BS EN ISO
20847:2004
BS 2000-496:
2004

Methods of test for petroleum and its products — BS 2000-496: Petroleum products — Determination of sulfur content of automotive fuels — Energy-dispersive X-ray fluorescence spectrometry

(Identical with IP 496-2005)

The European Standard EN ISO 20847:2004 has the status of a British Standard

ICS 75.080; 75.160.30

British Standards

National foreword

This British Standard is the official English language version of EN ISO 20847:2004. It is identical with ISO 20847:2004.

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.

Energy Institute, under the brand of IP publishes and sells all parts of BS 2000, and all BS EN petroleum test methods that would be part of BS 2000, both in its annual publication "Standard methods for analysis and testing of petroleum and related products and British Standard 2000 parts" and individually.

Further information is available from:

Energy Institute, 61 New Cavendish Street, London W1G 7AR.
Tel: 020 7467 7100. Fax: 020 7255 1472.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled "International Standards Correspondence Index", or by using the "Search" facility of the *BSI Electronic Catalogue* or of British Standards Online.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, the EN ISO title page, the EN ISO foreword page, the ISO title page, pages ii to v, a blank page, pages 1 to 11 and a back cover.

The BSI copyright notice displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 26 April 2004

ISBN 0 580 43676 4

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN ISO 20847

March 2004

ICS 75.080; 75.160.30

English version

Petroleum products - Determination of sulfur content of automotive fuels - Energy-dispersive X-ray fluorescence spectrometry (ISO 20847:2004)

Produits pétroliers - Détermination de la teneur en soufre des carburants pour automobiles - Spectrométrie de fluorescence de rayons X dispersive en énergie (ISO 20847:2004)

Mineralölerzeugnisse - Bestimmung des Schwefelgehalts von Automobilkraftstoffen - Energiedispersive Röntgenfluoreszenz-Spektrometrie (ISO 20847:2004)

This European Standard was approved by CEN on 1 March 2004.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Foreword

This document (EN ISO 20847:2004) has been prepared by Technical Committee ISO/TC 28 "Petroleum products and lubricants" in collaboration with Technical Committee CEN/TC 19 "Petroleum products, lubricants and related products", the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2004, and conflicting national standards shall be withdrawn at the latest by September 2004.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Endorsement notice

The text of ISO 20847:2004 has been approved by CEN as EN ISO 20847:2004 without any modifications.

INTERNATIONAL STANDARD

ISO 20847

First edition
2004-03-15

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

Reference number
ISO 20847:2004(E)

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 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.

blank

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.

NOTE Differences in window material thickness between batches, or the presence of even partial finger marks, are sufficient to affect results.

When carrying out measurements at low sulfur concentrations (< 100 mg/kg), follow the guidelines given in Annex B.

8 Calibration

8.1 General

Use either certified reference materials (4.3) or primary standards prepared from sulfur compounds (4.2) dissolved in diluent oil (4.1) as a basis for the preparation of the two primary calibration standards.

8.2 Preparation of primary standards

8.2.1 Prepare two primary standards with sulfur contents of approximately 5 000 mg/kg and 1 000 mg/kg.

8.2.2 Weigh, to the nearest 0,1 mg, the appropriate quantity of diluent oil (4.1) (see Table 1), into a flask (5.4) and add the appropriate quantity of the selected sulfur compound (4.2) or certified reference material (4.3), weighed to the nearest 0,1 mg. Mix the contents of the flask thoroughly at room temperature using the mixer (5.3).

Table 1 — Composition of primary standards based on nominal sulfur contents

Approximate sulfur content mg/kg	**White oil** g	**DBT** (4.2.2) g	**DBS** (4.2.3) g	**TNA** (4.2.4) g
1 000	50,0	0,29	0,23	0,21
5 000	50,0	1,48	1,17	1,07

8.2.3 Calculate the sulfur content, net of that included in the diluent oil, w_{S}, in milligrams per kilogram to three decimal places in each case, from the amounts of diluent oil and sulfur compound used as follows:

$$w_{\text{S}} = 10\,000 \times \frac{m_{\text{S}} w_{\text{Sc}}}{m_{\text{S}} + m_{\text{w}}}$$

where

m_{S} is the mass of sulfur compound, expressed in grams (g);

w_{Sc} is the sulfur content of the sulfur compound, expressed in percent mass, % (m/m);

m_{w} is the mass of white oil, expressed in grams (g).

8.2.4 Store primary standards in tightly closed glass containers in a dark cool place, preferably in a refrigerator. Before use, examine for any phase separation or discoloration, shake vigorously, and allow to stand to allow removal of air bubbles. Discard any standard that shows sediment, phase separation or discoloration.

8.3 Calibration standards

8.3.1 Prepare calibration standards from the primary standards (8.2) in the selected diluent oil (4.1), and calculate the exact sulfur content of the calibration standard using the equation given in 8.2.3. Prepare calibration standards of nominal sulfur content of 700 mg/kg and 300 mg/kg from the 5 000 mg/kg primary standard, and calibration standards of nominal sulfur content of 500 mg/kg and 100 mg/kg from the

1 000 mg/kg primary standard. Use the reference diluent oil (4.1) as the blank or zero point and the 1 000 mg/kg primary standard as the top point of the calibration. Calibration standards, of certified sulfur content in a specified diluent oil (e.g. diesel), are suitable for use for analysis of known similar materials. Where concentrations of less than 100 mg/kg are to be measured, additional standards of sulfur content 25 mg/kg and 50 mg/kg should be included in the calibration.

8.3.2 Store calibration standards in the same manner as primary standards (see 8.2.4).

NOTE Stability trials have shown that calibration standards are stable for up to six months when stored in a refrigerator.

8.4 Calibration procedure

8.4.1 When carrying out measurements at low sulfur contents (< 100 mg/kg), follow the guidelines given in Annex B.

8.4.2 Carry out the calibration procedure in accordance with the manufacturer's instructions, ensuring that both the sulfur K line and background intensity are measured and used to calculate net intensities for the sulfur line. If required for matrix corrections, the scattered radiation (e.g. from an X-ray tube line) shall also be measured (see Annex A).

8.4.3 Prepare the sample cup (5.1.3) by covering the base of the cup with window film, and fill to a minimum depth of 50 % of the cup capacity. If closed cells are used, provide a vent hole in the top to prevent bowing of the film during analysis of volatile samples. Ensure that there are no air bubbles between the window and the liquid, and that there are no wrinkles in the film or sagging of the window.

NOTE Scatter from the sample cell and the sample may vary with sample depth, and thus matrix corrections may be affected if the depth is not relatively consistent.

8.4.4 Obtain three readings on each calibration standard and run in random order, taking a fresh sample aliquot and cell for each reading. Set the counting times for the sulfur K peak, and the background measurement (and the scattered radiation if used) to be long enough to obtain an overall precision estimate of better than 3 % relative standard deviation (RSD) at 50 mg/kg sulfur content [i.e. at 50 mg/kg sulfur content, results should be within 3 mg/kg sulfur (95 % confidence)]. Measure the diluent oil as a blank.

NOTE The objective at low sulfur levels is to obtain adequate counts to satisfy the above requirements, with the reproducibility of measurement improved in relation to the number of counts collected. At very low sulfur levels, this counting time is related to instrument count rate and the background count rate (estimated from a sample with less than 1 mg/kg sulfur content). Where the manufacturer's data sheet does not recommend specific counting times, the user should refer to the instrument manufacturer for the correct equation to estimate the required counting time for each sulfur level.

8.4.5 Construct a calibration curve from the calibration standards. Check the curve at a minimum of three points with certified reference materials or laboratory secondary working standards of appropriate sulfur content and diluent type, with sulfur values either assigned from determinations on another instrument, or directly traceable to a primary standard. Results from this check shall be within the control limits allowed for each standard. If the results fall outside these limits (after repeat tests), repeat the primary calibration procedure (see 8.4.4).

Control limits are established from the laboratory statistical control charts, but initial values should be set before experience is established. Limits of the repeatability of this method, or 0,7 times the reproducibility, are reasonable starting points.

8.4.6 From the primary calibration graph, assign set-up standards and use them for frequent restandardization of the graph in order to compensate for changes in instrument stability and sensitivity. Check the graph regularly against calibration standards. Whenever tests on the calibration standards show sulfur content results which differ from their assigned values by more than the repeatability precision limits of the test method, standardize (prepare fresh set-up standards) or recalibrate the analyser. If the instrument does not meet the minimum precision requirements given in 8.4.4, or the set-up standards do not give acceptable results even after repeated recalibration, consult the instrument manufacturer. Provided the quality control check remains within the limits, recalibration is not required. If it is outside the limits, follow the calibration procedure given in 8.4.4.

NOTE 1 Set-up standards may be calibration standards (8.3), but are more commonly secondary standards such as oils or the manufacturer's supplied setting-up samples (SUS).

NOTE 2 Instrument drift may be influenced by temperature.

NOTE 3 The typical frequency of primary calibration checks is daily, or each time the instrument is used if less frequently.

9 Procedure

9.1 When carrying out measurements at low sulfur contents (< 100 mg/kg), follow the guidelines given in Annex B.

9.2 Prepare and fill the sample cup with the test portion as described in 8.4.3, taking the same precautions as for test portion capacity, venting and film continuity.

9.3 Take measurements for the sulfur K line and background (and scatter peak if used) using the same counting time as used for calibration. Repeat the measurements using a fresh test portion in a new cell, and calculate the mean net count.

NOTE Modern instruments may incorporate this calculation.

9.4 After every five to ten unknown sample analyses, analyse an appropriate quality control sample (4.4). Each day, analyse a blank sample. If the values of these quality control samples or the blank fall outside the control limits (see 8.4.5), recalibrate the instrument.

10 Calculation

Read the content of sulfur in the sample from the calibration curve, using the mean count for each test portion, or by direct reading from those analysers which have computing facilities.

11 Expression of results

Report the sulfur content to the nearest 1 mg/kg.

12 Precision

12.1 General

The precision, as determined by statistical examination in accordance with ISO 4259 ([1] and [2] in the Bibliography) of interlaboratory test results on eight motor gasoline samples and seven diesel samples, is given in 12.2 and 12.3.

12.2 Repeatability, r

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 values in only one case in 20.

For motor gasolines $r = 0{,}031\,2\,X + 9$

For diesels $r = 0{,}018\,8\,X + 8$

where X is the average of the results being compared, in milligrams per kilogram.

12.3 Reproducibility, R

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 following values in only one case in 20.

For motor gasolines	$R = 0{,}111\,6\,X + 11$
For diesels	$R = 0{,}016\,9\,X + 12$

where X is the average of the results being compared, in milligrams per kilogram.

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 procedure specified;

e) the date of the test.

Annex A
(informative)

Interferences

A.1 Spectral interferences

Spectral interferences occur when elements within the test portion emit X-rays that, due to the overlap of spectral peaks, the detector cannot resolve from sulfur K characteristic X-radiation. In general, for instruments employing a gas-filled proportional detector, interfering elements of contents greater than a tenth of the measured content of sulfur, or more than approximately 100 mg/kg, will produce such effects. Interfering elements include lead, silicon, phosphorus, calcium, potassium and the halides. Test portions containing these elements are excluded from the scope of this International Standard.

A.2 Matrix effects

A.2.1 General

Matrix effects are caused by variations in the concentrations of the elements within the test portion. Such variations directly influence X-ray absorption and will thus change the measured intensity for the sulfur K emission. Variations in oxygen content and/or the C:H mass ratio of the petroleum product under test will produce significant variations in measured values and therefore, if matrix matching is not to be used, it is critical that matrix effects are considered and compensated for.

A.2.2 Diluent selection

A.2.2.1 The reference diluent (4.1) for the production of calibration solutions from sulfur compounds is a highly paraffinic light oil, whereas test samples may contain varying amounts of aromatic and unsaturated hydrocarbons, and may contain oxygenated compounds. If compensation is not made for these variations, changes in the C:H mass ratio alone can lead to erroneous low values of up to 5 % relative, and significant concentrations of oxygenates will increase the errors beyond this value.

A.2.2.2 Compensation for matrix effects can be made by selecting a diluent for the calibration standards which closely matches the composition of the samples to be tested. Where only limited information is available on sample composition, such as the aromatic content of motor gasoline, simulated diluents of 2,2,4-trimethylpentane and toluene or xylene, mixed to the same approximate aromatic content, can be used. Where oxygenates are known to be present, matrix matching of the calibration standards for approximate oxygenate content is essential for the most accurate results.

A.2.2.3 Where oxygenates are not present, and the C:H mass ratio of the sample is known, or can be calculated, the following theoretical correction based on fundamental parameters can be applied to obtain a sulfur content corrected for the matrix effect when the diluent for the calibration standards is the reference diluent (4.1) (C:H mass ratio = 5,698).

$$w_{\mathrm{Sx}} = \frac{w_{\mathrm{Su}}}{1{,}076 - 0{,}013\,9C}$$

where

w_{Sx} is the corrected sulfur content;

w_{Su} is the sulfur content measured from the calibration curve;

C is the C:H mass ratio.

A.2.2.4 Where samples of unknown composition are tested in different laboratories, it is essential that the diluent used for the preparation of the calibration curves in the laboratories is the same, or at least similar, to enable the best comparison of results to be made. Where no agreement has been made, the diluent should be identified on the test report. The default diluent is the reference diluent oil (4.1).

A.2.3 Matrix correction using scattered tube radiation

Many modern instruments include the capability to correct for matrix effects by ratioing the measured sulfur intensity to some portion of the X-radiation scattered by the sample (e.g. characteristic tube lines or bremstrahlung). This can be effective for correcting for matrix differences between the test portion and the calibration standards but, unless counting times are calculated accordingly, it may lead to some degradation in measurement precision (see 5.1). The corrections provided by instrument manufacturers may not be universally applicable, and it is the responsibility of each user to develop matrix corrections that are accurate for their own applications (i.e. that cover the whole range of products which may be analysed on a routine basis). Regular checking of the corrections by the use of appropriate CRMs is recommended.

Annex B
(informative)

Guidelines for measuring low sulfur contents (less than 100 mg/kg)

B.1 Sample preparation

B.1.1 Prepare samples and cells in a clean, dust-free environment, away from the instrument and away from any samples or standards containing high concentrations of sulfur. Also ensure that unused cells and film are stored in a clean, dust-free environment when not in use (e.g. keep in a sealed plastic bag).

B.1.2 Never re-use disposable cells.

B.1.3 When assembling the cells, avoid touching the part of the film which will form the cell window with the fingers. Once cells are assembled, ensure that the window is free of wrinkles and that it does not come into contact with any surface prior to making the measurement (use a suitable rack to support the cells).

B.1.4 If the instrument incorporates a secondary window, change this after every sample (taking the same precautions as given in B.1.3).

B.1.5 Use a disposable pipette to transfer the sample to the cell (this avoids spillage and possible contamination of the outer parts of the cell).

B.2 Sample measurement

B.2.1 Transfer the sample to the cell immediately prior to measurement (in order to minimize the potential for cell leakage, sagging of the window or sample evaporation).

B.2.2 For volatile samples (e.g. motor gasoline) use a vented cap on the cell to minimize sample volatilization during measurement.

B.2.3 Check for pinhole leaks, or sagging of the cell window, just before inserting the sample cell into the instrument and again immediately after the measurement. In either case, any measurement should be rejected and a new cell prepared prior to carrying out (or repeating) the measurement. Also check the secondary window immediately after the measurement and reject any results if there is any evidence of liquid on the window (repeat the measurement using a fresh cell and new secondary window).

B.3 Calibration validation

B.3.1 In addition to running a check standard which is close in concentration to the samples being measured, it is strongly recommended that the calibration blank (e.g. white oil) be analysed on a daily basis. The measured content for the blank should be less than 3 mg/kg.

B.3.2 If the measured content for the blank is greater than the value given in B.3.1, restandardize the instrument by running the set-up standards (8.4.6) and repeat the measurement of the blank (use a fresh sample and fresh cell). If the result still falls outside the acceptable range, carry out a full calibration as described in 8.4.

B.3.3 It should be noted that, in order to obtain a good fit for the calibration at low concentrations, it may be necessary to change the weighting factor in the regression.

Bibliography

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

[2] ISO 4259:1992, Technical Corrigendum 1:1993 (English only)

[3] ISO 8754:2003, *Petroleum products — Determination of sulfur content — Energy-dispersive X-ray fluorescence spectrometry*

Energy Institute

61. New Cavendish Street
London
W1G 7AR

Tel: +44 (0)20 7467 7100
Fax: +44 (0)20 7255 1472
www.energyinst.org.uk

Buying Parts of BS 2000

Orders for BS 2000 publications should be addressed to:

The Library at the Energy Institute

British Standards Institution — Customer services
389 Chiswick High Road
London
W4 4AL

Tel: +44 (0)20 8996 9001
Fax: +44 (0)20 8996 7001
www.bsi-global.com

Order hard copy standards securely via:
www.bsi-global.com/bsonline

Copyright

IP

THE INSTITUTE
OF PETROLEUM