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भारतीय मानक मसौदा

पेट्रोलियम और उसके उत्पाद – परीक्षण पद्धतियाँ
भाग 101 लुब्रिकेटिंग ऑइल में फॉस्फोरस का वर्णमिति के द्वारा निर्धारण

(IS 1448 Part 101 का पहला पुनरीक्षण)

Draft Indian Standard

**METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS
PART 101 COLORIMETRIC DETERMINATION OF PHOSPHORUS
IN LUBRICATING OILS**

(First Revision of IS 1448 Part 101)

ICS 75.100

Methods of Sampling and Test for Petroleum and
related Products of Natural or Synthetic Origin
(excluding bitumen) Sectional Committee, PCD 01

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FOREWORD

(Formal clauses will be added later)

Phosphorus, often present in additives, plays a significant role in enhancing the performance and longevity of lubricants. Phosphorus in lubricating oils is vital not only for ensuring product quality but also for complying with environmental regulations aimed at controlling emissions and preserving the efficiency of emission control systems in vehicles and industrial machinery.

This standard was originally published in 1980. The revision has been brought out to keep pace with the latest technological developments and international practices. In this revision the following major changes have been incorporated:

- a) Photo-electric colorimeter has been replaced by spectrophotometer/ colorimeter;
- b) Analytical balance, muffle furnace, hot air oven, and water bath have been included in apparatus; and
- c) Use of crucible 'equivalent to No. 0' and volumetric flask of 1000 ml capacity have been included in apparatus.

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2: 2022 'Rules for rounding off numerical values (*second revision*)'.

1 SCOPE

This method is used for the determination of low concentrations of phosphorus in lubricating oils. Metallic elements, such as iron, lead, magnesium and barium in amounts commonly encountered in lubricating oils do not interfere. This method may also be used for the analysis of additive concentrates containing phosphorus in the pentavalent state but is not recommended if the material contains more than 10 percent by mass phosphorus.

2 OUTLINE OF THE METHOD

Organic matter in the sample is destroyed by ignition in the presence of zinc oxide. The residue is dissolved in sulphuric acid and a portion of the solution is reacted with ammonium molybdate and hydrazine sulphate. The intensity of the resultant colour is proportional to the amount of phosphorus present and is measured with a spectrophotometer / colorimeter.

3 APPARATUS

3.1 Spectrophotometer / Colorimeter — Capable of producing monochromatic light by means of colour filters (for colorimeter) or gratings (for spectrophotometer).

3.2 Analytical Balance — 0.1 mg sensitivity

3.3 Muffle Furnace — Heating capability 700 °C

3.4 Hot Air Oven — Capable to maintain a constant temperature at 105 °C

3.5 Water Bath

3.6 Hot Plate

3.7 Crucibles — Porcelain, low-form, No. 0 (or equivalent)

3.8 Volumetric Flasks — 100 ml and 1000 ml capacity

4 REAGENTS

4.1 Ammonium Molybdate Solution

Add cautiously (*see Note*) 300 ml of concentrated sulphuric acid to 500 ml of water. Cool to room temperature and add 20 g of ammonium molybdate tetrahydrate. Stir until solution is complete and dilute to one litre.

NOTE — Sulphuric acid should be added slowly with continuous stirring, to water contained in a beaker placed in a bath of cold water. It is recommended that a face shield or goggles should be worn during this operation.

4.2 Hydrazine Sulphate Solution

Dissolve 1.5 g of hydrazine sulphate in 1 litre of water. This solution deteriorates on standing. Discard what remains after 3 weeks and prepare a fresh solution.

4.3 Molybdate Hydrazine Mixture

Dilute 25 ml of ammonium molybdate solution (*see 4.1*) with 80 ml water, add 10 ml of hydrazine sulphate solution (*see 4.2*) and dilute to 100 ml with water. Prepare 50 ml for each determination to be made. Additional 50 ml is required for a blank. This mixture is unstable and shall be freshly prepared immediately before use.

4.4 Standard Phosphorus Stock Solution (1 mg Phosphorus per ml)

Dissolve 4.393 g of dried potassium dihydrogen phosphate (KH_2PO_4) in 150 ml of 1: 10 sulphuric acid and dilute to 1 litre in a volumetric flask with water.

NOTE — Commercially available reference materials can also be used.

4.5 Zinc Oxide — Dry and phosphorus free.

5 STANDARDIZATION OF APPARATUS

5.1 Prepare a standard phosphorus solution (0.01 mg phosphorus per ml) as follows:

Pipette 10 ml of the standard stock solution (*see 4.4*) into a 100 ml volumetric flask and dilute to the mark with water. Dilute 10 ml of this solution to 100 ml in a volumetric flask with water. Each millilitre contains 0.01 mg of phosphorus.

5.2 Pipette 1, 2, 4, 6, 8 and 10 ml portions of the standard solution (0.01 mg per ml) into 100 ml volumetric flasks (*see Note*). Add 50 ml of the molybdate hydrazine mixture (*see 4.3*) and dilute with water but not very close to the mark. Mix well and heat on a steam bath for 25 min. Cool immediately in a water bath to room temperature and adjust the volume to exactly 100 ml. Run a blank solution at the same time, giving to the same treatment but omitting the standard phosphorus solution. The colour developed by this procedure is stable for 24 h.

NOTE — It is desirable to set aside a number of flasks for this operation since the subsequent heating and cooling destroys their value for accurate volumetric analysis.

5.3 Measurements — Adjust the spectrophotometer or colorimeter so that 100 percent transmittance (zero optical density) is obtained on the blank at the wavelength of at 690 nm. Do not

disturb this adjustment during subsequent measurements. Determine and record the transmittance readings for each of the solutions.

5.4 Prepare a standard reference curve plotting colorimeter / spectrophotometer reading versus phosphorus content.

6 PROCEDURE

6.1 Weigh (M_2) a suitable sample into a No. 0, low-form, porcelain crucible and add (2 ± 0.1) g of zinc oxide. Ignite and when the sample will no longer burn freely, heat moderately until carbon is completely removed and cool.

NOTES

1 Ignition of sample using muffle furnace for 5 h at 700 °C effectively removes the carbon from sample

2 Use the following table to determine proper mass of the sample. When the amount of phosphorus expected is greater than 0.05 percent, dilute the sample after weighing it into the crucible with 5 or 6 drops of phosphorus-free white oil and mix well by gentle swirling:

<i>Expected Phosphorus Percentage by mass</i>	<i>Mass of Sample, g</i>
0.001	3.0
0.01	2.0
0.05	1.0
0.50	0.35
1.0	0.15
2.0	0.10
5.0	0.04
7.0	0.025
10.0	0.02

6.1.1 Transfer the content of the crucible to a 100 ml beaker and add 30 ml of dilute sulphuric acid (1: 10). Warm on a hot plate until the content is completely dissolved. Transfer to a 100 ml volumetric flask, filtering through a Whatman No. 42 (or equivalent) filter paper and washing with water if any insoluble matter is present. Dilute to the mark and mix.

6.2 Pipette an aliquot of the sample solution (A) estimated to contain 0.01 mg to 10 mg of phosphorus into another 100 ml volumetric flask. Add 50 ml of the molybdate hydrazine mixture (*see 4.3*) and proceed with the development and measurement of the colour as described in **5**. If a reading is obtained indicating a concentration of phosphorus greater than 0.10 mg, repeat the development of the colour using a smaller aliquot.

7 CALCULATION

$$\text{Phosphorus, percent} = \frac{10 \times M_1}{M_2 \times A}$$

where

M_1 = mg of phosphorus corresponding to the observed reading,

M_2 = mass of sample in g, and

A = aliquot in millilitres.

8 REPORT

8.1 Report results to the nearest 0.001 percent for values below 0.2 percent, to the nearest 0.01 percent for values between 0.2 percent and 5 percent and to the nearest 0.1 percent for values above 5 percent.

9 PRECISION

9.1 Results should not differ from the mean by more than the following amounts:

Sl. No.	Percent Phosphorus	Repeatability	Reproducibility
(1)	(2)	(3)	(4)
i.	0 to 0.01	0.0005	0.0009
ii.	Over 0.01 to 0.2	0.002	0.003
iii.	Over 0.2 to 2.0	0.02	0.03
iv.	Over 2.0 to 5.0	0.05	0.07
v.	Over 5.0 to 10.0	0.10	0.13