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Document Name: EI IP-501: Determination of aluminum, silicon, vanadium, nickel, iron, sodium, calcium, zinc and phosphorus in residual fuel oil

CFR Section(s): 40 CFR 1065.705 Table 1

Standards Body: Energy Institute

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Determination of aluminium, silicon, vanadium, nickel, iron, sodium, calcium, zinc and phosphorus in residual fuel oil by ashing, fusion and inductively coupled plasma emission spectrometry

FOREWORD

This standard is one part of that published previously as IP PM-CB. The procedure using atomic absorption spectrometry is now published as IP 470. The technique is essentially the same as that described in IP 377, with more elements being analyzed, and new precision values. The precision values for aluminium and silicon are taken from IP 377.

1 Scope

This standard specifies a procedure for the determination of aluminium, silicon, vanadium nickel, iron, sodium, calcium, zinc and phosphorus in residual fuel oils at levels detailed in the table below, by inductively coupled plasma emission spectrometry.

Element	Range mg/kg
Aluminium	5 to 150
Silicon	10 to 250
Sodium	1 to 100
Vanadium	1 to 400
Nickel	1 to 100
Iron	2 to 60
Calcium	3 to 100
Zinc	1 to 70
Phosphorus	1 to 60

Fuel oils with sulfur contents greater than 0,3 % m/m do not require an ashing aid. The precision data is based on fuel oils with sulfur contents greater than 0,3 % m/m.

Aluminium and silicon are normally found in association with each other in residual fuels, and may be specified, separately or in combination, as an estimate of catalyst fines content.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated. For undated references, the latest edition of the normative document referenced applies.

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

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

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

IP 475, *Petroleum liquids — Manual sampling.* (≡ ISO 3170

IP 476, *Petroleum liquids — Automatic pipeline sampling.* (≡ ISO 3171)

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

ISO 3819, *Laboratory glassware — Beakers.*

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

IP 367, *Petroleum products — Determination and application of precision data in relation to method of test.* (≡ ISO 4259)

3 Principle

A weighed test portion, is ignited and burnt, and the residual carbon removed by heating in a muffle furnace. The residue is fused with a dilithium tetraborate/lithium fluoride flux and the fused mixture digested in a solution of tartaric acid and hydrochloric acid. After dilution with water, the solution is aspirated into the plasma of an inductively coupled plasma emission spectrometer (ICPES) and the emission radiation of the resonance lines of the elements under analysis is measured, and compared to a calibration curve constructed from standard calibration solutions.

4 Reagents and materials

4.1 General

All reagents shall be of analytical reagent grade or of higher purity and water shall be of at least grade 3 purity as specified in ISO 3696.

4.2 Potassium hydrogensulfate ($KHSO_4$)

Fused solid.

4.3 Ashing agent

Sulfur, 99,9 % (*m/m*) minimum purity.

4.4 Propan-2-ol

4.5 Toluene

4.6 Toluene/propan-2-ol mixture (1 + 1)

Mix equal volumes of toluene and propan-2-ol.

4.7 Hydrochloric acid

Concentrated, 36 % (*m/m*) HCl.

4.7.1 Hydrochloric acid solution (1 + 1). Mix equal volumes of hydrochloric acid (4.7) and water.

4.7.2 Hydrochloric acid solution (1 + 2). Mix one volume of hydrochloric acid (4.7) with two volumes of water.

4.8 Flux

Mixture of 90 % (*m/m*) dilithium tetraborate ($Li_2B_4O_7$) and 10 % (*m/m*) lithium fluoride (LiF).

4.9 Tartaric acid

4.9.1 Tartaric acid/hydrochloric acid solution. Dissolve 5 g of tartaric acid in approximately 500 ml of water acidified with 40 ml of hydrochloric acid (4.7) and dilute to 1 000 ml with water.

4.10 Nitric acid

Concentrated, 70 % (*m/m*) HNO_3.

4.10.1 Nitric acid solution (1 + 1). Mix equal volumes of nitric acid (4.10) and water.

4.11 Standard solutions

4.11.1 Aluminium standard solution. Use either a commercially available aluminium standard solution of 1 000 mg/l aluminium content, or prepare in the manner described in 4.11.1.1.

4.11.1.1 Dissolve 1,000 g of aluminium metal wire, of minimum purity 99,9 % Al, in 50 ml hydrochloric acid (4.7) with gentle heating in a 400 ml beaker (5.13). Cool, transfer to a 1 000 ml volumetric flask (5.9), and dilute to the mark with water.

4.11.2 Silicon standard solution. Use either a commercially available silicon standard solution of 1 000 mg/l silicon content, or prepare in the manner described in 4.11.2.1.

4.11.2.1 Fuse 2,140 g of silicon dioxide, of minimum purity 99,99 % SiO_2, with 8 g of sodium hydroxide in a zirconium crucible fitted with a close-fitting lid (5.4) at dull re heat until a clear melt is obtained. Cool and dissolve the solidified melt in 100 ml of hydrochloric acid solution (4.7.2) in a 400 ml beaker (5.13). Cool, transfer to a 1 000 ml volumetric flask (5.9), make up to the mark with water, followed by immediate transfer to a plastic bottle (5.15) for longer-term storage.

4.11.3 Vanadium standard solution. Use either a commercially available vanadium standard solution of 1 000 mg/l vanadium content, or prepare in the manner described in 4.11.3.1.

4.11.3.1 Dissolve 1,000 g of vanadium metal, of minimum purity 99,9 % V, in 40 ml of nitric acid (4.10) with gentle heating in a 400 ml beaker

(5.13). Cool, transfer to a 1 000 ml volumetric flask (5.9) and make up to the mark with water.

4.11.4 Nickel standard solution. Use either a commercially available nickel standard solution of 1 000 mg/l nickel content, or prepare in the manner described in 4.11.4.1.

4.11.4.1 Dissolve 1,000 g of nickel metal of minimum purity 99,9 % Ni, in 40 ml of nitric acid solution (4.10.1) with gentle heating in a 400 ml beaker (5.13). Cool, transfer to a 1 000 ml volumetric flask (5.9) and make up to the mark with water.

4.11.5 Iron standard solution. Use either a commercially available iron standard solution of 1 000 mg/l iron content, or prepare in the manner described in 4.11.5.1.

4.11.5.1 Dissolve 1,000 g of iron metal of minimum purity 99,9 % Fe, in 40 ml of hydrochloric acid solution (4.7.1) with gentle warming in a 400 ml beaker (5.13). Cool, transfer to a 1 000 ml volumetric flask (5.9) and make up to the mark with water.

4.11.6 Sodium standard solution. Use either a commercially available sodium standard solution of 1 000 mg/l sodium content, or prepare in the manner described in 4.11.6.1.

4.11.6.1 Dissolve 2,542 g ± 0,001 g of sodium chloride (NaCl) in water in a 400 ml beaker (5.13). Transfer to a 1 000 ml volumetric flask (5.9), make up to the mark with water, and mix.

4.11.7 Calcium standard solution. Use either a commercially available calcium standard solution of 1 000 mg/l calcium content, or prepare in the manner described in 4.11.7.1.

4.11.7.1 Dissolve 2,498 g ± 0,001 g of calcium carbonate($CaCO_3$) in water in a 400 ml beaker (5.13) with 100 ml water and add dropwise 10 ml of hydrochloric acid solution (4.7.1). Transfer to a 1 000 ml volumetric flask (5.9), make up to the mark with water, and mix.

4.11.8 Zinc standard solution. Use either a commercially available zinc standard solution of 1 000 mg/l zinc content, or prepare in the manner described in 4.11.8.1.

4.11.8.1 Dissolve 1,000 g ± 0,001 g of zinc metal in minimum volume of hydrochloric acid solution (1 + 1)(4.7.1) in a 400 ml beaker (5.13). Transfer to a 1 000 ml volumetric flask (5.9), make up to the mark with water, and mix.

4.11.9 Phosphorus standard solution. Use either a commercially available phosphorus standard solution of 1 000 mg/l phosphorus content, or prepare in the manner described in 4.11.9.1.

4.11.9.1 Dissolve 4,264 g ± 0,001 g diammoniumhydrogenphosphate $(NH_4)_2HPO_4$ in water in a 400 ml beaker (5.13). Transfer to a 1 000 ml volumetric flask (5.9), make up to the mark with water, and mix.

5 Apparatus

5.1 General

The apparatus requirements are detailed in 5.2 to 5.16. All platinumware and glassware shall be sodium-free and carefully cleaned with hot hydrochloric acid solution (4.7.1) and rinsed thoroughly with water to eliminate contamination.

5.2 Inductively coupled plasma emission spectrometer

Use either a sequential or simultaneous spectrometer.

5.3 Platinum basin

Of 100 ml capacity with a minimum diameter of 70 mm. Clean the basin with fused potassium hydrogensulfate (4.2).

NOTE 1 - The following cleaning technique is recommended: place approximately 5 g of potassium hydrogensulfate (4.2) 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 water and dry.

5.4 Zirconium crucible

Of a capacity of 30 ml to 50 ml, and fitted with a close-fitting zirconium lid.

5.5 Mixer

Non-aerating, high-speed type.

5.6 Oven

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

5.7 Muffle furnace

Electric, capable of being maintained at temperatures of 525 °C ± 25 °C and 925 °C ± 25 °C, and preferable having apertures at front and rear to allow passage of a slow, natural draught of air. Ensure that the refractory walls are in good condition, with no loose particles.

5.8 Hot plate

Electric, with or without a magnetic stirring capability.

5.9 Volumetric flasks

100 ml and 1 000 ml capacity, complying with the requirements of ISO 1042, class A.

5.10 Pipettes

1 ml, 2 ml, 5 ml, 10 ml, 20 ml and 25 ml capacity, complying with the requirements of ISO 658, class A.

5.11 Pipettes

1 ml and 2 ml capacity, graduated in 0,1 ml subdivisions, complying with the requirements of ISO 835-2.

5.12 Measuring cylinders

10 ml, 25 ml, 50 ml and 100 ml capacity, with subdivided graduations, complying with the requirements of ISO 4788.

5.13 Beaker

400 ml capacity, squat form, complying with the requirements of ISO 3819.

5.14 Filter paper

'Ashless' grade, 0,01 % *(m/m)* ash content maximum.

5.15 Plastic bottles

100 ml and 1 000 ml capacity, suitable for long-term storage of dilute acid solutions.

5.16 Analytical balance

Capable of weighing to the nearest 0,2 mg.

6 Samples and sampling

6.1 Unless otherwise specified, laboratory samples shall be obtained by the procedures described in IP 475 or IP 476.

6.2 Thoroughly mix samples in their containers immediately prior to withdrawal of the test portions. Place the sample container in the oven (5.6) and maintain the sample at 50 °C to 60 °C until all the sample is fluid and of uniform viscosity. Insert the shaft of the mixer (5.5) into the sample container so that the head of the shaft is immersed to approximately 5 mm from the bottom of the container. Mix the sample for approximately 5 min.

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

7 Procedure

7.1 Test portion mass

Select a mass of test portion, between 20 g and 50 g, to yield approximately 5 - 50 mg of ash.

NOTE 3 - The mass of test portion is selected based on the ash content. If the levels of any elements is outside the validated calibration range, dilution of the test solutions are required.

7.2 Test solution preparation

7.2.1 Immediately after homogenization, transfer the test portion from the container to the weighed platinum basin (5.3). Re-weigh the basin and contents to the nearest 0,1 g to obtain the test portion mass.

7.2.2 If required, add 0,3 g of ashing agent (4.3) to the basin, distributing it as evenly as possible over the surface of the basin contents.

If only aluminium, silicon and iron are being determined, or if it is known that the ashing agent being used does not contribute significantly to the background blank, continue directly with the procedure described in 7.2.3 onwards. If however, the ashing agent has an unknown background effect, or if vanadium, nickel, sodium, calcium, zinc and/or phosphorus is to be included in the determination, prepare a blank test portion containing only the ashing agent, and use it for the complete procedure in this clause.

7.2.3 Warm the basin and contents gently with a

Bunsen flame until the test portion 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 test portion.

If foaming and frothing occur, discard the test portion and add 1 ml to 2 ml of propan-2-ol (4.4) before heating. If foaming and frothing are not sufficiently reduced, add 10 ml of toluene/propan-2-ol mixture (4.6) to a further test portion and mix thoroughly. Place several strips of filter paper (5.14) in the mixture before warming gently.

NOTE 5 - When the paper begins to burn, the greater part of the water will have been removed.

7.2.4 Place the basin and its contents in the muffle furnace (5.7), preheated to a temperature of 525 °C ± 25 °C. Ensure that the basin contents are not contaminated with refractory from the furnace walls, as this will contribute to erroneous silicon results. Maintain the muffle furnace at this temperature until all the carbon has been removed and only ash remains.

NOTE 6 - This may take overnight.

7.2.5 Cool the basin to room temperature, add 0,4 g of flux (4.8), and mix it with the ash. Place the basin and contents in the muffle furnace preheated to a temperature of 925 °C ± 25 °C for 5 min. Remove the basin and ensure contact of the flux with the ash. Replace the basin in the muffle furnace and maintain the temperature at 925 °C ± 25 °C for a further 10 min.

7.2.6 Remove the basin and cool the fusion melt to room temperature. Add 50 ml tartaric acid/hydrochloric acid solution (4.9.1) to the basin and place on the hot plate (5.8). Maintain at a moderate temperature without boiling.

NOTE 7 - Excessive evaporation of the solution could lead to precipitation of an insoluble form of silica.

NOTE 8 - 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.

7.2.7 Allow the solution to cool and then transfer it to a 100 ml volumetric flask (5.9) with water, washing the basin several times to ensure that the transfer is quantitative. Make up to the mark with water, and transfer immediately to a 100 ml plastic bottle (5.15).

NOTE 9 - Transfer to a plastic bottle is recommended as the dilute acid solution will contain tetrafluoroboric acid (HBF_4) from solution of 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 blank solution containing only 0,4 g flux (4.8) and 50 ml of the tartaric acid/hydrochloric acid solution (4.9.1), diluted to 100 ml, and transfer immediately to a 100 ml plastic bottle (5.15).

7.4 Preparation of calibration solutions

7.4.1 Aluminium, silicon, vanadium, nickel, iron, sodium, calcium, zinc and phosphorus. Prepare a 250 mg/l working solutions by diluting 25 ml of the 1 000 mg/l standard solution (4.11.1, 4.11.2, 4.11.3, 4.11.4, 4.11.5, 4.11.6, 4.11.7, 4.12.8, 4.12.9) to 100 ml with water. To each of thirty-six clean 100 ml volumetric flasks (5.9), add 0,4 g flux (4.8) and 50 ml of the tartaric acid/hydrochloric acid solution (4.9.1). To four 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. To another four 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. Continue to make similar solutions for each of the elements.

NOTE 10 - The calibration solutions contain 5 mg/l, 10 mg/l, 25 mg/l and 50 mg/l of aluminium, silicon, vanadium, nickel, iron, sodium, calcium, zinc and phosphorus each element respectively.

7.4.2 Storage. Transfer all standards immediately after preparation to 100 ml plastic bottles (5.15).

NOTE 12 - When aluminium, silicon, vanadium, nickel, iron, sodium, calcium, zinc and phosphorus are being determined together, it is possible to combine the 5 mg/l to 50 mg/l calibration solution, providing that there are no compatibility problems caused by the reagents used in the preparation of standard solutions given in 4.11.1 to 4.11.9, or contaminant levels of the other elements in the range that are likely to cause unacceptable blank levels of the respective elements being determined.

7.5 Setting up the spectrometer

7.5.1 General. Consult and follow the manufacturer's instructions for the operation of the inductively coupled plasma emission spectrometer

(5.2).

NOTE 13 - Design differences between spectrometers, ICP excitation sources and different 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 warm-up period, nebulize water through the plasma torch.

NOTE 14 - Some manufacturers may recommend even longer warm-up periods.

7.5.4 Wavelength profiling. Perform any wavelength profiling that may be 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.

When carrying out this test method for the first time, check the linearity of the spectrometer using the blank and working standards. If the response is linear over the analytic range, a two-point (blank plus high standard) or, if preferred, a three-point (blank plus intermediate plus high) calibration is sufficient. If linearity is not achieved, use multiple standards for the calibration curve.

7.5.7 Analysis of the test solution. Analyze the test portions 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 water for 10 s.

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

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

8 Calculation

Calculate E, the content of the element of interest as Al, Si, V, Ni, Fe, Na, Ca, Zn or P respectively in milligrams per kilogram from the following equation:

$$E = \frac{100cd}{m}$$

where

c is the element content of interest in mg/l as read from the calibration graph or direct readout;

d is the dilution factor, calculated from the volumes and aliquots taken to produce the test solution;

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

9 Expression of results

Report the element content of each element of interest to the nearest 1 mg/kg.

10 Precision

10.1 General

The precision given in 10.2 and 10.3 for elements other than aluminium and silicon was determined by statistical examination by IP 367 of interlaboratory test results on a matrix of residual fuels that was also used for the precision evaluation of the same range of elements except phosphorus by atomic absorption spectrometry, and given in IP 470. The values for aluminium and silicon are taken from IP 377.

10.2 Repeatability

The difference between two successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the value given in Table 2 only in one case in twenty.

10.3 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 normal and correct operation of the test method, exceed the values given in Table 2 only in one case in twenty.

Table 2 - Precision values

Element	Repeatability mg/kg	Reproducibility mg/kg
Aluminium	0,066 0 x	0,337 x
Silicon	0,064 3 x	0,332 x
Vanadium	0,6549 $x^{0,6}$	1,6799 $x^{0,6}$
Nickel	0,8153 $x^{0,55}$	1,6814 $x^{0,55}$
Iron	0,6358 $x^{0,55}$	0,9376 $x^{0,55}$
Sodium	0,5374 $x^{0,55}$	1,0667 $x^{0,55}$
Calcium	0,3734 $x^{0,65}$	0,6440 $x^{0,65}$
Zinc	0,3295 $x^{0,7}$	0,5082 $x^{0,7}$
Phosphorus	0,6008 $x^{0,55}$	1,2765 $x^{0,55}$
where x is the average of the results being compared, in mg/kg.		

Examples of actual precision for this test method, calculated from Table 2, are detailed in Table 3 below as a guideline for the user.

Table 3 - Examples of actual precision

	V mg/kg		Ni mg/kg		Fe mg/kg		Na mg/kg		Ca mg/kg		Zn mg/kg		P mg/kg	
mg/kg	r	R	r	R	r	R	r	R	r	R	r	R	r	R
1	0,65	1,68	0,82	1,68	0,64	0,94	0,54	1,07	0,37	0,64	0,33	0,51	0,60	1,28
10	2,61	6,69	2,89	5,97	2,26	3,33	1,91	3,78	1,67	2,88	1,65	2,55	2,13	4,53
50	6,85	17,57	7,01	14,46	5,47	8,06	4,62	9,17	4,75	8,19	5,09	7,86	5,17	10,97
100	10,38	26,62	10,26	21,17			6,47	13,43	7,45	12,85				
200	15,73	40,36												
300	20,07	51,47												
400	23,85	61,17												

Recordings at different wavelengths have been included in the precision study and listed in the below table as a guideline for the user.

Table 4 - Wavelengths

Element:	Most frequent used wavelength:	Other wavelengths used:
Vanadium	292,40	209,88 / 292,46 / 309,31/311,07
Nickel	231,60	221,68 / 232,00
Iron	259,94	-
Sodium	589,59	588,99
Calcium	317,93	393,36 / 422,67
Zinc	213,86	-
Phosphorus	214,91	213,61 / 121,43 / 178,22

11 Test report

The test report shall contain at least the following information:

a) a reference to this standard;

b) all details necessary for complete identification of the product tested;

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

d) any deviations, by agreement or otherwise, from the procedures specified;

e) the date of the test.