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A Honeywell Company

Trace Metals in Organics by ICP-OES

UOP Method 389-15

Scope

This method is for determining the concentrations of aluminum (Al), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), palladium (Pd), phosphorus (P), platinum (Pt), potassium (K), sodium (Na), strontium, (Sr), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn) in organic matrices such as crude petroleum, asphalts, vacuum tower bottoms, vacuum gas oils, atmospheric gas oils, diesel and jet fuels and their blending components, pyrolysis oils, and fatty acid derivatives by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). The lower limits of quantitation for the above elements, except palladium, are listed in Table 1 (see *Note*).

Table 1

Lower Limits of Quantitation, mg/kg (mass-ppm)

Al	0.05	Li	0.03	Pb	0.04
Ca	0.08	Mg	0.04	Pt	0.01
Co	0.02	Mn	0.01	Sn	0.10
Cr	0.04	Mo	0.01	Sr	0.01
Cu	0.01	Na	0.04	Ti	0.03
Fe	0.09	Ni	0.03	V	0.01
K	0.05	P	0.11	Zn	0.03

Determination of additional elements is possible if they are not volatilized during the ashing step and do not form insoluble sulfates. Two different reagents are used in sample preparation, depending upon the sample matrix.

Alternatively, some of the elements listed above may be analyzed by Atomic Absorption Spectroscopy (AAS). See UOP Method 391, "Trace Metals in Petroleum Products or Organics by AAS," for specific metals and their range of quantitation. Metals known to be non-volatile may be analyzed by UOP Method 407, "Trace Metals in Organics by Dry Ashing - ICP-OES."

References

ASTM Method D1193, "Specification for Reagent Water," www.astm.org

ASTM Practice D7455, "Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis," www.astm.org

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, USA. The UOP 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.

UOP Method 391, “Trace Metals in Petroleum Products or Organics by AAS,” www.astm.org

UOP Method 407, “Trace Metals in Organics by Dry Ashing - ICP-OES,” www.astm.org

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

Outline of Method

The sample is treated to reduce the volatility of the metals, then coked and ashed. The residue is treated with aqua regia and, after evaporation, is dissolved in acids. Scandium is added as an internal standard. The concentrations of elements in the resulting solutions are determined by ICP-OES.

Apparatus

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

Balance, laboratory, readable to 0.01 g

Beaker, quartz, low form, 250-mL, Ace Glass, Inc., Cat. No. 5334-14

Bottles, polypropylene, narrow mouth, screw cap, 1000-mL, VWR, Cat. No. 16067-124, several required

Bottle, wash, VWR, Cat. No. 89094-606, for deionized water

Cylinders, graduated, Class B, 5-, 10-, 25-, and 100-mL, VWR, Cat. Nos. 14201-610, -462, -364, and -718, respectively

Flasks, volumetric, Class A, 10-, 50-, and 1000-mL, VWR, Cat. Nos. 89000-398, -402, and -412, respectively

Flasks, volumetric, polypropylene, 25-, 50-, 100-, and 1000-mL, VWR, Cat. Nos. 83008-964, 29615-019, -007, and -062, respectively

Furnace, muffle, capable of operation at 600 °C, VWR, Cat. No. 30604-158

Hot plate, variable heat, maximum operating temperature 510 °C, VWR, Cat. No. 82026-752

Pipet, measuring (Mohr), 5-mL, VWR, Cat. No. 89003-458

Pipets, volumetric, Class A, 1-, 2-, 5-, 10-, 20-, 25-, 50-, and 100-mL, VWR, Cat. Nos. 89003-340, -342, -348, -350, -364, -362, -366-, and -368, respectively

Pipet filler, VWR, Cat. No. 53497-053

Regulator, argon, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Spectrometer, ICP-OES, computer controlled, having sufficient resolving power and dispersion to separate the analytical lines in the 160 to 800 nm region. The data system shall be capable of performing background corrections, blank corrections, mass/volume corrections and dilution corrections. A commercial grating spectrometer with a band pass of 0.018 nm or less in the first order is satisfactory. PerkinElmer, Optima 7300 DV.

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

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

Watch glasses, quartz, ribbed, 75-mm diameter, Wilmad-LabGlass, Cat. No. C-9990-75, several required

Reagents and Materials

References to catalogue numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. Unless otherwise specified, references to water mean deionized water.

Aqua regia. To prepare, mix 1 mL of concentrated nitric acid with 3 mL of concentrated hydrochloric acid. Prepare a fresh batch each time it is needed.

Argon, 99.995% minimum purity

Cleaning compound, Alconox detergent, VWR, Cat. No. 21835-032

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

Hydrochloric acid, concentrated, trace metals grade, VWR, Cat. No. EM-HX0608-2

Hydrofluoric acid, concentrated, trace metals grade, VWR, Cat. No. EM-HX0628-7, if needed, see *Procedure, Sample Preparation, Ashing*, Step 8

Nitric acid, concentrated, trace metals grade, VWR, Cat. No. EM-NX0408-2

Pipet, dropping, VWR, Cat. No. 52950-206

Scandium metal solution, aqueous, 1000-µg/mL, SPEX Certiprep, Inc., Cat. No. PLSC-2, for use as internal standard

Scandium metal solution, aqueous, 100-µg/mL. To prepare 50 mL, pipet 5.0 mL of the 1000-µg/mL scandium metal solution into a 50-mL volumetric flask. Fill to the mark with deionized water. Cap and invert several times to mix. The solution should remain stable for one month.

Scandium internal standard, 10-µg/mL. To prepare 1000 mL, pipet 10.0 mL of 1000-µg/mL scandium metal solution into a 1000-mL volumetric flask. Fill to the volume mark with water and mix. Store in a 1000-mL polypropylene bottle. The solution should remain stable for one month.

Scandium internal standard, 1-µg/mL. To prepare 1000 mL, pipet 1.0 mL of 1000-µg/mL scandium metal solution into a 1000-mL volumetric flask. Using a graduated cylinder, add 100 mL of concentrated hydrochloric acid. Fill to the volume mark with water and mix. Store in a 1000-mL polypropylene bottle. The solution should remain stable for one month.

Standard metal solutions, Al, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Sn, Sr, Ti, V, and Zn solutions of 1000-µg/mL concentrations, SPEX Certiprep, Inc., Cat. Nos. PLAL2-2, PLCA2-2, PLCO2-2, PLCR2-2, PLCU2-2, PLFE2-2, PLK2-2, PLLI2-2, PLMG2-2, PLMN2-2, PLMO2-2, PLNA2-2, PLNI2-2, PLP2-2, PLPB2-2, PLPD2-2, PLPT2-2, PLSN2-2, PLSR2-2, PLTI2-2, PLV2-2, and PLZN2-2, respectively

Sulfuric acid, concentrated, trace metals grade, VWR, Cat. No. EM-SX1248-6, if needed, see *Procedure, Sample Preparation, Ashing*, Step 7

Sulfur trioxide pyridine complex, [26412-87-3], Sigma-Aldrich, Cat. No. S7556, or Acros Organics, Cat. No. 13287-1000

Vials, autosampler, 15-mL, PerkinElmer, Cat. No. B0193233

Water, deionized, ASTM D1193 Type III reagent grade water, unless otherwise specified

Water, hot, tap

The following materials are not required to perform the analyses described herein and are not cited in the *Procedure* portion of the method. However, they may be useful for reference purposes, for verification of instrument performance, or as an aid in instrument maintenance. The diluted multi-element standard was used to develop part of the precision statement.

Element Blank Oil, 75 viscosity, Conostan Division, SCP Science

Wear Metal Multi-Element Standard, 500-µg/g (mg/kg) each, AccuStandard, Cat. No. WM-21-50X-8. Dilute by weight in Element Blank Oil to 5 mg/kg.

Preparation of Standards

The analyst is expected to be familiar with general laboratory practices. Dispose of all materials in an environmentally safe manner according to local regulations.

CAUTION: All subsequent steps involving additions of reagents and heating of samples must be performed in a properly operating fume hood, and appropriate personal protective equipment must be used. See the MSDS and any local requirements for each material used.

Standards are required for each element to be determined**.** They are prepared to contain a number of elements with compatible chemistries and no overlap of emission lines. Stock standard solutions are prepared first, from which lower level, matrix-matched, calibration standard solutions are then prepared.

- Calibration standards (including the blank), as well as the final sample preparation, contain the internal standard scandium at a concentration of 1 µg/mL

Preparation of Stock Standard Solutions

Prepare stock standard solutions of 100-µg/mL concentration of each element as follows:

1. Pipet 100 mL each of the Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, and Ni 1000-µg/mL commercial stock standards into a 1000-mL polypropylene volumetric flask. Dilute to the mark with deionized water. Label as Stock Standard A.
2. Pipet 100 mL each of the Sn, Pd, Pt, V, and Zn 1000-µg/mL commercial stock standards into a second 1000-mL polypropylene volumetric flask. Dilute to the mark with deionized water. Label as Stock Standard B.
3. Pipet 100 mL each of the Mo, P, and Ti 1000-µg/mL commercial stock standards into a third 1000-mL polypropylene volumetric flask. Dilute to the mark with deionized water. Label as Stock Standard C.
4. Pipet 100 mL each of the K and Na, 40 mL of the Li, and 20 mL of the Sr 1000-µg/mL commercial stock standards into a fourth 1000-mL polypropylene volumetric flask. Dilute to the mark with deionized water. Label as Stock Standard D.
    - Use only 40 mL of Li and 20 mL of Sr because the instrument is more sensitive to these elements. Their concentrations in the stock standard solutions are 40 µg/mL and 20 µg/mL, respectively.

Preparation of Blank and Calibration Standard Solutions

Sample preparation differs depending upon the composition of the sample. Lighter materials, kerosene, diesel, atmospheric gas oil, vacuum gas oil, and fatty acid derivatives, are prepared using *Preparation A*. These materials are typically lower in metals. Heavier materials, vacuum tower bottoms, crude, asphalt, and pyrolysis oil, are prepared using *Preparation B*. These materials are typically higher in metals. Blank and Calibration Standard Solutions must be matrix-matched to the sample preparation technique. *Preparation A* is used for metals stabilized with sulfur trioxide pyridine complex. *Preparation B* is used for metals stabilized with sulfuric acid.

Prepare 100 mL of matrix-matched Calibration Standards and a Blank as follows: