

POTASSIUM IN CATALYSTS BY ATOMIC ABSORPTION

UOP Method 878-87

SCOPE

This method is for determining potassium in fresh and used silica and non-silica containing catalysts by Atomic Absorption Spectrophotometry (AAS). The method is suitable for potassium determination over a range of 5 parts per million to several mass-percent.

OUTLINE OF METHOD

Silica-containing samples are treated with sulfuric and hydrofluoric acids until they are dissolved, while non-silica samples are treated with sulfuric acid. The sample solution is aspirated into the flame of the AAS unit and the response is compared spectrophotometrically to matrix-matched standard solutions. Sample results are reported on an as-received or volatile-free basis.

APPARATUS

Atomic absorption spectrophotometer, having direct readout (or recorder output) proportional to absorbance units, background corrector accessory and equipped with either a 100-mm triple slot or single slot burner head fabricated especially for use with an air-acetylene flame

Balance, readability 0.1-mg

Beaker, 250-mL, borosilicate glass, heat resistant type, or equivalent

Beaker, 250-mL, Teflon, Sargent-Welch Scientific, Cat. No. S-4694-E, or equivalent

Compressor, air, delivery of 50 L/min at 4.2 kg/cm² (1.8 cfm at 60 psi), Perkin-Elmer, Cat. No. 0303-0313, or equivalent

Cylinder, graduated, polypropylene, 10-mL, Sargent-Welch Scientific, Cat. No. S-24631-B, or equivalent

Flasks, volumetric, glass, 100-, 200-, 500- and 1000-mL, several of each required

Funnel, disposable, 55-mm diameter, Fisher Scientific, Cat. No. 16-320P, or equivalent

Gloves, polyethylene

Hollow cathode lamp, potassium

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).

Hot plate, adjustable heat

Mill, mixer, impact grinder and blender, Mixer/Mill, SPEX Industries, Inc., Cat. No. 8000, or equivalent

Pipets, total volume, Class A, 5-, 10-, 15-, 20- and 25-mL, several of each required

Pipetter, bottle-type, adjustable volume, Nalgene, 25-mL dispensing volume, Fisher Scientific, Cat. No. 13-683-55, or equivalent

Regulator, acetylene, two-stage, Perkin-Elmer, Cat. No. 303-0106, or equivalent

Regulator, air, two-stage, high purity, Matheson, Model 3104-590, or equivalent

Vial set, for mixer mill, tungsten carbide, SPEX Industries, Inc., Cat. No. 8004, or equivalent

Watch glass, borosilicate glass, 90-mm diameter

Watch glass, Teflon, 75-mm diameter

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 water mean deionized or distilled water.

Acetylene, cylinder, compressed gas, 99.6% minimum purity, Matheson, or equivalent

Air, compressed, filtered and dried, minimum of 414 kPa (60 psig) to AAS instrument

Aluminum chloride, 6-hydrate, 99.9% minimum purity, Sargent-Welch Scientific, Cat. No. SC-10537, or equivalent

Aluminum solution, 10,000- $\mu\text{g/mL}$. Dissolve 89.5 ± 0.01 g of aluminum chloride in water. Transfer to a one-liter volumetric flask and dilute to mark.

Hydrofluoric acid, 48%

Nitric acid, concentrated

Potassium chloride, 99.999% purity, SPEX Industries, Inc., Cat. No. K45, or equivalent

Potassium stock solution, 1000- $\mu\text{g/mL}$. Dissolve $1.9067 \text{ g} \pm 0.1 \text{ mg}$ of potassium chloride in water, add 10-mL of hydrochloric acid, transfer to a one-liter volumetric flask and dilute to mark.

Sodium chloride, 99.97% minimum purity, Sargent-Welch Scientific, Cat. No. SC-14765, or equivalent

Sodium solution, 10,000- $\mu\text{g/mL}$. Dissolve 25.42 ± 0.01 g of sodium chloride in water, transfer to a one-liter volumetric flask and dilute to the mark.

Sulfuric acid, concentrated

PROCEDURE

Preparation of Calibration Standards

Make a fresh 10- $\mu\text{g}/\text{mL}$ potassium standard as follows: Pipet 10 mL of 1000- $\mu\text{g}/\text{mL}$ potassium stock solution into a one-liter volumetric flask and fill to volume with water.

To prepare 0.5-, 1.0-, 1.5-, 2.0- and 2.5- $\mu\text{g}/\text{mL}$ potassium standards, pipet 5-, 10-, 15-, 20- and 25-mL aliquots of the 10- $\mu\text{g}/\text{mL}$ potassium standard solution into each of five 100-mL volumetric flasks, respectively. Do not add the standard solution to a sixth flask, which will be used as a blank. To each flask add 5 mL of concentrated sulfuric acid, 10 mL of 10,000- $\mu\text{g}/\text{mL}$ aluminum solution and 10 mL of 10,000- $\mu\text{g}/\text{mL}$ sodium solution. Cool the flasks and fill to volume with water.

Sample Preparation

Silica Containing Catalysts

Grind the sample in a mixer mill to a consistency of approximately 80 mesh or finer. Weigh to the nearest 0.1 mg approximately 1.0 g of the ground sample into a 250-mL Teflon beaker. If the potassium is to be reported on a volatile-free basis, obtain an LOI by UOP 275 at the same time the sample is weighed for the potassium determination. Add 10 mL of water and 10 mL of concentrated sulfuric acid to the beaker. Slowly add 10 mL of hydrofluoric acid from a polypropylene graduated cylinder, swirl to mix the contents of the beaker, and place the uncovered beaker on a 150 C hot plate. Heat until white fumes of sulfuric acid appear. Remove the beaker from the hot plate and allow it to cool. Check to see if the contents are dark-colored from organics or carbon that may have been in the sample. If dark, add a few drops of concentrated nitric acid and place the beaker back on the hot plate until white fumes again are evolved and the solution is no longer dark. Remove the beaker from the hot plate, allow it to cool and add approximately 40 mL of water to the sample with a graduated cylinder. Cover the beaker with a Teflon watch glass and return it to the hot plate. Let the sample boil until the solution is clear. Quantitatively transfer the contents of the beaker to a 200-mL volumetric flask.

Add 20 mL of 10,000- $\mu\text{g}/\text{mL}$ sodium solution, allow to cool and fill to the mark with water. If the potassium concentration in the sample solution is higher than the standards, dilute it with water and add 10 mL of 10,000- $\mu\text{g}/\text{mL}$ aluminum solution, 10 mL of 10,000- $\mu\text{g}/\text{mL}$ sodium solution and 5 mL of concentrated sulfuric acid per 100 mL.

Non-Silica Containing Catalysts

Grind the sample in a mixer mill to a consistency of approximately 80 mesh or finer. Weigh to the nearest 0.1 mg approximately 1.0 g of sample into a 250-mL borosilicate glass beaker. If the potassium is to be reported on a volatile-free basis, obtain an LOI by UOP 275 at the same time the sample is weighed for the potassium determination. Add 10 mL of water and 10 mL of sulfuric acid. Swirl to mix contents and cover with a watch glass. Place the beaker on a 150 C hot plate and heat until the sample dissolves. Add water if white sulfuric acid fumes evolve before the solids are totally dissolved. When the sample has dissolved, remove the beaker from the hot plate and allow it to cool. Add approximately 40 mL of water to the beaker and return it to the hot plate. Boil until all crystals have dissolved. Remove the beaker from the hot plate and allow it to cool. Quantitatively transfer the contents to a 200-mL volumetric flask. Add 20 mL of 10,000- $\mu\text{g}/\text{mL}$ sodium solution, allow to cool and fill to the mark with water. If the potassium concentration in the sample solution is higher than the standards, dilute it with water and add 10 mL of 10,000- $\mu\text{g}/\text{mL}$ aluminum solution, 10 mL of 10,000- $\mu\text{g}/\text{mL}$ sodium solution and 5 mL of concentrated sulfuric acid per 100 mL.

Potassium Determination

Operating Parameters for AAS Instrument

Potassium wavelength	766.5 nm
Slit setting	1.4 nm
Flame type	Air-acetylene (100-mm burner head, single or triple slot)
Filter	Red (required for some instruments)

Light the flame and allow it to stabilize for about 5 minutes. Using a 2.5- $\mu\text{g/mL}$ potassium standard, adjust the flame position and aspiration to give maximum response. The 2.5- $\mu\text{g/mL}$ potassium standard with aluminum and sodium will typically produce an absorbance of approximately 0.27 absorbance units (45% absorption).

Read solution absorbencies in the following order: blank, standards, samples and then read a standard again. Three standards are typically used, which are chosen to most closely bracket the concentrations of the samples. The final standard reading should compare to the first reading to within 3%. If not, reread the series.

If the potassium concentration in a sample is higher than the 2.5 $\mu\text{g/mL}$ standard, make appropriate dilutions to reduce the concentration, see **Sample Preparation**.

CALCULATIONS

Calculate the concentration of potassium in the sample, as received, as follows:

$$\text{Potassium, mass-\%} = \frac{200 \frac{F}{E} C}{10^4 M}$$

where:

C = concentration of potassium in the solution as determined by the instrument, $\mu\text{g/mL}$

E = aliquot taken from 200-mL volumetric flask, mL

F = volume of aspirating solution after dilution, mL

M = sample mass, g

10^4 = conversion factor to mass-%

200 = volumetric flask initial volume, mL

Calculate the concentration of potassium in the sample on a volatile-free (VF) basis, as follows:

$$\text{Potassium (VF), mass-\%} = 100 \frac{K}{100 - L}$$

where:

K = potassium concentration, calculated as above, mass-%

L = loss on ignition (LOI) at 900 C as determined by UOP Method 275, mass-%

PRECISION

The estimated standard deviation (esd) based on the indicated replicates is shown in the following table. Duplicate results by the same operator should not differ by more than the amounts shown in the "Allowable Difference" column (95% probability).

Number of Replicates	Potassium Content, mass-%	esd, mass-%	Allowable Difference, mass-%
6	0.030	0.0003	0.0012
6	10.6	0.10	0.36

TIME FOR ANALYSIS

The elapsed time for one analysis of catalyst with silica is 3.0 hours and for non-silica, 2.5 hours. The labor requirement is 1.5 hours for each.

REFERENCE

UOP Method 275

SUGGESTED SUPPLIERS

Fisher Scientific Company, 711 Forbes Ave., Pittsburgh, PA 15219
 Matheson, P.O. Box 96, Joliet, IL 60434
 Perkin-Elmer Corp., Instrument Div., Main Ave., Norwalk, CT 06856
 Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077
 SPEX Industries, Inc., P.O. Box 798, Metuchen, NJ 08840