

NICKEL, IRON, SULFUR AND VANADIUM IN DISTILLATE, RESIDUAL OILS AND PITCHES BY XRF

UOP Method 842-83

SCOPE

This rapid, nondestructive method is for determining nickel, iron and vanadium in distillate and residual oils and nickel, iron, vanadium and sulfur in solid pitches by energy dispersive x-ray fluorescence (XRF). The lower limit of detection for nickel, iron and vanadium is 2 mass-ppm. The lower limit of detection for sulfur in pitches is 100 mass-ppm.

The method assumes a linear relationship of percent metal vs. intensity when the concentration of the metal in the standards closely brackets the unknown. It also assumes that corrections for matrix absorption or inter-element effects are not required when properly calibrated standards of similar composition are used. Samples which are not homogeneous or that contain particulate material that precipitates on standing are not applicable.

The method is written for use with Kevex Model 0700-7000 Energy Dispersive instrument, however, other equivalent equipment is satisfactory.

OUTLINE OF METHOD

A sample of distillate or residual oil is poured into a polypropylene cup which is then fitted with a Mylar window, or if the oil sample is solid, it is ground and pressed into a pellet. The cup or pellet is introduced into the XRF instrument and a nitrogen purge is started on the sample chamber. The sample is irradiated by monochromatic x-rays and elements present in the sample emit characteristic spectral lines. These x-rays are detected, sorted and accumulated by the spectrometer. After background subtraction, the intensities are quantitatively compared to known standards which are actual samples of similar composition that have been analyzed for metals by AAS, UOP Method 800, and for sulfur by UOP Method 380.

APPARATUS

Cup windows, Mylar, Horiba, Cat. No. 350254, or equivalent

Die, 31-mm, chromium steel, SPEX Industries, Inc., Cat. No. 3623, or equivalent

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Die pellets, top and bottom, 31-mm, tungsten carbide, SPEX Industries, Inc., Cat. No. 3623 C, or equivalent

Grinder, Markson Science, Inc., Cat. No. R-15596, or equivalent

Pellet cups, flared, 30-mm, aluminum, SPEX Industries, Inc., Cat. No. 3619, or equivalent

Press, hydraulic, motorized, SPEX Industries, Inc., Cat. No. 3624, or equivalent

Sample cup, XRF, polypropylene, Chemplex Industries, Inc., Cat. No. 1850, or equivalent

X-ray fluorescence instrument, Kevex, Model 0700, fitted with helium purge and Vac Ion pump, coupled with Kevex μ X 7000 spectrometer, or equivalent

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified.

Butyl disulfide, BP 112/13 mm, Sargent-Welch Scientific Co., Cat. No. EK 1826-100GM, or equivalent

Iron octoate, Angstrom Inc., Cat. No. Fe-MO-8, or equivalent

Nitrogen, gas, 99.99% minimum purity

Nitrogen, liquid

Mineral oil, heavy, laboratory grade, Sargent-Welch Scientific Co., Cat. No. SC 13635-500ML, or equivalent

Nickel octoate, Angstrom Inc., Cat. No. Ni-MO-15, or equivalent

Standard, vanadium and nickel. This standard is available from the U.S. Department of Commerce, National Bureau of Standards, GM-5, 80 ppm vanadium and 90 ppm nickel, in residual oil.

Vanadium octoate, Angstrom Inc., Cat. No. V-MO-29, or equivalent

PROCEDURE

Sample Preparation

If the sample is a liquid, pour it into a sample cup to a minimum depth of approximately 1.25 cm; a larger volume may be used but will have no effect on the results. Viscous samples can be warmed on a hot plate before sampling to ensure homogeneity and ease in filling sample cups, however, the heating temperature should not exceed 60 C (140 F) because of damage to cups or Mylar film. Stretch a Mylar sheet over the cup opening and secure it using the ring portion of the cup. Invert the cup and label it on the bottom. Care should be exercised to ensure that the sample cup is tightly sealed and that no leakage occurs (see Note 1).

If the sample is a solid, grind a representative portion of approximately 25 g in the grinder for one minute. Samples which do not shatter easily will require chilling in dry ice. Set up the pellet die with the bottom 31-mm die pellet in place. Insert the flared pellet cup and place enough sample in it to fill the cup. Position the top die pellet in the die, insert the die plunger, place the combination in the hydraulic press and apply pressure to 165,000 kPa (24,000 psi) for one minute. Slowly release the pressure and remove the pellet cup containing the sample pellet. Examination should show no cracks or ripples and the surface should be mirror like. Turn the sample pellet over and label it on the bottom.

Preparation of Apparatus

The Kevex 0700 and 7000 Spectrometer are capable of operation with all parameters under microprocessor control.

Hardware and software calibration of the instrument is accomplished using the $K\alpha$ peaks of Al and Cu. A metallic disk containing aluminum and copper is positioned in the sample chamber above the x-ray tube and detector. A copper coin wrapped in aluminum foil is satisfactory. Hardware calibration is attained by successive adjustment to the pulse processor's amplifier. This aligns the aluminum and copper peak centroids to their proper energy levels. Software calibration is accomplished by having the microprocessor analyze the peak shapes of aluminum and copper and then storing this information in core memory.

A monitor reference number is determined which compensates for any changes in x-ray tube performance due to source fluctuations and allows spectra from samples and/or standards to be normalized to one another. The number is determined prior to all standards and sets of unknown samples. A separate monitor reference number must be determined for each excitation condition. All monitor reference numbers are determined by irradiating a Lucite pellet and collecting the intensity of the $K\alpha$ peak for each of the secondary targets.

Excitation conditions as shown in the following table and operating parameters are placed into the program memory for automatic recall during analysis. All samples are run under a nitrogen purge with a 100 second preset acquisition time.

Excitation Conditions

Liquid Samples

	<u>Fe</u>	<u>V</u>	<u>Ni</u>
Secondary Target	Ni	Fe	Ge
Voltage, kV	23	28	26
Current, mA	1.0	0.9	0.5

Solid Samples

	<u>S</u>	<u>Fe</u>	<u>V</u>	<u>Ni</u>
Secondary Target	Fe	Ge	Fe	Ge
Voltage, kV	20	26	20	26
Current, mA	0.9	0.5	0.9	0.5

For liquid oil samples a spectrum of mineral oil is acquired and retained in the computer memory of the instrument for later use as an iron, vanadium and nickel blank for background subtraction. Each blank spectrum must be acquired with the same excitation conditions as used with the metals (see Note 2). A blank is not used for solid samples; instead, an internal software program which is identified as a background modeling technique is used.

Calibration

Calibration of the instrument is accomplished by introducing appropriate standards containing metals, the concentrations of which bracket the expected concentrations of the unknowns and have the same matrix as the unknowns. The standards are preferably actual samples that have been analyzed for metals by atomic absorption through the use of UOP Method 800 or for sulfur by UOP Method 380. Alternatively, blends

may be prepared by weighing to the nearest 0.01 g octoates of Ni, Fe and V, and butyldisulfide in mineral oil. A NBS standard is also available for V and Ni in residual oil. Synthetic blends are discouraged because they will not compensate for matrix effects.

The spectra for the standards are acquired. For liquids, the mineral oil blank background spectrum is overlayed, normalized and subtracted from the spectra of the standards. For solids, a background modeling technique is used. The area under the $K\alpha$ peak of Ni, Fe, V or S is integrated and displayed as counts per second. After calibration data for the standards has been acquired and is stored in memory, a curve is constructed by the instrument computer using a least squares fitting technique. The equation for this curve along with comments, identification and metal mass-% concentrations, are used to quantitate unknown samples. All calculations and processes as just described are performed automatically by the Kevex instrument using laboratory written command sequences.

Sample Analysis

Load the samples into the instrument, close the sample chamber lid and start a timer. There is a constant nitrogen flush of the chamber, which will eliminate any residual atmospheric argon that may be present in the chamber. Argon, if present, would preferentially absorb and scatter x-rays thereby reducing the instrument sensitivity for sulfur and vanadium. After flushing for 10 minutes, begin the analysis.

Introduce sample identification and the position of the samples in the sample carousel into the computer. Automatic sample acquisition, measurement and sequencing are carried out until the last sample is processed.

CALCULATIONS

The mass-% metal calculation is carried out automatically by the Kevex 7000 μ X spectrometer according to the following equation:

$$\text{Metal, mass-\%} = \frac{b + m I}{R}$$

where:

- b** = Y intercept of the calibration curve line fit
- m** = slope of the calibration curve line fit
- I** = net peak intensity of the sample
- R** = monitor reference number

NOTES AND PRECAUTIONS

1. After filling the sample cup, it should be left on a paper towel for a period of time to be certain it does not leak. The nature of the covering materials is such that any sharp abrasion or slight flaw may rupture the film. Extensive damage to the instrument can result if the sample material contacts the detection window or x-ray generator.

2. All monitor references, metal blanks, calibration runs and unknown analyses must be performed at the same excitation conditions.

3. If the sample contains sediment, it must be filtered before measurement since deposition on the cell window will give erroneous results. In cases where sediment is considered to be part of the sample, an accurate determination cannot be made by this technique.

4. Samples containing volatile components may cause the cup window to bulge during analysis, thereby producing erroneous results. To prevent this, make a small vent hole in the bottom of the cup (which becomes the top when the cup is inverted for analysis).

5. To ensure stability and component longevity, the instrument if left on continuously and only shut down for periodic servicing.

6. The standards are run as samples, usually at the end of the sample trays. This provides a check on instrument stability and accuracy.

PRECISION

Based on 10 replicate determinations at each of the levels shown, the estimated standard deviation (esd) was calculated for both solid and liquid samples, and is listed in the following table. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

Solid Oil Samples

		Metal Concentration, mass-%	esd, mass-%	Allowable Difference, mass-%
V	}	0.27	0.020	0.064
		1.78	0.015	0.048
Ni	}	0.03	0.001	0.003
		0.15	0.003	0.009
Fe	}	50 ppm	3 ppm	10 ppm
		0.04	0.006	0.019
S		6.3	0.12	0.38

Liquid Oil Samples

		Metal Concentration, ppm	esd, ppm	Allowable Difference, ppm
V	}	16	0.7	2
		48	1.7	5
		80	3.2	10
Ni	}	7	0.7	2
		90	1.7	5
Fe	}	3	0.6	2
		44	1.5	5

TIME FOR ANALYSIS

The elapsed time for a single metal or sulfur determination in a liquid sample is 0.1 hour and in a solid sample, 0.15 hour. The labor requirement for each determination is 0.07 and 0.1 hour, respectively.

REFERENCES

UOP Method 380
UOP Method 800

SUGGESTED SUPPLIERS

Angstrom Inc., P. O. Box 248, Belleville, MI 48111
Chemplex Industries, Inc., 140 Marbledale Rd., Eastchester, NY 10707
Horiba Instruments, Inc., 1021 Duryea Ave., Irvine, CA 92714
Kevex International Corp., 1101 Chess Dr., Foster City, CA 94404
Markson Science, Inc., P. O. Box 767, Del Mar, CA 92014
Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077
SPEX Industries, Inc., P. O. Box 798, Metuchen, NJ 08840
U. S. Department of Commerce, National Bureau of Standards, Office of Standard Reference Materials,
Washington, DC 20234