

Methods of test for

Petroleum and its products

**Part 149. Petroleum products - Lubricating
oils and additives - Determination of
phosphorus content - Quinoline
phosphomolybdate method**

(Identical with IP 149/93)

Foreword

This British Standard, having been prepared under the direction of the Petroleum Standards Policy Committee, was published under the authority of the Standards Board and comes into effect on 28 February 1993. It is identical with ISO 4265 : 1986, prepared by Technical Committee 28, Petroleum products and lubricants, of the International Organization for Standardization (ISO).

This British Standard supersedes BS 7032 : 1988, which is withdrawn.

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 149 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 149 : 1993 is thus identical with IP 149/93. Square brackets marked in the margin of this IP Standard indicate text that differs from the previous edition.

ISO 4265 was previously published as a British Standard as BS 7032 (now withdrawn) which was subsequently renumbered and issued in the BS 2000 series.

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



Petroleum products — Lubricating oils and additives — Determination of phosphorus content — Quinoline phosphomolybdate method

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. 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 prior to use.

1 Scope and field of application

1.1 This International Standard specifies a quinoline phosphomolybdate method for the determination of the phosphorus content of unused lubricating oil and additive concentrates. The method is applicable to products containing any of the phosphorus compounds in normal use and having phosphorus contents between 0,005 and 10,0 % (m/m).

NOTE — There is no reason to doubt its applicability to filtered, used lubricating oils, but no systematic study of this application has been made.

1.2 The method is free from most interferences because the high insolubility of the quinoline phosphomolybdate precipitate leads to constant composition and freedom from most adsorbed or occluded impurities, especially from cations which would otherwise interfere in the subsequent titration of the precipitate.

NOTE — Barium, calcium, magnesium, zinc, iron, aluminium, alkali salts, citric acid and citrates, chromium up to 18 times the phosphorus content and titanium up to 3,5 times do not interfere with the method.

2 Reference

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

3 Principle

A test portion of known mass is ignited with excess of zinc oxide, whereby phosphorus is converted to phosphate. The residue is dissolved in hydrochloric acid and any sulfide formed is oxidized with potassium bromate. Phosphorus is then precipitated as quinoline phosphomolybdate and determined volumetrically by addition of excess standard volumetric alkali solution and back-titration with standard volumetric acid solution.

NOTE — Additive concentrates are diluted with phosphorus-free white oil to produce a working blend.

4 Reagents and materials

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Zinc oxide, finely divided.

4.2 Potassium bromate, solid.

4.3 Hydrochloric acid, solution, $c(\text{HCl}) \approx 1 \text{ mol/l}$.

4.4 Hydrochloric acid, concentrated solution, 36 % (m/m).

4.5 Sodium molybdate solution.

Dissolve 10 g of sodium hydroxide and 18 g of ammonia-free molybdenum trioxide in 200 ml of water and filter the solution.

NOTE — To avoid high blanks caused by silicate interference, store the solution in a polyethylene container.

4.6 Quinoline, redistilled synthetic or, if this is unobtainable, quinoline freshly distilled from the technical product. Collect the colourless distillate in the boiling range 232 to 238 °C. Store the quinoline in a dark-coloured bottle and in the dark.

4.7 Quinoline solution.

Dissolve 20 ml of the quinoline (4.6) in 800 ml of hot water acidified with 25 ml of the concentrated hydrochloric acid (4.4), add a little paper pulp (see the note), shake well, cool, filter and dilute to 1 litre with water. This solution is stable for about 1 month.

NOTE — Alternatively, a filter pad (5.6) may be dispersed in the solution.

4.8 Hydrochloric acid, standard volumetric solution, $c(\text{HCl}) = 0,1 \text{ mol/l}$, standardized to $\pm 0,001 \text{ mol/l}$.

4.9 Sodium hydroxide, standard volumetric solution, $c(\text{NaOH}) = 0,1 \text{ mol/l}$, standardized to $\pm 0,001 \text{ mol/l}$.

NOTE — To avoid high blanks caused by silicate interference, store the solution in a polyethylene container.

4.10 Phenolphthalein, 1 g/l solution in 95 % (V/V) ethanol.

4.11 Thymol blue, 1 g/l solution in 95 % (V/V) ethanol.

4.12 Mixed indicator.

Mix two volumes of the phenolphthalein solution (4.10) with three volumes of the thymol blue solution (4.11).

4.13 Lead acetate test paper.

4.14 Fluorescein test paper.

Prepare by dipping a strip of filter paper into a 1 g/l solution of fluorescein, sodium salt, in 95 % (V/V) ethanol.

4.15 White oil, containing less than 0,005 % (m/m) of phosphorus.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Silica crucibles, 40 mm internal diameter at the top and 50 mm in height. The internal surface shall be smooth and free from pitting.

5.2 Muffle furnace, capable of maintaining a temperature of 700 ± 25 °C, and fitted with ports to allow air circulation.

5.3 Hot-plate, heated by either electricity or steam, or boiling water-bath.

5.4 Filtering apparatus: a filter flask, of capacity 500 ml, provided with a glass crucible adapter fitted in a rubber bung together with a rubber sleeve.

5.5 Gooch crucible, porcelain, 35 mm diameter at the top.

5.6 Filter pad, 20 mm diameter.

5.7 Beakers, of capacity 25 and 500 ml.

5.8 Conical flask, of capacity 500 ml.

5.9 Burette, of capacity 50 ml, graduated in 0,1 ml subdivisions, complying with the requirements of ISO 385/1.

6 Blending procedure

6.1 For samples having a phosphorus content greater than 0,3 % (m/m), prepare a blend in the white oil (4.15) to give a phosphorus content in the range of 0,1 to 0,3 % (m/m).

6.2 Calculate the mass m_1 , in grams, of the test portion for a 10 g blend, using the equation

$$m_1 = \frac{2}{P}$$

where P is the approximate expected phosphorus content, expressed as a percentage by mass, of the test portion.

Calculate the mass m_2 , in grams, of white oil for an approximate 10 g blend using the equation

$$m_2 = 10 - m_1$$

6.3 Weigh, to the nearest 0,01 g, a test portion of mass m_1 into a 25 ml beaker (see 6.2).

6.4 Weigh, to the nearest 0,01 g, a mass m_2 of white oil (see 6.2).

6.5 Mix the test portion and white oil thoroughly by stirring and warming to approximately 50 °C.

7 Procedure

7.1 Test portion

The mass of test portion to be taken shall be estimated so that it contains not more than 3 mg of phosphorus (see table 1).

Table 1 — Suggested test portion size and volume of sodium hydroxide solution required

Phosphorus content of sample or blend % (m/m)	Approximate mass of test portion	Approximate volume of standard sodium hydroxide solution (4.9) required ¹⁾
	g	ml
0,005	3	1,3
0,010		2,5
0,05		13
0,10		25
> 0,10	1	8
0,20		17
0,30		25

1) See 7.2.8 for use of sodium hydroxide.

7.2 Determination

7.2.1 For additive concentrates, weigh, to the nearest 0.001 g, 1 g of the homogenized blend (6.5) into a silica crucible (5.1).

7.2.2 For lubricating oils, weigh, to the nearest 0.001 g, up to 3 g of the test portion into a silica crucible (5.1).

7.2.3 Cover the test portion with 8 g of the zinc oxide (4.1) and level the surface. Apply heat from a Meker burner to the surface until the zinc oxide becomes red hot, then gently heat the crucible from below with a small bunsen flame so that the oil burns off very gently. Finally, when no more vapour is evolved, ignite strongly and transfer to the muffle furnace (5.2), maintained at $700 \pm 25^\circ\text{C}$, to burn off residual carbon.

7.2.4 Allow the crucible to cool and carefully transfer its contents to a 500 ml beaker (5.7) (see the note), completing the transfer with a jet of water from a wash-bottle. Add about 50 ml of water to the contents of the beaker and rinse the crucible with a few millilitres of the concentrated hydrochloric acid solution (4.4). Add the acid rinsing to the beaker and then add sufficient concentrated hydrochloric acid solution to bring the total volume of acid added to 23 ml. Heat the contents of the beaker until all the zinc oxide is dissolved, then boil the mixture until all hydrogen sulfide has been expelled from the solution [boil until the lead acetate paper (4.13) is not coloured by the vapour].

NOTE — It is recommended that the dissolution of the zinc oxide be conducted under a fume hood with suitable extraction.

Allow to cool slightly, add 30 to 50 mg of the potassium bromate (4.2) and boil the mixture until all free bromine has been expelled from the solution [boil until the fluorescein paper (4.14) is not discoloured by the vapour].

NOTE — Glass apparatus should have good resistance to alkali. Scratched or etched beakers should not be used for the precipitation of quinoline phosphomolybdate.

7.2.5 Dilute the liquid to a volume of about 150 ml with water, add 30 ml of the concentrated hydrochloric acid solution (4.4) and 30 ml of the sodium molybdate solution (4.5), rinsing the sides of the beaker with a little water after each addition. Place the beaker on the hot-plate (5.3) and bring the liquid to the boil. Add a few drops of the quinoline solution (4.7) from a coarse-tipped burette or pipette, swirling the liquid during the addition. Bring it to the boil again and add 2 ml of the quinoline solution drop by drop with swirling. To the gently boiling liquid, add the quinoline solution in 2 to 3 ml increments until a total of 25 ml has been added, swirling during the addition. Stand the beaker on the edge of the hot-plate or on the boiling water bath (5.3) for 15 min for the precipitate to settle. Allow it to cool to ambient temperature.

7.2.6 Decant the clear supernatant liquid through the Gooch crucible (5.5), fitted with a filter pad (5.6) with applied suction, and wash the precipitate twice by decantation with 20 ml portions of the hydrochloric acid solution (4.3). Transfer the

precipitate to the filter pad with cold water and wash the beaker several times with volumes of 25 to 30 ml of water to free the beaker from acid.

Use these washes also to wash the precipitate on the filter pad, allowing each portion of liquid to pass through before pouring on the next. Continue to wash until one portion of wash liquid fails to decolorize the solution when passed into a clean flask containing a few drops of the phenolphthalein (4.10) and 1 drop of the standard sodium hydroxide solution (4.9). Six washes are usually sufficient.

7.2.7 Transfer the precipitate and filter pad to the conical flask (5.8) with a glass rod with a drawn-out pointed end. Insert a glass funnel into the flask and wash into it any portions of the precipitate remaining in the Gooch crucible using carbon dioxide-free water. Remove any traces of precipitate adhering to the funnel by wiping with a slip of moist filter paper; add this to the contents of the flask. Add carbon dioxide-free water until the volume of liquid in the flask is about 120 ml. Shake the flask until the filter pad and filter paper are disintegrated and the precipitate is thoroughly dispersed. Ensure that no lumps remain, otherwise difficulty may be encountered in dissolving them in the sodium hydroxide solution.

7.2.8 From the burette, slowly add the standard volumetric sodium hydroxide solution (4.9), shaking the flask vigorously to ensure complete solution of the precipitate. Continue to add the sodium hydroxide solution until the precipitate has dissolved and add approximately 5 ml in excess. Use table 1 to estimate the volume of alkali required. Record the volume V_1 of the standard volumetric sodium hydroxide solution (4.9) added.

7.2.9 Add about six drops of the mixed indicator (4.12) and titrate with the standard volumetric hydrochloric acid solution (4.8) until the colour changes from violet through grey and suddenly to pale yellow. Record the volume V_2 of the standard volumetric hydrochloric acid solution used in the back-titration.

7.2.10 Carry out a blank test in parallel with the determination following the same procedure and using the same quantities of the reagents [except the standard volumetric sodium hydroxide solution (4.9) and standard volumetric hydrochloric acid solution (4.8)], but omitting the test portion. In the final titration, add 5.0 ml of the standard volumetric sodium hydroxide solution (4.9) and titrate with the standard volumetric hydrochloric acid solution (4.8). Record this volume V_3 .

8 Expression of results

8.1 Method of calculation

8.1.1 Calculate the phosphorus content P , expressed as a percentage by mass, of a blended sample, using the equation

$$P = \frac{[(V_1 - V_2) - (5 - V_3)] \times 0.01191 \times (m_1 + m_2)}{m_0 \times m_1}$$

where

V_1 is the volume, in millilitres, of standard volumetric sodium hydroxide solution (4.9) added (7.2.8);

V_2 is the volume, in millilitres, of standard volumetric hydrochloric acid solution (4.8) used for the back-titration (7.2.9);

V_3 is the volume, in millilitres, of standard volumetric hydrochloric acid solution used for the blank test (7.2.10);

m_0 is the mass, in grams, of the blend taken for the determination;

m_1 is the mass, in grams, of original sample in the 10 g blend;

m_2 is the mass, in grams, of white oil in the 10 g blend.

NOTE — If the concentrations of the standard volumetric solutions used are not exactly as specified in the list of reagents and materials, appropriate corrections should be made.

8.1.2 Calculate the phosphorus content P , expressed as a percentage by mass, of an unblended sample, using the equation

$$P = \frac{[(V_1 - V_2) - (5 - V_3)] \times 0,011\,91}{m}$$

where

V_1 is the volume, in millilitres, of standard volumetric sodium hydroxide solution (4.9) added (7.2.8);

V_2 is the volume, in millilitres, of standard volumetric hydrochloric acid solution (4.8) used for the back-titration (7.2.9);

V_3 is the volume, in millilitres, of standard volumetric hydrochloric acid solution used for the blank test (7.2.10);

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

NOTE — If the concentrations of the standard volumetric solutions used are not exactly as specified in the list of reagents and materials, appropriate corrections should be made.

8.1.3 Report the results to the nearest 0,01 % (m/m) above 0,1 % (m/m) and to the nearest 0,001 % (m/m) below 0,1 % (m/m).

8.2 Precision

The precision of this method as obtained by statistical examination of inter-laboratory test results, is as follows.

8.2.1 Repeatability

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 the following values only in one case in twenty.

Level of result (x), %

0,005 to 0,079

0,08 to 10

Repeatability, %

0,032 ($x + 0,04$)

0,0318 $x^{0,992}$

where x is the average of the two results.

NOTE — Precision is given in table 2 for typical values of x .

8.2.2 Reproducibility

The difference between two single and independent 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 values only in one case in twenty.

Level of result (x), %

0,005 to 0,079

0,08 to 10

Reproducibility, %

0,074 ($x + 0,04$)

0,118 $x^{0,992}$

where x is the average of the two results.

NOTE — Precision is given in table 2 for typical values of x .

Table 2 — Precision for typical phosphorus contents

Phosphorus content x	Repeatability	Reproducibility
0,007	0,001	0,003
0,01	0,001	0,003
0,02	0,002	0,004
0,04	0,002	0,006
0,07	0,003	0,008
0,1	0,003	0,012
0,2	0,006	0,024
0,4	0,013	0,047
0,7	0,022	0,083
1,0	0,032	0,118
2,0	0,063	0,234
4,0	0,126	0,467
7,0	0,219	0,813
10,0	0,312	1,153

9 Test report

The test report shall contain at least the following information:

- the type and identification of the product tested;
- a reference to this International Standard;
- the result of the test;
- any deviation, by agreement or otherwise, from the procedure specified;
- the date of the test.