INTERNATIONAL STANDARD

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Petroleum and related products — Determination of chlorine and bromine content — Wavelength-dispersive X-ray fluorescence spectrometry

Produits pétroliers et produits connexes — Dosage du chlore et du brome — Spectrométrie par fluorescence X dispersive en longueur d'onde

Reference number
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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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15597 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Petroleum and related products — Determination of chlorine and bromine 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 chlorine and bromine content of liquid petroleum products, synthetic oils and fluids, and additives for petroleum products (including used oils) that are soluble in organic solvents of negligible or accurately known chlorine/bromine content. The method is applicable to products or additives having chlorine contents in the range 0,000 5 % (*m/m*) to 0,100 0 % (*m/m*), and bromine contents in the range 0,001 0 % (*m/m*) to 0,100 0 % (*m/m*). Other elements do not generally interfere, although lead may interfere at contents above 0,150 0 % (*m/m*) (see note 2).

NOTE 1 For the purposes of this International Standard, the term "% (*m/m*)" is used to represent the mass fraction of a material.

NOTE 2 Used lubricants may pose particular problems due to the range of potentially interfering elements at relatively high concentrations. For used lubricants generally, the lower limit of sensitivity may be 0,005 0 % (*m/m*) even when the provisions of the last paragraph of 9.3 are applied.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3170:1988, *Petroleum liquids — Manual sampling.*

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

ISO 4259:1992, *Petroleum products — Determination and application of precision data in relation to methods of test.*

3 Principle

The test portion and a bismuth 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 chlorine Kα at 0,472 9 nm and bismuth Mβ at 0,490 9 nm, or bromine Kα at 0,104 1 nm and bismuth Lα at 0,114 4 nm fluorescence thus excited, and the count rate of the background radiation at 0,480 7 nm or 0,108 5 nm, are measured, and the ratio of these net count rates is calculated. The chlorine and/or bromine content of the sample is determined from calibration curves prepared on the basis of chlorine and/or bromine calibration standards.

4 Reagents and materials

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

4.2 Chlorine compound, 1-chlorooctane or another oil-soluble chlorine compound of accurately known chlorine content, used for the preparation of the primary standards. The chlorine content shall be accurately known to the nearest 0,01 % (*m/m*).

4.3 Bromine compound, 1,1,2,2-tetrabromoethane or another oil-soluble bromine compound of accurately known bromine content, used for the preparation of the primary standards. The bromine content shall be accurately known to the nearest 0,01 % (*m/m*).

CAUTION — 1,1,2,2-tetrabromoethane is extremely toxic by inhalation and ingestion. Appropriate precautions for the handling operations of opening the container and weighing shall be followed.

4.4 Certified reference materials, obtained from a national standards body or accredited supplier with a range of certified chlorine and/or bromine contents for the production of calibration curves for routine analysis.

4.5 Bismuth compound, triphenylbismuth, of minimum purity 98 %.

4.6 2-ethylhexanoic acid, of minimum purity 98 %.

5 Apparatus

5.1 Wavelength-dispersive X-ray fluorescence spectrometer, any suitable spectrometer that allows the count rates of the Cl-Kα, Br-Kα, Bi-Mβ and Bi-Lα X-ray fluorescence to be measured, provided that the design incorporates the general features given in Table 1. It shall be set up according to the manufacturer's instructions.

Table 1 — General requirements of the spectrometer

Component	Requirement
Anode	Rhodium, scandium, chromium, or any other tube anode that allows the counting times to be adjusted to achieve the required precision
Collimator (if used)	Coarse for chlorine, narrow for bromine
Analysing crystal	Germanium for chlorine, lithium fluoride (LiF) for bromine, or any other crystal suitable for the required dispersion of the wavelengths in Table 2 within the angular range of the spectrometer
Optical path	Helium
Cell window	Polyester or polypropylene film, chlorine- and bromine-free, thickness 2 μm to 6 μm
Detector	Proportional counter with pulse-height analyser. For bromine, a scintillation counter with pulse-height analyser is preferred

5.2 Analytical balance, capable of weighing accurately to the nearest 0,1 mg.

5.3 Homogenizer, of the non-aerating, high-speed shear type, or **heatable magnetic** or **ultrasonic stirrer**.

5.4 Filters, of sintered glass, with a pore size of 10 μm to 60 μm.