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STANDARD

**ISO**
**10478**

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# Petroleum products — Determination of aluminium and silicon in fuel oils — Inductively coupled plasma emission and atomic absorption spectroscopy methods

*Produits pétroliers — Détermination de l'aluminium et du silicium dans les combustibles — Méthodes par spectroscopie d'émission à plasma induit et spectroscopie d'absorption atomique*

Reference number
ISO 10478:1994(E)

# 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.

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.

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# Petroleum products — Determination of aluminium and silicon in fuel oils — Inductively coupled plasma emission and atomic absorption spectroscopy methods

**WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.**

## 1 Scope

This International Standard specifies a method for determining the aluminium and silicon contents of fuel oils at concentrations between 5 mg/kg and 150 mg/kg for aluminium and 10 mg/kg and 250 mg/kg for silicon using inductively coupled plasma emission and atomic absorption spectroscopy.

## 2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 835-2:1981, *Laboratory glassware — Graduated pipettes — Part 2: Pipettes for which no waiting time is specified.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 3819:1985, *Laboratory glassware — Beakers.*

ISO 4788:1980, *Laboratory glassware — Graduated measuring cylinders.*

## 3 Principle

A weighed quantity of homogenized sample is heated in a clean platinum basin, the combustible material removed by burning and the carbon finally removed by heating in a muffle furnace at a temperature of 550 °C ± 25 °C. The residue is fused with a dilithium tetraborate/lithium fluoride flux, the fused mixture digested in a solution of tartaric acid and hydrochloric acid, and diluted to volume with water.

The solution is aspirated into either the plasma of an inductively coupled plasma emission spectrometer (ICPES), and the emission radiation of the resonance lines of aluminium/silicon measured and compared with that of standard calibration solutions, or the flame of an atomic absorption spectrometer (AAS) and the absorption of the resonance radiation of the aluminium/silicon measured and compared with that of standard calibration solutions.

## 4 Reagents

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity as specified in ISO 3696.

**4.1 Potassium hydrogensulfate**, ($KHSO_4$), fused solid.

**4.2 Flux**, mixture of 90 % (*m/m*) dilithium tetraborate ($Li_2B_4O_7$) and 10 % (*m/m*) lithium fluoride (LiF).

### 4.3 Propan-2-ol.

### 4.4 Toluene.

### 4.5 Toluene/propan-2-ol mixture (1 + 1).

Mix one volume of toluene with one volume of propan-2-ol.

**4.6 Hydrochloric acid**, concentrated, 36 % (*m/m*).

### 4.6.1 Hydrochloric acid solution (1 + 1).

Mix one volume of hydrochloric acid (4.6) with one volume of water.

### 4.6.2 Hydrochloric acid solution (1 + 2).

Mix one volume of hydrochloric acid (4.6) with two volumes of water.

### 4.7 Tartaric acid.

### 4.7.1 Tartaric acid/hydrochloric acid solution.

Dissolve 5 g of tartaric acid in approximately 500 ml of water acidified with 40 ml of hydrochloric acid (4.6) and dilute to 1 000 ml with water.

### 4.8 Standard solutions.

### 4.8.1 Aluminium standard solutions.

Use either a ready-made commercially available aluminium standard solution, 1 000 mg/l, or prepare by dissolving 1,000 g of aluminium metal (wire form, 99,99 % purity) in 50 ml of hydrochloric acid (4.6) with gentle heating in a 400 ml beaker (5.12). Cool, transfer and dilute the solution quantitatively with water to 1 000 ml in a volumetric flask (5.8).

### 4.8.2 Silicon standard solutions.

Use either a ready-made commercially available silicon standard solution, 1 000 mg/l, or prepare by fusing 2,140 g of silicon dioxide (99,99 % purity) with 8 g of sodium hydroxide in a zirconium crucible fitted with a close-fitting lid (5.2) at dull red heat until a clear melt is obtained. Cool and dissolve the solidified melt in 100 ml of hydrochloric acid/water solution (4.6.2) in a 400 ml beaker (5.12). Cool, transfer and dilute the solution quantitatively with water to 1 000 ml in a volumetric flask (5.8) followed by immediate transfer to a plastic bottle (5.14) for long-term storage.

## 5 Apparatus

Laboratory apparatus and apparatus described in 5.1 to 5.15 shall be used. Clean all glassware carefully with hot hydrochloric acid (4.6.1) and rinse thoroughly with water to eliminate contamination.

**5.1 Platinum basin**, 100 ml capacity, cleaned with molten potassium hydrogensulfate (4.1).

NOTE 1 The following cleaning technique is recommended: place 5 g of potassium hydrogensulfate (4.1) in the basin, heat in a muffle furnace at 550 °C ± 25 °C or over a Bunsen burner for 5 min. Allow to cool, wash out with distilled or deionized water and dry.

**5.2 Zirconium crucible**, with a close-fitting zirconium lid, 30 ml to 50 ml capacity.

**5.3 Mixer**, non-aerating, high-speed shear type.

**5.4 Electric oven**, capable of being maintained at a temperature between 50 °C and 60 °C.

**5.5 Electric muffle furnace**, capable of being maintained at temperatures of 550 °C ± 25 °C and 925 °C ± 25 °C, and preferably having apertures at front and rear to allow passage of a slow, natural draught of air.

**5.6 Electrical hotplate**, with or without a magnetic stirring capability.

### 5.7 Spectrometers.

### 5.7.1 Inductively coupled plasma atomic emission spectrometer.

Use either a sequential or simultaneous spectrometer, equipped with an ICP torch and RF generator to form and sustain the plasma.

### 5.7.2 Atomic absorption spectrometer.

Use an instrument with a modulated hollow cathode lamp or other source of modulated resonance radiation of aluminium/silicon; a dinitrogen oxide (nitrous oxide)/acetylene burner; and a light detector with a suitable measuring and readout system. The scale shall be linear in absorbance or in light intensity, or shall be directly in concentration units with curve correction.

**5.8 Volumetric flasks**, 100 ml and 1 000 ml, complying with ISO 1042, class A.

**5.9 Pipettes**, 1 ml, 2 ml, 5 ml, 10 ml, 20 ml and 25 ml, complying with ISO 648, class A.

**5.10 Pipettes**, 1 ml and 2 ml, graduated in 0,1 ml subdivisions, complying with ISO 835-2.

**5.11 Measuring cylinders**, 10 ml, 25 ml, 50 ml and 100 ml, with subdivided graduations, complying with ISO 4788.

**5.12 Beaker**, 400 ml squat form, complying with ISO 3819.

**5.13 Filter paper**, "ashless", 0,01 % (*m/m*) ash maximum.

**5.14 Plastic bottles**, unfilled virgin plastic, suitable for long-term storage of dilute acid solutions, 100 ml and 1 000 ml.

**5.15 Balance**, capable of being read to the nearest 0,2 mg.

## 6 Sample preparation

The sample shall be homogenized thoroughly before the test portion is taken. Place the sample container in an oven at a temperature between 50 °C and 60 °C and maintain the sample at this temperature until all the sample has melted and reached a uniform viscosity. Insert the shaft of the mixer (5.3) into the sample so that the head of the shaft is immersed to approximately 5 mm from the base of the container. Homogenize the sample for approximately 5 min. In the case of fluid samples which have stood undisturbed for several months, use a plastic rod to dislodge any sediment adhering to the base of the sample container before homogenization.

NOTE 2 Failure to use this homogenization procedure will invalidate results.

## 7 Procedure

### 7.1 Test portion

The mass of test portion taken from the sample (clause 6) shall weigh between 20 g and 50 g, and preferably contain approximately 1,3 mg of aluminium.

NOTE 3 The mass of test portion proposed, based on the aluminium content, will also suffice for the silicon determination, as both elements are usually found in fuel oils associated with each other.

### 7.2 Preparation of test solution

**7.2.1** Immediately after homogenization transfer the test portion from the homogenized sample to the weighed platinum basin (5.1); reweigh the basin and contents to the nearest 0,1 g to obtain the mass of the test portion taken.

**7.2.2** Warm the basin and contents gently with a Bunsen flame until the sample ignites. Maintain the contents of the basin at a temperature such that most of the combustible material is removed and only carbon and ash remain.

NOTE 4 If the sample contains considerable amounts of moisture, foaming and frothing may cause loss of sample.

If foaming and frothing occur, discard the sample and to a fresh portion add 1 ml to 2 ml of propan-2-ol (4.3) before heating. If foaming and frothing are not sufficently reduced, add 10 ml of a mixture of toluene/propan-2-ol (4.5) to a further test portion and mix thoroughly. Place several strips of ashless filter paper (5.13) in the mixture and warm gently (when the paper begins to burn, the greater part of the water will have been removed).

**7.2.3** Place the basin and contents in the muffle furnace (5.5) preheated to a temperature of 550 °C ± 25 °C. Maintain the muffle furnace at this temperature until all the carbon has been removed and only ash remains.

NOTE 5 This may require heating overnight.

**7.2.4** Cool the basin to room temperature and to the contents of the basin add 0,4 g of the flux (4.2) and mix it with the ash. Place the basin and contents for 5 min in a muffle furnace preheated to a temperature of 925 °C ± 25 °C. Remove the basin and ensure contact of the flux with the ash. Replace the basin in the muffle furnace and maintain at a temperature of 925 °C ± 25 °C for a further 10 min.

**7.2.5** Remove the basin, cool the fusion melt to room temperature and add 50 ml of tartaric acid/hydrochloric acid solution (4.7.1) to the basin. Place the basin and contents on a hotplate (5.6) and maintain at a moderate temperature without boiling.

NOTES

6 Excessive evaporation of the solution could lead to precipitation of an insoluble form of silica.

7 Prolonged heating may be required to dissolve the solidified melt completely and obtain a solution. Agitation or the use of magnetic stirring may be employed to speed dissolution of the solidified melt.

**7.2.6** Allow the solution to cool and transfer it to the 100 ml volumetric flask (5.8) with water, washing the basin several times to ensure transfer is quantitative. Make up to the mark with water. Transfer to a plastic bottle, 100 ml (5.14).

NOTE 8 Transfer to a plastic bottle is thought to be desirable, as the dilute acid solution will contain tetrafluoroboric acid from solution of the flux. However, storage tests have shown that there is no attack of glassware in the short term (up to one week); and that the solution does not contain free fluoride "ion" above the 5 mg/l level.

## 7.3 Preparation of blank solution

Prepare a zero-concentration solution containing only 0,4 g flux and 50 ml of the tartaric acid/hydrochloric acid solution (4.7.1) diluted to 100 ml and transfer to a plastic bottle, 100 ml (5.14).

## 7.4 Preparation of calibration solutions

### 7.4.1 Aluminium

Prepare a 250 mg/l aluminium working solution by diluting 25 ml of the 1 000 mg/l standard solution (4.8.1) to 100 ml with water. To each of four clean 100 ml volumetric flasks (5.8) add 0,4 g of the flux and 50 ml of the tartaric acid/hydrochloric acid solution (4.7.1). To successive flasks add 2 ml, 4 ml, 10 ml and 20 ml of the 250 mg/l aluminium working solution and dilute to 100 ml with water.

The calibration solutions then contain 5 mg/l, 10 mg/l, 25 mg/l and 50 mg/l of aluminium respectively.

### 7.4.2 Silicon

Prepare a 250 mg/l silicon working solution by diluting 25 ml of 1 000 mg/l standard solution (4.8.2) to 100 ml with water. To each of four clean 100 ml volumetric flasks (5.8) add 0,4 g of the flux and 50 ml of the tartaric acid/hydrochloric acid solution (4.7.1). To successive flasks add 2 ml, 4 ml, 10 ml and 20 ml of the 250 mg/l silicon working solution and dilute to 100 ml with water.

The calibration solutions then contain 5 mg/l, 10 mg/l, 25 mg/l and 50 mg/l of silicon respectively.

### 7.4.3 Storage

Transfer all standards to 100 ml plastic bottles (5.14).

NOTE 9 When both aluminium and silicon are being determined together, the 5 mg/l to 50 mg/l calibration solutions of each may be combined, providing there are no incompatibility problems caused by the reagents used in the preparation of the standard solutions 4.8.1 and 4.8.2.

## 7.5 Setting up and operating the inductively coupled plasma atomic emission spectrometer

### 7.5.1 General

Consult and follow the manufacturer's instructions for the operation of the instrument.

NOTE 10 Design differences between instruments, ICP excitation sources and different selected analytical wavelengths for individual spectrometers make it impracticable to specify the required manipulations in detail.

### 7.5.2 Peristaltic pump

If using a peristaltic pump, inspect the pump tubing and replace it, if necessary, before starting each day. Verify the solution uptake rate and adjust it to the desired rate.

### 7.5.3 ICP excitation source

Ignite the ICP excitation source at least 30 min before performing an analysis. During this warmup period nebulize distilled or deionized water through the plasma torch.

NOTE 11 Some manufacturers may recommend even longer warmup periods.

### 7.5.4 Wavelength profiling

Perform any wavelength profiling that is called for in the normal operation of the instrument.

### 7.5.5 Operation parameters

Assign the appropriate operating parameters to the instrument task file so that it is possible to determine the desired elements. Include the following parameters: element, wavelength, background correction points (optional), inter-element correction factors (optional), integration time and three consecutive repeat integrations.

### 7.5.6 Calibration curve

Prepare a five-point calibration curve using the blank and working standards at the beginning of analysis of each batch of samples.

### 7.5.7 Analysis of the test solution

Analyse the samples in the same manner as the calibration standards (i.e. same integration time, background correction points, plasma conditions etc.). Rinse the plasma torch between samples by nebulizing distilled or deionized water for at least 10 s.

If it is found that a test solution gives a concentration above that of the most concentrated calibration solution, dilute it in the same matrix, i.e. blank solution (7.3), to bring it within the range of the calibration solutions.

Analyse one of the calibration standards after every fifth test sample. If the concentration of any element is 5 % outside of the nominal value, make any adjustments to the instrument that are necessary and repeat the calibration.

## 7.6 Setting up and operating the atomic absorption spectrometer

### 7.6.1 General

Consult and follow the manufacturer's instructions for the operation of the atomic absorption spectrometer.

NOTE 12 Design differences between spectrometers make it impracticable to specify the required manipulations.

**WARNING — Correct operating procedures are required for safety as well as for reliability of results. An explosion can result from flame blowback unless the correct burner head and operating sequence are used.**

### 7.6.2 Settings for aluminium

Fit the aluminium hollow cathode lamp, set the monochromator to the specified wavelength (see table 1) and adjust the wavelength control to obtain maximum output. Aspirate an aluminium calibration solution (7.4.1) (e.g. 25 mg/l) into the flame. Make adjustments to burner height, burner alignment, acetylene flowrate and impact bead to give maximum absorbance (or minimum transmittance). Adjust the gain control to set the maximum within the recommended working region of the spectrometer (see manufacturer's operating instructions).

**Table 1 — Instrumental settings for aluminium**

| | |
|---|---|
| **Wavelength,** nm | 309,3 |
| **Fuel** | Acetylene |
| **Oxidant** | Dinitrogen oxide (nitrous oxide) |
| **Lamp current** | As recommended by the manufacturer, typically 60 % to 100 % of maximum |

### 7.6.3 Settings for silicon

Fit the silicon hollow cathode lamp, set the monochromator to the specified wavelength (see table 2) and adjust the wavelength control to obtain maximum output.

**Table 2 — Instrumental settings for silicon**

| | |
|---|---|
| **Wavelength,** nm | 251,6 |
| **Fuel** | Acetylene |
| **Oxidant** | Dinitrogen oxide (nitrous oxide) |
| **Lamp current** | As recommended by the manufacturer |

Follow a procedure similar to 7.6.2, aspirating a silicon calibration solution (7.4.2) (e.g. 25 mg/l) into the flame.

### 7.6.4 Calibration curve

A calibration curve shall be prepared prior to analysis of each group of samples and after any change in instrumental conditions, as variations occur in the instrument behaviour. The mode of calibration depends on the type of readout facility on the AAS.

NOTE 13 Readings may vary over short times from such causes as buildup of deposits on the burner slot or in the nebulizer. The visual appearance of the flame is a useful check to detect changes of condition.

### 7.6.5 Analysis of the test solution

#### 7.6.5.1 General

Analyse one of the calibration standards after every fifth sample. If the result indicates that the calibration has changed (see note 13), recalibrate the instrument.

If it is found that a test solution gives a concentration above that of the most concentrated calibration solution, dilute in the same matrix, i.e. blank solution (7.3), to bring it within the range of the calibration solution.

### 7.6.5.2 Spectrometers with meter readout

Aspirate the calibration solution, blank solution and test solution sequentially into the flame and record the meter readings. Aspirate the blank solution between each test solution.

If the spectrometer output is linear in absorbance, plot a calibration graph of net absorbance (calibration solution absorbance minus the blank solution absorbance) against concentration. From this calibration graph estimate the concentration of each sample solution after similarly computing its net absorbance.

If the spectrometer output is proportional to transmission (i.e. light intensity), calculate the net absorbance, $A$, using the following equation:

$$A = \lg \frac{(d_0)}{(d_1)}$$

where

$d_0$ is the meter reading due to the blank solution;

$d_1$ is the meter reading given by the calibration solution or test solution.

### 7.6.5.3 Spectrometers with digital readout and built-in (nonmicroprocessor-controlled) curvature correction and scale expansion facilities

Follow the manufacturer's operating instructions, aspirating the appropriate calibration solution, to set the digital readout to read directly in the required concentration units, carrying out a curvature correction program if necessary.

Aspirate the test solution and read the concentration of each test and blank solution directly from the concentration readout given by the digital display from the spectrometer.

### 7.6.5.4 Spectrometers with digital readout microprocessor-controlled calibration facilities

Follow the manufacturer's operating instructions, aspirating the appropriate calibration solution and using the recommended calibration program, to obtain a direct readout in concentration units; the concentration of each test and blank solution can thus be directly obtained after aspiration of the test solution.

## 8 Calculation

Calculate the aluminium and silicon contents as $Al$ or $Si$ respectively, in milligrams per kilogram sample, using the equations:

$$Al = \frac{100 c_1 d}{m}$$

$$Si = \frac{100 c_2 d}{m}$$

where

$c_1$ is the concentration of aluminium, in milligrams per litre, as read from either the readout of the inductively coupled plasma emission spectrometer (7.5.7), or the calibration curve (7.6.5.2) or the direct readout (7.6.5.3, 7.6.5.4) of the atomic absorption spectrometer;

$c_2$ is the concentration of silicon, in milligrams per litre, as read from either the readout of the inductively coupled plasma emission spectrometer (7.5.7), or the calibration curve (7.6.5.2) or the direct readout (7.6.5.3, 7.6.5.4) of the atomic absorption spectrometer;

$d$ is the dilution factor (7.5.7, 7.6.5.1). This factor shall be calculated to take into account the volumes and aliquots used to produce the test solution concentration falling within the calibration range; $d = 1$ unless the dilution procedures in 7.5.7 or 7.6.5.1 are carried out;

$m$ is the mass of the test portion, in grams.

## 9 Expression of results

Report the results to the nearest 1 mg/kg as aluminium/silicon content by either inductively coupled plasma emission spectroscopy or atomic absorption spectroscopy.

## 10 Precision

### 10.1 Precision data for results determined by inductively coupled plasma emission spectroscopy

#### 10.1.1 Repeatability, *r*

The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, in the normal and correct operation of the test method, would exceed the following value in only one case in twenty:

| | |
|---|---|
| Aluminium | $r = 0{,}0660X$ |
| Silicon | $r = 0{,}0643X$ |

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

#### 10.1.2 Reproducibility, *R*

The difference between two single and independent test results obtained by different operators working in different laboratories on nominally identical test materials, in the normal and correct operation of the test method, would exceed the following value in only one case in twenty:

| | |
|---|---|
| Aluminium | $R = 0{,}337X$ |
| Silicon | $R = 0{,}332X$ |

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

### 10.2 Precision data for results determined by atomic absorption spectroscopy

#### 10.2.1 Repeatability, *r*

The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, in the normal and correct operation of the test method, would exceed the following value in only one case in twenty:

| | |
|---|---|
| Aluminium | $r = 0{,}2968X^{2/3}$ |
| Silicon | $r = 0{,}3539X^{2/3}$ |

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

#### 10.2.2 Reproducibility, *R*

The difference between two single and independent test results obtained by different operators working in different laboratories on nominally identical test materials, in the normal and correct operation of the test method, would exceed the following value in only one case in twenty:

| | |
|---|---|
| Aluminium | $R = 0{,}7890X^{2/3}$ |
| Silicon | $R = 1{,}388X^{2/3}$ |

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

## 11 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) sufficient details for complete identification of the product tested;

c) the results of the test (see clause 9);

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

e) the date of the test.