INTERNATIONAL STANDARD

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Petroleum products — Determination of vanadium and nickel content — Wavelength-dispersive X-ray fluorescence spectrometry

Produits pétroliers — Dosage du vanadium et du nickel — Spectrométrie de fluorescence X dispersive en longueur d'onde

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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.

International Standard ISO 14597 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants.*

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Petroleum products — Determination of vanadium and nickel content — Wavelength-dispersive X-ray fluorescence spectrometry

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

1 Scope

This International Standard specifies a method for the determination of vanadium and nickel in liquid petroleum products. It may also be applied to semi-solid and solid petroleum products that are either liquefied by moderate heating or completely soluble in the specified organic solvent mixture. The method is applicable to products having vanadium contents in the range 5 mg/kg to 1 000 mg/kg, and nickel contents in the range 5 mg/kg to 100 mg/kg, although precision data have only been determined up to 100 mg/kg for vanadium and 60 mg/kg for nickel; higher contents may be determined by appropriate dilution.

Barium at concentrations above approximately 300 mg/kg interferes with the determination of vanadium, and iron at concentrations above approximately 500 mg/kg interferes with the determination of nickel. Other elements at concentrations above approximately 500 mg/kg may affect precision and accuracy due to spectral line overlap or absorption.

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

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

3 Principle

The test portion and a manganese solution as internal standard are mixed in a given mass ratio and exposed, in a sample cell, to the primary radiation of an X-ray tube.

The count rates of excited metal and reference material are measured, and the ratio of these count rates calculated. The vanadium and nickel contents of the sample are determined from calibration curves prepared on the basis of calibration standards.

4 Reagents and materials

4.1 White oil (light paraffin oil), high purity grade, sulfur content 1 mg/kg maximum.

4.2 Xylene or **mixed xylenes,** analytical reagent grade.

4.3 Solvent mixture, 1 part by volume of white oil (4.1) mixed with 2 parts by volume of xylene (4.2).

4.4 Acetyl acetone, minimum purity 99 % (*m*/*m*).

NOTE — For the purposes of this International Standard, the expressions "% (*m*/*m*)" and "% (*V*/*V*)" are used to represent the mass and volume fractions respectively.

4.5 2-ethylhexanoic acid, minimum purity 98 % (*m*/*m*).

4.6 Vanadium compound, bis (1-phenylbutane-1, 3-dionato)-oxo-vanadium(IV) or any other oil-soluble vanadium compound. The vanadium content shall be accurately known to the nearest 0,01 % (*m*/*m*).

4.7 Nickel compound, cyclohexane butanoic acid-nickel salts or any other oil-soluble nickel compound. The nickel content shall be accurately known to the nearest 0,01 % (*m*/*m*).

4.8 Manganese compound, manganese octoate or any other oil-soluble manganese compound. The manganese content shall be approximately 10 % (*m*/*m*).

NOTE — Manganese compounds may contain insoluble impurities entrapped during manufacture, e.g. oxides. If this is evident, the compound should be cleaned by dissolution in petroleum spirit, boiling range 60 °C to 80 °C, followed by filtration and evaporation.

4.9 Manganese solution.

Dissolve the manganese compound (4.8) in a solution of 95 % (*V*/*V*) solvent mixture (4.3) and 5 % (*V*/*V*) 2-ethylhexanoic acid (4.5) to produce a manganese content of approximately 500 mg/kg [0,05 % (*m*/*m*)]. Store the solution in a tightly-stoppered brown glass bottle protected from light within the temperature range of 18 °C to 28 °C.

NOTE — Under these conditions, the solution is stable for at least 3 months.

4.10 Certified reference standards, use materials from a national standards body or accredited suppliers, if available.

5 Apparatus

5.1 Wavelength-dispersive X-ray fluorescence spectrometer, use any suitable X-ray spectrometer capable of being operated under the conditions in table 1 and of measuring the wavelengths in table 2, or other giving equivalent results. It shall be set up according to the manufacturer's instructions.

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

5.3 Homogenizer, of non-aerating, high speed shear type or **heatable magnetic** or **ultrasonic stirrer**.

5.4 Flasks, of 50 ml capacity, narrow-necked, conical, made of borosilicate glass and fitted with ground-glass stoppers.

Table 1 — General requirements of spectrometer

Component	Requirement
Anode	Any tube anode may be used provided that the counting times be adjusted to achieve the required precision[1)]
Tube voltage and current	Set to provide maximum sensitivity for the lines in table 2 and within the power rating of the spectrometer
Analyzing cristal	Lithium fluoride (LiF) or any other crystal suitable for the dispersion of the wavelengths in table 2 within the angular range of the spectrometer
Optical path	Helium
Detector	Gas proportional detector with pulse-height analyser

1) If a chromium anode is used, either measure the Mn-K_{β} line (0,191 0 nm) and I_{UMn} at 0,188 5 nm, or measure the Mn-K_{α} line (0,210 3 nm) with a suitable tube filter to eliminate spectral interference from the Cr-K_{β} line and I_{UMn} at 0,219 0 nm.

6 Samples and sampling

6.1 Unless otherwise specified, samples shall be taken by the procedures described in ISO 3170 or ISO 3171.

6.2 Test portions from the samples shall be drawn after thorough mixing subdivision. Heat viscous, opaque, semi-solid or solid samples to a temperature which renders the sample liquid and homogenize using the homogenizer (5.3).

NOTE — Stratification in the sample cell, either of water or asphaltenic material, can lead to erroneous results.

7 Calibration solutions

7.1 General

Use either certified reference materials (4.10) or primary standards prepared from metal compounds (4.6 and 4.7) prepared as described in 7.2 as a basis for the preparation of stock solutions.

7.2 Preparation of stock solutions

7.2.1 Vanadium stock solutions

Weigh, to the nearest 0,1 mg, a quantity (m') of vanadium compound (4.6) to prepare stock solutions of approximately 1 000 mg/kg [0,10 % (m/m)] and 200 mg/kg [0,02 % (m/m)] vanadium content. Dissolve each of these in a mixture of 98,5 % (V/V) solvent mixture (4.3) and 1,5 % (V/V) acetyl acetone (4.4) and then weigh the solution to the nearest 0,1 mg ($m' + m''$). Mix the contents thoroughly using a homogenizer (5.3) and transfer to a tightly-stoppered brown glass bottle.

Calculate the exact vanadium content, w_{V2}, in mg/kg, to the nearest 1 mg/kg, from the mass of vanadium compound and mass of liquid using the following equation:

$$w_{\mathrm{V2}} = \frac{m' \times w_{\mathrm{V1}}}{m' + m''} \qquad \ldots (1)$$

where

m' is the mass, in grams, of the vanadium compound;

W_{V1} is the vanadium content, in milligrams per kilogram, of the vanadium compound;

m'' is the mass, in grams, of the solvent liquid.

NOTE — The stock solutions have a limited shelf life and as soon as turbidity is evident they should be discarded in an environmentally acceptable manner.

7.2.2 Nickel stock solution

Weigh, to the nearest 0,1 mg, a quantity (m') of nickel compound (4.7) to prepare a stock solution of approximately 100 mg/kg [0,01 % (m/m)] nickel content. Dissolve this in a mixture of 95 % (V/V) solvent mixture (4.3) and 5 % (V/V) of 2-ethylhexanoic acid (4.5) and then weigh the solution to the nearest 0,1 mg ($m' + m''$). Mix the contents thoroughly using a homogenizer (5.3) and transfer to a tightly-stoppered brown glass bottle.

Calculate the exact nickel content, W_{Ni2}, in mg/kg, to the nearest 1 mg/kg, from the mass of nickel compound and mass of liquid using the following equation:

$$W_{Ni2} = \frac{m' \times W_{Ni1}}{m' + m''} \qquad \ldots (2)$$

where

m' is the mass, in grams, of nickel compound;

W_{Ni1} is the nickel content, in milligrams per kilogram, of the nickel compound;

m'' is the mass, in grams, of the solvent liquid.

7.3 Preparation of standard solutions

7.3.1 High range vanadium

Into 50 ml flasks (5.4), weigh to the nearest 0,1 mg, the appropriate quantity of the 1 000 mg/kg vanadium stock solution (7.2.1) to produce approximately 25 g of each standard solution with vanadium contents of approximately 800 mg/kg, 600 mg/kg, 500 mg/kg, 400 mg/kg and 300 mg/kg. Add solvent mixture (4.3) to make up to approximately 25 g and re-weigh to the nearest 0,1 mg. Calculate the vanadium content, W_{V3}, in mg/kg, of each standard solution to the nearest 1 mg/kg, using the following equation:

$$W_{V3} = \frac{(m_2 - m_1)W_{V2}}{m_3 - m_1} \qquad \ldots (3)$$

where

m_1 is the mass, in grams, of the flask;

m_2 is the mass, in grams, of the flask plus stock solution;

m_3 is the mass, in grams, of the flask plus stock solution plus solvent mixture;

W_{V2} is the vanadium content, in milligrams per kilogram, of the stock solution.

NOTE — Dissolution and mixing is aided by the use of the homogenizer (5.3) and mild heat.

7.3.2 Low range vanadium

Prepare standard solutions as described in 7.3.1 using the 200 mg/kg stock solution (7.2.1) to give standard solutions of approximately 175 mg/kg, 150 mg/kg, 125 mg/kg, 100 mg/kg, 75 mg/kg, 50 mg/kg, 25 mg/kg and 5 mg/kg. Calculate the vanadium content to the nearest 1 mg/kg using equation (3) given in 7.3.1.

7.3.3 Nickel

Prepare standard solutions as described in 7.3.1 using the nickel stock solution (7.2.2) to give standard solutions of approximately 75 mg/kg, 50 mg/kg, 25 mg/kg, 10 mg/kg and 5 mg/kg.

7.4 Preparation of calibration solutions

7.4.1 Preparation

Weigh 20,00 g ± 0,01 g of each of the standard solutions (7.3) and the stock solutions (7.2) into separate flasks (5.4), and add 2,00 g ± 0,01 g of the manganese solution (4.9). Mix, using the homogenizer (5.3) at a maximum temperature of 50 °C, and cool to a temperature of 18 °C to 28 °C. Transfer to tightly-stoppered brown glass bottles.

7.4.2 Storage

Store certified reference standards in accordance with the instructions of the certifying organization and use within the timescale specified.

Store standards prepared from solvent mixture and standard solutions in a cool dark place.

NOTE — The stability of prepared standards, under the above storage conditions, has been found to exceed three months.

8 Calibration

8.1 General

After the spectrometer has been set up and checked (5.1) purge the optical path thoroughly with helium.

8.2 Calibration curves

Transfer each of the calibration solutions (7.4.1) to a sample cell and, in a sequence of increasing metal content, place them in the spectrometer for exposure to the primary radiation. Measure the count rates, I, of the excited V-K$_\alpha$, Ni-K$_\alpha$, Mn-K$_\alpha$ or Mn-K$_\beta$, and also the respective background radiations, I_U, at the wavelengths given in table 2.

Table 2 — Wavelengths of X-ray fluorescence and background radiation

Element	Wavelength nm
Vanadium, I_V	0,250 5
Vanadium background, I_{UV}	0,239 2
Nickel, I_{Ni}	0,165 9
Nickel background, I_{UNi}	0,163 8
Manganese, I_{Mn}	
a) Mn-K$_\alpha$	0,210 4
b) Mn-K$_\beta$	0,190 6
Manganese background, I_{UMn}	0,219 0

The setting of the spectrometer shall be such that at least 50 000 counts are registered for the Mn-K$_\alpha$ or Mn-K$_\beta$ line over the measurement period. In addition, the measuring time for each element shall be sufficient to achieve a coefficient of variation of less than 1 % at the top concentration levels ($w_V = 1\,000$ mg/kg, $w_{Ni} = 100$ mg/kg). The coefficient of variation, C, is calculated from the following equation:

$$C = \frac{100\sqrt{N_p + N_b}}{(N_p + N_b)} \qquad \text{. . . (4a)}$$

where

N_p is the number of counts collected on the Ni-K$_\alpha$ (I_{Ni}) or V-K$_\alpha$ (I_V) peak;

N_b is the number of counts collected at the relevant background wavelength (I_U).

If the peak to background ratio, $I{:}I_U$, is greater than 10:1, formula (4a) reduces to

$$C = \frac{100}{\sqrt{N_p}} \qquad \text{. . . (4b)}$$

For a coefficient of variation of 1 %, formula (4b) gives N_p equal to 10 000.

The measuring time, T_p, for the elements, or T_b, for background is calculated from the following equations:

$$T_p = \frac{N_p}{R_p} \qquad \text{. . . (5a)}$$

$$T_b = T_p\sqrt{\frac{R_b}{R_p}} \qquad \text{. . . (5b)}$$

where

R_p is either I_{Ni} or I_V;

R_b is I_U.

The times calculated from the above equations shall generally be regarded as minimum times. Rounding to practical time intervals shall be to the nearest longer time.

The net count ratio, R_0, for vanadium and nickel calibration solutions is calculated using the following general equation:

$$R_0 = \frac{I - I_U}{I_{Mn} - I_{UMn}} \qquad \text{. . . (6)}$$

where

I is I_V or I_{Ni} as appropriate;

I_U is I_{UV} or I_{UNi} as appropriate.

Calibration curves (see note to clause 10) are constructed by plotting the net count ratio, R_0, against metal content, mg/kg, of the calibration solutions. Two vanadium curves, covering the range 200 mg/kg to 1 000 mg/kg, and 5 mg/kg to 200 mg/kg, and one nickel curve covering the range 5 mg/kg to 100 mg/kg shall be constructed.

8.3 Checking

In regular use, check at least two points on each calibration curve not less frequently than monthly. Fuller checks shall be carried out at intervals not greater than six months. If the check result differs from the curve by more than the repeatability of this International Standard, a new calibration curve shall be constructed.

9 Procedure

Weigh 20,00 g ± 0,01 g of the sample to be analyzed (see note 1) into a flask (5.4) and add 2,00 g ± 0,01 g of the manganese solution (4.9). Mix, using the homogenizer (5.3) at a maximum temperature of 80 °C. Cool to a temperature of 18 °C to 28 °C and transfer a test portion to a sample cell. Measure the count rates for excited and background radiations and calculate the net count ratio, R_0, in the manner described in 8.2 [equation (6)].

NOTES

1 For the purpose of this procedure, the term "sample" includes solutions prepared from additives, semi-solid or solid petroleum products that have been appropriately pre-treated and/or diluted.

2 If the test portion solidifies on cooling, the measured results will not be noticeably affected, as the density change is compensated by the internal manganese standard.

10 Calculation

Read the vanadium and nickel contents from the calibration curves constructed in 8.2. If the vanadium content is above 1 000 mg/kg, or the nickel content is above 100 mg/kg, dilute the sample with solvent mixture (4.3) and repeat the procedure specified in clause 9.

NOTE — Modern instruments include a computer system which stores the calibration curves and calculates and produces a digital readout of the concentration values.

11 Expression of results

Report the vanadium content, in mg/kg, to the nearest 1 mg/kg if below 200 mg/kg, and to the nearest 5 mg/kg if between 200 mg/kg and 1 000 mg/kg. Report the nickel content to the nearest 1 mg/kg.

12 Precision

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 normal and correct operation of the test method, exceed the values in table 3 in only one case in twenty.

12.2 Reproducibility

The difference between two single and independent test 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 in table 3 in only one case in twenty.