1. Scope

1.1 These test methods cover the determination of nickel, vanadium, iron, and sodium in crude oils and residual fuels by flame atomic absorption spectrometry (AAS). Two different test methods are presented.

1.2 Test Method A, Sections 7-12—Flame AAS is used to analyze a sample that is decomposed with acid for the determination of total Ni, V, and Fe.

1.3 Test Method B, Sections 13-17—Flame AAS is used to analyze a sample diluted with an organic solvent for the determination of Ni, V, and Na. This test method uses oil-soluble metals for calibration to determine dissolved metals and does not purport to quantitatively determine nor detect insoluble particulates.

1.4 The concentration ranges covered by these test methods are determined by the sensitivity of the instruments, the amount of sample taken for analysis, and the dilution volume. A specific statement is given in Note 3.

1.5 For each element, each test method has its own unique precision. The user can select the appropriate test method based on the precision required for the specific analysis.

1.6 This standard does not purport to address all of the safety concerns, if any, 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. Specific warning statements are given in Notes 1, 2, 5 and 6.

1.7 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

2. Referenced Documents

2.1 ASTM Standards:
D 1193 Specification for Reagent Water
D 1548 Test Method for Vanadium in Heavy Fuel Oil
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

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E 288 Specification for Laboratory Glass Volumetric Flasks
E 969 Specification for Volumetric (Transfer) Pipets

3. Summary of Test Methods

3.1 Test Method A—One to twenty grams of sample are weighed into a beaker and decomposed with concentrated sulfuric acid by heating to dryness. The residual carbon is burned off by heating at 525°C in a muffle furnace. The inorganic residue is digested in dilute nitric acid, evaporated to incipient dryness, dissolved in dilute nitric acid and made up to volume with dilute nitric acid. Interference suppressant is added to the dilute nitric acid solution. The solution is nebulized into the flame of an atomic absorption spectrometer. A nitrous oxide/acetylene flame is used for vanadium and an air/acetylene flame is used for nickel and iron. The instrument is calibrated with matrix-matched standard solutions. The measured absorption intensities are related to concentrations by the appropriate use of calibration data.

3.2 Test Method B—Sample is diluted with an organic solvent to give a test solution containing either 5 % (m/m) or 20 % (m/m) sample. The recommended sample concentration is dependent on the concentrations of the analytes in the sample. For the determination of vanadium, interference suppressant is added to the test solution. The test solution is nebulized into the flame of an atomic absorption spectrometer. A nitrous oxide/acetylene flame is used for vanadium and an air/acetylene flame is used for nickel and sodium. The measured absorption intensities are related to concentrations by the appropriate use of calibration data.

4. Significance and Use

4.1 When fuels are combusted, metals present in the fuels can form low melting compounds that are corrosive to metal parts. Metals present at trace levels in petroleum can deactivate catalysts during processing. These test methods provide a means of quantitatively determining the concentrations of vanadium, nickel, iron, and sodium. Thus, these test methods can be used to aid in determining the quality and value of the crude oil and residual oil.

5. Purity of Reagents

5.1 Reagent grade chemicals shall be used for all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analyt-
ical Reagents of the American Chemical Society where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 When determining metals at concentrations less than 1 mg/kg, use ultra-pure grade reagents.

5.3 Purity of Water—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

6. Sampling and Sample Handling

6.1 The objective of sampling is to obtain a sample for testing purposes that is representative of the entire quantity. Only representative samples obtained as specified in Practices D 4057 and D 4177 shall be used. Do not fill the sample container more than two-thirds full.

6.2 Prior to weighing, stir the sample and then shake the sample in its container. If the sample does not readily flow at room temperature, heat the sample to a sufficiently high and safe temperature to ensure adequate fluidity.

**TEST METHOD A—FLAME ATOMIC ABSORPTION AFTER ACID DECOMPOSITION OF THE SAMPLE**

7. Apparatus

7.1 Atomic Absorption Spectrometer, complete instrument with hollow cathode lamps and burners with gas supplies to support air-acetylene and nitrous oxide-acetylene flames (Warning—see Note 1).

**NOTE 1: Warning—Hazardous. Potentially toxic and explosive. Refer to the manufacturer's instrument manual for associated safety hazards.**

7.2 Sample Decomposition Apparatus (optional)—This apparatus is described in Fig. 1. It consists of a Vycor or Pyrex 400-mL beaker for the test solution, an air bath (Fig. 2) that rests on a hot plate and a 250 W infrared lamp supported 2.5 cm above the air bath. A variable transformer controls the voltage applied to the lamp.

7.3 Glassware—Vycor or Pyrex 400-mL beakers, volumetric flasks of various capacities and pipettes of various capacities. When determining concentrations below 1 mg/kg, all glassware must be thoroughly cleaned (or soaked overnight) with 5 % HNO₃ and rinsed five times with water.

7.4 Electric Muffle Furnace, capable of maintaining 525 ± 25°C and sufficiently large to accommodate 400-mL beakers. The capability of an oxygen bleed is advantageous and optional.

7.5 Steam Bath.

7.6 Temperature Controlled Hot Plate, (optional).

7.7 Drying Oven, (optional), explosion-proof, if used to heat crude oils to obtain fluidity.

8. Reagents

8.1 Aqueous Standard Solutions—Individual aqueous

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Note—All parts 16 gage (1.5 mm, 0.060 in.) aluminum. All dimensions are in inches.

<table>
<thead>
<tr>
<th>in.</th>
<th>Metric Equivalents</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.4</td>
</tr>
<tr>
<td>1¼</td>
<td>38.1</td>
</tr>
<tr>
<td>2</td>
<td>50.8</td>
</tr>
<tr>
<td>3½</td>
<td>77.8</td>
</tr>
</tbody>
</table>

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10. Preparation of Test Solutions

10.1 Into a beaker, weigh an amount of sample estimated to contain between 0.0025 and 0.12 mg of each metal to be determined. A typical mass is 10 g. Add 0.5 mL of H₂SO₄ for each gram of sample.

Note 3—If it is desired to extend the lower concentration limits of the test method, it is recommended that the decomposition be done in 10-g increments up to a maximum of 100 g. It is not necessary to destroy all the organic matter each time before adding additional amounts of the sample and acid. When it is desired to determine higher concentrations, reduce the sample size accordingly.

10.2 At the same time prepare reagent blanks using the same amount of sulfuric acid as used for sample decomposition. Reagent blanks should be carried through the same procedure as the samples.

Note 4: Caution—Reagent blanks are critical when determining concentrations below 1 mg/kg. To simplify the analysis, use the same volume of acid and the same dilutions as used for the samples. For example, if 20 g of sample is being decomposed, use 10 mL of sulfuric acid for the reagent blank.

10.3 The use of the air bath apparatus (Fig. 2) is optional. Place the beaker in the air bath, which is located in the hood. The hot plate is off at this time. Heat gently from the top with the infrared lamp (Fig. 1) while stirring the test solution with a glass rod. As decomposition proceeds (indicated by a frothing and foaming), control the heat of the infrared lamp to maintain steady evolution of fumes. Give constant attention to each sample mixture until all risk of spattering and foaming is past. Then, gradually increase the temperature of both the hot plate and lamp until the sample is reduced to a carbonaceous ash.

10.4 If the air bath apparatus is not used, heat the sample and acid on a temperature controlled hot plate. As described in 10.3, monitor the decomposition reaction and adjust the temperature of the hot plate accordingly.

Note 5: Precaution—Hot fuming concentrated sulfuric acid is very corrosive and a strong oxidizing acid. The analyst should work in a well-ventilated hood and wear rubber gloves and a suitable face shield to protect against spattering acid.

10.5 Place the sample in the muffle furnace maintained at 525 ± 25°C. Optionally, introduce a gentle stream of oxygen into the furnace to expedite oxidation. Continue to heat until the carbon is completely removed.

10.6 Dissolve the inorganic residue by washing down the wall of the beaker with about 10 mL of the 1+1 HNO₃. Digest on a steam bath for 15 to 30 min. Transfer to a hot plate and gently evaporate to incipient dryness.

10.7 Wash down the wall of the beaker with about 10 mL of dilute nitric acid (5 % V/V). Digest on the steam bath until all salts are dissolved. Allow to cool. Transfer quantitatively to a volumetric flask of suitable volume and make up to volume with dilute nitric acid. This is the test solution.

10.8 Pipette aliquots of the test solution into two separate volumetric flasks. Retain one flask for the determination of nickel and iron. To the other flask add aluminum interference suppressant for vanadium determination (refer to Table 1) and dilute up to mark with dilute nitric acid (5 % V/V). Similarly, prepare a reagent blank solution for vanadium analysis.

11. Preparation of Apparatus

11.1 Consult the manufacturer’s instructions for the operation of the atomic absorption spectrometer. This test method assumes that good operating procedures are followed. Design differences between spectrometers make it impractical to exactly specify required instrument settings.

11.2 Set up the instrument to determine each analyte sequentially.

12. Calibration and Analysis

12.1 For each analyte in turn, perform the following operation.
TABLE 2 AAS Conditions for the Determination of Vanadium, Nickel, and Sodium Following Solvent Dilution of the Sample

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Concentration Range, mg/kg</th>
<th>Interference Supressant</th>
<th>Flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>318.4</td>
<td>0.5-15</td>
<td>15 mg/kg Al(^{a})</td>
<td>N(_2)O-C(_2)H(_2)</td>
</tr>
<tr>
<td>Nickel</td>
<td>232.0</td>
<td>0.5-20</td>
<td>None</td>
<td>Ar-C(_2)H(_2)</td>
</tr>
<tr>
<td>Sodium</td>
<td>589.0</td>
<td>0.1-5</td>
<td>None</td>
<td>Ar-C(_2)H(_2)</td>
</tr>
</tbody>
</table>

\(^{a}\) Prepared from an organometallic standard, mineral oil, and dilution solvent.

12.2 Nebulize the appropriate blank standard and zero the instrument.

12.3 Nebulize the working standards, determine the absorbance and construct a calibration curve of absorbance versus analyte concentration utilizing the instrument’s concentration mode if available, otherwise plot these values.

12.4 Use the check standard to determine if the calibration for each analyte is accurate. If the results obtained on the check standard are not within ±5% of the expected concentration for each analyte, take corrective action and repeat the calibration.

12.5 Nebulize the test solutions and measure and record the absorbance. If appropriate, blank correct this absorbance by subtracting the reagent blank absorbance.

12.6 After measuring absorbances for a test solution, check the blank standard. If this does not read zero, check the system and then repeat steps 12.2 through 12.5.

12.7 Test solutions that give absorbances greater than that figures.

18. Calculation

18.1 For Test Method A, calculate the concentration of each analyte in the sample using the following equation:

\[
\text{analyte concentration, mg/kg} = (C \times V \times F)/W
\]

where:

- \(C\) = concentration of the analyte in the test solution (corrected for the concentration determined in the reagent blank), \(\mu g/mL\),
- \(V\) = volume of the test solution, mL,
- \(F\) = dilution factor, volume/volume or mass/mass, and
- \(W\) = sample mass, g.

18.2 For Test Method B, calculate the concentration of each analyte in the sample using the following equation:

\[
\text{analyte concentration, mg/kg} = C \times F
\]

where:

- \(C\) = concentration of the analyte in the test solution, mg/kg, and
- \(F\) = dilution factor, volume/volume or mass/mass.

19. Report

19.1 Report the following information:

19.1.1 Report concentrations in mg/kg to two significant figures.
TABLE 4 Calculated Repeatability (mg/kg) at Selected Concentrations (mg/kg)

<table>
<thead>
<tr>
<th>Element</th>
<th>Test Method</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Vanadium</td>
<td>A</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4.8</td>
</tr>
<tr>
<td>Nickel</td>
<td>A</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.13</td>
</tr>
<tr>
<td>Iron</td>
<td>A</td>
<td>0.98</td>
</tr>
<tr>
<td>Sodium</td>
<td>B</td>
<td>0.12</td>
</tr>
</tbody>
</table>

TABLE 5 Reproducibility

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration Range, mg/kg</th>
<th>Test Method</th>
<th>Reproducibility, mg/kg(^{\text{a}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>50–500</td>
<td>A</td>
<td>0.33X(^{0.90})</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td></td>
<td>1.2X(^{0.90})</td>
</tr>
<tr>
<td>Nickel</td>
<td>10–100</td>
<td>A</td>
<td>1.3X(^{0.63})</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td></td>
<td>0.06X(^{1.2})</td>
</tr>
<tr>
<td>Iron</td>
<td>3–10</td>
<td>A</td>
<td>1.45X(^{0.45})</td>
</tr>
<tr>
<td>Sodium</td>
<td>1–20</td>
<td>B</td>
<td>0.07X(^{1.0})</td>
</tr>
</tbody>
</table>

\(^{a}\) X = mean concentration, mg/kg.

TABLE 6 Calculated Reproducibility (mg/kg) at Selected Concentrations (mg/kg)

<table>
<thead>
<tr>
<th>Element</th>
<th>Test Method</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Vanadium</td>
<td>A</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>27.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>A</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.95</td>
</tr>
<tr>
<td>Iron</td>
<td>A</td>
<td>4.1</td>
</tr>
<tr>
<td>Sodium</td>
<td>B</td>
<td>0.69</td>
</tr>
</tbody>
</table>

20. Precision and Bias\(^{8}\)

20.1 Precision—The precision of this test method was determined by statistical analysis on interlaboratory test results. For Test Methods A and B, six cooperators participated in the interlaboratory study. Seven samples (four residual oils and three crude oils) comprised the test set. One residual oil was NIST SRM 1618.\(^{6}\) One crude oil was NIST SRM 8505.\(^{9}\)

20.1.1 Repeatability—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the values in Tables 3 and 4 only in one case in twenty.

20.1.2 Reproducibility—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test materials, would in the long run, in the normal and correct operation of the test method, exceed the values in Tables 5 and 6 only in one case in twenty.

20.2 Bias—Bias was evaluated from results obtained on two NIST samples. For Test Method A, the means of the reported values for V and Ni do not differ from the corresponding expected values by more than the repeatability of the test method. For Test Method B, the mean of the reported values for V does not differ from the corresponding expected value by more than the repeatability of the test method, and the mean of the reported values for Ni is higher than the expected value by an amount approximately equal to twice the repeatability of the test method. Standard reference materials for Fe and Na are not available, so bias was not determined for these elements.

21. Keywords

21.1 atomic absorption spectrometry; AAS; iron; nickel; sodium; vanadium