**ASTM INTERNATIONAL**

**Designation: D8252 – 23**

# Standard Test Method for
# Vanadium and Nickel in Crude and Residual Oil by X-ray Spectrometry[1]

This standard is issued under the fixed designation D8252; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ($\varepsilon$) indicates an editorial change since the last revision or reapproval.

## 1. Scope*

1.1 This test method covers the quantitative determination of total vanadium and nickel in crude and residual oil in the concentration ranges shown in Table 1 using X-ray fluorescence (XRF) spectrometry.

1.2 Sulfur is measured for analytical purposes only for the compensation of X-ray absorption matrix effects affecting the vanadium and nickel X-rays. For measurement of sulfur by standard test method use Test Methods D4294, D2622 or other suitable standard test method for sulfur in crude and residual oils.

1.3 This test method is limited to the use of X-ray fluorescence (XRF) spectrometers employing an X-ray tube for excitation in conjunction with wavelength dispersive detection system or energy dispersive high resolution semiconductor detector with the ability to separate signals of adjacent and near-adjacent elements.

1.4 This test method uses inter-element correction factors calculated from XRF theory, the fundamental parameters (FP) approach, or best fit regression.

1.5 Samples containing higher concentrations than shown in Table 1 must be diluted to bring the elemental concentration of the diluted material within the scope of this test method.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6.1 The preferred concentrations units are mg/kg for vanadium and nickel.

1.7 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry

D6259 Practice for Determination of a Pooled Limit of Quantitation for a Test Method

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D7343 Practice for Optimization, Sample Handling, Calibration, and Validation of X-ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants

E1621 Guide for Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry

## 3. Terminology

3.1 *Definitions:*

3.1.1 *alpha corrections, n*—influence correction factors that compensate for inter-element X-ray matrix effects; alpha corrections may be determined by best-fit regression, XRF Fundamental Parameters (FP), or XRF theory (called theoretical alphas).

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**\*A Summary of Changes section appears at the end of this standard**

**TABLE 1 Elements and Ranges of Applicability**

| Element | PLOQ in mg/kg | Max Concentration in mg/kg |
|---|---|---|
| Vanadium | 1.9 | 50 |
| Nickel | 2.2 | 50 |

3.1.2 *Bremsstrahlung, n*—the component of X-ray tube source beam due to radiation emitted when electrons from the tube cathode stop their motion (also called the continuum or white noise).

3.1.3 *channel, n*—*in WDXRF*, the wavelength channel used to measure X-ray intensity for an element of interest.

3.1.4 *concentration, n*—mass fraction wt/wt%, mass%, or mg/kg.

3.1.5 *energy dispersive X-ray fluorescence spectrometry, n*—XRF spectrometry applying energy dispersive detection of radiation.

3.1.6 *fundamental parameters, n*—calibration approach based on XRF theory in which the fundamental constants and equations relating element concentration and X-ray intensity are used to model how X-ray move in and out of matter.

3.1.7 *matrix effects, n*—X-ray absorption and enhancement that occurs in the sample due to the interaction of X-rays and the atoms of the materials.

3.1.8 *monochromatic source excitation, n*—Bremsstrahlung component of background is negligible and typically ignored; a secondary target is used in the X-ray source beam between X-ray tube and sample that virtually removes Bremsstrahlung component of the source beam.

3.1.9 *polychromatic source excitation, n*—Bremsstrahlung component of background is significant and cannot be ignored; the X-ray tube may irradiate the sample directly in an open position, or use primary filters in the X-ray source beam between X-ray tube and sample that selectively shape or remove Bremsstrahlung in an energy or wavelength range.

3.1.10 *region of interest, n*—*in EDXRF*, the energy region used to measure X-ray intensity for an element of interest.

3.1.11 *wavelength dispersive X-ray fluorescence spectrometry, n*—XRF spectrometry applying wavelength dispersive detection of radiation.

3.1.12 The terms *apparatus*, *spectrometer*, and *instrument* are often used interchangeably.

3.2 *Abbreviations:*

3.2.1 *cps*—count per second, the unit used for X-ray intensity

3.2.2 *EDXRF*—energy dispersive X-ray fluorescence

3.2.3 *LLOQ*—laboratory limit of quantification, the limit of quantification of a single spectrometer as defined as three times the instrument 3σ detection limit (see Practice D6259)

NOTE 1—See Sections 3, 5, and 6 of Practice D6259 relating to LLOQ.

3.2.4 *MXRF*—monochromatic XRF (can be MEDXRF or MWDXRF)

3.2.5 *PLOQ*—pooled limited of quantification based on pooled data of instrumentation used in the ILS (see Practice D6259)

3.2.6 *PXRF*—polychromatic XRF (can be EDXRF or WDXRF)

3.2.7 *ROI*—region of interest

3.2.8 *WDXRF*—wavelength dispersive X-ray fluorescence

3.2.9 *XRF*—X-ray fluorescence

## 4. Summary of Test Method

4.1 A sample is placed in the X-ray beam and is irradiated by the source X-ray beam, causing characteristic fluorescent X-ray intensities for all excited elements to be emitted from the sample. The characteristic fluorescent X-rays from vanadium and nickel are then related to concentration based on the apparatus calibration.

4.2 The resultant net element intensities are obtained after subtracting the background intensities measured during the analysis and correcting for overlapping lines from elements having transitions at the same or close to the elemental lines being measured. (The detection resolution exhibited by WDXRF, or EDXRF using a semiconductor detector, minimizes or obviates the need for peak overlap corrections in this test method.) Various standard algorithms are used to compensate for background and elemental peak overlaps, depending on use of WDXRF or EDXRF and polychromatic or monochromatic source X-rays; see manufacturer's guidelines.

4.3 Net element intensities are then correlated to known concentration values and corrected for X-ray absorption/enhancement effects. X-ray absorption/enhancement correction factors, also called alpha corrections, are determined by best-fit regression, fundamental parameters, or theoretical means. See manufacturer's guidelines for algorithms calculating matrix absorption/enhancement correction factors.

4.4 Measurement of net element intensities for unknown samples are then compared to the stored calibration to determine elemental concentration of the unknown samples.

4.5 *Wavelength Dispersive XRF (WDXRF):*

4.5.1 WDXRF excitation type may be polychromatic or monochromatic.

4.5.2 Appropriate crystals that diffract each element's X-rays to the detector are chosen to isolate each desired element peak and any required background signals, and these intensities are measured by the detection system of the WDXRF spectrometer. The appropriate background intensity in each element peak is calculated and subtracted from the initial gross peak intensity. See manufacturer's guidelines for selection of crystals, peak positions, background signals, and background correction method.

**TABLE 2 Peak Position Wavelengths for Elements of Interest**

| Element Line | Peak Position (nm) |
|---|---|
| S-Kα | 0.5373 |
| V-Kα | 0.2505 |
| Ni-Kα | 0.1659 |

4.5.3 Table 2 shows typical peak position in nm for the elements of interest; see manufacturer's guidelines.

4.6 *Energy Dispersive XRF (EDXRF):*

4.6.1 EDXRF excitation type may be polychromatic or monochromatic.

4.6.2 The X-ray intensity in the ROI of each desired element peak and any required background regions is measured by the detector of the EDXRF spectrometer. The appropriate background intensity in each element peak is calculated and subtracted from the initial gross peak intensity. See manufacturer's guidelines for selection of element ROI, any appropriate background regions, and background correction method.

4.6.3 Table 3 shows typical peak centroid position in keV for the elements of interest; see manufacturer's guidelines.

## 5. Significance and Use

5.1 This test method provides a rapid and precise elemental measurement with simple sample preparation. Typical analysis times are approximately 4 min to 5 min per sample with a preparation time of approximately 1 min to 3 min per sample.

5.2 The quality of crude oil is related to the amount of sulfur present. Knowledge of the vanadium and nickel concentration is necessary for processing purposes as well as contractual agreements.

5.3 The presence of vanadium and nickel presents significant risks for contamination of the cracking catalysts in the refining process.

5.4 This test method provides a means of determining whether the vanadium and nickel content of crude meets the operational limits of the refinery and whether the metal content will have a deleterious effect on the refining process or when used as a fuel.

## 6. Interferences

6.1 XRF exhibits inter-element X-ray absorption/enhancement matrix effects in which the atoms present in the material can affect the fluorescent X-ray intensities. Instrument software includes absorption/enhancement correction adjustments to the calibration employing theoretical means, FP, or empirical best-fit regression.

6.2 XRF spectrometers may exhibit element peak overlaps depending on the full-width half-max resolution of the detection system. Instrument software typically includes procedures to measure and subtract spectral peak overlap interferences.

6.3 Crude and residual oil contain relatively high concentrations of sulfur, typically 0.1 % to 5 %. The sulfur signal is measured and appropriate corrections are employed to compensate for sulfur's absorption of V and Ni X-rays. See manufacturer's guidelines.

6.4 Crude and residual oil may contain other elements including chlorine, calcium, and iron typically less than 0.1 % each and may exhibit spectral overlap and/or X-ray absorption/enhancement effects.

6.5 Crude oils may have trace amounts of sodium and magnesium in addition to phosphorus introduced through hydraulic fractionation liquids in the form of phosphate or phosphonate esters. Levels of these elements are generally less than 0.01 % and may have no significant influence on the estimation of the elements of interest.

6.6 Crude oils containing high amounts of water greater than 3.1 % by mass (approximately 2.8 % by mass oxygen) can have a high oxygen content leading to significant absorption of sulfur X-rays and corresponding low results. It may be necessary to remove excess water by centrifuging the sample, or other suitable means of removing the excess water.

## 7. Apparatus

7.1 WDXRF analyzer may be used if its design incorporates, as a minimum, the following features. Required design features include (unless otherwise specified):

7.1.1 *Pulse-Height Analyzer,* or other means of energy discrimination.

7.1.2 *Detector,* for the detection of X-rays with wavelengths in the range of interest (from about 0.1 nm to about 0.6 nm or optimized for single element analyzers). Typically sealed gas proportional counter, flow gas proportional counter, or scintillation counter is used.

7.1.3 *Analyzing Crystals*—The choice of analyzing crystals is made based on the element to be determined. The same crystals must be used for measuring calibration standards and unknown samples.

7.1.4 *Excitation Source,* X-ray tube and any required primary filters or monochromator, capable of exciting sulfur Kα, vanadium Kα, and nickel Kα radiation.

7.2 EDXRF analyzer may be used if its design incorporates, as a minimum, the following features. Required design features include (unless otherwise specified):

7.2.1 *X-ray Tube,* capable of exciting sulfur Kα, vanadium Kα, and nickel Kα radiation.

7.2.1.1 *Monochromator(s) (Optional),* for analyzers utilizing monochromatic excitation of sulfur Kα, vanadium Kα, and nickel Kα radiation. See manufacturer's guidelines.

7.2.2 *X-ray Detector,* with high sensitivity and a resolution value (Full Width at Half Maximum, FWHM) not to exceed 350 eV at 5.9 keV.

7.3 The following apply to both WDXRF and EDXRF instrumentation.

7.3.1 *X-ray Transparent Film,* for containing and supporting the test specimen in the sample cell while providing a low-absorption window for X-rays to pass to and from the sample. Sample cup and safety window film must be resistant to chemical attack by the sample, and should be free of sulfur, vanadium, and nickel. Film corrections will need to be applied if these elements are present in the film used. See spectrometer

**TABLE 3 Energy Positions for Peak Centroids for Elements of Interest**

| Element Line | Centroid Peak of Region of Interest (keV) |
|---|---|
| S-Kα | 2.307 |
| V-Kα | 4.949 |
| Ni-Kα | 7.472 |