INTERNATIONAL STANDARD

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Petroleum products — Determination of low concentration of sulfur in automotive fuels — Energy-dispersive X-ray fluorescence spectrometric method

Produits pétroliers — Détermination de la teneur en soufre en faible concentration dans les carburants pour automobiles — Méthode spectrométrique 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 13032 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*, in collaboration with ISO Technical Committee TC 28, *Petroleum products and lubricants*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

Introduction

This International Standard is directed specifically at the lower end of the concentration range covered in ISO 20847[2]. By selecting the instrument type, a better signal-to-background ratio for sulfur K-$L_{2,3}$ emission is assured. A knowledge of the general composition of the sample for analysis is advantageous in obtaining the best test result.

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

Where matrix matching is not used and where the C:H mass ratio of the test sample is known or can be determined, accuracy can be improved by the use of Equation (A.1) (see A.2.3) to correct the result to the C:H mass ratio of the calibration standards, i.e. the reference diluent oil (see 4.1).

Some instruments include the capability for instrument-based matrix correction; notes on the use of this approach to compensate for matrix effects in the test sample are provided in A.3 for information.

This International Standard is based on IP test method PM DU[3] developed by the Energy Institute.

INTERNATIONAL STANDARD **ISO 13032:2012(E)**

Petroleum products — Determination of low concentration of sulfur in automotive fuels — Energy-dispersive X-ray fluorescence spectrometric method

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 sulfur content in automotive gasoline containing up to 3,7 % (m/m) oxygen [including those blended with ethanol up to 10 % (V/V)], and in diesel fuels [including those containing up to about 10 % (V/V) fatty acid methylester (FAME)] having sulfur contents in the range 8 mg/kg to 50 mg/kg.

Other products can be analysed and other sulfur contents can 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 automotive gasoline, gasoline having a content of greater than 8 mg/kg lead replacement or to product and feedstock containing lead, silicon, phosphorus, calcium, potassium or halides at concentrations greater than one tenth of the concentration of sulfur measured or more than 10 mg/kg, whichever is the greater.

NOTE For the purposes of this International Standard, the terms "% (m/m)" and "% (V/V)" are used to represent the mass fraction, μ, and the volume fraction, ϕ, 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-$L_{2,3}$ characteristic X-radiation is measured and the accumulated count is compared with a calibration curve constructed from sulfur standards covering the range of sulfur contents under examination.

NOTE The exciting radiation can be either direct or indirect via a polarizing or secondary target.

4 Reagents and materials

4.1 Diluent oil

The reference diluent oil is white oil (light paraffin oil) of high purity grade, with a maximum sulfur content of 0,5 mg/kg. 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 contents of the material to be analysed and should consist of high-purity components of less than 0,5 mg/kg sulfur content.

NOTE 1 Suitable components for the matched matrix diluent include *n*-heptane, 2,2,4-trimethylpentane, toluene, xylenes, ethanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) and tertiary amyl methyl ether (TAME).

NOTE 2 For the analysis of diesel fuels containing FAME, the accuracy of results can be improved by use of a matched matrix diluent oil of the white oil with FAME.

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 (CRMs) shall be used instead.

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

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

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

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

4.3 Reference materials (CRMs)

CRMs from accredited suppliers, containing a range of sulfur concentrations, are suitable alternatives to the compounds listed in 4.2.2 to 4.2.5 for use as calibration standards.

4.4 Quality control samples

Stable samples representative of the materials being analysed, which have a sulfur content that is known by this test method over a substantial period of time, or are 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 instrument

5.1.1 Performance characteristics.

For a 10 mg/kg sulfur standard (see 8.3), the instrument shall be capable of meeting the following performance characteristics:

$$\left(R_\text{s} - R_\text{b}\right)\Big/\sqrt{R_\text{b}} \geq 1{,}3 \tag{1}$$

and

$$C_V\left(R_\text{s}\right) < 5\ \% \tag{2}$$

where

R_S is the gross count rate (counts per second) for the sulfur region of interest for a 10 mg/kg sulfur standard;

R_b is the gross count rate (counts per second) for the same region of interest for a blank sample [diluent oil (4.1)];

C_V is the coefficient of variation (relative standard deviation) based on 10 individual measurements of the calibration standard.

The 10 mg/kg sulfur standard shall be a CRM (4.3) or shall be prepared from one of the compounds given in 4.2.2 to 4.2.5 following the procedures described in Clause 8.

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

For X-ray detectors with a resolution greater than 200 eV at 2,3 keV, all characteristic X-ray lines originating from the X-ray tube anode shall have an energy above 3,3 keV to ensure minimal background variation due to scatter from the X-ray tube anode lines.

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 polyester or polycarbonate film with a thickness of 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 silicon, calcium and sulfur in some types of film. However, the effects are normally cancelled out where samples and standards are analysed using the same batch of film. It is important that samples, standards and blanks be measured using the same batch of film to avoid bias.

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

5.1.5 Means of discriminating between sulfur K-$L_{2,3}$ characteristic X-radiation and other X-rays of higher energy (if required, for example filters).

5.1.6 Signal conditioning and data-handling electronics, including the functions of pulse counting and an energy region for the S peak as a minimum.

5.2 Analytical balance, 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 in accordance with 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 (spark free).

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

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

NOTE Additional sample handling recommendations are given in IP 558 (ASTM D7343[4]).

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 If required, purge the optical system with helium (minimum 99 % purity) following the manufacturer's guidelines on flush time and flow rate 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 Note to 5.1.3).

Keep handling of window material to the absolute minimum. Follow the guidelines given in Annex B.

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

8 Calibration

8.1 General

Use either CRMs (4.3) or primary standards prepared from the selected sulfur compound (4.2) dissolved in diluent oil (4.1) as a basis for the preparation of the two primary standards. The user shall always validate his/her calibration with CRMs whose matrices match his/her samples.

NOTE Recommendations on selection of diluent oil are provided in Annex A. Accuracy can be improved by utilizing the manufacturer's recommended instrument-based matrix correction (see Annex A). For this method, see the manufacturer's recommended corrections.

8.2 Preparation of primary standards

8.2.1 Prepare two primary standards with sulfur contents of approximately 500 mg/kg and 1 000 mg/kg.

8.2.2 Weigh, to the nearest 0,1 mg, the appropriate quantity of the selected sulfur compound (4.2) or CRM (4.3) (see Table 1) into a flask (5.4) and add the appropriate quantity of diluent oil (4.1), 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[a] g	DBS[b] g	TNA[c] g
1 000	50,0	0,29	0,23	0,21
500	50,0	0,144	0,114	0,105

[a] See 4.2.2.

[b] See 4.2.3.

[c] See 4.2.4.

8.2.3 Calculate the sulfur content, S, in milligrams per kilogram, to one decimal place in each case, from the amounts of diluent oil and sulfur compound used, as follows:

$$S = 10\,000 \times \frac{(m_\text{s} c_\text{s} + m_\text{d} c_\text{d})}{(m_\text{s} + m_\text{d})} \tag{3}$$

where

m_s is the mass of sulfur compound, expressed in grams (g);

c_s is the sulfur content of the sulfur compound, expressed as a mass percentage [% (m/m)];

c_d is the sulfur content of the diluent oil, expressed as a mass percentage [% (m/m)];

m_d is the mass of diluent oil, expressed in grams (g).

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

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

8.3 Calibration standards

8.3.1 Prepare calibration standards of nominal concentrations as shown in Table 2, from the primary standards (8.2) in the selected diluent oil (4.1) and calculate the exact sulfur content of the calibration standard, S_x, in milligrams per kilogram, as follows:

$$S_x = \frac{(m_{\text{s},x} c_{\text{s},x} + m_\text{d} c_\text{d})}{(m_{\text{s},x} + m_\text{d})} \tag{4}$$

where

$m_{\text{s},x}$ is the mass of sulfur primary standard, expressed in grams (g);

$c_{\text{s},x}$ is the sulfur content of the primary standard, expressed in milligrams per kilogram (mg/kg);

c_d is the sulfur content of the diluent oil, expressed in milligrams per kilogram (mg/kg);

m_d is the mass of diluent oil, expressed in grams (g).

Prepare calibration standards of nominal sulfur content of 5 mg/kg, 10 mg/kg and 50 mg/kg from the 500 mg/kg primary standard and calibration standards of nominal sulfur content of 30 mg/kg, 70 mg/kg and 100 mg/kg from the 1 000 mg/kg primary standard.

Use the reference diluent oil (4.1) as the nominal zero point, in milligrams per kilogram, for the calibration. Calibration standards of certified sulfur content in a specified diluent oil (e.g. diesel) are suitable for analysing known similar materials.

The stability of the calibration standards should be checked on a regular basis by comparing with freshly prepared standards to establish maximum shelf-life.

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

Table 2 — Nominal composition of calibration standards

Sulfur content mg/kg	**Mass of diluent oil** g	**Primary standard** mg/kg	**Mass of primary standard** g
0	100	—	—
5	99,0	500	1,0
10	98,0	500	2,0
30	97,0	1 000	3,0
50	90,0	500	10,0
70	93,0	1 000	7,0
100	90,0	1 000	10,0

8.4 Calibration procedure

8.4.1 Whenever carrying out measurements, follow the guidelines given in Annex B.

8.4.2 If required for matrix corrections, the scattered radiation (e.g. from an X-ray tube line) shall also be measured (see Annex A). The energy difference between the region of interest selected for the scattered radiation and the sulfur K-$L_{2,3}$ line shall not exceed 10 keV.

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's capacity. If closed cups 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 cup and the sample can vary with sample depth; thus, matrix corrections can be affected if the depth is not relatively consistent.

8.4.4 Obtain two readings on each calibration standard and run in random order, taking a fresh sample aliquot and cup for each reading. Set the counting times for the sulfur K-$L_{2,3}$ peak, the background measurement and the scattered radiation, if they are used, so that they are long enough to obtain an overall precision estimate of better than 3 % coefficient of variation (relative standard deviation) at a 10 mg/kg sulfur content [i.e. at a 10 mg/kg sulfur concentration, results should be within 0,6 mg/kg sulfur (95 % confidence interval)]. Measure the diluent oil as a blank.

NOTE The objective at low sulfur levels is to obtain adequate counts to satisfy the requirements in 8.4.4, with a precision of measurement that improves in relation to the number of counts collected. At very low sulfur levels, this counting time is related to the 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 (8.3.1). Check the curve at a minimum of three points with CRMs 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 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. The repeatability limits 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 re-standardization 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. Providing the quality control check remains within the limits, recalibration is not required. If outside the limits, follow the calibration procedure given in 8.4.4.

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

NOTE 2 Instrument drift can be influenced by temperature settings.

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

9 Procedure

9.1 When carrying out measurements, follow the guidelines given in Annex B.

9.2 Whenever more than one calibration is set up on the instrument for this method, ensure that the calibration selected is suitable for the sample to be analysed (see Annex A).

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

9.4 Take measurements for the sulfur K-$L_{2,3}$ line (and background and scatter peak, if either is used) using the same counting time as used for calibration. Repeat the measurements, using a fresh test portion in a new sample cup and calculate the mean sulfur concentration.

NOTE Modern instruments can incorporate this calculation.

9.5 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), re-standardize the instrument as described in 8.4.6, then repeat measurement of the quality control sample and blank using fresh sample cups. If repeated measurements still remain outside control limits, recalibrate the instrument as described in 8.4.4.

10 Calculation

Read the concentration 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 0,1 mg/kg.

12 Precision

12.1 General

The precision given is derived from statistical analysis, carried out as described in ISO 4259[1], of the results of interlaboratory testing of a matrix of fuels, including nine gasoline fuels and nine diesel fuels.

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 is expected in the long run, in the normal and correct operation of the test method, to exceed the following value in absolute value in only one case in 20.

$$r = 0{,}005\,X + 1{,}07 \tag{5}$$

where X is the average of the two results being compared, in milligrams per kilogram (mg/kg).

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, is expected in the long run, in the normal and correct operation of the test method, to exceed the following value in only one case in 20.

$$R = 0{,}016\,X + 3{,}70 \tag{6}$$

where X is the average of the two results being compared, in milligrams per kilogram (mg/kg).

13 Test report

The test report shall contain at least the following information:

a) reference to this International Standard, i.e. ISO 13032:2012;

b) type and complete identification of the product tested;

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

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

e) date of the test;

f) if appropriate, the diluent oil used to prepare the primary and calibration standards.

Annex A
(informative)

Matrix effects

A.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, thus, change the measured intensity for the sulfur K-$L_{2,3}$ emission. Variations in oxygen content and/or the C:H mass ratio of the petroleum product under test can produce significant variations in measured values and, therefore, if matrix matching is not used, it is critical that matrix effects be considered and compensated for.

A.2 Diluent selection

A.2.1 The reference diluent (4.1) for the production of calibration solutions from sulfur compounds has a high content of 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 [more than 3,7 % (m/m) oxygen in the sample] increase the errors beyond this value.

A.2.2 Compensation for matrix effects should be carried out by selecting a diluent for the calibration standards which closely matches the composition of the samples under test. 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, may be used. Where oxygenates are known to be present in significant concentration [more than 3,7 % (m/m) oxygen in the sample], matrix matching of the calibration standards for approximate oxygenate content is essential for the most accurate results.

A.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 whenever the diluent for the calibration standards is the reference diluent (4.1) (C:H mass ratio = 5,698).

$$S_\mathrm{c} = \frac{S_\mathrm{u}}{1{,}076 - 0{,}013\,9C} \qquad \text{(A.1)}$$

where

S_c is the corrected sulfur content;

S_u is the sulfur content measured from the calibration curve;

C is the C:H mass ratio of the sample.

If C of the diluent oil is not that shown for the default (i.e. 5,698), Equation (A.1) might not hold and a new equation would need to be constructed.

A.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 be the same, or at least similar, to enable the best comparison of results. 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.3 Instrument-based matrix correction

A.3.1 Many modern instruments include the capability to correct for matrix effects. Some of the correction models that can be used for this method are the following.

A.3.2 Rationing the measured sulfur intensity to some portion of the X-radiation scattered by the sample (e.g. characteristic Compton tube lines or Bremstrahlung) is one model. This can be effective for correcting matrix differences between the test portion and the calibration standards; however, unless counting times are calculated accordingly, it can lead to some degradation in measurement precision (see 5.1). The use of energy regions, which do not provide infinite thickness with respect to their energy position, requires that a constant mass be used.

A.3.3 The use of theoretical calculated fundamental parameter alphas is another model. This method uses a combination of measurements to ascertain the organic non-analysed matrix concentration of a sample and uses a fundamental parameters model to correct the sulfur concentration for the presence of elements such as oxygen. Use of this model allows a single calibration to be used for a wide range of matrix types. Additional measurements of mass are usually required to obtain the most accurate use of this model.

NOTE For this method, see the manufacturer’s recommended corrections. It is intended that the user always validate his/her calibration with CRMs whose matrices match his/her samples.

Annex B
(normative)

Guidelines for measuring low sulfur concentrations

B.1 Sample preparation

B.1.1 Prepare samples and cups 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 cups and film are stored in a clean, dust-free environment whenever not in use (e.g. keep in a sealed plastic bag).

B.1.2 Never re-use disposable cups.

B.1.3 While assembling the cups, avoid touching with fingers the part of the film which forms the cup window. Once cups 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 cups).

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 cup (this avoids spillage and possible contamination of the outer parts of the cup).

B.2 Sample measurement

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

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

B.2.3 Check for pinhole leaks or sagging of the cup window, just before inserting the sample cup into the instrument and again immediately after the measurement. In either case, any measurement shall be rejected and a new cup 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 cup 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 concentration for the blank should be (0 ± 1) mg/kg.

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

B.3.3 In order to obtain a good fit for the calibration at low concentrations, it can be necessary to change the weighting factor in the regression, following the manufacturer’s recommendations.

Bibliography

[1] ISO 4259:2006, *Petroleum products — Determination and application of precision data in relation to methods of test*

[2] ISO 20847:2004, *Petroleum products — Determination of sulfur content of automotive fuels — Energy-dispersive X-ray fluorescence method*

[3] IP PM DU, *Determination of sulfur content in low sulfur automotive fuels — Energy-dispersive X-ray fluorescence spectrometry method*

[4] IP 558 (ASTM D7343), *Code of practice for optimization, sample handling, calibration, and validation of X-ray fluorescence spectrometry methods for elemental analysis of petroleum products and lubricants*

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