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Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS

[P : 4]

ASH, SULPHATED ASH AND WATER SOLUBLE ASH

(*Second Revision*)

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Adapted from the Joint ASTM-IP Standards No. ASTM D 482/80-IP 4/75 and ASTM D 874/82-IP 163/78 and LIC 80-01 D-1969 issued by the Standard Inspection Laboratory of ESSO Research and Engineering Co, USA.

1. SCOPE

1.1 Four methods are prescribed for the determination of ash, sulphated ash and water soluble ash of petroleum products and greases.

1.2 Method A is suitable for the determination of ash from distillate and residual fuel oils, gas turbine fuels, crude oils, lubricating oils, waxes and other petroleum products, in which any ash-forming materials present are normally considered to be undesirable impurities or contaminants (*see* Note 1). The method is limited to petroleum products which are free from added ash-formimg additives, including certain phosphorus compounds (*see* Note 2).

NOTE 1 — In certain type of samples, all of the ash forming metals may not be retained quantitatively in the ash. This is particularly true of distillate oils which require a special ashing procedure in order to retain metals quantitatively.

NOTE 2 — This method is not intended for the analysis of unused lubricating oils containing additives, for such samples use Method C; neither it is intended for the analysis of lubricating oils containing lead, nor for used engine crankcase oils.

BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

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1.3 Methods B_1 and B_2 are prescribed for the determination of ash from greases.

1.4 Method C describes a procedure for determining the sulphated ash from unused lubricating oils containing additives and from additive concentrates used in compounding. These additives usually contain one or more of the following metals: barium, calcium, magnesium, zinc, potassium, sodium and tin. The elements of sulphur, phosphorus, and chlorine may also be present in combined form.

1.4.1 Application of this method to sulphated ash levels below 0·02 percent is restricted to oils containing ashless additives. The lower limit of the method is 0·005 percent sulphated ash.

1.4.2 There is evidence that magnesium does not react in the same way as other alkali metals in this test. If magnesium additives are present the data should be interpreted with caution.

1.4.3 There is evidence that samples containing molybdenum may give low results because molybdenum compounds may not be fully recovered at the temperature of ashing.

1.5 Method D is applicable to all types of petroleum oils, either unused or used. When the sample under test contains lead compounds or some of the alkali metals, the result does not express the true metallic content, since some of the metals will be lost by vaporization.

2. TERMINOLOGY

2.0 For the purpose of these methods, the following definitions shall apply.

2.1 Ash — The inorganic residue left after the ignition of the sample under prescribed conditions, calculated as the percentage by mass of the original sample.

2.2 Sulphated Ash — The ash that remains after the sample has been carbonized and the residue subsequently treated with sulphuric acid and heated to constant mass.

2.3 Water Soluble Ash — The water soluble portion of the ash of the sample, calculated as the percentage by mass of the original sample.

3. METHOD A — ASH FROM PETROLEUM PRODUCTS

3.1 Outline of the Method — The sample contained in a suitable vessel is ignited and allowed to burn until only ash and carbon remain. The carbonaceous residue is reduced to an ash by heating in a muffle furnace at 775°C, cooled, and weighed.

3.2 Apparatus

3.2.1 *Evaporating Dish or Crucible* — made of platinum, silica, or porcelain, of 90 to 120-ml capacity.

3.2.2 *Electric Muffle Furnace* — capable of maintaining a temperature of 775°C ± 25°C, and preferably having suitable apertures at the front and rear so as to allow a slow natural draught of air to pass through.

3.3 Procedure

3.3.1 Heat the evaporating dish or crucible at 700°C to 800°C for 10 minutes or more. Cool to room temperature in a suitable container (*see* Note) and weigh to the nearest 0·1 mg.

NOTE — The container in which the dish or crucible is cooled should not contain a desiccating agent. In addition, all weighings of the crucibles should be performed as soon as the crucibles have cooled. If it should be necessary that the crucibles remain in the desiccator for a longer period, then all subsequent weighings should be made after allowing the crucibles and contents to remain in the desiccator for the same length of time.

3.3.2 The quantity of sample to be taken depends upon the ash content of the material. Weigh into the dish or crucible sufficient sample (up to a maximum of 100 g) to give up to 20 mg of ash. For sample mass which require more than one filling of the dish, obtain the mass from the difference between the initial and final mass of a suitable sample container. Weigh the sample to the nearest 0·1 percent. Heat the dish or crucible and sample until the contents become capable of being ignited with a flame. Maintain at such a temperature that the sample continues to burn at a uniform and moderate rate, leaving only ash and carbon when the burning ceases.

CAUTION — The sample may contain water, which can cause spattering. The operator should heat the sample cautiously in a hood while wearing safety goggles.

NOTE — If the sample contains sufficient moisture to cause foaming and loss of material, discard the sample and to an additional sample add 1 to 2 ml of 99 percent *iso*-propyl alcohol before heating. If this is not satisfactory, add 10 ml of an equivolume mixture of toluene and *iso*-propyl alcohol and mix thoroughly. Place several strips of ashless filter paper in the mixture and heat; when the paper begins to burn, the greater part of the water is found to have been removed.

3.3.3 Heat the residue in the muffle furnace at 775 ± 25°C until all carbonaceous material has disappeared. Cool the dish to room temperature in a suitable container as prescribed in **3.3.1**, and weigh to the nearest 0·1 mg.

3.3.4 Reheat the dish at 775°C for 20 to 30 minutes, cool in a suitable container as prescribed in **3.3.1** and reweigh. Repeat the heating and weighing until consecutive weighings differ by not more than 0·5 mg.

3.4 Calculation — Calculate the mass of the ash as a percentage of the original sample, as follows:

$$\text{Ash, percent by mass} = \frac{100\,m}{M}$$

where

m = mass in g of ash, and
M = mass in g of sample.

3.5 Reporting — Report the result to the nearest 0·01 as the ash, Method A stating the mass of sample taken.

3.6 Precision — Results of duplicate tests shall not differ by more than the following amounts:

Ash percent	*Repeatability*	*Reproducibility*
0·001 to 0·079	0·003	0·005
0·080 to 0·180	0·007	0·024

4. METHOD B — ASH FROM GREASES

4.1 General

4.1.1 Two methods are prescribed for determining ash from greases, Method B_1 is a rapid routine method and is substantially the same as Method A (*see* **3**). Method B_2, which involves sulphation, gives more concordant results than Method B_1, but requires more time and manipulation and *shall be used as a referee method.*

4.1.2 Method B_2 is also preferred because Method B_1 is sometimes unsatisfactory for the following reasons:

a) Sodium carbonate derived from the soap may react with inorganic fillers;
b) The ash may react with the porcelain crucible during the long continued heating necessary to burn off all carbon;
c) If much sodium or potassium carbonate is present, the ash is fusible and often encloses carbon, making complete removal of the latter very difficult;
d) Results are low when easily reducible oxides of volatile metals are present; and
e) There is uncertainty as to when calcium carbonate has been completely ignited to calcium oxide.

4.2 Outline of Method — In Method B_1, the sample is heated gently until it burns and the residue is ignited until it is free from carbon.

Alcohol may be added to prevent the foaming of wet samples. In Method B_2, the partially ignited residue is treated with dilute sulphuric acid and the sulphated ash weighed.

4.3 Apparatus

4.3.1 *Dish or Squat-Form Crucible* — of silica, porcelain or platinum, and of about 15 ml capacity. A platinum dish shall not be used if the sample contains lead, zinc or other metals which attack platinum at high temperature.

4.4 Method B_1

4.4.1 *Procedure* — Heat the dish to redness, allow it to cool in a desiccator, and weigh. Weigh 2 to 5 g of the sample to the nearest 0·01 g. Heat the dish gently until the grease burns at the surface (*see* Note). Burn off the combustible matter slowly and heat the residue strongly with a flame or in a muffle furnace until the ash is free from carbon. Cool the dish and contents in a desiccator and weigh them.

NOTE — When the sample contains sufficient water to cause foaming and loss, add 1 to 2 ml of absolute alcohol before heating it.

4.4.2 *Calculation and Reporting* — Calculate the mass of the residue as a percentage of the mass of the sample to the nearest 0·1 and report as Ash, Method B_1.

4.4.3 *Precision* — Since the oxide-carbonate ratio in the ash obtained by this method may vary with the intensity and duration of heating, precision limits have not been established.

4.5 Method B_2

4.5.1 *Reagents*

a) *Dilute sulphuric acid* — approximately 10 percent (*m/v*).

b) *Methyl orange indicator* — containing one gram of methyl orange in one litre of water.

c) *Ammonium carbonate*

4.5.2 *Procedure* — Carry out the ashing of the sample as prescribed in **4.4.1** till the ash is nearly free from carbon. Cool the dish and its contents and dissolve the soluble portion of the ash in a little water. Add a slight excess of dilute sulphuric acid carefully from a pipette inserted under a watch-glass covering the dish. Warm the dish and its contents on a boiling water-bath until effervescence ceases. Rinse the watch-glass with water into the dish. Test the solution with methyl orange indicator to ensure the presence of free acid. Evaporate the contents of the dish to dryness and ignite them at a low red heat, adding a small quantity of dry ammonium carbonate to drive off the excess of sulphur trioxide. Cool the dish and contents in a desiccator and weigh them.

4.5.3 *Calculation and Reporting* — Calculate the mass of the residue as a percentage of the mass of the sample to the nearest 0·1 and report it as Ash, Method B_2.

4.5.4 *Precision* — Unless fillers or easily reducible compounds of volatile metals are present, results of duplicate tests shall not differ by more than the following amounts:

Repeatability	*Reproducibility*
10 percent of mean	10 percent of mean

5. METHOD C — SULPHATED ASH FROM UNUSED LUBRICATING OILS AND ADDITIVES

5.0 Outline of the Method — The sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulphuric acid and heated at 775°C until oxidation of carbon is complete. The ash is then cooled, re-treated with sulphuric acid, and heated at 775°C to constant mass.

5.1 Significance and Use — The sulphated ash may be used to indicate the concentration of known metal-containing additives in new oils. When phosphorus is absent, barium calcium, magnesium, sodium and potassium are converted to their sulphates and tin (stannic) and zinc to their oxides (*see* Note 1). Sulphur and chlorine do not interfere but when phosphorus is present with metals, it remains partially or wholly in the sulphated ash as metal phosphates.

NOTE 1 — Since zinc sulphate slowly decomposes to its oxide at the ignition temperature specified in the method, samples containing zinc may give variable results unless the zinc sulphate is completely converted to the oxide.

NOTE 2 — This method is not intended for the analysis of used engine oils or oils containing lead. Neither it is recommended for the analysis of non-additive lubricating oils, for which Method A should be used.

NOTE 3 — For best results on samples containing less than 0·1 percent sulphated ash, platinum dishes should be used. The precision values shown in **5.7** for this type of sample were so obtained.

5.2 Apparatus

5.2.1 *Dish* — An evaporating dish or crucible made of porcelain, fused silica, or platinum of 50 to 100-ml capacity. For samples yielding less than 0·02 percent sulphated ash, a platinum evaporating dish or crucible of 120- to 150-ml capacity is specified, except for samples containing elements injurious to platinum.

NOTE — A platinum vessel should not be used if the sample is likely to contain elements, such as phosphorus, which attack platinum under the conditions of the test.

5.2.2 *Electric Muffle Furnace* — The furnace shall be capable of maintaining a temperature of 775°C ± 25°C and preferably have apertures at the front and rear to allow a slow natural draught of air to pass through the furnace.

5.3 Reagents

5.3.1 *Low-Ash Mineral Oil* — White oil (*see* IS : 1083-1978*) having a sulphated ash lower than the limit capable of being determined by this method.

NOTE — Determine the sulphated ash of this oil by the procedure given in **5.4.1** to **5.4.11** using 100 g of white oil weighed to the nearest 0·5 g in a 120 to 150 ml platinum dish. Deduct the sulphuric acid blank as described in **5.4.11**.

5.3.2 *Sulphuric Acid (Relative Density 1·84)* — Concentrated sulphuric acid (H_2SO_4).

5.3.3 *Sulphuric Acid (1 : 1)* — Prepare by slowly adding one volume of concentrated sulphuric acid (relative density 1·84) to one volume of water.

> CAUTION — Sulphuric acid is highly corrosive and has a high heat of hydration. Protective clothing, including gloves and face mask, should be worn during manipulations involving this acid.

5.4 Procedure

5.4.1 Select the size of the evaporating dish or crucible according to the quantity of sample necessary (*see* **5.4.3**).

5.4.2 Heat the evaporating dish or crucible at 775°C for at least 10 minutes. Cool to room temperature in a suitable container and weigh to the nearest 0·1 mg.

NOTE — The container in which the dish is cooled should not contain a desicating agent.

5.4.3 Weigh into the dish a quantity of sample given by the following equation:

$$M = \frac{10}{A}$$

where

M = mass in g of sample, and

A = expected percent of sulphated ash.

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*Specification for industrial white oils (*first revision*).

5.4.3.1 Do not take a quantity in excess of 80 g. In the case of lubricating oil additives yielding a sulphated ash of 2 percent or more, dilute the weighed sample in the dish with approximately 10 times its mass of low ash mineral oil.

NOTE — If the amount of sulphated ash found differs from the expected amount by more than a factor of two, repeat the analysis with a different mass of sample calculated from the first analysis.

5.4.4 Heat the dish or crucible and sample carefully until the contents can be ignited with a flame. Maintain at such a temperature that the sample continues to burn at a uniform and moderate rate. When burning ceases, continue to heat gently until no further smoke or fumes are evolved.

NOTE — If the sample contains sufficient moisture to cause foaming and loss of material from the dish, discard the sample, and to an additional sample add 1 to 2 ml of 99 percent *iso*-propyl alcohol before heating. If this is not satisfactory, add 10 ml of a mixture of equal volumes of toluene and *iso*-propyl alcohol and mix thoroughly. Place several strips of ashless filter paper in the mixture and heat; when the paper begins to burn, the greater part of the water will have been removed.

5.4.5 Allow the dish to cool to room temperature, then completely moisten the residue by the dropwise addition of sulphuric acid (relative density 1·84). (*See* Caution under **5.3.3**). Carefully heat the dish at a low temperature on a hot plate or over a gas burner, avoiding spattering, and continue heating until fumes are no longer evolved.

5.4.6 Place the dish in the furnace at 775°C ± 25°C and continue heating until oxidation of the carbon is complete or almost complete.

5.4.7 Allow the dish to cool to room temperature. Add three drops of water and ten drops of sulphuric acid (1 : 1). Move the dish so as to moisten the entire residue. Again heat the dish as in **5.4.5**.

5.4.8 Again place the dish in the furnace at 775 ± 25°C and maintain at that temperature for 30 minutes. Cool the dish to room temperature in a suitable container (*see* Note under **5.4.2**).

NOTE — Zinc dialkyl or alkaryl dithiophosphates and blends containing these additives may give a residue which is partially black at this stage. In this case, repeat **5.4.7** and **5.4.8** until a white residue is obtained.

5.4.9 Weigh the dish and residue to the nearest 0·1 mg.

5.4.10 Repeat **5.4.8** and **5.4.9** until two successive weighings differ by no more than 1·0 mg.

NOTE — Normally one repeat will suffice, unless a high proportion of zinc is present, when three or four heating periods may be required.

5.4.11 For samples expected to contain 0·02 percent or less of sulphated ash, determine a sulphuric acid blank by adding 1 ml of the concentrated sulphuric acid to a tared platinum dish or crucible, heating until fumes are no longer evolved and then heating in the furnace at 775 ± 25°C for 30 minutes. Cool the dish or crucible to room temperature in a suitable container and weigh to the nearest 0·1 mg. If any ash is found in the sulphuric acid, an adjustment to the mass of sulphated ash obtained is made by subtracting the mass of ash contributed by the sulphuric acid, determined from the total volume of sulphuric acid used and the mass of ash found for the 1 ml blank, from the total mass in grams of sulphated ash for the sample. Use this corrected mass *m*, in calculating the percent sulphated ash.

5.5 Calculation — Calculate the mass of sulphated ash as a percentage of the original sample as follows:

$$\text{Sulphated ash, percent by mass} = \frac{100\,m}{M}$$

where

m = mass in g of ash, and

M = mass in g of sample.

5.6 Reporting — Report the result to the nearest 0·001 percent for samples below 0·02 percent and to the nearest 0·01 percent for higher levels as the sulphated ash.

5.7 Precision — For sulphated ash levels between 0·005 and 0·10 percent, the precision of this method is as follows:

Repeatability	*Reproducibility*
$0{\cdot}47 \times y^{0{\cdot}85}$	$0{\cdot}189 \times y^{0{\cdot}85}$

where y is average of two results in units of percent sulphated ash.

6. METHOD D — WATER SOLUBLE ASH

6.1 Outline of the Method — The water soluble ash is determined by boiling the ash, as obtained by Method A or Method C, in water, filtering and evaporating the filtrate to dryness.

6.2 Procedure — Place the dish or crucible containing the ash, as obtained by Method A or Method C, in a beaker, add about 350 ml of water, cover the beaker with a watch-glass and boil gently for about 15 minutes. Remove the dish or crucible from the water and wash any residue into the beaker with a fine jet of water. Heat the beaker until the volume of water is reduced to about 50 ml. Filter through a filter paper (Whatman No. 30 or its equivalent) collecting the filtrate in a tared glass evaporating dish of 200-ml capacity. Rinse the beaker and the filter paper with hot water. and filter the rinsings into the evaporating dish. Place the evaporating dish on a steam bath, and evaporate the contents to dryness. Remove the evaporating dish from the steam-bath, wipe the outside with a clean cloth, and put it into an oven maintained at 105°C. At the end of one hour remove the dish from the oven, cool in desiccator and weigh again. Repeat the drying until the mass is constant.

6.3 Calculation and Reporting — Calculate the mass of the water soluble ash as a percentage of the mass of the sample, and report it to two significant figures as Water Soluble Ash, Method D.

6.4 Precision — The precision limits of this method have not been established.