



A Honeywell Company

Trace Metals in Organics by AAS

UOP Method 391-09

Scope

This method is for determining trace concentrations of copper (Cu), iron (Fe), nickel (Ni), potassium (K), sodium (Na), and vanadium (V) by Atomic Absorption Spectrophotometry (AAS). It can be applied to petroleum products such as crude oils, gasolines, kerosenes, diesel fuels, and residues, or varied organic mixtures (including nitroanilines, amines, chlorobenzenes, phenols and other related materials) produced or used in chemical manufacturing. The range of quantitation is from 0.5 to 100 mg/kg (mass-ppm).

In addition to the elements listed above, aluminum (Al), calcium (Ca), cobalt (Co), chromium (Cr), magnesium (Mg), manganese (Mn), palladium (Pd), platinum (Pt), and zinc (Zn) may also be analyzed by AAS using the techniques described herein; but these elements have not been evaluated for sensitivity or repeatability. Also, lead (Pb), molybdenum (Mo), phosphorus (P), and tin (Sn) may be analyzed by Graphite Furnace - Atomic Absorption Spectrophotometry (GF-AAS), which is outside the scope of this method.

Alternatively, the elements listed above may be analyzed by Inductively Coupled Plasma – Optical Emission Spectrophotometry (ICP-OES). See UOP Method 389, “Trace Metals in Organics by Wet Ashing - ICP-OES,” for specific metals and their range of quantitation.

References

UOP Method 389, “Trace Metals in Organics by Wet Ashing - ICP-OES,” www.astm.org

UOP Method 999, “Precision Statements in UOP Methods,” www.astm.org

Outline of Method

The sample is wet ashed with fuming sulfuric acid and the resulting organic residue (char) is oxidized in a muffle furnace. The remaining inorganic residue is dissolved in a mixture of acids and diluted to a specific volume. Cesium is added as an ionization suppressant. The sample solution is aspirated into the flame of an AAS instrument and quantitation is achieved by comparison to matrix-matched standard solutions.

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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Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, top-loading, capacity 500-g, readability 0.01-g

Beakers, 400-mL, heat-resistant type, quartz, Ace Glass, Cat. No. 5334-18

Bottle, dropping, acid, 60-mL, VWR, Cat. No. 89001-566

Bottle, wash, polypropylene, 500-mL, VWR, Cat. No. 16651-904

Cylinder, graduated, 10-mL, Class B, VWR, Cat. No. 89000-248

Flasks, volumetric, Class A, 100- and 1000-mL, VWR, Cat. Nos. 89001-964 and -966, respectively

Flasks, volumetric, polypropylene, 50- and 100-mL, VWR, Cat. Nos. 29615-018 and -007, respectively

Furnace, muffle, capable of operation at 540°C, VWR, Cat. No. 30604-158

Gloves, neoprene/natural rubber, acid resistant, VWR, Cat. No. 32917-206 (for size large)

Hot plate, variable temperature to 400°C, VWR, Cat. No. 11301-106

Pipet, dispensing, Class B, 10-mL, VWR, Cat. No. 89003-506

Pipets, volumetric transfer, Class A, 1-, 2-, 4-, 5-, 6-, 8-, 10-, 15-, 20-, 30-, 40-, and 100-mL, VWR, Cat. Nos. 89045-056, -058, -062, -064, -066, -070, -074, -076, -078, -082, -084, and -088, respectively

Pipet filler, VWR, Cat. No. 53497-055

Regulator, acetylene, with flash arrestor, single-stage, PerkinElmer, Cat. No. 03030106

Regulator, air, two-stage, high-purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, nitrous oxide, single-stage, PerkinElmer

Spectrophotometer, AAS, computer controlled, with lamps for the elements to be analyzed. The computer must be capable of performing background corrections, blank corrections, and weight/volume and dilution corrections. PerkinElmer, Analyst 800.

Lamps, hollow cathode, AAS, copper, iron, nickel, potassium, sodium, and vanadium, PerkinElmer

Stirring rods, quartz, JSRitter, Cat. No. 21-905

Thermometer, surface type, 0 to 550°C, VWR, Cat. No. 61157-254

Tongs, beaker, VWR, Cat. No. 82027-374

Tongs, crucible, VWR, Cat. No. 82027-372, for muffle furnace use

Watch glasses, ribbed, 100-mm diameter, Wilmad-LabGlass, Cat. No. C-9990-100

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. References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean deionized or distilled water.

Acetylene, cylinder, compressed gas, 99.6% minimum purity

Air, compressed

Cesium solution, 10,000- $\mu\text{g/mL}$, SPEX, Cat. No. PLCS2-3X (used as an ionization suppressant)

Hydrochloric acid, concentrated, VWR, Cat. No. VW-3110-3

Nitric acid, concentrated, VWR, Cat. No. VW4815-6

Nitrous oxide, cylinder, 99% minimum purity

Pipet, transfer, disposable plastic, 155-mm length, VWR, Cat. No. 414004-004

Standard metal solutions, Cu, Fe, K, Na, Ni, and V solutions of 1000- $\mu\text{g/mL}$ concentrations, SPEX Industries, Inc., Cat. Nos. PLCU2-2, PLFE2-2, PLK2-2, PLNA2-2, PLNI2-2, and PLV2-2, respectively

Sulfuric acid, concentrated, VWR, Cat. No. VW6840-3

Sulfuric acid, fuming, 27 to 30% excess SO_3 , VWR, Cat. No. AA39187-36

Water, deionized or distilled

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of AAS, and the equipment being used.

Preparation of Calibration Standards

1. Pipet 10 mL of 1000- $\mu\text{g/mL}$ of each of the standard metal solutions into separate 1000-mL volumetric flasks. Dilute to the mark with water, cap and invert several times to thoroughly mix. Label with the element and concentration (10- $\mu\text{g/mL}$). Store the prepared solution in the volumetric flask and prepare new solutions after three months.
2. Prepare 1-, 2-, 3-, and 4- $\mu\text{g/mL}$ iron standards by pipeting 10-, 20-, 30-, and 40-mL aliquots of the 10- $\mu\text{g/mL}$ iron solution into each of four 100-mL volumetric flasks, respectively. Label with the element and concentration.
3. Prepare 1-, 2-, and 3- $\mu\text{g/mL}$ nickel standards by pipeting 10-, 20-, and 30-mL aliquots of the 10- $\mu\text{g/mL}$ nickel solution into each of three 100-mL volumetric flasks, respectively. Label with the element and concentration.
4. Prepare 5-, 10-, 20-, and 30- $\mu\text{g/mL}$ vanadium standards by pipeting 5-, 10-, 20-, and 30-mL aliquots of the 100- $\mu\text{g/mL}$ vanadium solution into each of four 100-mL volumetric flasks, respectively. Label with the element and concentration.
5. Prepare 1-, 2-, and 3- $\mu\text{g/mL}$ copper standards by pipeting 10-, 20-, and 30-mL aliquots of the 10- $\mu\text{g/mL}$ copper solution into each of three 100-mL volumetric flasks, respectively. Label with the element and concentration.

6. Prepare 0.2-, 0.4-, 0.6-, 0.8-, and 1- $\mu\text{g/mL}$ sodium standards by pipeting 2-, 4-, 6-, 8-, and 10-mL aliquots of the 10- $\mu\text{g/mL}$ sodium solution into each of five 100-mL polypropylene volumetric flasks, respectively. Label with the element and concentration.
7. Prepare 0.5-, 1-, 1.5-, and 2- $\mu\text{g/mL}$ potassium standards by pipeting 5-, 10-, 15-, and 20-mL aliquots of the 10- $\mu\text{g/mL}$ potassium solution into each of four 100-mL volumetric flasks, respectively. Label with the element and concentration.
8. Add 10 mL of 10,000- $\mu\text{g/mL}$ cesium solution and 5 mL of concentrated sulfuric acid with a graduated cylinder to each of the 23 flasks prepared in Steps 2 through 7 above.
 - The contents of the flasks will get warm when the sulfuric acid is added.
9. Add 10 mL of 10,000- $\mu\text{g/mL}$ cesium solution and 5 mL of concentrated sulfuric acid with a graduated cylinder to an empty 100-mL polypropylene flask. This is used as the calibration blank for all of the standards. Label as the calibration blank.
10. Allow all the flasks to cool to ambient temperature, dilute to the mark with water, cap and invert several times to thoroughly mix.
 - The prepared solutions are stored in the volumetric flasks. Fresh solutions must be prepared after one month.

Sample Preparation

The sample size of petroleum products is dependent on the levels of metals expected in the sample. As a general rule, the lighter and more free-flowing the material, the less trace metals it contains. For a gasoline or other light materials, a 100-g sample size is recommended; for a viscous residue, 10 g is generally sufficient. For samples having intermediate viscosity, or samples where no estimate of metals content can be made, a 50-g sample size is recommended.

The sample size of other organic mixtures is dependent on their expected reaction with fuming sulfuric acid. Determine the potential for vigorous chemical reactions before attempting to wet ash an organic sample for the first time by mixing approximately 5 g of sample with 1 mL of fuming sulfuric acid and heating. To maximize sensitivity, the largest mass of sample that can be safely handled is usually used. As a rule, 400-mL quartz beakers are used for all ashings involving organics to minimize loss of sample as a result of sudden or unexpected vigorous reactions.

Use appropriate safety precautions including gloves when performing any of the procedures below. All sample digestions are performed in a hood. Use beaker tongs when transferring beakers to or from hot plates or the muffle furnace.

Use an additional quartz beaker, without sample, to carry a reagent (acid) blank through the procedure below each time a set of samples is prepared.

1. Obtain a representative sample in the following manner: if the material to be sampled is free-flowing, shake the container by hand for several minutes prior to sampling. Heat viscous or waxy samples prior to shaking.
2. Weigh the sample, to the nearest 0.01 g, into a 400-mL quartz beaker.
 - If multiple samples are being weighed, cover the beakers with watch glasses to prevent contamination.
3. Measure 10 mL of fuming sulfuric acid into a graduated cylinder. Using a transfer pipet, add the fuming sulfuric acid to the beaker, dropwise, in a hood, after removing the watch glass (if used in Step 2). Use a stirring rod to carefully mix the sample and acid.

- Add the acid slowly. If a vigorous reaction ensues, stop addition until the reaction subsides. Then add the remainder of the acid in increments, allowing the reaction to proceed at a slow, controlled rate.
4. After any initial reaction subsides, place the beaker on a warm hot plate and occasionally stir. Increase the heat slowly while continuing to stir at intervals until the sludge that forms hardens sufficiently to be broken into small lumps with the stirring rod. Leave the stirring rod in the beaker.
 5. Increase the hot plate temperature to the point where sulfuric acid fumes begin to evolve. After the fuming ceases, increase the temperature to 400°C and heat until only a dry organic char remains.
 6. Place the beaker containing the organic char and stirring rod just inside a 540°C muffle furnace with the door fully open.
 - The muffle furnace must be located in a hood or under a canopy hood since acid vapors are generated during heating.
 7. When SO₃ fumes are no longer visible, move the beaker to the rear of the furnace and close the door.
 8. Leave the samples in the furnace until all of the organic char is burned off and only ash remains. The door may be opened occasionally to check for completion.
 - The elapsed time for Steps 6 through 8 will vary from 4-16 hours depending on the sample composition.
 - A slow flow of air in the muffle furnace will speed up the organic char burn off, but is not a method requirement.
 - Minimization of laboratory dust or contamination from the muffle furnace liner is important for trace analysis.
 9. Remove the beaker containing the stirring rod from the muffle furnace, cover it with a watch glass, and allow it to cool to ambient temperature.
 - A watch glass is used to prevent contamination.
 10. Gently wet the ash with a fine stream of water from a wash bottle before removing the watch glass.
 - The water is introduced through the spout opening of the beaker, alongside the stirring rod.
 11. Using a graduated cylinder, add 2.5 mL of concentrated sulfuric acid and 1.0-mL of concentrated hydrochloric acid to the beaker.
 12. Using the acid dropping bottle, slowly add three drops of concentrated nitric acid and allow it to run down the inner wall of the beaker.
 - The acid is run down the inner wall to minimize the possibility of a splash or spatter.
 13. Heat the beaker on a hot plate in the hood until sulfuric acid fumes begin to evolve. Remove the beaker from the hot plate and allow it to cool to ambient temperature.
 14. Transfer the beaker contents to a 50-mL polypropylene volumetric flask, quantitatively, with water.
 15. Using a graduated cylinder, add 5 mL of 10,000-µg/mL cesium solution to the flask. Dilute to the mark with water, cap and invert several times to thoroughly mix.

Instrumental Analysis

- Set the instrument for one of the elements to be read following the instrument manufacturer's instructions for that element. Typical instrument settings are listed in Table 1.
 - The settings shown are recommendations and may be changed if the manual for the instrument being used recommends other parameters.

Table 1
AAS Instrument Parameters

<u>Element</u>	<u>Wavelength, nm</u>	<u>Slit, nm</u>	<u>Background Correction</u>	<u>Flame Type</u>	<u>Burner, mm</u>
Iron	248.3	0.2	Yes	air-C ₂ H ₂	100
Nickel	232.0	0.2	Yes	air- C ₂ H ₂	100
Vanadium	318.4	0.7	No	N ₂ O- C ₂ H ₂	50
Copper	324.7	0.7	No	air- C ₂ H ₂	100
Sodium	589.0	0.4	No	air- C ₂ H ₂	100
Potassium	766.5	1.4	No	air- C ₂ H ₂	100

- Analyze the standards and samples in the following order: calibration blank, standards, reagent (acid) blank, samples, and then reanalyze one of the standards. If the last standard does not match its initial reading to within 3% relative, check for problems with the instrument or the procedure and reanalyze the entire series.
 - If a sample reading exceeds the highest standard reading, dilute the sample so that the metal concentration is within the standard range, maintaining the matrix-match by proper addition of sulfuric acid and cesium solution.
- Reset the instrument for each additional element, proceeding through Steps 1 and 2 above.

Calculations

Calculate the concentration of any of the metals in the original sample to the nearest 0.1 mg/kg for concentrations below 10 mg/kg and to the nearest mg/kg for concentrations between 10 and 100 mg/kg using Equation 1:

$$\text{Metal, mg/kg} = \frac{50(A - B)C}{DM} \quad (1)$$

where:

A = concentration of metal in initial or second, if required, dilution from instrument readout, $\mu\text{g/mL}$

B = concentration of metal in reagent (acid) blank, from instrument readout, $\mu\text{g/mL}$

C = total volume of second dilution, mL

D = aliquot taken from initial dilution, mL

If no second dilution is required, **C/D = 1**.

M = sample mass, g

50 = initial dilution volume, mL

This calculation will normally be performed by the computer data reduction software after the analyst enters the appropriate values for mass and dilution.

Precision

Precision statements were determined using UOP Method 999. Copper was not present in the sample tested. It is expected that the repeatability for copper would be similar to that reported for the other elements.

Repeatability

A nested design was carried out for determining elements in one sample with two analysts in one laboratory. Each analyst carried out tests on the sample performing four tests on the sample. The total number of tests for each sample component was eight. The precision data are summarized in Table 2. Two tests performed by the same analyst sequentially should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed by different analysts should not differ by more than the repeatability allowable difference with 95% confidence.

Table 2
Repeatability and Site Precision, Metals, mg/kg

<u>Metal</u>	<u>Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Iron	1.2	0.10	0.4	0.15	0.9
Nickel	10.2	0.29	1.1	0.29	1.2
Potassium	0.1	0.02	0.1	0.03	0.1
Sodium	0.6	0.08	0.3	0.14	0.9
Vanadium	10.5	0.30	1.2	0.45	2.5

The data in Table 2 are short-term estimates of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the site precision.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time is determined by the wet ashing step, and may vary between 5 and 16 hours per sample. The labor requirement is dependent on the number of elemental determinations. Generally, the wet ashing requires one hour and then each elemental determination requires 0.5 hour (all 6 elements would require 4 hours). Multiple sample analyses reduce the labor requirements per sample.

Suppliers

Ace Glass, Inc., P.O. Box 688, 1430 North West Blvd., Vineland, NJ 08362-0688 (856-691-3333)
www.aceglass.com

JSRitter, 50 Cove St. Portland, ME 04101 (207-772-3822) www.jsritter.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

PerkinElmer Analytical Instruments, 710 Bridgeport Avenue, Shelton, CT 06484-4794 (203-925-4600) www.perkinelmer.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700) www.vwr.com

Wilma-LabGlass, 1002 Harding Hwy., Buena, NJ 08310 (856-697-3000)
www.wilma-labglass.com