



A Honeywell Company

Trace Metals in Methanol by ICP-OES

UOP Method 1003-13

Scope

This method is for determining trace concentrations of calcium (Ca), iron (Fe), magnesium (Mg), potassium (K), and sodium (Na) in methanol by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). The lower limits of quantitation for these elements are listed in Table 1.

Table 1					
<u>Lower Limits of Quantitation, mg/kg (mass-ppm)</u>					
Ca	0.04	K	0.08	Na	0.04
Fe	0.10	Mg	0.08		

Determination of additional elements is possible if they are not volatilized during the evaporation step of the sample preparation.

References

- ASTM Method D1193, "Specification for Reagent Water," www.astm.org
- UOP Method 389, "Trace Metals in Organics by ICP-OES," www.astm.org
- 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 slowly evaporated with nitric acid on a hot plate to reduce the volatility of the metals. The residue is diluted with hydrochloric acid and an internal standard is added. The concentrations of elements in the resulting solution 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

Bottle, wash, 500 mL, VWR, Cat. No. 2402-0500, for deionized water

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. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) 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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Cylinder, graduated, Class B, 10- and 100-mL, VWR, Cat. No. 89000-264 and -270, respectively

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

Flasks, volumetric, polypropylene, 100- and 1000-mL, VWR, Cat. Nos. 29615-007, and -062, respectively

Hot plate, variable heat, with temperature display, VWR, Cat. No. 12365-474

Pipets, volumetric, Class A, 1-, 2-, 5-, 10-, and 100-mL, VWR, Cat. Nos. 89003-340, -342, -348, -350, 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 8300 DV or equivalent. The use of an autosampler is recommended for efficiency

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

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

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

Centrifuge tubes, 15 mL, polypropylene, Fisher Scientific, Cat. No. 05-538-51

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

Hydrochloric acid, 10%, To prepare 1000 mL, using a graduated cylinder, add 100 mL of the concentrated hydrochloric acid, into a 1000-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.

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

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

Scandium metal solution, aqueous, 1000- $\mu\text{g/mL}$, SPEX Industries, Inc., Cat. No. PLSC-2, for use as an internal standard

Scandium metal solution, aqueous, 10- $\mu\text{g/mL}$. To prepare 100 mL, pipet 1.0 mL of the 1000- $\mu\text{g/mL}$ scandium metal solution into a 100-mL volumetric flask. Fill to the mark with 10% hydrochloric acid. Cap and invert several times to mix. The solution should remain stable for one month.

Standard metal solutions, Ca, Fe, K, Mg, and Na solutions of 1000- $\mu\text{g/mL}$ concentrations, SPEX Industries, Inc., Cat. Nos. PLCA1-2X, PLFE2-2X, PLK1-2X, PLMG2-2X, and PLNA2-2X, respectively

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

Water, hot, tap

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of ICP-OES, and the equipment being used. Dispose of all materials in an environmentally safe manner according to local regulations.

CAUTION: All subsequent steps involving the use of acids must be performed in a properly operating fume hood, and appropriate personal protective equipment must be worn. See the SDS and any local requirements for each material used.

Preparation of Standards

Standards are required for each element to be determined. 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 Ca, Fe, and Mg 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 and Na 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 B.

Preparation of Blank and Calibration Standard Solutions

Blank and calibration standard solutions must be matrix matched to the sample preparation technique.

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

1. Pipet an amount of standard stock solutions as shown in Table 2 into 100-mL polypropylene volumetric flasks.

	Table 2		
	Calibration Standards and Blank Preparation		
	Volume of 100-$\mu\text{g/mL}$ Ca, Fe, Mg Stock Standard A, mL	Volume of 100-$\mu\text{g/mL}$ K, Na Stock Standard B, mL	Volume of 10-$\mu\text{g/mL}$ Internal Standard Scandium Solution, mL

Blank	0	0	10
1.00 $\mu\text{g/mL}$ (Ca, Fe, K, Mg, Na)	1	1	10
10.00 $\mu\text{g/mL}$ (Ca, Fe, K, Mg, Na)	10	10	10

2. Dilute to the mark with 10% hydrochloric acid.

3. The standards contain 1.0 and 10.0 µg/mL of their respective elements. The solutions should remain stable for one month.

Cleaning of Quartz Beakers

Clean the 250-mL quartz beakers used for sample preparation before each use as follows:

1. Wash the beakers with cleaning compound and hot tap water. Rinse with deionized water. Rinse the watch glasses with deionized water.
2. Using a graduated cylinder, add 10 mL of concentrated hydrochloric acid to each beaker, bring to boiling on a hot plate, cool, dispose of the acid, and rinse again 4 to 5 times with deionized water. Dry on a warm hot plate, and allow to cool to ambient temperature.
3. Use the same day.

Sample Preparation

1. Weigh into a quartz beaker, to the nearest 0.01 g, 50 g of sample. If the concentrations of the metals are expected to be high, or are not known, start with 25 g.
 - Ensure that a representative sample is obtained.
2. Add, using a graduated cylinder, 2 mL of nitric acid.
3. Cover the beaker with a watch glass.
4. Place the covered beaker on a hot plate at ambient temperature. Slowly apply heat.
 - A slow increase in heating rate is necessary to avoid loss of sample by “spitting” and will generally require about 1.5 -1.75 hours to reach a final hot plate temperature of 250°C.
5. Increase the temperature every 5 mins by ~10°C. When the temperature reaches 250°C, hold the temperature and evaporate to approximately to 1 mL.
 - Do not exceed 250°C. Loss of some of the more volatile elements may occur.
6. Allow the beaker and contents to cool to room temperature.
7. Add approximately 2 mL 10% hydrochloric acid and swirl to mix.
8. Quantitatively transfer the contents of the beaker into a 10-mL volumetric flask using the 10% hydrochloric acid.
9. Add 1.0 mL of the 10-µg/mL internal standard scandium solution.
10. Dilute to the mark with 10% hydrochloric acid.
11. Transfer the diluted sample to a 15-mL centrifuge autosampler tube and proceed to Spectrometric Procedure.

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 prior to aspiration of the samples. Table 3 lists recommended wavelengths to be used for the analyses.

- Other wavelengths may be used if there is overlap in transmission lines for the elements analyzed. The alternative wavelengths must retain sufficient sensitivity to achieve the necessary limits of detection.

Spectrometric Procedure

1. Prepare the spectrometer as described under *Preparation of Spectrometer*.
2. Enter the appropriate mass of the sample taken, and the final 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, dilute the sample with 10% hydrochloric acid to bring it into a reading range of the standards. Then repeat Steps 2 and 3.

Table 3
Recommended Wavelengths for each Element

Element	Concentration Range in Sample, mg/kg*	λ, nm
Ca	0.04-20	422.673 (or 317.933)
Fe	0.10-20	238.204
K	0.08-20	766.491
Mg	0.08-20	279.553
Na	0.04-20	589.592
Sc	Internal standard	424.683

Calculations

Calculations are normally performed by the computer data reduction software after the analyst enters the appropriate values for the mass of the sample taken, the dilution volume, and the internal standard concentration.

The equivalent manual calculation is shown in Equation 1.

$$\text{Concentration of a specific element in the original sample, mg/kg} = \left(\frac{10 R}{W} \right) \left(\frac{C}{D} \right) \quad (1)$$

where:

- C** = total volume of second dilution, *Spectrometric Procedure*, Step 4, mL, if required
D = volume of diluted sample aliquot taken, *Spectrometric Procedure*, Step 4, mL, if required
 If no second dilution is required, $C/D = 1$
R = concentration of element in diluted sample, from instrument readout, $\mu\text{g/mL}$
W = mass of sample used, *Sample Preparation*, Step 1, g
10 = initial dilution volume, *Sample Preparation*, Step 6, mL

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.

Precision

Precision statements were determined using UOP Method 999.

Repeatability and Site Precision

A nested design was carried out for determining metals in a methanol sample. The sample was analyzed by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of eight analyses. Using a stepwise analysis of variance procedure,

the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table 4. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 4 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 4 with 95% confidence.

Table 4
Repeatability and, Site Precision, mg/kg

<u>Analytes</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within</u> <u>Day esd</u>	<u>Allowable</u> <u>Difference</u>	<u>Within</u> <u>Lab esd</u>	<u>Allowable</u> <u>Difference</u>
Ca	1.32	0.015	0.06	0.041	0.18
Fe	1.02	0.018	0.07	0.018	0.07
K	0.99	0.029	0.11	0.061	0.37
Mg	1.05	0.035	0.14	0.046	0.21
Na	2.33	0.049	0.19	0.073	0.33

The data in Table 4 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

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 approximately 2 hours, depending upon sample preparation. The labor requirement for one analysis is 2 hours. In groups of 5 or more samples, the labor requirement for each analysis is 0.5 hour.

Suggested Suppliers

Ace Glass, Inc., 1430 North West Blvd., Vineland, NJ 08362, USA, 1-856-691-3333,
www.aceglass.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219, USA, 1-412-490-8300,
www.fishersci.com

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA, 1-215-641-2700,
www.mathesontrigas.com

PerkinElmer Analytical Instruments, 710 Bridgeport Ave., Shelton, CT 06484, USA, 1-203-925-4600, www.perkinelmer.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840, USA, 1-732-549-7144,
www.spexcsp.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com

Wilmad-LabGlass, 1002 Harding Hwy., Buena, NJ 08310, USA, 1-856-697-3000, www.wilmad-labglass.com