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

Produits pétroliers et connexes — 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

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*, in collaboration with 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 accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 13032:2012), which has been technically revised.

The main changes are as follows:

— extension of the Scope to include paraffinic diesel fuel and neat fatty acid methyl ester (FAME);

— update of precision statements as well as the concentration range which are based on results of a new interlaboratory study, for gasoline and diesel type fuels, and FAME type samples.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document is directed specifically at the lower end of the concentration range covered in ISO 20847. By selecting the instrument type, a better signal-to-background ratio for sulfur K-$L_{2,3}$ emission is ensured. 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 document; the corresponding Siegbahn X-ray line notation (S Kα or S $K\alpha_{1,2}$) is being phased out.

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

WARNING — The use of this document can involve hazardous materials, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel prior to application of the document and to fulfil other applicable requirements for this purpose.

1 Scope

This document specifies an energy dispersive X-ray fluorescence (EDXRF) test method for the determination of sulfur content in automotive fuels. This document is applicable to:

— gasoline containing up to 3,7 % oxygen by mass (including those blended with ethanol up to 10 % by volume) having sulfur contents in the range of 6,9 mg/kg to 56,7 mg/kg,

— diesel fuels including those containing up to about 30 % fatty acid methyl ester (FAME) by volume, paraffinic diesel fuel, and neat FAME, having sulfur contents in the range of 5,0 mg/kg to 60,2 mg/kg.

The sulfur content in other products can be determined according to the test method specified in this document; however, no precision data for products other than automotive fuels and for results outside the specified range have been established for this document.

For reasons of spectral overlap, this document is not applicable to leaded automotive gasoline, gasoline having a content of greater than 8 mg/kg lead 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.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 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. The accumulated number of counts in a given time or count rate is compared with a calibration curve constructed from sulfur standard solutions covering the range of sulfur contents under examination.

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

5 Reagents and materials

5.1 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 required to be analysed (e.g. motor gasoline), the accuracy of results can 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.

For the analysis of FAME, the oxygen content shall be adjusted to the sample matrix. The use of a mixture of white oil with methyl oleate (see 5.2.6) or organic acid (see 5.2.7) is recommended as a diluent oil.

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 composed of a mixture of white oil and methyl oleate (see 5.2.6) or organic acid, to adjust the oxygen content and the sample matrix.

5.2 Sulfur compounds

5.2.1 Sulfur compounds of known sulfur content. These shall be used for the preparation of the primary standards. The compounds given in 5.2.2 to 5.2.5 are suitable and their nominal sulfur contents are given. Where the purity of these compounds is less than 99 % by mass, either the concentrations and nature of all impurities shall be known, or certified reference materials (CRMs) (5.3) shall be used instead.

5.2.2 Dibenzothiophene (DBT), with a nominal sulfur content of 17,399 % by mass.

5.2.3 Dibutylsulfide (DBS), with a nominal sulfur content of 21,915 % by mass.

5.2.4 Thionaphthene (Benzothiophene) (TNA), with a nominal sulfur content of 23,890 % by mass.

5.2.5 Dibutyldisulfide (DBDS), with a nominal sulfur content of 35,950 % by mass.

5.2.6 Methyl oleate, for use as a blank solution with a sulfur content of less than 1 mg/kg when FAME is analysed. Check the blank solution prior to use with the spectrometer (6.1). A signal for sulfur shall not be detectable (i.e. the intensity shall be lower that the intensity equivalent to 1 mg/kg). Other oxygen-containing and sulfur-free blank solutions, such as octanol, may also be used. Methyl oleate may also be used in combination with white oil to make a matrix-matched base for diesel fuels containing FAME.

5.2.7 Organic acid, for use as a blank solution with a sulfur content of less than 1 mg/kg when FAME is analysed. Check the blank solution prior to use with the spectrometer (6.1). A signal for sulfur shall not be detectable (i.e. the intensity shall be lower that the intensity equivalent to 1 mg/kg). Other oxygen-containing and sulfur-free blank solutions, such as octanol, may also be used. Organic acid may also be used in combination with white oil to make a matrix-matched base for diesel fuels containing FAME.

5.3 Reference materials

Certified reference materials (CRMs) from suppliers complying with ISO 17034, containing a range of sulfur concentrations, are suitable alternatives to the calibration standard solutions based on compounds listed in 5.2.2 to 5.2.5 for use as calibration standards.

5.4 Quality control samples

Quality control samples are 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. Before use, ensure that the material is within its shelf-life.

6 Apparatus

6.1 Energy-dispersive X-ray fluorescence instrument, with the following performance characteristics.

a) For a 10 mg/kg sulfur standard (see 9.3), the instrument shall be capable of meeting the performance characteristics as described by Formulae (1) and (2):

$$(R_s - R_b)/\sqrt{R_b} \geq 1{,}3 \quad (1)$$

and

$$C_V(R_s) < 5\,\% \quad (2)$$

where

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

R_b is the gross count rate (expressed in counts per second) for the same region of interest for a blank sample [diluent oil (5.1, 5.2.6, 5.2.7) or a mixture of either 5.2.6 or 5.2.7 with 5.1)];

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

NOTE The term "relative standard deviation" is deprecated by the term "coefficient of variation".

The 10 mg/kg sulfur standard shall be a CRM (5.3) or shall be prepared from one of the compounds given in 5.2.2 to 5.2.7 following the procedures described in Clause 9.

b) 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.

c) Removable sample cup, providing a sample depth of at least 5 mm and equipped with replaceable X-ray transparent thin film. It is important that samples, standards, quality control standards and blanks are measured using the same batch of film to avoid bias.

d) X-ray transparent film.

This is a thin film which shall possess the necessary combination of consistency and chemical and physical properties. It is typically made of polypropylene, polyester, polycarbonate or other materials with a thickness between 2 µm and 6 µm. Aromatics can dissolve polycarbonate or polypropylene films. It is thus preferable to choose films made of polyesters or other chemically resistant materials. Some types of film can

contain traces of silicon, calcium and sulfur. However, the effects are normally cancelled when samples and standards are analysed with the same batch of film.

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

f) Means of discriminating between sulfur K-L2,3 characteristic X-radiation and other X-rays of higher energy, if required for example filters.

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

6.2 **Analytical balance**, capable of weighing to the nearest 0,1 mg.

6.3 **Mixer**, magnetic stirrer with PTFE-coated stirring rods.

6.4 **Flasks**, narrow-necked, conical and made of borosilicate glass. Seal and stopper that are compatible with the matrix, sized so that the head space is minimal.

7 Sampling and sample handling

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

7.2 Store samples which contain light fractions in a refrigerator (spark free).

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

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

NOTE Additional sample handling recommendations are given in IP 558[4] and ASTM D7343.[5]

8 Apparatus preparation

8.1 Analyser

8.1.1 Set up the analyser (6.1) in accordance with the manufacturer's instructions. Wherever possible, the instrument shall be continuously switched on to maintain optimum stability.

8.1.2 Purge the optical system with helium (minimum 99 % purity) following the manufacturer's guidelines on flush time and flow rate to ensure the stability of measurements.

NOTE Analysis can be carried out without a helium purge, however the precision data were obtained using results only from instruments using a helium purge.

8.2 Sample cups

It is recommended to use disposable sample cups. 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, i.e. X-ray transparent film [(6.1 d)], for each run of verification and sampling analysis.

Keep handling of window material to the absolute minimum. The instructions listed in Annex B shall be followed.

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

9 Calibration

9.1 General

Use either CRMs (5.3) or primary standard solutions prepared from the selected sulfur compound (5.2) dissolved in diluent oil (5.1) as a basis for the preparation of the two primary standard solutions. Users shall always validate their calibration with CRMs whose matrices match their samples. If FAME is analysed, use a diluent blank solution in accordance with 5.1 to minimize potential matrix effects.

NOTE 1 Recommendations on selection of diluent oil are provided in Annex A. Some instruments include the capability for instrument-based matrix correction through which accuracy can be improved. Notes on the use of this approach to compensate for matrix effects in the test sample are provided in A.3 for information. For this method, see the manufacturer's recommended corrections.

NOTE 2 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 using Formula (A.1) to correct the result to the C:H mass ratio of the calibration standard solutions, i.e. the reference diluent oil (see 5.1).

9.2 Preparation of primary standard solutions

9.2.1 Prepare two primary standard solutions with sulfur contents of approximately 500 mg/kg and 1 000 mg/kg. Prepare the two primary standard solutions independently.

9.2.2 Weigh, to the nearest 0,1 mg, the appropriate quantity of the selected sulfur compound (5.2) or CRM (5.3) (see Table 1) into a flask (6.4) and add the appropriate quantity of diluent oil (5.1), weighed to the nearest 0,1 mg.

Mix the contents of the flask thoroughly at room temperature using the mixer (6.3).

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

Approximate sulfur content mg/kg	Diluent blank g	DBT[a] g	DBS[b] g	TNA[c] g	DBDS[d] g
1 000	50,0	0,29	0,23	0,21	0,14
500	50,0	0,144	0,114	0,105	0,07

[a] See 5.2.2.
[b] See 5.2.3.
[c] See 5.2.4.
[d] See 5.2.5.

9.2.3 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 described in Formula (3):

$$S = 10\,000 \times \frac{(m_s c_s + m_d c_d)}{(m_s + m_d)} \quad (3)$$

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 (%);

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

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

9.2.4 Store primary standard solutions 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 standard solutions are stable for up to six months if stored in a refrigerator.

9.3 Calibration standard solutions

9.3.1 Prepare calibration standard solutions of nominal concentrations as shown in Table 2, from the primary standard solutions (9.2) in the selected diluent oil (5.1) and calculate the exact sulfur content of the calibration standard solution, S_x, in milligrams per kilogram, as described in Formula (4):

$$S_x = \frac{(m_{s,x}\, c_{s,x} + m_d\, c_d)}{(m_{s,x} + m_d)} \quad (4)$$

where

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

$c_{s,x}$ is the sulfur content of the primary standard solution, 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 standard solutions of nominal sulfur content of 5 mg/kg, 10 mg/kg and 50 mg/kg from the 500 mg/kg primary standard and calibration standard solutions of nominal sulfur content of 30 mg/kg, 70 mg/kg and 100 mg/kg from the 1 000 mg/kg primary standard solution.

Use the reference diluent oil (5.1) as the calibration standard with the lowest concentration. 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 standard solutions should be checked on a regular basis by comparing with freshly prepared standard solutions to establish maximum shelf-life.

9.3.2 Store calibration standard solutions in the same manner as primary standard solutions (see 9.2.4).

Table 2 — Nominal composition of calibration standard solutions

Sulfur content mg/kg	Mass of diluent g	Primary standard solution mg/kg	Mass of primary standard solution 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

9.4 Calibration procedure

9.4.1 Whenever carrying out measurements, the instructions given in Annex B shall be followed.

9.4.2 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.

9.4.3 Prepare the sample cup [6.1 c)] by covering the base of the cup with window film and fill to a minimum height of 50 % of the cup's capacity. Typically, the minimum amount by mass to be used for a 28 mm/32 mm diameter cup is 5 g; for a 40 mm diameter cup, 10 g is used. 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.

9.4.4 Obtain two readings on each calibration standard solution 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 coefficient of variation, C_V, at a 10 mg/kg sulfur content of better than 5 % relative [i.e. at a 10 mg/kg sulfur concentration, results should be within 0,6 mg/kg sulfur (95 % confidence interval)]. Measure the diluent to test for possible contamination.

NOTE The objective of meeting the requirements in 9.4.4 is to obtain an adequate number of counts at low sulfur levels, and therefore obtain an adequate precision of measurement.

Where the manufacturer's data sheet does not recommend specific counting times, the user should refer to the instrument manufacturer for the correct formula to estimate the required counting time for each sulfur level.

9.4.5 Construct a calibration curve from the calibration standard solutions (9.3.1), also following recommendations from A.2.2, A.3.2 or A.3.3. Check the curve at a minimum of three points with CRMs or laboratory secondary standard solutions of appropriate sulfur content and diluent type, with sulfur values either assigned from determinations on another instrument or directly traceable to a primary standard solution. Results from this check shall be within the control limits allowed for each standard solution. If the results fall outside these limits after repeat tests, repeat the calibration procedure (see 9.4.4).

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

9.4.6 From the primary calibration graph, assign calibration standard solutions to be used for re-standardization of the graph in order to compensate for changes in instrument stability and sensitivity.

EXAMPLE Standard solutions with nominal contents of 10 mg/kg, 30 mg/kg, and 100 mg/kg and the blank diluent are selected. Then the calibration using quality control samples (5.4) is validated.

Whenever tests on the calibration standard solutions show sulfur content results which differ from their assigned values by more than the repeatability precision limits of the test method, standardize (prepare fresh calibration standards) or recalibrate the analyser. If the instrument does not meet the minimum precision requirements given in 9.4.4, or if the set-up standard solutions 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 9.4.4.

NOTE 1 Instrument drift can be influenced by temperature settings.

NOTE 2 Typical frequency of calibration checks is daily or each time the instrument is used, if less frequently.

10 Procedure

10.1 When carrying out measurements, the requirements given in Annex B shall be followed.

10.2 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).

10.3 Prepare and fill the sample cup with the test portion as described in 9.4.3, taking the same precautions as taken for test portion capacity, venting and film continuity.

10.4 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.

10.5 After every five to 10 unknown sample analyses, analyse an appropriate quality control sample (5.4). Each day, analyse a blank sample. If the values of these quality control samples or the blank fall outside the control limits (see 9.4.5), re-standardize the instrument as described in 9.4.6, then repeat measurement of the quality control samples using fresh sample cups. If repeated measurements still remain outside control limits, recalibrate the instrument as described in 9.4.5.

11 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.

12 Expression of results

Report the sulfur content to the nearest 0,1 mg/kg.

13 Precision

13.1 General

The precision details given in Formulae (5) to (8) are derived from the statistical analysis,[6] carried out as described in ISO 4259-1, of the results of interlaboratory testing of a matrix of fuels, including gasoline, diesel, paraffinic diesel and FAME fuels.

NOTE The precision data were obtained using results only from instruments using helium purge.

13.2 Repeatability, *r*

The difference between two independent results obtained using this method for test material considered to be the same in the same laboratory, by the same operator using the same equipment within short intervals of time, in the normal and correct operation of the method that is expected to be exceeded with an approximate probability of 5 % due to random variation, can be calculated using Formula (5) or Formula (6), where appropriate:

$$r = 0{,}026\,24 \times (X + 78{,}5) \quad \text{for gasoline; or} \tag{5}$$

$$r = 0{,}002\,512 \times (X + 512{,}2) \quad \text{for diesel, paraffinic diesel and neat FAME (B100) fuels;} \tag{6}$$

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

13.3 Reproducibility, *R*

The difference between two independent results obtained using this method for test material considered to be the same in different laboratories, where different laboratory means a different operator, different equipment, different geographic location, and under different supervisory control, in the normal and correct operation of the method that is expected to be exceeded with an approximate probability of 5 % due to random variation, can be calculated using Formula (7) or Formula (8), where appropriate:

$$R = 0{,}041\,14 \times (X + 78{,}5) \quad \text{for gasoline; or} \tag{7}$$

$$R = 0{,}004\,855 \times (X + 512{,}2) \quad \text{for diesel, paraffinic diesel and neat FAME (B100) fuels;} \tag{8}$$

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

14 Test report

The test report shall contain at least the following information:

a) a reference to this document, i.e. ISO 13032:2024;

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

c) the diluent oil used to prepare the primary and calibration standards;

d) the result of the test (see Clause 12);

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

f) any unusual features observed;

g) the date of the test.

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 (5.1) for the production of calibration solutions from sulfur compounds has a high content of paraffinic light oil, whereas test samples can contain varying amounts of aromatic and unsaturated hydrocarbons, and can 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 % oxygen by mass 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 standard solutions, 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 % oxygen by mass in the sample), matrix matching of the calibration standard solutions 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 theoretical correction based on fundamental parameters as given by Formula (A.1) can be applied to obtain a sulfur content corrected for the matrix effect whenever the diluent for the calibration standard solutions is the reference diluent (5.1) (C:H mass ratio = 5,698).

$$S_c = \frac{S_u}{1{,}076 - 0{,}013\,9C} \qquad \text{(A.1)}$$

where

S_c is the corrected sulfur content, in milligrams per kilogram (mg/kg);

S_u is the sulfur content measured from the calibration curve, in milligrams per kilogram (mg/kg);

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

If C of the diluent oil is not as shown for the default (i.e. 5,698), it is possible that Formula (A.1) will not hold and a new formula 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.

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 specified in A.3.2 and A.3.3.

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 Bremsstrahlung) 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. 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 alphas or fundamental parameter methods 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 validates the calibration with CRMs whose matrices match the samples.