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भारतीय मानक मसौदा

पेट्रोलियम और उसके उत्पाद — परीक्षण पद्धतियाँ

आईसीपी- परमाणु उत्सर्जन स्पेक्ट्रोमीटर द्वारा अनयूज्ड लुब्रिकेटिंग ग्रीस में तत्वों को ज्ञात करना

Draft Indian Standard

PETROLEUM AND ITS PRODUCTS — TEST METHODS — DETERMINATION OF ELEMENTS IN UN-USED LUBRICATING GREASES BY INDUCTIVELY COUPLED PLASMA — ATOMIC EMISSION SPECTROMETER

(ICS 75.100)

Methods of Sampling and Test for Petroleum and related Products of Natural or Synthetic Origin (excluding bitumen) Sectional Committee, PCD 01	Last date for receipt of comment is **03 October 2025**

FOREWORD

(*Formal clause will be added later*)

ICP-AES (Inductively Coupled Plasma – Optical Emission Spectrometry) also referred to as Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) is an analytical technique used for detection and quantification of elements. In this technique, element-specific emission spectra produced by radio-frequency inductively coupled plasma are measured by optical spectrometry. Because of its superior detection capabilities and the ability to handle both simple and complex matrices, it has been proven to be a powerful tool for rapid and concurrent determination of elements in petroleum products viz lubricating oils, greases, fuels, and distillates of crude oils.

In the preparation of this standard, considerable assistance has been derived from the following standards:

ASTM D4951-14 — Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

ASTM D5185-18 — Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

ASTM D7303-23 — Standard Test Method for Determination of Metals in Lubricating Greases by Inductively Coupled Plasma Atomic Emission Spectrometry

IP 561-2008 — Determination of silicon, chromium, copper, nickel and iron in used grease - Inductively coupled plasma atomic emission spectroscopy (ICP-AES) method

This method does not purport to address safety problems, if any, associated with its use. It is the responsibility of the user of this method to use appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

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

1 SCOPE

1.1 This test method is applicable for determination of elements in un-used (fresh) lubricating greases by inductively coupled plasma atomic emission spectrometry (ICP-AES). Elements covered in this method should be in the form of soap (fatty acid salts) based thickeners and oil soluble additives. Organophilic clay type greases and poly methyl siloxane type greases also exhibit desired solubility in kerosene and chlorinated benzene mixture for ICP-AES analysis.

1.2 The test procedure covers the determination of Al, Ba, B, Ca, Mg, Mo, P, Li, Na, Si, Sb and Zn in the concentration range 0.01 mass percent to 2.25 mass percent for sulphur analysis, sulphur free solvents (Kerosene & 1,2,4 Trichlorobenzne) to be used which is not in the scope of current standard.

NOTE — The specific elements along with the suggested wavelengths are referred in Table 1. Other elements also can be determined based on capability of the instrument.

2 SUMMARY OF TEST METHOD

2.1 Sample Preparation

A weighed portion of a thoroughly homogenized lubricating grease is diluted fifty times by weight (5 g) with trichlorobenzene in glass container (round bottom or beaker) and kept the container in ultrasonicator with water bath maintained at 50 °C for 15 min. After partial/ complete solubilization, add the 45 g of dilution solvent containing ISD to the contents and continue the ultrasonication or alternate manual stirring may be used till the grease components are solubilized and clear solution appears. A mandatory internal standard is added to the dilution solvent to compensate for variations in test specimen introduction efficiency. The solutions are introduced to the ICP instrument by free aspiration or an optional peristaltic pump. By comparing emission intensities measured with the standards, the concentrations of elements in the test specimen are calculated.

Table 1 Suggested Wavelengths for Various Elements
(*Clause* 1.2 *Note*)

Sl. No.	**Element**	**Wavelength, *nm***	**Property / Source**
(1)	(2)	(3)	(4)
i)	Aluminium (Al)	394.401, 396.152	Thickener
ii)	Antimony (Sb)	206.834, 217.582	Additive
iii)	Barium (Ba)	249.678, 249.772	Thickener, Additive
iv)	Boron (B)	455.403, 493.408	Additive
v)	Calcium (Ca)	317.933, 396.847	Thickener, Additive
vi)	Magnesium (Mg)	279.553, 280.270	Additive
vii)	Molybdenum (Mo)	202.032, 204.598	Additive
viii)	Phosphorus (P)	213.618, 214.914	Additive
ix)	Potassium (K)	766.491, 769.897	Additive
x)	Lithium (Li)	610.365, 670.783	Thickener
xi)	Sodium (Na)	588.995, 589.592	Thickener
xii)	Silicon (Si)	212.412, 251.611	Thickener, Additive
xiii)	Zinc (Zn)	202.548, 206.200	Additive

NOTES

1)These wavelengths (1st and 2nd preference) are only suggestive. Wavelength of maximum isotopic abundance should be selected for superior sensitivity. If interference is found, alternate wavelength can be selected.

2)Analysis of Greases with oil insoluble thickeners and additives (Graphite, MoS_2, PTFE, Clay, Perfluoropolyethers) is not possible to analyze this method and attempt may lead to blocking of nebulizer.

3 SIGNIFICANCE AND USE

Greases mainly consist of thickener and base oil along with performance boosters like anti-ware, extreme pressure, antioxidants, viscosity modifiers, corrosion inhibitors, friction modifiers, detergents etc. The economics of grease manufacturing process involves the optimization (mass percent) of various components desired to achieve the target performance.

4 REAGENTS AND MATERIALS

Reagent grade solvents/chemicals shall be used in all tests. It is intended that all solvent/ reagents conform to the metal free and the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.1 Internal Standard — Oil soluble cadmium, cobalt, scandium or yttrium (or any suitable metal) 1000 mg/kg is required when using internal standardization.

4.2 Multi Element Organometallic Standards (CRM) — Oil soluble standard containing 900 mg/kg of each element as per requirement.

4.3 Hydrocarbon Solvent — Kerosene or mixed xylenes or *o*-xylene, tetralin. Dilution solvent components are free of analytes and dilution solvent is capable of completely dissolving standards and samples of interest.

NOTE — Plasma ignition and sample introduction conditions to be optimized as per the ICP-AES manufacturer recommendations for reducing the carbon build-up on injector tube.

4.4 Chlorinated Solvent (Warning-Health & Environmental Hazard) - 1,2,4 -Trichlorobenzene. Dilution solvent components are free of analytes and dilution solvent is capable of completely dissolving standards and samples of interest.

4.5 High Purity Argon Gas —99.999 percent minimum purity

4.6 High Purity Nitrogen Gas — 99.999 percent minimum purity

4.7 High Purity 80 percent Argon & 20 percent Oxygen Mixture — 99.999 percent minimum purity

NOTE — The gases requirement is being only suggestive. Instrument manufacturer recommendations to be followed.

5 APPARATUS

5.1 Analytical Balance — Minimum capacity 220 g capable of weighing to the nearest 0.1 mg.

5.2 Inductively-Coupled Plasma Atomic Emission Spectrometer

Either a sequential or simultaneous spectrometer is suitable, if equipped with a quartz Inductively Coupled Plasma (ICP) torch and Radio Frequency (RF) generator to form and sustain the plasma.

5.3 Nebulizer — Reduces the possibility of clogging and minimizes aerosol particle effects.

NOTE — A Babington-type high-solids nebulizer is strongly recommended.

5.4 Peristaltic Pump

A peristaltic pump is strongly recommended to provide a constant flow of solution. The pumping speed should be maintained at 30 rpm and may be reduced or increased to get the stable plasma analytical zone. The pump tubing shall withstand at least 6 h exposure to the dilution solvent. Suitable tubing compatible to 10 percent trichlorobenzene in kerosene should be used as per the instrument manufacturer advice.

5.5 Ultrasonicator and Water Bath (with temperature controller)

NOTE — Alternate manual stirring is an alternate to ultrasonicator if the samples producing clear solution in selected solvent mixture.

5.8 General Laboratory Glassware

5.8.1 *Round bottom flask* (100 ml),

5.8.2 *Glass beakers* (250 ml),

5.8.3 *Spatula* (*PTFE or Teflon coated*),

5.8.4 *Measuring cylinder* (50/100 ml),

5.8.5 *Self-standing centrifuge bottles/tubes* (50 ml),

5.8.6 *Dispensing Bottle* (50/1000 ml).

6 SAMPLE PREPARATION

The reliability of analysis is based on representative sample used for testing. In order to achieve homogeneity of sample, the samples shall be thoroughly mixed in their containers immediately prior to testing.

7 SAMPLE ANALYSIS PROCEDURE

7.1 Sample quantity for test take sufficient quantity of homogeneous test sample so as to meet the requirements of the analyse with the lowest expected concentration as mentioned in Table 2.

Table 2 Sample Quantity for Test
(*Clause* 7.1)

Sl. No.	**Expected Concentration of Element, Mass percent**	**Mass of Test Portion, g**
(1)	(2)	(3)
i)	0.01 - 1.12	0.10 (± 0.01g)
ii)	1.12 - 2.25	0.05 (± 0.01g)

7.1.1 *Setting up the Spectrometer*

7.1.1.1 *General*

Consult and follow the manufacturer’s instructions for the operation of the inductively coupled plasma emission spectrometer.

7.1.1.2 *Peristaltic Pump*

If using peristaltic pump, inspect the pump tubing and replaced it, if necessary, before starting each day. Verify the solution uptake rate and adjust it to the desire rate.

7.1.1.3 *ICP Excitation Source*

Ignite the ICP excitation source for at least 30 min before performing an analysis. During this warm-up period, nebulise dilution solvent.

7.1.1.4 *Wavelength Profiling*

Perform any wavelength profiling that may be called for in the normal operation of the instrument.

7.1.1.5 *Operation Parameters*

Assign the appropriate operating parameters to the instrument task file so that it is possible to determine the desire elements (Table 3). Include the following parameters:

a) element,
b) wavelength,
c) background correction points,
d) inter-element correction factors if any, and
e) integration time and three consecutive repeat integrations.

Table 3 Typical Spectrometer Settings for Elemental Analysis
(*Clause* 7.1.1.5)

Sl. No.	**Parameter**	**Set Value**
(1)	(2)	(3)
1	Plasm gas flow, Argon	15.0 l/min
2	Auxiliary Flow, Argon	1.5 l/min
3	Nebulizer flow, Argon	0.45 l/min
4	Makeup gas flow, Argon 80 percent Oxygen 20 percent	15 percent
5	Peristaltic pump speed	30 rpm
6	RF power	1.40 kW
7	View mode	Radial
8	Integration time	10 sec
9	Stabilization time	15 sec
10	Viewing height	8 mm
11	Uptake delay	60 sec
12	Rinse time	30 sec

NOTE — These instrument settings are only suggestive. Instrument manufacturer recommendations to be followed.

7.2 Internal Standard Method

The internal standard procedure requires that every test specimen solution have the same concentration (or a known concentration) of an internal standard (Sc/Y/Co/Cd) element that is not present in the original specimen. Specimen to specimen changes in the emission intensity of the internal standard element can be used to correct for variations in the test specimen introduction efficiency, which is dependent on the physical properties of the test specimen.

7.2.1 *Preparation of Internal Standard Solution* (5 *mg/kg*)

Weigh 2 g of 1000 mg/kg cadmium, cobalt, scandium or yttrium (or any other suitable metal) organo-metallic concentrates into a 500 ml volumetric flask and add dilution solvent (kerosene) till the mark with constant stirring / mixing. Prepare fresh, at least weekly, and transfer this solution into a dispensing bottle.

7.2.2 *Preparation of Test Specimen and Standards*

7.2.2.1 *Blank*

Prepare a blank containing TCB (5 g) and Kerosene (45 g).

7.2.2.2 *Calibration Standard,* (1.0 µg/g)

Weigh 0.056 g of the 900 mg/kg multi-element standard CRM into 100 ml volumetric flask. Add 4.94 g of TCB and 45 g of the dilution solvent kerosene containing ISD.

7.2.2.3 *Calibration Standard*, (10.0 µg/g)

Weigh 0.556 g of the 900 mg/kg multi-element standard CRM into 100 ml volumetric flask. Add 4.44 g of TCB and 45 g of the dilution solvent kerosene containing ISD.

7.2.2.4 *Calibration Standard*, (25 µg/g)

Weigh 1.389 g of the 900 mg/kg multi-element standard CRM into 100 ml volumetric flask. Add 3.61 g of TCB and 45 g of the dilution solvent kerosene containing ISD.

7.2.2.5 *QC Check Standards* (5.0 ug/g)

Weigh 0.278 g of the 900 mg/kg multi-element standard CRM into 100 ml volumetric flask. Add 4.72 g of TCB and 45 g of the dilution solvent kerosene containing ISD.

7.2.2.6 *Test Specimen*

A weighed portion (0.1 g) of a thoroughly homogenized lubricating grease is diluted with fifty times by weight (5 g) with trichlorobenzene in glass container (round bottom or beaker) and kept the container in ultrasonicator with water bath maintained at 50 °C for 10min. After partial /complete solubilization, add the 45 g of dilution solvent kerosene containing ISD (Co/Cd/ Y/Sc) to the contents and continue the ultrasonication till the grease components are solubilized and clear solution appears.

7.2.3 *Calibration*

7.2.3.1 The linear range shall be established once for the particular instrument being used. This is accomplished by running intermediate standards between the blank and the working standard and by running standards containing higher concentrations than the working standard. Analyses of test specimen solutions shall be performed within the linear range of response.

7.2.3.2 *Working Standards with Internal Standard*

At the beginning of the analysis of each batch of specimens, perform a three-point calibration consisting of the blank and working standard with internal standard. Use the check standard to determine if each element is in calibration. When the results obtained with the check standard are within 5 percent of the expected concentrations for all elements, proceed with test specimen analyses. Otherwise, make any adjustments to the instrument that are necessary and repeat the calibration. Repeat this procedure with the check standard every five samples.

7.2.3.3 Based on the standard’s emission intensities and those of the internal standard, calculate an intensity ratio for each element by the following equation:

$$I\ (Re) = [I\ (e) - I\ (Be)]\ /\ I\ (is)$$

where,

$I\ (Re)$ = intensity ratio for element e;
$I\ (e)$ = intensity for element e;
$I\ (Be)$ = intensity of the blank for element e; and
$I\ (is)$ = intensity of internal standard element.

7.2.4 *Procedure and Calculation*

7.2.4.1 *Analysis*

Analyse the test specimen solutions in the same manner as the calibration standards (that is, same integration time, background correction points, plasma conditions, and so forth). Between test specimens, nebulise dilution solvent containing polychlorinated benzenes for 60 s. Calculate elemental concentrations by multiplying the determined concentration in the diluted test specimen solution by the dilution factor. Calculation of concentrations can be performed manually or by computer software when such a feature is available (or as per the manufacturers guidelines).

7.2.4.2 *Quality Control with Check Standard*

Analyse the check standard after every fifth sample, and if any result is not within 5 percent of the expected concentration, recalibrate the instrument and re-analyse the test specimen’s solutions back to the previous acceptable check standard analysis.

7.2.4.3 *Analysis with Internal Standardization*

Analyse the test specimen solutions and calculate an intensity ratio for each of the elements found in the test specimen solutions using equation (*see* **7.2.3.3**). From that, intensity ratios, concentrations of the elements can be calculated.

8 EXPRESSION OF RESULTS

Report mg/kg or mass percent concentrations to three significant figures.

NOTE — For additive elements use mg/kg whereas for thickener elements use mass percent.

9 BIAS

The method is empirical and depends on various conditions, no statement of bias can be made.

9 PRECISION

The precision of this test method is expressed in terms of Relative Standard Deviation (RSD). The RSD for intra lab shall be max 5 percent and RSD for inter lab shall be max 10 percent.