



A Honeywell Company

Trace Metals in Organics by Dry Ashing - ICP-OES

UOP Method 407-09

Scope

This method is for determining the concentrations of the metals aluminum (Al), calcium (Ca), cobalt (Co), chromium (Cr), 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, and polymers, by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). Most of the elements can be determined within the concentration range of 0.02 to 200 mg/kg when a 50-g sample is ashed. Higher or lower concentrations can be determined by changing sample weight, dilution volume, and/or modifying the instrument operating parameters. Determination of additional elements is possible if they are not volatilized during the ashing step. See *Note*.

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.

References

ASTM Method D482, “Ash from Petroleum Products,” www.astm.org

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

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

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

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

Outline of Method

The sample is weighed into a quartz beaker. It is ignited and allowed to burn until it no longer supports a flame. The carbonaceous residue is further treated in a muffle furnace at 540°C to complete the ashing. If percent ash is being determined, the empty, full and ignited weights of the beaker are recorded. After ashing, the sample is dissolved in dilute hydrochloric acid containing scandium as an internal standard. The concentrations of elements in the resulting solutions are determined by ICP-OES.

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

Polypropylene labware and containers must be used wherever possible to eliminate the possibility of contamination caused by the leaching of elements from glassware. In some instances, propylene labware may not be readily available, e.g., volumetric pipets. Glassware may be used for short-term dispensing purposes if it is cleaned before and after use. Glassware must never be used for storage of calibration solutions or samples.

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

Balance, readability 0.001-g

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

Bottles, polypropylene, narrow mouth, screw cap, 30-mL, VWR, Cat. No. 16067-022

Bottle, wash, VWR, Cat. No. 16651-595, for deionized water

Cylinder, graduated, polypropylene, 10-mL, VWR, Cat. No. 83008-860

Desiccator, VWR, Cat. No. 25021-022, with high temperature plate, VWR, Cat. No. 89038-070

Flasks, volumetric, polypropylene, 50-, 100-, and 1000-mL, VWR, Cat. Nos. 29615-018, -007, and -062, respectively, several of each required

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

Gloves, thermal protection, VWR, Cat. No. 32885-407, optional

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

Meker burner, VWR, Cat. No. 89038-544

Pipets, Mohr, polypropylene, 1- and 10-mL, Thomas, Cat. Nos. 7480N48 and 7480N84, respectively

Pipets, volumetric, Class A, 5, 10- and 100-mL, VWR, Cat. Nos. 89045-064, -074, and -088, 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 5300 V.

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

Support, cast iron tripod, VWR, Cat. No. 62760-003

Support, wire gauze, VWR, Cat. No. 66232-029

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

Tongs, beaker, VWR, Cat. No. 82027-372

Reagents and Materials

References to catalog 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.

Argon, 99.995% minimum purity

Cleaning compound, Alconox detergent, VWR, Cat. No. 21835-032. Dilute 1:100 in deionized water for use.

Desiccant, VWR, Cat. No. EM-DX0017-1

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

Hydrochloric acid, HCl, concentrated, high purity, VWR, Cat. No. VW3110-3

Hydrochloric acid, diluted to 1 in 10. Fill a 1000-mL volumetric flask approximately half full with deionized water. Pipet 100 mL of concentrated HCl into the flask. Dilute to the mark with deionized water.

Natural gas, for Meker burner

Nitric acid, HNO₃, concentrated, high purity, VWR, Cat. No. VW4815-6

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

Scandium internal standard solution, 100-μg/mL. To prepare 1000 mL, pipet 100.0 mL of 1000-μg/mL scandium 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.

Scandium internal standard solution, 10-μg/mL. To prepare 1000 mL, pipet 10.0 mL of 1000-μg/mL scandium 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.

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 Industries, 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

Pipets, disposable transfer, VWR, Cat. No. 16001-188

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

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

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.

Procedure

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

CAUTION: All subsequent steps involving heating of samples and addition of acids must be performed in a properly operating fume hood, and appropriate personal protective equipment must be worn. See MSDS for each material used.

Preparation of Standards

Standards are required for each element to be determined. Standards 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.

Preparation of Stock Standard Solutions

Prepare stock standard solutions of 100- $\mu\text{g/mL}$ concentration of each element as follows:

1. Pipet 100 mL each of the Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, and Ni 1000- $\mu\text{g/mL}$ 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 K, Li, Na, P, Ti, V, and Zn 1000- $\mu\text{g/mL}$ 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, Pb, Sn, and Sr 1000- $\mu\text{g/mL}$ 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 Pd and Pt 1000- $\mu\text{g/mL}$ commercial stock standards into a fourth 1000-mL polypropylene volumetric flask. Dilute to the mark with deionized water. Label as Stock Standard D.

Preparation of Blank and Calibration Standard Solutions

Prepare 100 mL of matrix matched calibration standards and a blank as follows:

1. Label five 100-mL polypropylene volumetric flasks 10-mg/kg Calibration Standard A, B, C, D, and Blank.
2. Pipet into each of the five flasks 1.0 mL of the 1,000- $\mu\text{g/mL}$ scandium solution.
3. Pipet 10.0 mL of Stock Standard A into the flask labeled 10-mg/kg Calibration Standard A. Fill to the mark with diluted HCl. Follow the same procedure for Standards B, C, and D. The standards contain 10.0 $\mu\text{g/mL}$ of their respective elements. Fill the flask labeled Blank to the mark with diluted HCl.

Preparation of Spectrometer

Start up the ICP-OES and ignite the plasma according to the manufacturer's recommendations. Allow a minimum of 30 minutes for warm up after the plasma is ignited before starting the analysis. Using the recommended elemental emission wavelengths, calibrate the spectrometer prior to the analysis of the sample solution. Perform a wavelength calibration prior to the start of the analysis if

recommended by the manufacturer. Aspirate the standards and blank to establish the calibration for each element to be measured. Table 1 lists recommended wavelengths to be used for the analyses.

Preparation of Quartz Beakers

Clean the 250-mL quartz beakers before each use as follows:

1. Wash the beakers with cleaning compound and rinse with deionized water.
2. Using a graduated cylinder, add 10 mL of concentrated hydrochloric acid, bring to boiling on a hot plate and allow to cool. Rinse again 4 to 5 times with deionized water.
 - Dispose of the hydrochloric acid and all other chemicals used in an environmentally safe manner according to local regulations.
3. Store in a clean area.

Table 1
Recommended Wavelengths for each Element

Element	Concentration Range in Sample, mg/kg*	λ, nm	Element	Concentration Range in Sample, mg/kg*	λ, nm
Al	0.05-500	396.152	Na	0.05-500	589.592
Ca (low)	0.05-5	393.366	Ni	0.10-100	231.604
Ca (high)	5.0-500	422.673	P	0.10-500	213.618
Co	0.05-200	228.616			or
Cr	0.05-50	206.149			214.914
Cu	0.02-200	324.754	Pb	0.10-100	220.353
Fe	0.02-200	238.204	Pd	0.05-200	340.458
K	0.05-500	766.491	Pt	0.05-200	265.945
Li	0.02-200	610.364	Sc	internal standard	424.683
		or	Sn	0.20-200	189.989
		670.781	Sr	0.02-200	407.771
Mg	0.02-200	279.553	Ti	0.20-200	334.941
Mn	0.02-200	257.610	V	0.02-200	292.402
Mo	0.05-50	202.030	Zn	0.02-200	206.200

* Based on an ashed 50-g sample, diluted to 50 mL for the higher concentrations and 10 mL for the lower concentrations.

Sampling

Sample size depends primarily on the type of sample and the concentrations of metals expected to be present. Several sample types and amounts used, based upon typical metals concentrations, are listed in Table 2. Because elements can be extracted from glass, the sample should be collected in plastic bottles.

Weigh into a quartz beaker, to the nearest 0.01 g, an amount of sample appropriate to sample type and the expected metals concentration. See Table 2.

- Ensure that a representative sample is obtained. Viscous samples may be gently heated until they flow freely. Hot tap water is generally satisfactory, however, more viscous samples may require use of

boiling water. Shake the warmed samples vigorously or stir with a quartz rod and then weigh a sample for analysis to the nearest 0.01 g.

- Contamination is possible especially because of the trace concentrations, in many cases sub-mass-ppm, of common metals. If sufficient sample is available, duplicate analyses may be performed as a check. If duplicate analyses are performed, report the individual results.

Table 2
Sample Types and Sample Size Used

<u>Sample</u>	<u>Amount used, g</u>	<u>Sample</u>	<u>Amount used, g</u>
Crude Petroleum	5 to 10	Atmospheric Gas Oil	50 to 100
Asphalt	5 to 10	Diesel and Jet Fuel	50 to 100
Vacuum Tower Bottoms	5 to 10	Polymers	5 to 10
Vacuum Gas Oil	20 to 50		

Sample Preparation, Dry Ashing

Determination of Percent Ash, if Requested

- Heat the quartz beakers that are to be used for ashing the sample at 540°C for a minimum of 10 minutes.
- Remove from furnace, place in a desiccator, cool to room temperature and weigh to 0.001 g.
- Add sample and record the weight. Weigh after ignition, see *Dry Ashing*, and calculate % ash, if requested, and report % ash and the temperature used.
 - Make all weighings to the nearest 0.001 g. If the determination of % ash is not requested, weighing the sample to the nearest 0.01 g is sufficient for metals analysis.

Dry Ashing

Dry ash the samples as described below. Additional information about dry ashing is available in ASTM Method D482, "Ash from Petroleum Products."

- Turn on the muffle furnace and set the temperature at 540°C.
 - The muffle furnace must be used in a hood.
- Ignite and ash the sample:
 - In a hood, carefully heat the quartz beaker containing the sample with a Meker burner, or equivalent, until the contents are ignited.
 - Maintain the temperature so that the sample continues to burn at a uniform and moderate rate. Only a carbonaceous residue is present when the burning ceases.
 - Allow the ignited matter to cool.
- Place a ribbed watch glass over the ignited sample and, using tongs, place in the 540°C muffle furnace. Check progress by determining if smoke is evolving from the furnace.
 - Do not exceed 540°C; loss of some of the more volatile elements may occur.
- When smoke is no longer apparent, open the muffle furnace and examine the samples. If black matter is present continue heating. If there is no black matter, or no further change is noticed, remove the quartz beakers from the muffle furnace using tongs. Allow to cool to room temperature and weigh if % ash is requested.

- Caution, use care when removing the hot beakers from the furnace. Thermal gloves may be used in addition to tongs, if desired.
 - If % ash is requested, cool the beaker in a desiccator and weigh before proceeding to Step 5.
5. Rinse the sides of the beaker with deionized water and add a few drops of HCl. If insoluble matter is present, add a few drops of HNO₃. Heat on a hot plate to near dryness, cool, pipet in 5.0 mL of the 100-μg/mL scandium internal standard solution and 5 mL concentrated HCl; heat gently to dissolve.
 6. Label a polypropylene 50-mL volumetric flask with sample information. Quantitatively transfer the sample into the flask using deionized water, and dilute to the mark with deionized water. The solution is ready to be analyzed by ICP.

Spectrometric Procedure

1. Prepare the spectrometer as described under *Preparation of Spectrometer*.
2. Enter the appropriate sample mass and dilution volume for each sample into the data system.
3. Aspirate the blank, the standards, and the samples. The data system will calculate the mg/kg metal in the original sample and print the result.
4. If the concentration of one or more elements in the sample is above the concentration in the Calibration Standard, pipet an aliquot of the sample into a volumetric flask and dilute with the 10-μg/mL scandium in diluted HCl sample diluent to bring it into a reading range of the standards.
 - The volume of the aliquot of sample pipetted and the size of the volumetric flask used depends upon the amount of dilution required.

Calculations

Calculate the mg/kg of each element in the original sample using the mg/kg value from the instrument readout for each element following Equation 1.

$$\text{Concentration of a specific element in original sample, mg/kg} = \frac{RV}{DW} \quad (1)$$

where:

D = dilution factor, the pipetted volume of the prepared sample divided by the final dilution volume, see *Spectrometric Procedure*, Step 4, if required; **D** = 1 if no additional dilution is required

R = concentration of element in diluted sample, from instrument readout, μg/mL

V = dilution volume, from *Dry Ashing*, Step 6, mL

W = mass of sample used, g

This calculation will normally be performed by the computer data reduction software after the analyst enters the appropriate values for **D**, **V**, and **W**.

The data system, using known dilutions and concentration levels, determines the correct number of significant figures to report. In general, results are reported to the nearest 0.01 mg/kg, but not exceeding three significant figures. If duplicate analyses are performed, report both results.

Note

This method is an alternative to UOP Method 389, “Metals in Organics by Wet Ashing – ICP-OES.” The sulfuric acid used in the wet ashing procedure in UOP Method 389 tends to reduce the volatility of some elements. It does, however, have the disadvantage of contributing to higher blanks. It is necessary to verify that the metals of interest are not volatilized during the dry ashing procedure

in this method. This is typically done by analyzing the samples by this method and by UOP Method 389, and comparing the results. If the results are in agreement, this method may then be used for similar samples. Alternatively, if the elements of interest are known to be present as non-volatile compounds, this method may be used directly.

Precision

Precision statements were determined using UOP Method 999.

Repeatability and Site Precision

Samples containing higher and lower concentrations of elements were analyzed in one laboratory. The analyst carried out tests on two separate days, performing two tests on each sample each day. The precision data for estimated standard deviation and allowable difference are summarized in Table 3. Two tests performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

The data in Table 3 are short-term estimates of repeatability and site precision. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term site precision.

Reproducibility

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

Time for Analysis

The elapsed time for one analysis is about 6 to 8 hours. The labor requirement for one analysis is 2 hours. In groups of 5 or more samples, the labor requirement for each analyses is 1.5 hours.

Suggested Suppliers

AccuStandard, 125 Market St., New Haven, CT 06513 (203-786-5290) www.accustandard.com

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

Conostan Division, SCP Science, 21800 Clark Graham, Baie D'Urfé, QC, Canada H9X 4B6 (514-457-0701) www.scpscience.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 Ave., 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

Thomas Scientific, Swedesboro, NJ 08085 (856-467-2000) www.thomassci.com

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

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

Table 3
Repeatability and Site Precision, mg/kg

<u>Element</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>
Al	0.46	0.007	0.03	0.010	0.05
Al	9.83	0.030	0.12	0.031	0.14
Ca	0.48	0.022	0.09	0.025	0.11
Ca	10.06	0.022	0.09	0.051	0.31
Co	0.42	0.012	0.05	0.012	0.05
Co	9.87	0.033	0.15	0.047	0.19
Cr	0.42	0.011	0.05	0.015	0.06
Cr	9.79	0.113	0.51	0.152	0.60
Cu	0.42	0.012	0.05	0.014	0.06
Cu	9.74	0.072	0.32	0.101	0.40
Fe	0.45	0.014	0.06	0.017	0.07
Fe	9.94	0.039	0.17	0.055	0.21
Li	4.99	0.005	0.02	0.015	0.05
Mg	0.43	0.006	0.03	0.007	0.03
Mg	9.68	0.073	0.30	0.077	0.33
Mn	0.43	0.004	0.02	0.005	0.02
Mn	9.90	0.028	0.13	0.032	0.13
Mo	0.39	0.011	0.05	0.015	0.06
Mo	9.87	0.097	0.43	0.111	0.44
Na	0.52	0.081	0.35	0.088	0.37
Na	10.14	0.184	0.80	0.204	0.83
Ni	0.42	0.015	0.07	0.021	0.08
Ni	9.83	0.013	0.05	0.015	0.07
Pb	0.40	0.031	0.14	0.040	0.16
Pb	4.88	0.055	0.22	0.143	0.64
Pd	0.91	0.038	0.17	0.053	0.21
Pd	9.57	0.072	0.32	0.092	0.36
Sn	0.67	0.038	0.17	0.052	0.20
Sr	0.43	0.004	0.02	0.006	0.02
Ti	0.41	0.007	0.03	0.018	0.08
Ti	9.82	0.112	0.50	0.138	0.54
V	0.41	0.009	0.04	0.012	0.05
V	9.93	0.024	0.09	0.034	0.15
Zn	0.43	0.006	0.03	0.007	0.03
Zn	9.75	0.037	0.14	0.039	0.18