BRITISH STANDARD

BS ISO 15597:2001
BS 2000-503:2004

Methods of test for Petroleum and its products — BS 2000-503: Determination of chlorine and bromine content — Wavelength-dispersive X-ray fluorescence spectrometry

(Identical with IP 503-2004)

ICS 75.080

British Standards

National foreword

This British Standard reproduces verbatim ISO 15597:2001 and implements it as the UK national standard.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

Cross-references

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INTERNATIONAL STANDARD

ISO 15597

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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

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Contents

Page

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 0,0005 % (*m*/*m*) to 0,1000 % (*m*/*m*), and bromine contents in the range 0,0010 % (*m*/*m*) to 0,1000 % (*m*/*m*). Other elements do not generally interfere, although lead may interfere at contents above 0,1500 % (*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 0,0050 % (*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 0,4729 nm and bismuth Mβ at 0,4909 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.

5.5 Flasks, of 25 ml to 100 ml capacity, narrow-necked, conical, made of borosilicate glass, and fitted with ground-glass stoppers.

6 Samples and sampling

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

6.2 Test portions from the samples shall be drawn after thorough mixing and subdivision. Heat viscous samples to a temperature which renders the sample fluid, and homogenize, using the homogenizer or stirrer (5.3) as necessary.

NOTE For the purpose of this procedure, the term “sample” includes solutions prepared from additives, semi-solid or solid petroleum products that have been appropriately pre-treated and/or diluted.

7 Calibration solutions

7.1 General

Use either certified reference materials (4.4) or primary standards prepared from chlorine compounds (4.2) and/or bromine compounds (4.3) dissolved in white oil (4.1) as a basis for the preparation of the appropriate range of stock solutions.

7.2 Preparation of stock solutions

7.2.1 Chlorine and bromine stock solutions

Weigh, to the nearest 0,1 mg, a quantity of chlorine compound (4.2) or bromine compound (4.3) to prepare stock solutions of approximately 0,10 % by mass of chlorine or bromine, calculated to the nearest 0,001 % (*m/m*), and dissolve in white oil (4.1) at room temperature. Mix the contents thoroughly using a homogenizer (5.3), and store in a glass-stoppered flask (5.5).

It is recommended that a polytetrafluorethylene (PTFE) or glass-coated magnetic stirrer and stirring device be used to mix the contents of the flask.

Calculate the exact chlorine and/or bromine content, w_2, in percent by mass, to three decimal places, in each case from the amounts of white oil and compound used as follows:

$$w_2 = \frac{m_c \times w_1}{m_c + m_0} \tag{1}$$

where

m_c is the mass of the chlorine or bromine compound, expressed in grams;

w_1 is the chlorine or bromine content of the compound, expressed in percent by mass;

m_0 is the mass of white oil, expressed in grams.

7.2.2 Bismuth solution

Weigh, to the nearest 0,1 mg, a quantity of triphenylbismuth (4.5) sufficient to make a 1 % by mass solution in white oil. Dissolve the triphenylbismuth in white oil by stirring and warming to a temperature not exceeding 80 °C. Add 5 % (*m/m*) 2-ethylhexanoic acid (4.6) to the solution. Remove any residual turbidity by filtering the gently heated mixture through the filter (5.4). Store in a tightly stoppered flask or bottle.

When protected against moisture, the bismuth solution can be kept for several months. Any turbidity should be taken as an indication that the solution is no longer suitable for use.

7.3 Preparation of standard solutions

Prepare standard solutions of chlorine and/or bromine contents of 0,000 5 % (*m/m*), 0,001 0 % (*m/m*), 0,002 0 % (*m/m*), 0,005 0 % (*m/m*), 0,010 0 % (*m/m*), 0,025 0 % (*m/m*) and 0,050 0 % (*m/m*) from the stock solutions (7.2.1), by weighing, to the nearest 0,1 mg, a quantity of the stock solution to produce approximately 25 g of standard solution, into a flask (5.5), and diluting this with white oil (4.1). Reweigh to the nearest 0,1 mg and mix thoroughly at room temperature. Calculate the content of chlorine or bromine, w_3, in percent by mass, in each solution to the nearest 0,000 01 % (*m/m*) by means of equation (2) below. Transfer the solutions to tightly stoppered dark glass bottles with the content recorded on each bottle.

$$w_3 = \frac{w_2\left(m_2 - m_1\right)}{m_3 - m_1} \tag{2}$$

where

m_1 is the mass of the flask, expressed in grams;

m_2 is the mass of the flask plus stock solution, expressed in grams;

m_3 is the mass of the flask plus stock solution plus white oil, expressed in grams.

7.4 Preparation of calibration solutions

Weigh a series of flasks (5.5) and add a quantity of each standard solution (7.3) to separate flasks. Also add a quantity of each stock solution (7.2.1) and of the white oil (4.1) to additional separate weighed flasks. Reweigh. Mix each of these with bismuth solution (7.2.2) in the ratio 10:1. Mix thoroughly at room temperature. The quantity of each resulting solution shall be sufficient to adequately fill the sample cells for the spectrometer.

NOTE Normally, 25 g ± 0,1 g of solution plus 2,5 g ± 0,01 g of bismuth solution gives an adequate volume.

7.5 Storage of standards

Store certified reference materials in accordance with the instructions of the certifying organization, and use within the time-scale specified.

Store standards prepared from white oil and chlorine and/or bromine compounds in dark glass-stoppered bottles in a cool dark place.

8 Calibration

8.1 General

After the spectrometer (5.1) has been set up and checked, purge the optical path thoroughly with helium.

8.2 Measurements

Transfer each of the calibration solutions (7.4) to a sample cell and, in a sequence of increasing chlorine or bromine content, place them in the spectrometer for exposure to the primary radiation.

Measure the count rates, I, at the wavelengths specified in Table 2, and just one background radiation at an appropriate wavelength for the X-ray tube being used.

NOTE Lead interferes with background measurements on the short wavelength side of the bromine line.

Keep the total duration of the radiation as short as possible, measuring the X-ray fluorescence radiation for each solution for chlorine and/or bromine followed by bismuth. For the chlorine or bromine radiation, do not exceed a measurement time of 100 s, or 40 s if an end-window tube is used.

Choose a measurement procedure that results in at least 50 000 pulses for the Bi-Mβ or Bi-Lα radiation during the total measurement period.

Table 2 — Wavelengths of the X-ray fluorescence and background radiation

Radiation		Wavelength nm
Chlorine	Cl-Kα	0,472 9
Bismuth (Cl)	Bi-Mβ	0,490 9
Background, Cl	B, Cl	0,480 7
Bromine	Br-Kα	0,104 1
Bismuth (Br)	Bi-Lα	0,114 4
Background, Br	B, Br	0,108 5

Calculate the net count ratios, $R_{0,\mathrm{Cl}}$ and $R_{0,\mathrm{Br}}$ from equation (3) or equation (4).

$$R_{0,\mathrm{Cl}} = \frac{I_{\mathrm{Cl}} - I_{\mathrm{B,Cl}}}{I_{\mathrm{Bi,Cl}} - I_{\mathrm{B,Cl}}} \tag{3}$$

$$R_{0,\mathrm{Br}} = \frac{I_{\mathrm{Br}} - I_{\mathrm{B,Br}}}{I_{\mathrm{Bi,Br}} - I_{\mathrm{B,Br}}} \tag{4}$$

where

I_{Cl} is the count rate for Cl-Kα;

$I_{\mathrm{Bi,Cl}}$ is the count rate for Bi-Mβ;

$I_{\mathrm{B,Cl}}$ is the count rate for background radiation (chlorine);

I_{Br} is the count rate for Br-Kα;

$I_{\mathrm{Bi,Br}}$ is the count rate for Bi-Lα:

$I_{\mathrm{B,Br}}$ is the count rate for background radiation (bromine).

8.3 Calibration curves

Plot the count ratio, R_0, of the individual calibration solutions as a function of the chlorine and/or bromine content, to give calibration curves for chlorine and/or bromine.

NOTE A polynomial equation may be required for mathematical analysis of the experimental data.

8.4 Checking

Check the calibration curves regularly, and after each fresh preparation of bismuth solution. In regular use, check at least two points on each calibration curve not less frequently than every six months. If the check result differs from the curve by more than the repeatability of this International Standard, construct a new calibration curve.

9 Procedure

9.1 Ensure that all laboratory glassware is free from chlorine or bromine, and that the laboratory air does not contain any vapour from halogenated solvents.

9.2 Weigh, to the nearest 0,1 mg, 25 g ± 0,1 g of the sample to be analysed into a flask (5.5), and add 2,5 g ± 0,01 g of the bismuth solution (7.2.2), weighed to the same accuracy. Stopper immediately and homogenize thoroughly using the homogenizer (5.3) and gently heat to a temperature not exceeding 50 °C.

9.3 Cool the solution to room temperature, transfer it to a sample cell and place it in the spectrometer for exposure to the primary radiation. Measure the count rates, I, at the specified wavelengths, together with the background radiations. Measure the count rates, I_{Bi}, for the appropriate bismuth lines and calculate the count ratio, $R_{0,\mathrm{Cl}}$ or $R_{0,\mathrm{Br}}$, from equation (3) and/or equation (4).

If bubble formation is found to be a problem, and if both chlorine and bromine contents are required, divide the solution into two sample cells to reduce the overall radiation period, and determine the concentrations separately.

If interfering elements, e.g. lead at contents above 0,15 % (*m/m*), are present, then the use of a primary collimator with higher resolution than would normally be used for the measurement of Cl-Kα is recommended.

10 Calculation

Read the chlorine and/or bromine content from the calibration curves constructed in accordance with 8.3. If the chlorine or bromine content is above that specified in the scope of this International Standard, dilute the sample with white oil (4.1) and repeat the procedure specified in 9.2 and 9.3.

NOTE Many modern instruments contain a microprocessor that retains the calibration curve and produces a digital readout.

11 Expression of results

Report the chlorine and/or bromine content of the sample to the nearest 0,000 1 % (*m/m*), or to the nearest 1 mg/kg.

12 Precision

12.1 General

The precision, as determined by statistical examination, in accordance with ISO 4259, of interlaboratory test results is given in 12.2 and 12.3.

12.2 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 values given in Table 3 in only one case in twenty.

12.3 Reproducibility

The difference between two single and independent test 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 values given in Table 3 in only one case in twenty.

Table 3 — Precision values

Halogen content % (*m*/*m*) [mg/kg]	**Repeatability** % (*m*/*m*) [mg/kg]		**Reproducibility** % (*m*/*m*) [mg/kg]	
Chlorine				
0,000 5 to 0,001 0 [5 to 10]	0,000 15	[1,5]	0,000 3	[3]
> 0,001 0 to 0,005 0[> 10 to 50]	0,000 3	[3]	0,000 6	[6]
> 0,005 0 to 0,010 0[> 50 to 100]	0,000 5	[5]	0,001 0	[10]
> 0,010 0 to 0,100 0[> 100 to 1 000]	3 % relative [a]		10 % relative [a]	
Bromine				
0,001 0 to 0,005 0 [10 to 50]	0,000 2	[2]	0,000 5	[5]
> 0,005 0 to 0,010 0[> 50 to 100]	0,000 3	[3]	0,001 0	[10]
> 0,010 0 to 0,100 0[> 100 to 1 000]	3 % relative [a]		10 % relative [a]	

[a] Based on the mean value calculated from two results.

13 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) the type and complete identification of the product tested;

c) the result of the test (see clause 11);

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

e) the date of the test.

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