

ALUMINUM, SILICON AND SILVER IN ACETIC ACID BY ICP-OES

UOP Method 972-01

SCOPE

This method is for determining trace (mass-ppm) concentrations of aluminum, silicon and silver in acetic acid by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The lower limits of detection for aluminum, silicon, and silver are 0.1 mass-ppm, 1 mass-ppm, and 0.01 mass-ppm, respectively. The upper range of determination is approximately 100 mass-ppm. The method is also applicable, but has not been verified, for the determination of other metals.

OUTLINE OF METHOD

The sample is diluted with water and hydrochloric acid and then aspirated into an ICP emission spectrometer that has been calibrated with matrix matched standards.

APPARATUS

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

Balance, readability 0.1-mg

Bottle, narrow mouth, HDPE, Nalgene, 250-mL, Fisher Scientific, Cat. No. 03-313-5B, several required

Cylinders, polypropylene, graduated, Nalgene, 25-, 50-, and 100-mL, Fisher Scientific, Cat. Nos. 08-572B, 572C, and 572D, respectively

Flasks, volumetric, polymethylpentene, Nalgene, 50-, 100-, and 250-mL, Fisher Scientific, Cat. Nos. 10-198-52A, 52C, and 52E, respectively

Flask, volumetric, polypropylene, Nalgene, 200-mL, Fisher Scientific, Cat. No. 10-198-50C

Gloves, polyethylene

Pipetters, automatic, Rainin, EP-2500 and EP-10ML, Rainin Instrument

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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Pipets, Pyrex Brand, volumetric transfer, Class A, 2- and 25-mL, Fisher Scientific, Cat. Nos. 13-651-11A, -11H, respectively

Spectrometer, Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), Perkin-Elmer Optima 3000 DV. Must be equipped with sapphire injector tube.

Water purification system, Barnstead NANOpure II, three module, equipped with Pretreatment (D0835), Ultrapure (D0809) and Organic Free (D0820) replacement cartridges, available from Fisher Scientific, for preparing ASTM D 1193 Type I reagent grade water

REAGENTS AND MATERIALS

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

Acetic acid, Ultrex II, J.T. Baker, Cat. No. 6903-05

Aluminum standard solution, 1,000- $\mu\text{g/mL}$, Spex, Cat. No. PLAL1-2X

Hydrochloric acid, Certified ACS Plus, Fisher Scientific, Cat. No. A144-212

Hydrochloric acid solution, 10-vol%, add 25 mL concentrated hydrochloric acid to a 250-mL volumetric flask. Fill to mark with water, cap, and mix. Transfer to a 250-mL HDPE bottle.

- Normally, acid is added to water. However, with these materials at these volumes, there is no spattering or significant exotherm caused by adding water to acid. Preparation of larger volumes may require different techniques.

Hydrofluoric acid, Reagent ACS, 49%, Fisher Scientific, Cat. No. A147-1LB

Hydrofluoric acid solution, 10-vol%, add 12.5 mL hydrofluoric acid to a 250-mL polymethylpentene volumetric flask. Fill to mark with water, cap, and mix. Transfer to a 250-mL HDPE bottle.

- Normally, acid is added to water. However, with these materials at these volumes, there is no spattering or significant exotherm caused by adding water to acid. Preparation of larger volumes may require different techniques.

Pipet tips, Rainin, RC-2500 and RC-10ML, Rainin Instrument

Silicon standard solution, 1,000- $\mu\text{g/mL}$, Spex, Cat. No. PLSI9-2X

Silver standard solution, 1,000- $\mu\text{g/mL}$, Spex, Cat. No. PLAG2-2X

Yttrium standard solution, 1,000- $\mu\text{g/mL}$, Spex, Cat. No. PLY2-2X

Yttrium standard solution, 100- $\mu\text{g/mL}$, pipet 25 mL of 1,000- $\mu\text{g/mL}$ yttrium standard solution into a 250-mL volumetric flask. Fill to mark with water, cap and mix. Transfer into a 250-mL Nalgene bottle.

Water, 18.3-megohm/cm, Type 1 Reagent Grade, from Water purification system. Use this water wherever water is specified.

PROCEDURE

Preparation of Calibration Standards

Prepare all solutions fresh weekly.

1. To prepare the blank solution.

Using a polypropylene graduated cylinder, add into a 100-mL polymethylpentene flask, 10 mL of concentrated acetic acid and 34 mL of concentrated hydrochloric acid. Using a pipetter, add 1 mL of the 100- $\mu\text{g/mL}$ yttrium standard solution, dilute to volume with water, cap and mix well.

- Yttrium is used as the internal standard.

1. To prepare the standard solution.

Using a polypropylene graduated cylinder, add into a 100-mL polymethylpentene flask 10 mL of concentrated acetic acid and 34 mL of concentrated hydrochloric acid. Using pipettors, add 2 mL of the 1,000- $\mu\text{g/mL}$ aluminum standard solution, 2 mL of the 1,000- $\mu\text{g/mL}$ silver standard solution and 1 mL of the 1,000- $\mu\text{g/mL}$ silicon standard solution. Using a pipetter, add 1 mL of the 100- $\mu\text{g/mL}$ yttrium standard solution. Dilute to volume with water, cap and mix well. The resulting ICP calibration solution will contain 20 $\mu\text{g/mL}$ of aluminum and silver, 10 $\mu\text{g/mL}$ silicon and 1.0 $\mu\text{g/mL}$ yttrium.

For samples with metal contents known to be low, a standard solution with lower levels of analytes should be prepared.

2. To prepare the rinse solution.

Prepare a rinse solution analogous to the blank, but do not add an internal standard. Using a graduated cylinder, add to a 200-mL polypropylene flask, 20 mL acetic acid, 68 mL hydrochloric acid and dilute to volume with water. Cap, mix and transfer into a 250-mL HDPE bottle.

Sample Preparation

Place an uncapped 50-mL polymethylpentene flask on an analytical balance and tare. Using a pipetter add 5 mL of the acetic acid sample to the flask and record the weight the sample. Add 17 mL of hydrochloric acid and, using a pipetter, add 0.5 mL of the 100- $\mu\text{g/mL}$ yttrium standard solution. Dilute to volume with water, cap and mix.

- The addition of hydrochloric acid ensures that any silver present in the sample stays in solution.

Sample Analysis

Set up the ICP spectrometer according to the instrument manufacturer's guidelines, allowing the system to equilibrate for at least 30 minutes after the plasma is ignited prior to starting the analysis. Table 1 lists the recommended wavelengths for each element. Other wavelengths may be used if it can be shown that the precision is not affected. Use of a corrosion resistant and silicon free sample introduction system is required. To achieve the desired detection limits, axial view is to be used.

1. Clean the sample transport system prior to calibration and between samples. Silicon has a memory in ICP and the instrument must be prepared by aspirating the hydrofluoric acid solution for 15 min. followed by the hydrochloric acid solution for 15 min.
2. Aspirate the rinse solution and monitor the intensities for the elements of interest; a flat response is desired.
3. Standardize the instrument by aspirating the blank, followed by the standard. Allow sufficient wash-out time between aspirations.
4. Run the blank as a sample to ensure the wash-out brings the baseline to zero for the elements of interest.
 - Silicon is harder to rinse out than the other elements.
5. Analyze the samples allowing sufficient wash-out time between aspirations.
6. Check the calibration and baseline stability after every 3-5 samples by aspirating the calibration standard solution and the blank.
 - Any calibration checks and the final standard readings should return the concentrations of the elements in the standard within $\pm 5\%$ relative. If not, recalibrate and re-aspirate the samples.

Table 1

**Elements Sought, Recommended Wavelengths
and Recommended Standard Concentrations**

<u>Element</u>	<u>Wavelength, nm</u>	<u>Concentration, $\mu\text{g/mL}$</u>
Al	396.134	20.0
Ag	328.053	20.0
Si	252.600	10.0
Y	371.023	1.0

CALCULATIONS

All calculations are performed by the instrument software and the results are displayed and printed in mass-% or ppm ($\mu\text{g/g}$).

NOTE

Samples should be taken in plastic bottles. Aluminum and silicon will be leached from glass. In addition, it is good practice to analyze trace metal containing samples as rapidly as possible as the metals may be lost from solution by adsorption on the container.

PRECISION

Precision statements were determined using UOP Method 999.

ASTM and UOP Repeatability

A nested design was carried out for determining aluminum, silver, and silicon in acetic acid with two analysts in one laboratory. Each analyst carried out tests on four separate days, performing four tests each day. The total number of tests for each element was 32. The precision data are summarized in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable difference with 95% confidence.

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

Reproducibility

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

Table 2
ASTM and UOP Repeatability, mass-ppm

Element	Mean Conc.	ASTM Repeatability		UOP Repeatability	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference
Al	3.85	0.067	0.22	0.26	0.9
Ag	1.00	0.011	0.03	0.049	0.17
Si	4.77	0.36	1.2	0.78	2.5

TIME FOR ANALYSIS

The elapsed time for one analysis is 0.5 hours. The labor requirement is 0.5 hours. Multiple samples can be run at the rate of four samples per hour.

REFERENCE

ASTM Method D 1193, www.astm.org
UOP Method 999, "Precision Statements in UOP Methods,"

SUGGESTED SUPPLIERS

J. T. Baker, 222 Red School Lane, Phillipsburg, NJ 08865 (908-859-2151) www.mallchem.com
Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300) www.fishersci.com
Perkin-Elmer Inc., 761 Main Ave., Norwalk, CT 06859-0001 (203-762-4003) www.perkinelmer.com
Rainin Instrument Co., Inc., 5400 Hollis Street, Emeryville, CA 94608-9880 (781-935-3050)
www.rainin.com
Spex Certiprep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.com