Solution* – 0.05% aqueous.

4.6. *Phenolphthalein Solution* – 1% in the alcohol.

4.7. *Anhydrous Sodium Sulphate* – ignited (see Note 2, Section 6).

4.8. *Sodium Sulphate Solution* – 10% hydrated salt in water.

4.9. *Potassium Hydroxide Solution* – approx 0.5 N aqueous.

4.10. *Acetone.*

NOTE to clause 4. The designation of the amount-of-substance concentrations in normalities (N) and molarities (M) should be replaced by designation in moles per litre (mol/L).

NOTE to 4.1. 'IM Solution' should be replaced by '1 mol/L Solution'.

NOTE to 4.2. Ethanol and methylated spirits, complying respectively with BS 507 and BS 3591, are suitable. The preferred unit for expressing concentration is percentage by volume; IMS 74 op corresponds to 99.23 % (V/V). (See footnote *)

NOTE to 4.3. 'weight per ml 0.714–0.716 g at 20°C' should be replaced by ' $\rho_{20} = 0.714 - 0.716 \text{ g/mL}$ '.

NOTE to 4.7. Delete reference to Note 2, Section 6.

NOTE to footnote 1. BS 2000 : Part 136 is identical with IP 136.

* Previously IP 136/65, Method B; IP 136/65, Method A is now a joint ASTM-IP method, D94-IP 136.

*It should be noted that the use of industrial methylated spirits is governed by the Methylated Spirits Regulations 1983 (SI 1983 No. 252). It is not permissible to use duty-free ethanol, received under the provisions of the Alcohol Liquors Duties Act 1979 Section 10, for purposes for which industrial methylated spirits is an acceptable alternative to ethanol.

5. SAFETY PRECAUTIONS

5.1. All operations using diethylether must be carried out in a fume cupboard. Ensure that the handling of diethylether is carried out away from flames or other sources of heat as this solvent is extremely flammable. Electric ovens fitted with internal make and break contacts must not be used for removing traces of ether.

5.2. During ether extractions take care to release the pressure at frequent intervals.

6. PROCEDURE

6.1. Use an amount of sample such that not more than half of the potassium hydroxide added reacts in the test [Note 1].

The following quantities are suggested:

For oils containing more than 70% fatty matter – approx 2 g.

For oils containing 30 to 70% fatty matter – approx 5 g.

For oils containing less than 30% fatty matter – approx 10 g.

NOTE 1: If it is known or suspected that very volatile hydrocarbons are present, it is recommended that they be removed from the original material with the aid of some form of diluent trap, the non-volatile residue being subjected to the procedure described below.

6.2. Weigh the oil sample (to the nearest mg) into the saponification flask. Add 50 ml of the alcoholic potassium hydroxide solution. Connect the flask to a reflux condenser and place on the asbestos mat on an electric hot plate (or on a steam heated hot plate). Boil the contents gently for 3 h; 1 h is sufficient for pure fatty oils. Before disconnecting the flask wash down the condenser with 10 ml of alcohol. Cool the contents of the flask and transfer them to a 500 ml separating funnel. Rinse out the flask with 150 ml of water, followed by successive portions of ether to a total of 50 ml. Add all the rinsings to the separating funnel.

6.3. Shake the mixture (**CAUTION: See Section 5.2**) and allow the funnel to stand until the two layers separate and clarify. Drain off the lower aqueous alcoholic layer into the flask used for the saponification.

NOTE 2: If it is found that separation is very slow due to a high soap concentration, it may be helpful to add some anhydrous sodium sulphate or sodium chloride. Separation may be improved by removal of the alcohol with a suitable distillation apparatus. This may affect the quoted precision of the method.

6.4. Drain the ether layer into a second 500 ml funnel containing 20 ml water. If the ether layer contains any solid suspended matter filter it into the funnel using a small, dry, fat-free filter; wash the filter subsequently with small amounts of ether and allow the washings to run into the main ether layer. Transfer the aqueous layer back to the first funnel and extract twice more with 50 ml portions of ether. After each extraction run the aqueous solution back into the saponification flask. Add each ether layer in turn to the second funnel, filtering if necessary. Shake the contents of the funnel gently, allow the layers to separate, then run off the water into the aqueous alcoholic solution contained in the saponification flask.

6.5. *Unsaponifiable Matter* – Add 2–3 ml of dilute hydrochloric acid to the contents of the second separating funnel and shake vigorously. Wash the ethereal solution with 20 ml of water and reject the washings.

6.5.1. Wash the ethereal solution with a further 20 ml of water and transfer these washings to the first separating funnel. Make three successive washings with 20 ml of aqueous potassium hydroxide solution then wash with 20 ml portions of water until the washings are no longer alkaline to phenolphthalein solution. Add all these washings to the first funnel.

6.5.2. Transfer the ethereal solution from the second funnel to a 500 ml flask, rinse the funnel with a little ether and add to the flask. Add 20 ml of ether to the first funnel. Shake gently and allow the phases to separate. Transfer the aqueous layer to the second funnel and wash the ether layer in the first funnel with successive 5 ml portions of water until the washings are no longer alkaline to phenolphthalein solution. Add all washings to the second funnel and transfer the ether layer to the main ether extract in the flask.

NOTE to 6.2. Delete the words 'and place on an asbestos mat on an electric hot plate (or on a steam heated hot plate)'. The flask should be heated using the steam bath or mantle (see 3.2).