

MOLYBDENUM IN PLATFORMING CATALYSTS AND FINES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

UOP Method 833-82

SCOPE

This method is for determining molybdenum in fresh or used alumina Platforming[®] catalysts and catalyst fines by Atomic Absorption Spectrophotometry (AAS). The method is suitable for molybdenum determination over a range of about 5 parts per million to several percent. It is specifically intended for use in conjunction with UOP Methods 274 and 823 for determining molybdenum in samples that have been ignited at 900 C. It should not be used for any other purpose.

OUTLINE OF METHOD

A ground 900 C ignited sample is treated with sulfuric and hydrochloric acid until all the alumina is dissolved. The sample solution is aspirated into the flame of the AAS unit and the response is compared spectrophotometrically to standard solutions of known metal content and concentrations of reagents matching the sample solutions.

APPARATUS

Atomic absorption spectrophotometer, capable of measuring radiation over the wavelength range of 200 to 800 nm. The instrument must have the basic capability of measuring low level signals corresponding to approximately 1% absorption or 0.004 absorbance units. Equip the instrument with a 5-cm single slot burner head especially fabricated for use with a nitrous oxide-acetylene flame.

Balance, capable of weighing to 0.1 mg

Beakers, 250- and 400-mL, Pyrex, heat resistant type, or equivalent

Beaker covers, 90- and 125-mm diameter, glass

Crucible, high form, porcelain, Coors Size No. 00, Sargent-Welch Scientific Co., Cat. No. S-23685 D, or equivalent

Desiccator, aluminum, 115-mm ID, Sargent-Welch Scientific Co., Cat. No. S-25140A, or equivalent

Filter Paper, Whatman No. 42, or equivalent

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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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The 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.

Flasks, Volumetric, 100-, 500- and 1000-mL, several of each required

Furnace, electric, muffle, 900 ± 25 C

Hammer mill, laboratory type, with screen having perforations of 0.61-mm (0.024-inch), Sargent-Welch Scientific Co., Cat. No. S-60870, or equivalent

Hollow cathode lamp, molybdenum

Hood, fume, an area from which evolved smoke and acid fumes may be safely exhausted

Hot plate

Pipets, total volume, 5-, 10-, 15-, 20- and 50-mL, class A type, several of each required

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. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit use without reducing the accuracy of the determination. References to water mean deionized.

Acetylene, cylinder, compressed gas, regular welders grade or equivalent. The recommended size is 1A, 8.5 m^3 , (300 cu ft), equipped with a C_2H_2 regulator, Perkin-Elmer Corp., Cat. No. 303-0106, or equivalent, and flash arrestors, Matheson series 6103, for safety.

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

Alumina catalyst base

Ammonium hydroxide, concentrated

Hydrochloric acid, concentrated

Hydrogen peroxide, 30%

Molybdenum trioxide, powder, 99.99% purity, Spex Industries, Inc., or equivalent

Molybdenum solution, 1000 $\mu\text{g/mL}$. Weigh 1.5003 g of MoO_3 into a 250-mL beaker and add 100 mL of a 1:1 mixture of NH_4OH and water. Stir to dissolve, heat slightly if needed. Transfer to a one-liter volumetric flask and dilute to mark with water.

Molybdenum solution, 500 $\mu\text{g/mL}$. Pipet 50-mL of 1000 $\mu\text{g/mL}$ solution into a 100-mL volumetric flask and dilute to the mark with water.

Nitric acid, concentrated

Nitrous oxide, cylinder, size No. 1, 14.7 m^3 , (520 cu ft) equipped with a 2-stage heated regulator, Perkin-Elmer Corp., Cat. No. 303-0204, or equivalent

Sulfuric acid, concentrated

READING STANDARDS

The molybdenum determination by AAS is very sensitive to the presence of aluminum. For this reason, the aluminum content must be closely matched.

Matrix Stock Solution, 20,000 $\mu\text{g Al}_2\text{O}_3/\text{mL}$

Into a 400-mL beaker add 10 g of alumina catalyst base and 100 mL of a (1:1) mixture of concentrated sulfuric acid and water. Cover the beaker with a beaker cover and heat at low boiling until the alumina has dissolved and the solution is clear. Allow to cool and cautiously add 100 mL of water while swirling the beaker. Transfer contents of the beaker to a 500-mL volumetric flask and add 50 mL of concentrated hydrochloric acid. Allow to cool and dilute to the mark.

Preparation of Standards

Prepare a 50 $\mu\text{g/mL}$ molybdenum solution as follows: Pipet 50 mL of the 500 $\mu\text{g/mL}$ molybdenum solution (see *REAGENTS AND MATERIALS*) into a 500-mL volumetric flask and dilute to the mark with water. Make 2.5, 5.0, 7.5 and 10.0 $\mu\text{g/mL}$ molybdenum standards as follows:

Pipet 5-, 10-, 15- and 20-mL aliquots of the 50 $\mu\text{g/mL}$ molybdenum solution into each of four 100-mL flasks, respectively. Pipet 50-mL aliquots of the matrix stock solution into each of the four flasks and dilute to the mark with water.

PROCEDURE

Sample Preparation

Fresh and Used Catalyst

Grind the sample in the hammer mill to a consistency of 80 mesh or finer. Weigh to the nearest 0.1 mg about 1.0 g of the ground sample into a tared Coors crucible. Determine the mass of the catalyst after ignition at 900 C (See UOP Method 275). After obtaining this mass, quantitatively transfer the ignited catalyst, using caution to prevent loss from dusting, to a 250-mL beaker. Rinse any sample remaining in the crucible into the beaker, using a minimum amount of water. Add 10 mL of water and 5 mL of concentrated sulfuric acid. Cover the beaker, place it on a hot plate and heat the mixture until the alumina has dissolved. Remove the beaker from the hot plate and allow to cool. Add 10 mL of water and 5 mL of concentrated hydrochloric acid. Mix by swirling and heat. Add 30% hydrogen peroxide dropwise until platinum has dissolved. Boil to dispel excess hydrogen peroxide.

Remove the beaker from the hot plate and allow the solution to cool until it can be manipulated by hand. If insoluble residue remains, filter the solution through Whatman 42 filter paper and collect the filtrate in a 100-mL volumetric flask. Dilute to the mark.

Extraneous Materials

Grind the sample in the hammer mill to a consistency of 80 mesh or finer. Weigh 1.0 g of sample to the nearest 0.1 mg into a tared Coors porcelain crucible and ignite to constant mass at 900 C in a muffle furnace. Determine the mass of the catalyst after ignition. Quantitatively transfer the ignited catalyst, using caution to prevent loss from dusting, to a 250-mL beaker. Rinse any sample remaining in the crucible into the beaker, using a minimum amount of water.

Add about 5 mL of water and 5 mL of concentrated sulfuric acid to the beaker. Cover the beaker with a beaker cover. Add approximately 3 mL of concentrated nitric acid and 6 mL of concentrated hydrochloric acid to the contents of the beaker and allow the mixture to digest at room temperature for approximately 30

minutes (a slight warming on the hot plate may be necessary to start the digestion reaction). Place the beaker on the hot plate and evaporate the contents to sulfuric acid fumes. Remove the beaker from the hot plate and allow it to cool. Add 25 mL of water, 5 mL of concentrated hydrochloric acid and six drops of 30% hydrogen peroxide to the beaker. Boil until all of the hydrogen peroxide has been dispelled which is indicated by a slow steady boiling. Allow the solution to cool until the beaker can be manipulated by hand. If insoluble residue remains, filter through Whatman 42 filter paper and collect the filtrate in a 100-mL volumetric flask. Allow to cool and dilute to the mark with water.

Molybdenum Determination

Operating Parameters for AAS Instrument

Molybdenum wavelength	313.3 nm
Slit Setting	0.7 nm
Flame type	Nitrous oxide-acetylene flame (5-cm burner head) reducing (rich, red)

Using the 10 $\mu\text{g/mL}$ molybdenum standard, adjust the flame position and aspiration to give maximum response. The 10 $\mu\text{g/mL}$ molybdenum standard with aluminum will typically produce an absorbance reading of about 0.19 absorbance units (about 35% absorption).

Sample Readings

Aspirate the sample into the AAS unit and compare the absorbance obtained to the absorbances of the molybdenum standards. If a calibration curve is not used, compare the absorbance of the sample to that of the closest standard. If the sample reads higher than the 10 $\mu\text{g/mL}$ molybdenum standard, make appropriate dilutions to bring it into reading range. Add alumina matrix solution to the diluted sample to match the alumina and acidity in the standards.

CALCULATIONS

Calculate the concentration of molybdenum in the 900 C ignited sample as follows:

$$\text{Mo, mass-\%} = \frac{\left(\frac{A_s - B}{A_{\text{std}} - B} \right) C_{\text{std}} \frac{F}{E}}{W 10^2}$$

where:

- A_s** = absorbance of sample
- A_{std}** = absorbance of standard
- B** = absorbance of blank
- C_{std}** = concentration of standard, $\mu\text{g/mL}$
- E** = aliquot taken from 100-mL volumetric flask, mL
- F** = volume of aspirating solution after dilution, mL
- W** = sample mass, g

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 be considered suspect unless they differ by more than the amounts shown in the "Allowable Difference" column (95% probability).

Number of Replicates	Molybdenum Content, mass-%	esd, mass-%	Allowable Difference, mass-%
6	0.21	0.0033	0.012
6	0.51	0.0093	0.034

TIME FOR ANALYSIS

The elapsed time for one analysis of fresh or used catalyst is 2.5 hours, and for extraneous material 3.0 hours. The labor requirement is 1.5 and 2.0 hours, respectively.

REFERENCE

UOP Method 275

SUGGESTED SUPPLIERS

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