
**Petroleum products — Low levels of
vanadium in liquid fuels — Determination by
flameless atomic absorption spectrometry
after ashing**

*Produits pétroliers — Détermination des basses teneurs en vanadium dans les
combustibles liquides — Méthode par spectrométrie d'absorption atomique sans
flamme après calcination*



Foreword

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International Standard ISO 8691 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

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Petroleum products — Low levels of vanadium in liquid fuels — Determination by flameless atomic absorption spectrometry after ashing

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 vanadium content in the range of 0,4 mg/kg to 4,0 mg/kg in gas turbine fuels and domestic fuel oils by means of flameless atomic absorption spectrometry.

NOTE 1 Fuel oils containing vanadium may cause operational difficulties in the presence of sodium, for example when being burnt in boilers or used for the operation of gas turbines.

2 Normative references

The following International 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 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

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

ISO 3170:1988, *Petroleum liquids — Manual sampling*.

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling*.

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

3 Principle

The sample is incinerated in a crucible and brought to glowing heat (500 °C) in a muffle furnace. The ash is dissolved in hydrochloric acid (1 mol/l), and the vanadium content in the hydrochloric acid solution is determined by flameless atomic absorption spectrometry.

4 Reagents and materials

During the analysis, use only reagents of recognized analytical grade, and water equivalent to Grade 3 of ISO 3696.

4.1 Hydrochloric acid, aqueous solution of concentration 1 mol HCl/litre solution.

4.2 Sulfuric acid, concentrated, 98 % (m/m) minimum H₂SO₄.

4.3 Sulfur, flowers, ash content maximum 10 mg/kg.

4.4 Xylene (dimethylbenzene).

4.5 Xylenesulfonic acid.

Pour 100 ml of xylene (4.4) and 50 ml of sulfuric acid (4.2) into a clean beaker. Stir the mixture and gradually raise the temperature to 95 °C ± 5 °C. Continue heating and stirring until just one clear phase remains (30 min to 40 min). Cool and transfer the xylenesulfonic acid to a clean, stoppered bottle.

NOTE 2 A thin layer of xylene may remain on the top.

4.6 Ammonium trioxovanadate, NH_4VO_3 .

4.7 Vanadium standard solution, of vanadium content 100 mg/kg.

Use either a commercially available vanadium solution, or prepare as follows:

Dissolve 229,7 mg of ammonium trioxovanadate (4.6) in hydrochloric acid (4.1) in a 1-litre volumetric flask (5.6), and fill up to the mark with hydrochloric acid (4.1).

4.8 Inert gas (argon or nitrogen), 99,9 % purity minimum.

5 Apparatus

Ordinary laboratory apparatus and:

5.1 Atomic absorption spectrometer (AAS).

5.2 Flameless atomizer, with inert gas supply and coolant water connection.

5.3 Graphite tube absorption cell, comprising a pyrocoated tube or carbon-rod atomizer system.

5.4 Recording device, comprising a strip-chart recorder with maximum 0,5 s time setting, or electronic readout facilities either with or without microprocessor controls.

5.5 Analytical balance, either single- or double-pan, with a sensitivity of 0,1 mg or better.

5.6 Flasks, one-mark volumetric flasks of 100 ml and 1 litre capacities, in accordance with ISO 1042.

5.7 Burette, of 2 ml nominal capacity, in accordance with ISO 385-1.

5.8 Crucible, platinum or silica, approximately 15 ml capacity and 25 mm diameter, with lid.

5.9 Crucible tongs.

If a platinum crucible is used, use tongs with platinum tips.

5.10 Muffle furnace, electrically heated and adjustable to a temperature of $500\text{ }^\circ\text{C} \pm 25\text{ }^\circ\text{C}$.

5.11 Micropipette, 20 μl capacity, in conjunction with a graphite tube cuvette.

5.12 Syringe, graduated, with adjustable capacity of 2 μl , in conjunction with a carbon-rod atomizer.

6 Samples

Take samples in accordance with ISO 3170, ISO 3171 or an equivalent national standard.

7 Preparation of reference solutions

Freshly prepare reference solutions from the vanadium standard solution (4.7) by adding the quantities shown in table 1 into a series of 100 ml volumetric flasks (5.6), and making up to the mark with hydrochloric acid (4.1).

Table 1 — Reference solutions

Volume of vanadium standard solution, ml	0,2	0,5	1,0	1,5	2,0
Vanadium content of reference solution, mg/kg	0,2	0,5	1,0	1,5	2,0

8 Preparation of apparatus

8.1 Atomic absorption spectrometer

Use a vanadium hollow-cathode lamp and set the wavelength at 318,3 nm. Adjust the wavelength setting for maximum radiation intensity. Set the lowest possible time constant. Do not apply a deuterium background corrector.

8.2 Flameless atomizer

After a new graphite tube has been fitted, adjust the vanadium hollow-cathode lamp and cuvette or graphite tube holder to give optimum energy yield.

The absorbance/concentration ratio of the determination is dependent upon the individual graphite tube. Therefore, each series of measurements shall be made with the same graphite tube.

Adjust the inert gas supply, and the coolant water supply.

Since this International Standard allows the use of either of two basically different systems of atomic absorption spectrometry, guide values for the conditions of determination, which can be adjusted for the control unit concerned, are given in 8.2.1 and 8.2.2.

8.2.1 Determination with a graphite tube absorption cell

Use the micropipette (5.11) to fill the absorption cells with 20 µl of the test solution (9.1). Between two consecutive determinations, heat to a maximum temperature three times for 5 s (see table 2).

8.2.2 Determination with a carbon-rod atomizer

Use the syringe (5.12) to fill the absorption cells with 2 µl of the test solution (9.1). While injecting the solutions, ensure that the syringe needle rests in the inside of the tube opposite to the injection hole, and that the syringe is emptied quickly. Between two consecutive determinations, heat to a maximum temperature for 1 s (see table 2).

Table 2 — Guide values for test conditions depending on source of atomization

Stage of test	Source of atomization	
	Graphite tube cuvette	Carbon-rod atomizer
Filling cuvette	20 µl pipette (5.11)	2 µl syringe (5.12)
Drying stage	30 s at 100 °C	30 s at 100 °C
Incineration stage	10 s at 700 °C	10 s at 700 °C
Atomizing stage	20 s at 2 700 °C	3 s at 2 400 °C
Cleanup stage: heat to maximum temperature	3 times for 5 s	Once for 1 s

8.3 Recording device

Operate the recording device (5.4) undamped with tenfold sensitivity.

NOTE 3 The atomizing peak is represented by a quick ballistic signal. Damping in the AAS apparatus and in the recorder would cause absorbance losses and curved reference lines.

Electronic readout facilities, with or without microprocessor controls, shall be operated according to the manufacturer's instructions.

9 Test procedure

9.1 Preparation of test solution

Before weighing, homogenize the sample by shaking and/or stirring vigorously. Weigh 2 g to 4 g of the sample to the nearest 0,01 g into a preweighed clean crucible (5.8). Add 0,4 g of sulfur (4.3), or 1 g of

xylenesulfonic acid (4.5) and heat the crucible on a clay triangle in a fume cupboard until the sample ignites and burns out slowly.

NOTE 4 If a large number of samples is burned, an electric incinerator is recommended.

Put the crucible into the muffle furnace (5.10) and heat at a temperature of 500 °C ± 25 °C for at least 1 h, or overnight if necessary. After ashing, remove the crucible from the furnace, put on the lid and allow it to cool to between 60 °C and 70 °C, or to a temperature at which the hydrochloric acid can be added safely without boiling.

Remove the lid and dissolve the ash in the crucible with 3 ml of the hydrochloric acid (4.1). Replace the lid on the crucible and keep it within the temperature range 60 °C to 70 °C for 30 min, e.g. by placing it in a hot air oven. Then allow the crucible and the solution to cool to room temperature and weigh to the nearest 0,01 g, with the lid of the crucible removed.

After weighing, replace the lid on the crucible containing the sample solution and complete the remainder of the determination within one hour of the weighing.

9.2 Vanadium determination

9.2.1 General measurement procedure

Set up the apparatus in accordance with clause 8 and the manufacturer's instructions. Fill the cuvette with a reference solution or test solution as described in 8.2.1 or 8.2.2, depending on the source of atomization used. Immediately switch on the programme on the control unit (see 8.2.1 or 8.2.2). Allow the recorder to draw out a graph for approximately 10 s from the start of the atomizing stage until completion of the atomizing peak.

To evaluate the atomizing peak, first draw a perpendicular line from the absorbance maximum, then extend the base line at the beginning of the atomizing peak up to the intersection point with the perpendicular line. Measure the height from this theoretical baseline to the absorbance maximum.

9.2.2 Calibration

9.2.2.1 Measure the absorbance maximum for the zero point by filling the cuvette with hydrochloric acid (4.1). This is recorded as the absorbance maximum of the blank, with a vanadium content calculated from extrapolation of the curve constructed in 9.2.2.2.

9.2.2.2 Repeat the measurement on each of the reference solutions (table 1), consecutively introducing them into the cuvette in order of increasing

concentration. Between atomization of each two consecutive reference solutions, heat the atomizer as described in 8.2.1 and 8.2.2.

Plot the values for the vanadium absorbances of the reference solutions against the vanadium concentrations, expressed in milligrams vanadium per kilogram solution.

9.2.2.3 Carry out determinations of the vanadium absorbance of test sample solutions in triplicate. Locate the vanadium absorbance of the test sample solution on the reference curve derived in 9.2.2.2. Repeat the determination for the reference solution whose absorbance comes closest in value to that of the sample solution. Determine the result by calculating the mean of the three values derived for the sample solution absorbance.

10 Calculation

Calculate the vanadium content, V , of the sample in milligrams per kilogram, using the following equation:

$$V = \frac{A_s C_s G_s}{A_s^1 m} - \frac{A_b C_b G_b}{A_b^1 m}$$

where

- A_s is the absorbance of the sample solution;
- A_s^1 is the absorbance of the reference solution closest to that of the sample solution;
- A_b is the absorbance of the blank solution;
- A_b^1 is the absorbance of the reference solution closest to that of the blank solution;
- C_s is the vanadium content, expressed in milligrams per kilogram, of the reference solution with absorbance closest to that of the sample solution;
- C_b is the vanadium content, expressed in milligrams per kilogram, of the reference solution with absorbance closest to that of the blank solution;
- G_s is the mass of hydrochloric acid sample solution, expressed in grams;

G_b is the mass of hydrochloric acid blank solution, expressed in grams;

m is the mass of the sample, expressed in grams.

11 Expression of results

Report the vanadium content calculated in accordance with clause 10, expressed in milligrams per kilogram, to the nearest 0,05 mg/kg.

12 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows:

12.1 Repeatability

The difference between successive 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 value of 0,1 mg/kg only in one case in 20.

12.2 Reproducibility

The difference between two single and independent results, obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of the test method, exceed the value of 0,2 mg/kg only in one case in 20.

13 Test report

The test report shall contain at least the following information:

- a) sufficient details for complete identification of the product tested;
- b) a reference to this International Standard;
- c) the result of the test (see clause 11);
- d) any deviation, by agreement or otherwise, from the procedures specified in this International Standard;
- e) the date of the test.