

VANADIUM, NICKEL AND IRON IN PETROLEUM OILS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

UOP Method 800-79

SCOPE

This method is for determining concentrations of vanadium, nickel and iron in all types of petroleum oils by atomic absorption spectrophotometry (AAS). The method covers a range of vanadium from 0.3 ppm to several hundred ppm and a range of 0.1 to 100 ppm or higher for both nickel and iron.

OUTLINE OF METHOD

The oil sample is wet ashed with fuming sulfuric acid and the resultant char is burned off in a muffle furnace (see Note 1). The remaining inorganic residue (ash) is dissolved in sulfuric and hydrochloric acids. A solution of potassium chloride is added as an ionization suppressant for vanadium (see Note 2). The sample solution is aspirated into the flame of the AAS unit and is compared spectrophotometrically to standard solutions containing known metals content and concentrations of reagents matching the sample solutions.

APPARATUS

Atomic absorption spectrophotometer, capable of measuring radiation over the wavelength range of 200 nm to 800 nm. The instrument must have the basic capability of measuring low level signals corresponding to approximately 1% absorption or 0.004 absorbance units per mg/l vanadium. The instrument must be equipped as follows:

Automatic background corrector, deuterium arc source or equivalent

Auxiliary amplification, capable of at least 10X scale expansion of the basic instrument signal. A strip-chart recorder, 1 mV full scale (with attenuator) can satisfy this requirement

Burner heads, 10-cm single or multiple slot capable of supporting an air-acetylene flame, 5-cm single slot fabricated especially for use with a nitrous oxide-acetylene flame

Hollow cathode electronic lamp supply, regulated, and filtered to minimize baseline drift

Printer or recorder, or equivalent device to establish a permanent record of results obtained. A recorder is recommended and the one previously described will serve this purpose also

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).

Balance, analytical, capable of weighing to 0.1 mg

Balance, platform or trip-scale, 500-g capacity with accuracy to ± 0.01 g, Mettler top loading No. PC1210, or equivalent

Bath, ice, any type of low form plastic or metal container which will hold 3 to 4 400-ml beakers

Beakers, 250- and 400-ml, heat-resistant type. Vycor or quartz glass is satisfactory

Bottle, dropping, acid, 50-ml capacity

Bottle, wash, polyethylene "squeeze" type, 500-ml capacity

Dryer and filter, assembly, in air line to instrument such as Perkin-Elmer No. 303-0299 or equivalent

Flasks, volumetric, several of each. 25-, 50-, 100-, 200-, 250-, 500-ml and 1-liter regular lab supply

Gloves, rubber, industrial type, No. 834 Playtex or equivalent

Graduate, 10-, 25-, 50-ml borosilicate glass or equivalent

Hood, an area from which evolved smoke and acid fumes may be safely exhausted

Hot plate, electric, a continuous and variable surface temperature of 60 to 400 F is required, similar to Corning PC-100 or equivalent

Lamp, heat, such as National Torch Lamp, Cat. No. V2930 from CRC Inc.

Lamps, hollow cathode, one each of Fe, Ni and V, available from Westinghouse, Tekmar, Perkin-Elmer, or equivalent

Muffle furnace, electric. Must be capable of maintaining 550 ± 20 C. A furnace having as large an internal capacity as possible, to accommodate several 400-ml beakers at one time is desirable. Should be equipped with evacuation hood and a supply to entrained air.

Pipet, 10-ml, Mohr type; Type 1 Class B

Pipets, 1-, 2-, 5-, 10-, 15-, 20- and 100-ml; several of each Class A type

Stirring rods, Vycor, heavy duty 3/8 x 7-inch

Thermometer, surface type, such as PTC[®] 50-1000 F range, SGA Scientific or equivalent

Tongs, beaker

Watch glasses, 90 mm diameter, borosilicate glass

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical 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 to sufficiently high purity to permit use without lessening the accuracy of the determination. References to water mean distilled or deionized water.

Acetylene, cylinder compressed gas, regular welders grade is satisfactory. Recommend size 1A (300 cu ft), equipped with a C₂H₂ regulator, i.e., Perkin-Elmer No. 303-0106 or equivalent

Air, compressed, filtered and dried, minimum of 60 psig to AAS instrument

Hydrochloric acid, concentrated

Iron, metal, sponge or wire, 99.999% purity, SPEX Industries, or equivalent

Iron solution, 1000 mg/l. Weigh 1.000 g of primary standard iron sponge or wire into a 250-ml beaker. Add 100 ml of water and 10 ml of concentrated hydrochloric acid. Cover the beaker with a watch glass and warm gently until the wire or sponge is completely dissolved. Cool the solution and transfer it quantitatively to a 1-liter volumetric flask. Dilute to the mark with water and mix.

Iron solution, 100 mg/l. Pipet 100 ml of the 1000 mg/l standard into a 1-liter flask and dilute to mark with water and mix.

Iron solution, 10 mg/l. Pipet 10 ml of the 1000 mg/l standard into a 1-liter flask and dilute to the mark with water and mix.

Nickel, metal sponge, 99.999% purity, SPEX Industries, or equivalent

Nickel solution, 1000 mg/l lab stock standard. Weigh 1.000 g pure metal into a 250-ml beaker, wet with approximately 100 ml of water and slowly add 30 ml of nitric acid. Cover with watch glass and heat gently until dissolution is complete. Transfer quantitatively to a 1-liter flask; dilute to mark with water and mix.

Nickel solution, 100 mg/l. Pipet 100 ml of the 1000 mg/l standard into a 1-liter flask. Dilute to mark with water and mix.

Nickel solution, 10 mg/l standard. Pipet 10 ml of the 1000 mg/l stock standard solution into a 1-liter flask and dilute to mark with water and mix.

Nitrous oxide, cylinder, size No. 1 520 cu ft equipped with a 2-stage heated regulator, i.e., Perkin-Elmer No. 303-0204 or equivalent.

Potassium chloride, reagent grade (Baker Analyzed)[®] KCl or equivalent

Potassium chloride solution, 10 g/l K releasing agent (Note 3). Dissolve 19.1 g of KCl in 1 liter of water.

Sulfuric acid, concentrated

Sulfuric acid, fuming, containing 27-33% excess SO₃

Vanadium, metal pieces or turning, 99.999% purity. SPEX Industries, or ROC/RIC, or equivalent

Vanadium solution, 1000 mg/l standard. Weigh 1.000 g of standard metal into a 250-ml beaker and cautiously add 10 ml of nitric acid, cover with watch glass and gently heat until dissolution is complete. Add 100 ml of H₂O, heat to a boil, transfer quantitatively into a 1-liter flask. Dilute to mark with water and mix.

Vanadium solution, 100 mg/l. Pipet 100 ml of the 1000 mg/l standard into a 1-liter flask, dilute to the mark with water and mix.

Vanadium solution, 10 mg/l. Pipet 10 ml of the 1000 mg/l standard into a 1-liter flask, dilute to the mark with water and mix.

CALIBRATION BLENDS

Stock Solutions

Multi-element Stock Solution I (100 mg/l V, 10 mg/l Ni, 10 mg/l Fe)

Into a 1-liter volumetric flask, pipet 100 ml of the 1000 mg/l vanadium reagent, 10 ml of the 1000 mg/l nickel reagent and 10 ml of the 1000 mg/l iron reagent. Dilute to the mark and mix. Label this solution and date. This standard is stable for 3-6 months.

Multi-element Stock Solution II (10 mg/l V, 10 mg/l Ni, 10 mg/l Fe)

Into a 1-liter volumetric flask pipet 10 ml of the 1000 mg/l vanadium reagent, 10 ml of the 1000 mg/l Ni reagent and 10 ml of the 1000 mg/l Fe reagent. Dilute to the mark and mix. Label and date. Solution is stable 3-6 months.

Acid-KCl Matrix Stock Solution

Transfer 200 ml (± 0.5 ml) of the KCl reagent (containing 10 g/l K) into a 1-liter volumetric flask. Add 150-200 ml of water and cool the flask and contents in an ice water bath. With the flask in the ice bath, cautiously swirl the contents of the flask while slowly adding 200 ml (± 0.5) of concentrated sulfuric acid. After flask and contents have been cooled below room temperature, add 100 ml (± 0.5) of concentrated hydrochloric acid and dilute to the mark with water.

Standard Reading Solutions

High Range (10-50 mg/l V and 1-5 mg/l Ni and Fe)

Pipet 0, 10, 20, 30, 40 and 50 ml of the Multi-element Stock Solution I into six 100-ml volumetric flasks, respectively. Add about 20 ml of H₂O to the first three flasks to bring the water level up to that of the other flasks. Pipet 50 ml of the Acid-KCl Stock Solution into each of the flasks and make the required dilutions to the mark with water and mix well. Label each solution carefully, as for example, the sixth solution: "RS 50,5,5" (Reading Standard 50 mg/l V, 5 mg/l Ni, 5 mg/l Fe). Label the solution with no metals added as "RS H-Blank"—the calibration blank for the high range.

Intermediate Range (2.5-10 mg/l V and 0.25-1 mg/l Ni and Fe)

Pipet 0, 2.5, 5.0, 7.5 and 10 ml of the Multi-element Stock Solution II into five 100-ml volumetric flasks, respectively. Add about 30 ml of water then pipet 50 ml of the Acid-KCl Stock Solution into each flask and swirl. Dilute to the mark and mix. Label solution as above, i.e., "RS I-Blank" and "RS 2.5, 0.25, 0.25" to "RS 10, 1, 1".

Low Range (0.1-2.5 mg/l V, Ni and Fe)

Pipet 0, 1, 3, 5, 7, 10, 15 and 25 ml of Multi-element Stock Solution II into eight 100-ml volumetric flasks, respectively. Add sufficient water to bring the volume to about 40 ml maximum. Pipet 50 ml of the Acid-KCl Stock Solution into each flask and swirl. Dilute to the mark with water and mix. Label as "RS L-Blank", "RS 0.1", "RS 0.3", to "RS 2.5", where the numbers refer to the concentrations of each metal present (see Note 4).

PROCEDURE

Sample Processing

The sample is wet ashed using approximately 1 ml of fuming sulfuric acid per gram of sample ashed. One half of the total amount to be used is added at the start of the ashing. The other half is added in three increments after the reaction between the oil and acid subsides. Sample size is dependent upon the estimated amount of vanadium or nickel present. If the concentration of vanadium is less than 10 ppm or the nickel less than 1 ppm, 50 to 70 g sample sizes are ashed. Twenty to twenty-five gram sample weights are used for all other concentrations up to several hundred ppm. Five to ten grams are ashed for all types of asphalt and similar petroleum bottoms estimated to contain macro amounts of vanadium. These types of samples are difficult to break down and require at least two 10-ml increments of fuming sulfuric acid—an exception to the guideline of 1 ml per gram of sample.

Obtain a representative sample of the oil by shaking it in its container for several minutes. Viscous or waxy samples should be heated until fluid prior to shaking. At the same time the samples are processed, process a wet ash blank (as described under *Blank Processing*) according to the following wet ash and ash dissolution procedure.

Ash 5-25 g samples in 250-ml Vycor beakers and 50-70 g samples in 400-ml Vycor beakers. Transfer the appropriate amount of oil sample to a Vycor beaker and, based on the sample weight used, cautiously add to the sample from a graduate approximately one half of the estimated amount of fuming sulfuric acid to be used (1 ml per gram of sample). Cover the beaker with a watch glass and begin heating it on a hot plate at 200-300 F (use a surface hot plate thermometer). Soon the oil will react with the fuming sulfuric acid producing varying amounts of coke-like char (voluminous white fumes will indicate reaction). The amount produced will depend on the type of oil sample ashed. If excess foaming occurs, remove from heat and replace when foaming subsides. Continue to heat until initial reaction is completed. Remove the beaker from the hot plate and with a Vycor rod, break up the hard char mass and free it from the bottom of beaker; stir and then add slowly and cautiously, 1/3 of the remaining estimated volume of fuming sulfuric acid. Cautiously stir and when reaction again subsides, add the second 1/3 of fuming sulfur acid, stir and when reaction subsides add the remainder. At this point and throughout the ashing procedure leave the Vycor rod in the beaker. Raise the surface temperature of the hot plate to 400-500 F and continue the heating process. If the oil splatters, cover the beaker with a watch glass. At 10-15 minute intervals resume the stirring and continue to break up the char mass. If a watch glass has been used, leave it ajar so SO₃ fumes may escape.

When the bulk of unreacted oil is charred and excess sulfuric acid has been evaporated, raise the surface temperature to 650-700 F. Stir occasionally and with the aid of a heat lamp, drive off the remaining sulfuric acid. Cover the beaker containing the Vycor rod and with the watch glass left ajar, place it in a muffle furnace at 1000 F ± 50 F. After 2 hours, remove the watch glass and continue the heating process until the char is reduced to ash (preferably overnight). Replace the watch glass and remove the beaker from the muffle furnace. After the beakers have cooled and before removing the watch glass, use the squeeze bottle to spray about 5 ml of water under the edge of the watch glass to anchor the light ash. Rinse down the Vycor rod, watch glass and sides of the beaker with about 10-15 ml of water from a squeeze bottle.

At this point, separate the samples containing an anticipated low concentration of metals (normally the 50-70 g sample sizes) from the others. The low-level samples are to be processed using exactly half the volume of the reagents as the others and are to be diluted to a final 50-ml volume instead of a 100-ml volume. In the instructions which follow in the next paragraph, *the volume of reagents to be used for the low-level samples are given in parentheses*.

Add 10 ml (5 ml) of the potassium chloride solution to the beaker and tare weight the beaker and contents to zero on a top-loading balance (Note 3). Remove the beaker from pan and tilt it at an angle and using a 10-ml graduate, cautiously add slightly less than 10 ml (5 ml) of concentrated sulfuric acid pouring down the side of the beaker. Do not swirl the beaker at this point but replace it on the balance pan. Using the dropping bottle, adjust the weight of sulfuric acid to equal 18.4 g or 10.0 ml (9.2 g or 5.0 ml) of concentrated sulfuric acid. Remove from pan and place in ice bath without swirling. Cool for 5 minutes then swirl gently. Continue to cool and swirl and when solution is cold to the touch, pipet in 5 ml (2.5 ml) of concentrated hydrochloric acid. Rinse down the sides of beaker with 3-5 ml of water. Cover with a watch glass and heat to boiling or until dissolution of ash is completed.

Cool and quantitatively transfer the beaker contents to an appropriately-sized clean volumetric flask as follows (see Note 4). Transfer the low-level samples, which were processed with half the normal volume of reagent, to 50-ml volumetric flasks and transfer the others to 100-ml volumetric flasks. Dilute to the mark with water, mix and label appropriately.

Wet Ash Blank Processing

Prepare and process the wet ash blanks in the following manner. Into a 250-ml Vycor beaker transfer the same volume of fuming sulfuric acid as was used in wet ashing the oil sample (see Note 10). Evaporate to dryness on a hot plate and cool. Continue to process this blank in the same manner as instructed in the previous section *Sample Processing*, starting at the point in instructions where ashed sample is removed from the muffle and cooled. Begin with “After the beakers have cooled...etc.”

Dilute the low-level wet ash blanks to 50-ml final volume with one half of the reagents the same as the low-level samples, otherwise, dilute to 100-ml with normal amount of reagents.

Vanadium Analysis

Instrument Adjustments

Turn on the hollow cathode lamp and observe the manufacturer’s warm-up instructions. Set the lamp current to about 50% of its rated maximum current. Adjust slits to an opening of 0.5 nm. Select a normal wavelength of 318.4 nm and then fine adjust the wavelength setting to give the maximum peak (see Note 5). Now open the slits to 0.7 to 1.0 nm. (If equipment being used does not provide for manual fine adjustment of the wavelength, follow manufacturer’s wavelength selection procedure.)

Position the burner head so its slot is parallel to and about one-half inch below the hollow cathode light beam. This is an approximate setting. Ignite the nitrous-oxide acetylene burner according to the instrument manufacturer’s instructions. Adjust the acetylene to produce a red cone flame without streaks of white (indicating excess acetylene).

Aspirate the 100 mg/l vanadium reagent and adjust the various parameters beginning with the lateral and vertical burner position. Make only small adjustments. Adjust the acetylene flow. Replace the 100 mg/l V reagent with the 50-5-5 reading standard, and fine tune all parameters to reflect a *minimum* of 45% absorption (0.26 absorbance). A nebulizer adjustment also can be included at this point to maximize response, although one manufacturer forbids nebulizer adjustments with the nitrous-oxide-acetylene flame. It is not dangerous if done carefully. Make only *minute* counter and clockwise nebulizer adjustments while watching the flame; a loss of the red cone is a warning to proceed no further in that direction.

Sample Readings

To obtain a preliminary indication of the concentration of vanadium present, aspirate the original sample

solutions (or if necessary for an on-scale reading, as for dark, blue-green colored solutions, a measured dilution of the original sample) and note their absorbance. Make the appropriate quantitative dilution of the original sample solutions which read more than 5% higher than the 50 mg/l V standard in order to produce readings preferably corresponding to a 20-30 mg/l V standard. When diluting an aliquot of the original sample solution, always dilute to the mark using an exact 1:1 volume mixture of the Acid-KCl Stock Solution and water. Set aside those sample solutions which indicated a concentration of vanadium less than 10 mg/l and proceed to process the samples within the 10 to 50 mg/l range.

Aspirate the reading standards for the 10-50 mg/l V high range, including the RS Blank, and record their absorbances. Continually aspirate water before and after the reading solutions to flush out the corrosive acids and to maintain the burner head at a constant temperature. Construct a standard curve by plotting absorbance versus mg/l vanadium concentrations. If there was a difference in the reading between the RS Blank and water, use the former reading for the zero point; otherwise, use the water zero. Now aspirate the samples, including the wet ash blank, and record their absorbance. If more than four samples have been aspirated, repeat one or two standards to make sure response conditions have remained the same since aspirating the standards. From the curve plotted, determine the concentration of vanadium in mg/l in each of the final sample solutions.

In a similar manner aspirate the intermediate reading standards for the 2.5 to 10.0 mg/l V range and record their absorbances. Obtain the readings for those sample solutions whose absorbances fall within this range. From a curve plot of the absorbance versus vanadium concentration (mg/l) for the reading standards, determine the vanadium concentration in the final sample solutions in mg/l V.

For sample solutions whose absorbance readings fall below the 2.5 mg/l V standard, a more sensitive setting of the instrument is required or scale-expansion of the readout device is utilized. Follow the instructions given above under *Instrument Adjustments*. Then set the instrument at a sensitivity which will produce a near full-scale readout deflection when aspirating the 10 mg/l V reading standard. Next aspirate the 5 mg/l V reading standard and record the response. Then aspirate four of the low-level reading standards, namely 0.5, 1.0, 1.5 and 2.5 mg/l V including the RS Blank and record and plot all responses (Note 6). If the RS Blank has a higher response than the water zero, use the former for the curve zero. Aspirate the sample solutions, including the wet ash blank, record the responses and from the curve determine the corresponding concentrations of vanadium in mg/l.

Nickel Analyses

Nickel is determined in the premixed air-acetylene flame using a single or multiple 10-cm slot burner head at the primary wavelength of nickel at 232 nm. The automatic background correction device should be activated for this analysis (Note 7).

Turn on the hollow cathode lamp and apply a current equivalent to 50% of the manufacturer's maximum rated current. Turn on the background corrector and after the required warm-up time for both light sources, equalize the energy between the two as suggested by the manufacturer. Ignite the burner according to the manufacturer's procedure as outlined in the instrument manual.

With the instrument set in the regular, unexpanded signal mode, aspirate the 5 mg/l nickel standard (RS 50,5,5). Maximize absorption response by adjusting the critical parameters, i.e., burner position, fuel/oxidant ratio (lean) and nebulizer flow to achieve a minimum of 35% absorption (0.19 absorbance). It is anticipated that the final sample solutions read in the vanadium analyses should be satisfactory for the nickel analyses. If not, aspirate the original sample solutions and note the concentration range of the samples. Set aside those samples which read below 1 mg/l nickel. Dilute and adjust the matrix of the solutions which exceed the 5 ppm standard by more than 5%. When diluting an aliquot of the original

sample solution, always dilute to the mark using an exact 1:1 volume mixture of the Acid-KCl Stock Solution and water. Diluted samples should read in the range of about 2-3 mg/l nickel.

Aspirate the high range reading standards for the 1-5 mg/l nickel range including the RS Blank and record their net absorbance (signal minus background). An absorbance reading higher than the zero water reading for the RS Blank with the background corrector engaged suggests that nickel was introduced as a contaminant and the RS Blank reading should be used as the zero or first point of the curve. Aspirate the samples in the 1 to 5 mg/l nickel range and record their absorbance responses.

Construct a curve from the standard readings by plotting absorbance versus concentrations of nickel, mg/l. Determine from this curve the concentration of nickel in the sample solution. Calculate the concentration of nickel in the sample by applying the correct dilution factor (if used) and sample weight of oil ashed.

For sample solutions whose absorbances fall below that of the 1 mg/l reading standard (RS 10,1,1), typically vacuum gas oils, for example, the following low range reading standards will be used: RS 0.1, RS 0.3, RS 0.5, RS 0.7 and RS 1.0.

Put the instrument into a 10X signal expansion mode or the equivalent (see Note 8). Aspirate the 1 mg/l reading standard (RS 1.0) and maximize response to record a net recorder deflection of 30% (30 chart divisions) while the background correction is engaged. Aspirate the 0.1 to 1.0 mg/l standards and record their response including the RS Blank. In this large expansion mode it is possible to record a slight negative baseline (1 or 2 chart divisions) for the RS Blank. In this case, use this negative baseline as a zero reference. Any positive RS Blank reading (above the water baseline) should be used as the standard curve zero. Construct the best possible curve by plotting chart divisions versus concentration of nickel, mg/l. Aspirate the sample solutions, including the wet ash blank, record the absorbances and from the curve determine the corresponding concentrations of nickel mg/l.

Iron Analysis

Iron is determined in the premixed air-acetylene flame under the same conditions as the nickel analyses. The primary wavelength of iron at 248.3 nm is used. Light the hollow cathode iron lamp and apply a current at 50% of the maximum rated current listed for this lamp. Activate the background corrector and equalize the energy between two sources.

Aspirate the high range standard, RS 50,5,5 (5 mg/l Fe), and fine tune the instrument so that the absorption response is 35-40% (0.19, 0.22 absorbance). The same physical parameters, including the background corrector, used for the nickel analyses or previous 1 to 5 ppm Fe range are applicable for this analysis. Aspirate the remainder of the high range standards and follow the same procedure as in the nickel analyses for preparation of the standard curve in the 1-5 mg/l Ni range. Aspirate the sample solutions and record the absorbance for those in this range.

For sample solutions producing absorbances below that produced by the 1 mg/l reading standard (RS 10,1,1), prepare a calibration curve using the same set of low range standards used in the nickel analyses. The instrument mode should be a 5X to 10X signal expansion; one which will record a discernable signal above the baseline noise of at least 3 chart divisions while aspirating the 0.1 ppm iron matrix standard. Aspirate the standard RS 1.0 (1 mg/l Fe) and record the maximum chart deflection. Then aspirate the rest of the standards in descending concentration order, 0.7, 0.5, 0.3, 0.1 mg/l Fe including the proper RS Blank. If the RS Blank shows a recorder chart deflection of more than the baseline, use this response for the first point of the standard curve.

Aspirate the sample solutions, including the wet ash blank (see Note 9), record the absorbances and from the curve determine the corresponding concentration of iron in mg/l.

CALCULATIONS

$$\text{Metals, ppm} = \frac{(AF - B)V}{W}$$

where:

A = concentration of metal present in the sample solution whose absorbance was measured from the curve, mg/l

B = appropriate wet ash blank value, mg/l (see Note 10)

F = 1 for undiluted sample stock solution,
or

F = the dilution factor, R/S, for diluted samples

where:

R = total volume of final diluted sample solution used to obtain A, ml

S = volume of the aliquot of the original sample stock solution used to prepare R, ml

V = total volume of original sample stock solution, ml

W = weight of sample ashed, g

NOTES

1. There are several techniques associated with the destruction of petroleum oils and their subsequent conversion from an organic phase to an acid aqueous phase. This conversion here is desirable because it ensures that both organic and inorganic species of analyte in the oil will be solubilized and present in the sample solution during its aspiration into the flame of the AAS.

In the “direct” analysis of the oil, a procedure where a portion of the oil is diluted with xylene or another appropriate solvent and then is aspirated directly into the flame of the AAS, most likely, only the organically soluble analyte is recorded, because inorganic or elemental forms of analyte may or may not be reduced to ground state atoms in the fleeting moment they are present in the flame region of the cathode light beam.

Another procedure of conversion is “dry” ashing. In this procedure a portion of the oil is set afire in a large platinum crucible and kept burning until only a char remains. The char is then reduced to ash in a muffle furnace. The ash is dissolved in appropriate acids, diluted with water and brought to a specific volume. This technique is suspected of metal losses because of the mechanics of the burning oil.

In the wet ashing procedure chosen for this method, a representative portion of the oil is reacted with fuming sulfuric acid to produce a coke-like char. The unreacted oil and excess sulfuric acid is evaporated and the char is semidried over a hot plate. The sulfated char is then reduced to ash in a muffle furnace. The ash is dissolved in a specific amount of sulfuric and hydrochloric acids, diluted with water and brought to a fixed volume after the addition of a solution of potassium chloride.

A superior (but time consuming and tedious) conversion is the “wet digestion” technique. This technique involves digesting the representative oil sample with sulfuric and nitric acids. When the organic matter has been destroyed the excess sulfuric acid is fumed down to less than 10 ml, the acid is diluted with water, transferred, to a tared 250-ml Vycor beaker, evaporated to sulfuric fumes again and cooled. The sulfuric acid is adjusted to be exactly 10 ml (18.4 g), then hydrochloric acid and a potassium chloride solution are

added. This solution is diluted with water and brought to a specific volume. The wet ashing results compare favorably with the wet digestion results. Because of the excessive amount of time it takes to convert large samples by wet digestion (25-50 g), a semiautomatic digestion device is mandatory but is not readily available for purchase and may have to be custom-made.

2. The addition of the potassium salt is necessary for the vanadium analysis because of the nitrous-oxide acetylene flame used. This is a very high energy flame and tends to elevate atoms to higher energy levels (ionization) than appropriate for absorption. To dissipate excess amounts of energy from this flame (which is necessary to break up refractory-like molecules such as the oxide of vanadium) an easily ionized element such as sodium or potassium is added to absorb the excess energy. This then increases the population of ground state vanadium atoms contributing to increased absorption and better sensitivity for the analyses. The potassium does not effect either the iron or nickel analyses.

3. In some cases the weight of the beaker plus water and KCl solution will exceed the tare limit of the balance. In this case set the tare to the nearest 100 g (i.e., 100.0 or 200.0).

4. All glassware should be periodically cleaned with 1:1 hot hydrochloric acid solution, especially if glassware has been exposed to any high metal concentrations. All glassware for trace metal analysis should be cleaned and set aside for this work.

5. For this analyses the absorbing wavelength (line) for vanadium shall consist of a group of three vanadium absorbing wavelengths which reside within three angstroms of each other. The lines in increasing wavelength are 318.3 nanometer (nm), 318.4 nm, and 318.5 nm. The first line 318.3 nm is actually a doublet 318.341 and 318.398 (difficult to resolve with most commercial instruments). As a doublet, this is a very intense line which also gives the most response (percent absorption/l ppm V). This doublet is normally isolated for the method of standard addition but its isolation is not necessary or required for this analyses since only comparison of similar solutions are performed. The isolation of the doublet requires narrow entrance and exit slits, (spectral band pass) approximately 50 microns or less.

The three wavelengths of interest are resolved through the use of wider slit openings, 70 to 100 microns. The use of the wider slits allows lower photomultiplier (gain) and hollow cathode lamp current, a procedure which produces quieter instrument performance (less electronic deviation—"noise") which is mandatory for any sizeable signal expansion.

Our suggested procedure for the resolution of the triple wavelengths of vanadium is to narrow the slits to 50 microns or less and isolate the doublet at its maximum peak, then open the slits to 70-100 microns, turn down the gain and hollow cathode lamp current to the required energy level. This procedure assures that all of the desirable doublet is included in the resolution of the triple lines. One precaution to observe is that the hollow cathode lamp current should be run at least 50% of its rated maximum current. This is so that its beam will have the necessary intensity to overcome the excessive high energy produced by the nitrous-oxide flame.

6. One of the accepted criteria for a valid signal is that it be greater than twice the noise (electronic) level. Aspirate the vanadium standards in descending concentration order accepting those lower concentration readings which are at least twice the electronics noise level as discerned from the baseline at 10X expansion.

7. In the wavelength region of 180-300 nm there is a noticeable amount of molecular and nonatomic absorption; the SO_4 molecule produces such an unwanted absorption in the nickel wavelength region used in this analysis. There are several ways to compensate for this unwanted absorption which if not corrected for, will produce erroneously high results. An approximate correction can be made using a subtraction of any signal made from the acid blank. The use of a non-absorbing line is another way, but the best and

quickest correction is the use of the deuterium arc automatic background corrector (BGC) coupled with the proper wet ash blank. Although the BGC will correct the molecular and non-atomic absorption, it will not reflect a true correction if there was any analyte contamination (Fe, Ni, or V) of the various acids or reagents used. The acid blank should be “read” along with the standards. Its reading should be compared to water. In most instances, they should both equal zero if automatic background correction is being used.

8. Select a tenfold signal expansion mode which produces the quietest recorder baseline (least amount of electronic deviation) while aspirating water. This can be an instrument concentration mode, recorder signal expansion mode or a combination of both.

9. Trace amounts of iron in the sulfuric acids used can contribute a small signal at 10X expansion. It is important that the proper wet ash blank be made, i.e., 50 ml of fuming H_2SO_4 when used for a 50 g ashed sample, and 70-ml fuming H_2SO_4 when 70 g of oil is ashed.

10. In practice one can standardize on three sample sizes corresponding to the three calibration ranges described. Hence, three nominal volumes of fuming H_2SO_4 will be used and three wet ash blanks will be defined. Blank values may be obtained for intermediate volumes of reagents by interpolation. Wet ash blanks must be redetermined for each new batch or bottle of bulk reagents.

PRECISION

The estimated standard deviation (esd) or relative standard deviation (rsd) for vanadium, nickel and iron at various concentrations are shown below. Duplicate results by the same operator should not be considered suspect unless they differ by more than the amounts shown in the “allowable difference” column (95% probability).

<u>Element</u>	<u>Replicates</u>	<u>Range, ppm</u>	<u>Precision</u>	<u>Allowable Difference</u>
Vanadium	5 pairs	0.2 to 2.5	0.043 esd	0.16 ppm
	15 pairs	2.5 to 2000	1.7% rsd	6.5% of Mean
Nickel	5 pairs	0.1 to 2	0.028 esd	0.11 ppm
	15 pairs	2 to 2000	1.5% rsd	5.7% of Mean
Iron	5 pairs	1 to 15	0.27 esd	1.0 ppm
	10 pairs	15 to 1500	1.7% rsd	6.5% of Mean

TIME FOR ANALYSIS

All time estimates are based on the simultaneous processing of four samples for the determination of the three metals, V, Ni and Fe. Elapsed time of analysis will vary from 5 to 22 hours depending on the amount of sample ashed. A 70 g sample, for sample, will require about 16 hours of muffle furnace time (overnight).

The man-hour requirement for processing four samples simultaneously will vary from 5 to 7 hours, depending on sample size, but on the average, the labor requirement is 1.5 man-hours per sample for determining V, Ni and Fe by this method.

SUGGESTED SUPPLIERS

CRC Inc., 2310 Superior Ave., N.E., Cleveland, OH 44114
 Perkin-Elmer Corp., Instrument Div., Main Ave., Norwalk, CT 06852
 Sargent-Welch, 7300 N. Linder Ave., Skokie, IL 60076
 SPEX Industries, Inc., P.O. Box 798, Metuchen, NJ 08840