International Standard 3987

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Petroleum products — Lubricating oils and additives — Determination of sulphated ash

Produits pétroliers — Huiles lubrifiantes et additifs — Détermination des cendres sulfatées

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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It has been approved by the member bodies of the following countries :

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The member body of the following country expressed disapproval of the document on technical grounds :

France

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Petroleum products — Lubricating oils and additives — Determination of sulphated ash

1 Scope and field of application

1.1 This International Standard specifies a procedure for determining the sulphated ash from unused lubricating oils containing additives and from additive concentrates used in compounding (see note 1). These additives usually contain one or more of the following metals : barium, calcium, magnesium (see note 2), zinc, potassium, sodium, and tin. The elements sulphur, phosphorus, and chlorine may also be present in combined form. Application of this method to sulphated ash levels below 0,02 % (m/m) is restricted to oils containing ashless additives. The lower limit of applicability of the method is 0,005 % (m/m) sulphated ash.

1.2 The sulphated ash may be used to indicate the concentration of known metal-containing additives in new oils. If phosphorus is absent, barium, calcium, magnesium, sodium and potassium are converted to their sulphates and tin (IV) and zinc to their oxides (see note 3). Sulphur and chlorine do not interfere, but, if phosphorus is present with the metals, it remains partially or wholly in the sulphated ash as metal phosphates.

NOTES

1 This method is not intended for the analysis of used engine oils containing lead, nor is it recommended for the analysis of non-additive lubricating oils.

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

3 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.

2 Reference

ISO 3170, *Petroleum products — Liquid hydrocarbons — Manual sampling.*

3 Definition

sulphated ash : The residue remaining after the sample has been carbonized, and the residue subsequently treated with sulphuric acid and heated to constant mass.

4 Principle

Ignition of a test portion and burning until only ash and traces of carbon remain. After cooling, treatment of the residue with concentrated sulphuric acid and heating at 775 °C until the oxidation of carbon is complete. Cooling of the ash, treatment with dilute sulphuric acid, and heating at 775 °C to constant mass.

5 Reagents and materials

Use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

5.1 Low-ash mineral white oil, having a sulphated ash yield lower than the limit capable of being determined by this method.

NOTE — Determine the sulphated ash of this oil by the procedure given in clause 8 but 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 8.11.

5.2 Sulphuric acid (H_2SO_4), ϱ 1,84 g/ml, concentrated.

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

5.3 Sulphuric acid, (1 + 1) solution, prepared by slowly adding 1 volume of the concentrated sulphuric acid (5.2) to 1 volume of water.

6 Apparatus

6.1 Evaporating dish or **crucible,** made of porcelain, fused silica, or platinum, of 50 to 100 ml capacity. For samples yielding less than 0,02 % (m/m) sulphated ash, a platinum evaporating dish or crucible of 120 to 150 ml capacity should be used, 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.

6.2 Electric muffle furnace, capable of maintaining a temperature of 775 ± 25 °C and preferably having apertures at the front and rear to allow a slow natural draught of air to pass through the furnace.

7 Sampling

Samples for the determination of sulphated ash content shall be taken in accordance with the instructions specified in ISO 3170.

8 Procedure

8.1 Select an evaporating dish or crucible of suitable size according to the quantity of sample necessary (see 8.3).

8.2 Heat the evaporating dish or crucible in the muffle furnace (6.2) controlled at 775 ± 25 °C for at least 10 min. 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 desiccating agent.

8.3 Weigh, to the nearest 0,1 mg, into the dish, a test portion, according to the expected percentage by mass of sulphated ash, calculated from the formula

$$m_1 = \frac{10}{m_0}$$

where

m_0 is the expected percentage by mass of sulphated ash;

m_1 is the mass, in grams, of the test portion.

Do not take a test portion in excess of 80 g. In the case of lubricating oil additives yielding a sulphated ash greater than 2 % (m/m), dilute the weighed test portion in the dish with approximately 10 times its mass of low ash mineral oil (5.1).

NOTE — If the amount of sulphated ash found differs from the expected amount by more than a factor of two, repeat the analysis using a mass of test portion which takes into account the result of the first analysis.

8.4 Carefully heat the dish or crucible and the test portion at a low temperature on a hot plate or over a gas burner, avoiding spattering, until the contents can be ignited with a flame. Maintain at such a temperature that the test portion 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 test portion contains sufficient moisture to cause foaming and loss of material from the dish, discard the test portion, and, to an additional test portion, add 1 to 2 ml of 99 % (V/V) propanol-2 before heating. If this is not satisfactory, add 10 ml of a mixture of equal volumes of toluene and propanol-2 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.

8.5 Allow the dish to cool to room temperature, then completely moisten the residue by the addition, drop by drop, of the concentrated sulphuric acid (5.2). 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.

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

8.7 Allow the dish to cool to room temperature. Add 3 drops of water and 10 drops of the sulphuric acid solution (5.3). Move the dish so as to moisten the entire residue. Again heat the dish as specified in 8.5.

8.8 Replace the dish in the furnace controlled at 775 ± 25 °C and maintain at that temperature for 30 min. Cool the dish to room temperature in a suitable container (see note to 8.2).

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, the operations specified in 8.7 and 8.8 should be repeated until a white residue is obtained.

8.9 Weigh the dish and residue to the nearest 0,1 mg.

8.10 Repeat the operations specified in 8.8 and 8.9 until two successive weighings differ by not more than 1,0 mg.

NOTE — Normally repetition once will suffice, unless a high proportion of zinc is present, in which case three or four heating periods may be required.

8.11 For samples expected to contain 0,02 % (m/m) or less of sulphated ash, determine a sulphuric acid blank by adding 1 ml of the concentrated sulphuric acid (5.2) 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 min. Cool the dish or crucible to room temperature in a suitable container (see note to 8.2) 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, make 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 of sulphated ash for the test portion. Use this corrected mass as the value, m_2, in calculating the percentage by mass of sulphated ash.

9 Expression of results

9.1 Method of calculation

Calculate the sulphated ash, as a percentage by mass, of the original sample using the following formula

$$\frac{m_2}{m_1} \times 100$$

where

m_1 is the mass, in grams, of the test portion;

m_2 is the mass, in grams, of ash.

Express the result to the nearest 0,001 % (m/m) for samples having sulphated ash levels below 0,02 % (m/m), and to the nearest 0,01 % (m/m) for samples having higher levels.

9.2 Precision

The precision of the method, as obtained by statistical examination of inter-laboratory results, is a follows :

9.2.1 Repeatability

The difference between two 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 value only in one case in twenty :

$$0{,}047\ X^{0{,}85}$$

where X is the average of the two test results expressed as percentages by mass of sulphated ash.

9.2.2 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 value only in one case in twenty :

$$0{,}189\ X^{0{,}85}$$

where X is the average of the two test results expressed as percentages by mass of sulphated ash.

9.2.3 Specimen values

Specimen values, calculated in accordance with 9.2.1 and 9.2.2, are given in the following table.

Table — Precision

Sulphated ash % (m/m)	Repeatability	Reproducibility
0,005	0,000 5	0,002
0,01	0,000 9	0,004
0,05	0,003 7	0,015
0,1	0,006	0,027
0,5	0,026	0,105
1,0	0,047	0,189
10,0	0,33	1,34
20,0	0,60	2,4
30,0	0,85	3,4
40,0	1,1	4,3

10 Test report

The test report shall contain at least the following information :

a) the type and identification of the product tested;

b) a reference to this International Standard;

c) the result of the test (see 9.1);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.