

MERCURY IN CATALYSTS BY GF-AAS

UOP Method 894-91

SCOPE

This method is for determining mercury in alumina or silica-alumina supported catalysts by Graphite Furnace-Atomic Absorption Spectroscopy (GF-AAS). The detection range is from one to several hundred mass-ppm. The method is applicable where Cold Vapor Atomic Absorption Spectroscopy cannot be used due to interference from aluminum and platinum group metals.

OUTLINE

The mercury is extracted from the catalyst with aqua regia and treated with hydrogen peroxide. The extract is introduced into the furnace of the GF-AAS unit and quantitation is achieved by comparison of the sample absorbance to the absorbances of prepared standards. The concentration of mercury in the original sample is calculated on an as-received basis.

APPARATUS

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

Atomic absorption spectrophotometer, computer controlled or equipped with a recorder output proportional to absorbance units, a graphite furnace accessory, Deuterium or Zeeman background correction accessory, and an automatic sampling system with 20- μ L capacity

Balance, readability 0.1-mg

Balance, top loading, readability 0.01-g

Beaker, borosilicate glass, 100-mL

Flasks, glass, volumetric, Class A, 10-, 50- and 100-mL

Centrifuge, general purpose, 9,000 rpm, with 4-place rotor, buckets and adapters for 50-mL conical tubes, Fisher Scientific, Cat. Nos. 04-977-6K, 04-976-4100, 04-975-100RND (2 required) and 04-974-100C (2 required), respectively

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.

Centrifuge tube, borosilicate glass, with PTFE stopper, 50-mL, Fisher Scientific, Cat. No. 05-538-40B

Calculator, electronic, capable of least squares analysis, Sharp EL-52-T available from Elek-Tek

Cylinder, graduated, glass, 100-mL

Funnel, disposable, polypropylene, 65-mm diameter, Fisher Scientific, Cat. No. 10-320A

Hot plate, stirring, variable surface temperature of 25 to 350°C

Mercury lamp, electrodeless discharge lamp (EDL), Perkin Elmer, Cat. No. 0303-6244

Pipet, Eppendorf, 20- μ L capacity, Fisher Scientific, Cat. No. 21-278-8

Pipet, volumetric, glass, Class A, 25-mL

Pipet, Mohr, one-milliliter

Pipet tips, 20- μ L, for Eppendorf pipet, Fisher Scientific, Cat. No. 21-371-1

Stirring bar, Teflon coated, 25-mm, Fisher Scientific, Cat. No. 14-511-63

Thermometer, digital pyrometer, with hand held surface probe, Fisher Scientific, Cat. Nos. 13-904-50 and 13-904-50D, respectively

Watch glass, 65-mm diameter, borosilicate glass

REAGENTS AND MATERIALS

Unless otherwise specified, all reagents and materials shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available. References to water mean deionized or distilled.

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Aqua regia, 80%. Using a graduated cylinder, add 60 mL of concentrated hydrochloric acid and 20 mL of concentrated nitric acid to a 100-mL volumetric flask in a fume hood. Bring the solution to volume with water. Mix thoroughly by pouring the contents into the graduated cylinder and then back into the volumetric flask. Store loosely capped to avoid pressure build up.

Argon, minimum purity 99.996%

Hydrogen peroxide, 30%, Baker Ultrex, J. T. Baker, Cat. No. 5107-01

Hydrochloric acid, pure, Baker “Instra-analyzed Reagent”, J. T. Baker, Cat. No. 9530-33

Mercury standard, 1000 μ g/mL, Inorganic Ventures

Nitric acid, ultrapure, Baker Ultrex II, J. T. Baker, Cat. No. 6901-05

UOP R-9[®] support, UOP

PROCEDURE

Extraction of Mercury from Catalyst Samples

1. Weigh approximately 2.0 g, to the nearest 0.1 mg, of the alumina or silica/alumina catalyst sample into a 100-mL beaker.
2. Weigh approximately 2.0 g, to the nearest 0.1 mg, of R-9 support into a second 100-mL beaker.
 - This is used as the blank for either alumina or silica/alumina catalyst samples.
3. Use a graduated cylinder to add 40 mL of 80% aqua regia to both the sample and blank. Add stirring bars and cover the beakers with watch glasses.
 - Care must be exercised in handling aqua regia.
4. Place the covered beakers on stirring hot plates. Stir at a moderate rate and heat the mixture at a surface hot plate temperature of $90 \pm 5^{\circ}\text{C}$ for one hour.
5. Remove the beakers from the hot plates and allow them to cool to ambient temperature.
6. Decant the supernatant liquid from each beaker into separate, tared centrifuge tubes. Rinse the beakers with one to two milliliters of water and transfer the rinsings into the centrifuge tubes while minimizing the transfer of solids. Cap the tubes.
7. Determine the mass of the centrifuge tubes containing the sample and the blank, and adjust the mass of the lighter tube to that of the heavier by adding water.
 - The mass of the centrifuge tubes should be approximately the same so they are balanced during spinning.
8. Centrifuge the tubes at 9,000 rpm for 30 minutes.
9. Transfer the clear supernatant solution from each tube into 100-mL volumetric flasks.
10. Add 10 mL of concentrated hydrochloric acid to each flask.
11. Allow the solutions to cool to ambient temperature and make up to volume with water. Cap and invert several times to thoroughly mix the contents.

Preparation of Standard and Sample Solutions

1. Pipet 25 mL of 1000- $\mu\text{g/mL}$ mercury standard into a 50-mL volumetric flask and dilute to volume with water. Cap the flask and invert several times to thoroughly mix the contents.
 - This intermediate standard contains 500- $\mu\text{g/mL}$ mercury.
2. Pipet 25 mL of 500- $\mu\text{g/mL}$ standard solution and 25 mL of the 1000- $\mu\text{g/mL}$ standard solution into separate 100-mL volumetric flasks. Bring to volume with water, cap and invert several times to mix thoroughly.
 - These intermediate standards contain 125- and 250- $\mu\text{g/mL}$ of mercury.
3. Pipet 20 μL of each of the three mercury intermediate standards into separate 10-mL volumetric flasks. Bring to volume with the blank solution prepared under *Extraction of Mercury from Catalyst Samples*. Cap and invert several times to mix thoroughly.

- These working standards contain 0.25-, 0.50- and 1.00- $\mu\text{g/mL}$ mercury, respectively.
4. Fill two separate 10-mL volumetric flasks to the mark with the prepared sample and blank solution, respectively.
 5. Add 0.2 mL, by pipet, of 30% hydrogen peroxide to the blank, each of the three working standards, and to the sample solution.
 6. Carefully mix the solutions by capping and inverting. Vent any released gases.
 - The gases released must be vented carefully to avoid loss of solution.

Analysis by GF-AAS

1. Set the instrument according to the manufacturer's recommendation, using the settings in the following Table.

Table 1

Wavelength	253.6 nm
Slit	0.7 nm
Tube type	standard
Dry temperature	150°C
Drying time, sec	20
Char temperature	150°C
Charring time, sec	20
Atomizing temperature	1200°C
Atomizing time, sec	7
Background correction	on
Furnace sample size	20 μL
Argon purge gas	on
Argon flow rate	30 mL/min
Gas interrupt	on
Recorder speed	20 mm/min
Recorder chart expansion	X1

2. Fill the autosampler cups with sample, blank and the three working standard solutions prepared in Steps 3 through 6 under *Preparation of Standard and Sample Solutions*.
3. Determine the mercury absorbance for each solution by running the blank and the calibration standards followed by the samples.
 - A 2500°C cycle of the furnace must be performed between injections to clean the furnace tube. On older instruments this must be done manually; on newer instruments it can be programmed.
4. Verify the instrument stability by repeating one standard.
 - If the value does not agree within 5% of the initial reading, repeat the determination starting with Step 2.
 - If the absorbance due to the mercury concentration in any sample exceeds the absorbance of the highest standard, make appropriate volumetric dilutions of the sample to bring it within range of the standards. The blank must also be diluted by the same amount, and new standards prepared using the diluted blank in a manner similar to that described in Step 3 under *Preparation of Standard and Sample Solutions*. Then proceed with Steps 4 through 6 of that section, substituting the diluted sample and diluted blank for the original sample and blank. Complete the analysis by following Steps 1 through 4 of this section.

CALCULATIONS

1. Calculate a least squares fit of the standard concentrations, in $\mu\text{g/mL}$, and absorbances, in peak height, for mercury. Perform the least squares fit on a calculator capable of performing a least squares linear regression.
 - Newer AAS units may be able to perform this calculation automatically.
2. Check the linearity of the standard absorbance vs. concentration plot by determining the correlation coefficient, Q .
 - If the value of Q is 0.999 or higher, proceed with the calculations.
 - If the value of Q is less than 0.999, one or more of the absorbances is outside the linear range and the calibration standards must be remade and the analysis repeated.
 - In no case can one of the standards be dropped to perform the linear regression using only two standards.
3. Calculate the $\mu\text{g/mL}$ concentration (C) of mercury in the sample solution by substitution of the sample absorbance, in peak height, into the equation for the best straight line. If a dilution of the sample solution was required, multiply the value determined in Step 3 by the dilution factor to obtain the dilution corrected value of C for use in the equation below.
4. Calculate the concentration of mercury in the as-received catalyst to the nearest mass-ppm using the following equation:

$$M = \frac{100 C}{W}$$

where:

C = concentration of mercury in sample solution, $\mu\text{g/mL}$, from Step 3 above

M = mass-ppm of the mercury in the sample, $\mu\text{g/g}$

W = mass of the catalyst extracted, g

100 = volume of solution, mL

PRECISION

Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests) in one laboratory, the within-laboratory estimated standard deviations (esd) on two synthetic samples were calculated at the mercury concentrations shown in Table 2. Two tests performed in the one laboratory by different analysts on different days should not differ by more than the allowable differences shown (95% probability).

Table 2

Mercury, mass-ppm	Catalyst Support	Within-Lab esd, mass-ppm	Allowable Difference, mass-ppm
42	silica-alumina	1.6	5
37	alumina	0.9	3

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 six hours. The labor requirement is four hours.

SUGGESTED SUPPLIERS

J.T. Baker Chemical Co., 222 Redschool Ln., Phillipsburgh, NJ 08865

Elek-Tek, 6557 Lincoln Ave., Chicago IL 60645

Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219

Inorganic Ventures, Inc. 195 Lehigh Ave., Lakewood, NJ 08701

Perkin Elmer Corp., Instrument Div., 761 Main Ave., Norwalk, CT 06859-0177

UOP, Monirex Systems, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017