INTERNATIONAL STANDARD

ISO 14596

Second edition
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Petroleum products — Determination of sulfur content — Wavelength-dispersive X-ray fluorescence spectrometry

Produits pétroliers — Détermination de la teneur en soufre — Spectrométrie de fluorescence X dispersive en longueur d'onde

Reference number
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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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 14596 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This second edition cancels and replaces the first edition (ISO 14596:1998), which has been technically revised. It also incorporates the Technical Corrigendum ISO 14596:1998/Cor. 1:1999.

Petroleum products — Determination of sulfur content — Wavelength-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 a method for the determination of the sulfur content of liquid petroleum products, additives for petroleum products, and semi-solid and solid petroleum products that are either liquefied by moderate heating or soluble in organic solvents (see 4.1) of negligible or accurately known sulfur content. The method is applicable to products or additives having sulfur contents in the range 0,001 % (*m*/*m*) to 2,50 % (*m*/*m*); higher contents can be determined by appropriate dilution. Other elements do not interfere at concentrations anticipated in the materials subject to this analysis.

NOTE For the purposes of this International Standard, the term "% (*m*/*m*)" is used to represent the mass fraction of a material.

High concentrations of phosphorus or chlorine [typically above 3 % (*m*/*m*)] can cause bias in the sulfur result by absorbing Zr-Lα and S-Kα to different extents. It is necessary in these cases to carry out studies to determine whether this potential interference is significant.

When larger amounts of molybdenum are present (typically above 50 mg/kg to 100 mg/kg), increased background radiation and spectral overlap with the sulfur signal can occur. It is necessary in these cases to inspect the relevant spectral regions, for example, to investigate the significance of this potential source of bias.

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 and a zirconium solution as internal standard are mixed in a given mass ratio and exposed, in a sample cell, to the primary radiation of an X-ray tube.

The count rates of the S-Kα at 0,537 3 nm and Zr-Lα1 at 0,607 0 nm fluorescence thus excited and the count rate of the background radiation at 0,545 nm are measured and the ratio of these net count rates calculated. The sulfur content of the sample is determined from a calibration curve prepared on the basis of sulfur calibration standards.

NOTE The Siegbahn X-ray line notation (S-Kα) is used in this International Standard; the corresponding IUPAC X-ray line notation is S K-$L_{2,3}$.

4 Reagents and materials

4.1 White oil (light paraffin oil, paraffinum perliquidum), high-purity grade, sulfur content 1 mg/kg maximum.

4.2 Sulfur compounds, of sulfur content accurately known to the nearest 0,01 % (m/m), used for the preparation of the primary standards.

The compounds given in 4.2.1 to 4.2.3 are suitable, and their nominal sulfur contents are given. Where the purity of these compounds is less than 99 %, certified materials are required, or the nature of all impurities and their contents should be accurately known to the nearest 0,01 % (m/m).

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

4.2.2 Dibutyl sulfide (DBS), with a nominal sulfur content of 21,915 % (m/m).

4.2.3 Thionaphthene (benzothiophene) (TNA), with a nominal sulfur content of 23,890 % (m/m).

4.3 Certified sulfur reference materials.

Use materials from a national standards body or accredited suppliers, if available.

4.4 Zirconium solution A.

Zirconium octoate solution with a zirconium content in the range of 12 % (m/m) to 18 % (m/m) or another oil-soluble, sulfur-free zirconium compound dissolved in white oil (4.1) to provide a zirconium mass fraction in the range of 12 % (m/m) to 18 % (m/m).

4.5 Zirconium solution B.

Dissolve the zirconium solution A (4.4) with white oil (4.1) to provide a zirconium mass fraction of approximately 1 % (m/m).

5 Apparatus

5.1 Wavelength-dispersive X-ray fluorescence (WDXRF) spectrometer, consisting of any suitable spectrometer that incorporates the design features listed in Table 1. It shall be set up according to the manufacturer's instructions.