INTERNATIONAL STANDARD

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Petroleum products — Determination of sulfur content of automotive fuels — Energy-dispersive X-ray fluorescence spectrometry

Produits pétroliers — Détermination de la teneur en soufre des carburants pour automobiles — Spectrométrie de fluorescence de rayons X dispersive en énergie

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 20847 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Introduction

This International Standard is directed specifically at the lower end of the concentration range covered in ISO 8754 ([3] in the Bibliography), which covers sulfur contents from 0,01 % (*m/m*) up to 5,00 % (*m/m*). By restriction of instrument type, a better signal to background ratio for sulfur K emission is assured and by the use of matrix matched calibration standards or other means of matrix corrections (as detailed below), the precision and accuracy of results for samples having varying C:H mass ratios and oxygen contents are improved. A knowledge of the general composition of the sample for analysis is advantageous in obtaining the best test result.

Where matrix matching is not used and where the C:H mass ratio of the test sample is known or can be determined, accuracy may be improved by the use of the equation given in A.2.2 to correct the result to the C:H mass ratio of the calibration standards, i.e. the reference diluent oil (4.1).

Some instruments include the capability for the separate measurement of scattered radiation from the X-ray tube, and notes for information are provided in A.2.3 on the use of this scattered radiation for compensation for matrix effects in the test sample.

Petroleum products — Determination of sulfur content of automotive fuels — Energy-dispersive X-ray fluorescence spectrometry

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies an energy dispersive X-ray fluorescence (EDXRF) test method for the determination of the sulfur content of motor gasolines, including those containing up to 2,7 % (*m/m*) oxygen, and of diesel fuels, including those containing up to 5 % (*V/V*) fatty acid methyl ester (FAME), having sulfur contents in the range 30 mg/kg to 500 mg/kg. Other products may be analysed and other sulfur contents may be determined according to this test method; however, no precision data for products other than automotive fuels and for results outside the specified range have been established for this International Standard. For reasons of spectral overlap, this International Standard is not applicable to leaded motor gasolines, lead-replacement gasolines containing 8 mg/kg potassium to 20 mg/kg potassium, or to products and feedstocks containing lead, silicon, phosporus, calcium, potassium or halides at concentrations greater than one-tenth of the concentration of sulfur measured.

NOTE For the purposes of this International Standard, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent the mass fraction and the volume fraction of a material, respectively.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3170:2004, *Petroleum liquids — Manual sampling*

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling*

3 Principle

The test portion, in a cup fitted with an X-ray transparent window, is placed in a beam of exciting radiation from an X-ray tube. The intensity of the sulfur K characteristic X-radiation is measured, and the number of accumulated counts is compared with a calibration curve constructed from sulfur standards covering the range of sulfur contents under examination.

NOTE The exciting radiation may be either direct, or indirect via a secondary target.

4 Reagents and materials

4.1 Diluent oil

4.1.1 The reference diluent oil is white oil (light paraffin oil) of high purity grade, with a sulfur content of 1 mg/kg maximum. However, if only one type of matrix is to be analysed (e.g. motor gasoline), the accuracy of results may be improved by using a matrix-matched diluent. These should match approximately the aromatic and oxygen content of the material to be analysed, and should consist of high purity components of less than 1 mg/kg sulfur content.

NOTE Suitable components for the matched matrix diluent include heptane, 2,2,4-trimethylpentane, toluene, xylenes, ethanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME) and fatty acid methyl ester (FAME).

4.1.2 For the analysis of diesel fuels containing FAME at contents greater than 5 % (*V/V*), a matched matrix diluent oil of the white oil with FAME shall be used.

4.2 Sulfur compounds

4.2.1 General

Sulfur compounds of known sulfur content shall be used for the preparation of the primary standards. The compounds given in 4.2.2 to 4.2.5 are suitable, and their nominal sulfur contents are given. Where the purity of these compounds is less than 99 % (*m/m*), either the concentrations and nature of all impurities are to be known or certified reference materials shall be used.

4.2.2 **Dibenzothiophene (DBT)**, with a nominal sulfur content of 17,399 % (*m/m*).

4.2.3 **Dibutylsulfide (DBS)**, with a nominal sulfur content of 21,915 % (*m/m*).

4.2.4 **Thionaphthene (Benzothiophene) (TNA)**, with a nominal sulfur content of 23,890 % (*m/m*).

4.2.5 **Dibutyldisulfide (DBDS)**, with a nominal sulfur content of 35,950 % (*m/m*).

4.3 Reference materials

Certified reference materials (CRMs) from accredited suppliers, containing a range of sulfur concentrations, are suitable alternatives to the compounds listed in 4.2 for use as calibration standards.

4.4 Quality control samples

Stable samples representative of the materials being analysed, that have a sulfur content that is known by this test method over a substantial period of time, or supplied commercially with a certified value. Ensure before use that the material is within its shelf life.

5 Apparatus

5.1 Energy-dispersive X-ray fluorescence analyser

5.1.1 **Energy-dispersive X-ray fluorescence analyser**, having facilities for measuring and subtracting the background to give net sulfur intensities.

The instrument shall be capable of measuring the content of sulfur at 50 mg/kg with an error due to counting statistics of 3 % relative standard deviation (RSD) maximum.

5.1.2 **Source of X-ray excitation**, with significant flux at X-ray energies above 2,5 keV.

5.1.3 Removable sample cup, providing a sample depth of at least 5 mm, and equipped with replaceable X-ray transparent film.

NOTE The transparent film is normally of polyester or polycarbonate with a thickness between 2 µm and 6 µm. Polyester film is the preferred choice as samples of very high aromatic content can dissolve polycarbonate film. There are possibly trace amounts of calcium in polyester film, but any absorption or enhancement effects would be cancelled out when samples and standards are analysed using the same material. It is important that samples, standards and blanks are measured using the same batch of film to avoid bias.

5.1.4 X-ray detector, with high sensitivity, and resolution not exceeding 800 eV at 2,3 keV.

5.1.5 Means of discriminating between sulfur K characteristic X-radiation and other X-rays of higher energy (e.g. filters).

5.1.6 Signal conditioning and data handling electronics, including the functions of pulse counting, and a minimum of two energy regions (to correct for background X-rays). When matrix matching of samples and standards is not used, the instrument shall also be able to measure an energy region corresponding to scattered radiation, and to use this measurement to compensate for matrix effects (see Annex A). The latter measurement can also be used as the second energy region specified above and used to calculate the background.

NOTE Differences in carbon/hydrogen ratios, or oxygen contents, between samples and standards can cause matrix effects which may lead to a bias in the analytical result.

5.2 Analytical balance, single-pan or double-pan, capable of weighing to the nearest 0,1 mg.

5.3 Mixer, magnetic stirrer with PTFE-coated stirring rods.

5.4 Flasks, of 100 ml capacity, narrow-necked, conical, and made of borosilicate glass.

6 Sampling and sample handling

6.1 Unless otherwise specified, samples shall be taken by the procedures described in ISO 3170 or ISO 3171.

6.2 Store samples which contain light fractions (e.g. motor gasoline and naphtha) in a refrigerator.

6.3 Mix samples by gently shaking by hand prior to the removal of the test portion.

6.4 Allow test portions to attain ambient temperature prior to analysis.

7 Apparatus preparation

7.1 Analyser

7.1.1 Set up the analyser (5.1) in accordance with the manufacturer's instructions. Wherever possible, the instrument shall be continuously switched on to maintain optimum stability.

7.1.2 Purge the optical system with helium (99 % purity) following the manufacturer's guidelines on minimum flush time to ensure stability of measurements.

7.2 Sample cups

It is recommended that disposable sample cups be used. If disposable cups are not used, thoroughly clean the sample cups with an appropriate solvent and dry before use. Do not re-use disposable cups. Use the same batch of window material for each run of verification and sampling analysis (see the note to 5.1.3). Keep handling of window material to the absolute minimum.