Standard Test Method for Palladium in Molecular Sieve Catalyst by Atomic Absorption[1]

This standard is issued under the fixed designation D5153; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of palladium in molecular sieve-containing fresh catalysts with about 0.5 weight % of palladium.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E456 Terminology Relating to Quality and Statistics

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

D7442 Practice for Sample Preparation of Fluid Catalytic Cracking Catalysts and Zeolites for Elemental Analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy

2.2 *U.S. Federal Specification:*

Federal Spec. NNN-P-395C Tolerance for Class A Pipets[3]

3. Summary of Test Method

3.1 The test sample is treated with a mixture of sulfuric and hydrofluoric acids. Upon dissolution, the excess hydrofluoric acid is expelled. Aqua regia and lanthanum chloride are added and the solution is diluted to a specific volume. Palladium concentration is determined by atomic absorption spectrophotometry. Absorbance of the samples is bracketed using a set of narrow range, matrix matched standards. A second sample, taken at the same time as the analysis sample, is used to determine loss on ignition.

4. Significance and Use

4.1 This test method provides a means of determining the palladium content in fresh catalysts containing molecular sieves.

4.2 This test method is not intended to cover samples containing precious metals other than palladium.

5. Apparatus

5.1 *Analytical Balance,* capable of weighing to nearest 0.1 mg.

5.2 *Atomic Absorption Spectrophotometer.*

5.3 *Beakers,* TFE-fluorocarbon, 100-mL.

5.4 *Crucibles,* porcelain, 10-mL.

5.5 *Crucible Cover,* porcelain, for 10-mL crucible.

5.6 *Desiccator.*

5.7 *Flasks,* Erlenmeyer, 2000-mL.

5.8 *Graduated Cylinders,* glass, 5-mL, 10-mL, 25-mL, 50-mL, 250-mL, 500-mL, 1000-mL.

5.9 *Graduated Cylinder,* plastic, 10-mL.

5.10 *Hot Plate.*

5.11 *Muffle Furnace,* electrically heated, capable of 1000°C.

5.12 *Pipets,* 4-mL, 6-mL, 8-mL, 10-mL.

5.13 *Volumetric Flasks,* 100-mL, 500-mL.

5.14 *Watch Glasses,* TFE-fluorocarbon, for 100-mL beaker.

5.15 *Weighing Papers.*

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

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[1] This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.03 on Chemical Composition.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from Standardization Documents Order Desk, DODSSP, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111-5098.

all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Specification D1193.

6.3 *Hydrochloric Acid,* concentrated, 36.5–38.0 wt. % or 12 M, sp gr 1.18.

6.4 *Hydrofluoric Acid,* concentrated, 48.0–51.0 wt. % or 28.9 M, sp gr 1.17.

NOTE 1—Refer to Section 8 of Practice D7442-08 for hazards associated with handling of acids.

6.5 *Nitric Acid,* concentrated, 69.0–71.0 wt. % or 15.7 M, sp gr 1.41.

6.6 *Sulfuric Acid,* concentrated, 95.0–98.0 wt. % or 18 M, sp gr 1.84.

6.7 *Aluminum Oxide* (Al_2O_3).

6.8 *Lanthanum Chloride* ($LaCl_3 \cdot 7H_2O$).

6.9 *Palladium Wire,* 99.99 %.

6.10 *Aqua Regia*—Mix three parts by volume of concentrated hydrochloric acid (12 M) and one part by volume of concentrated nitric acid (15.7 M) immediately before use.

6.11 *Sulfuric Acid,* 15.8–16.3 wt. % or 3M. Cautiously add 250 mL of concentrated sulfuric acid (18 M) to 1250 mL of water—mix well and allow to cool.

6.12 *Palladium Standard Solution,* 500 mg/L. Dissolve 0.2500 ± 0.0001 g of palladium wire (99.99 %) in 25 mL of aqua regia. Evaporate the solution to dryness on a steam bath. Dissolve the remaining salts by addition of 25 mL of concentrated hydrochloric acid (12 M) and 25 mL of distilled water. Transfer the solution to a 500 mL volumetric flask and dilute to volume when cool.

NOTE 2—A commercially available atomic absorption palladium reference solution may be used if it is known to be reliable.

6.13 *Lanthanum Chloride Solution*—Dissolve 25.5 g of lanthanum chloride ($LaCl_3 \cdot 7H_2O$) in distilled water, dilute to 100 mL and mix well. This solution serves as an ionization suppressor in atomic absorption.

6.14 *Desiccant,* molecular sieve, type 4A.

7. Procedure

7.1 *Preparation of Calibration Standards:*

7.1.1 If the concentration of aluminum oxide in the sample is unknown, digest a representative sample in acid and determine the aluminum concentration by atomic absorption spectrophotometry.

7.1.2 Transfer 30 mL of sulfuric acid (3M) to five TFE-fluorocarbon beakers.

7.1.3 To each beaker add the equivalent weight of aluminum oxide that would be present in 0.8000 g of sample as determined in 7.1.1.

NOTE 3—If it is available, 0.800 g of catalyst base material may be substituted for the aluminum oxide.

7.1.4 Transfer 0, 4, 6, 8 and 10 mL of the 500 mg/L palladium standard to the five TFE-fluorocarbon beakers.

7.1.5 Add 10 mL of concentrated hydrofluoric acid to each beaker.

7.1.6 Cover the beakers with TFE-fluorocarbon lids and digest on a hot plate at medium heat until all solid material is in solution (including any brown stains that may appear on the beaker walls) and light fumes are evolved.

NOTE 4—If brown stains do not redissolve, discard sample and prepare again.

7.1.7 Cool the solutions. Dilute to 70 mL with distilled water. Add 10 mL of aqua regia. Boil gently for a few minutes on a hot plate.

7.1.8 When the solution is cool, transfer quantitatively to a 500-mL volumetric flask.

7.1.9 Add 5 mL of the lanthanum chloride solution to each flask. Dilute to volume when the solution has reached room temperature.

7.1.10 The concentration of palladium will be 0, 4, 6, 8 and 10 mg/L.

NOTE 5—The standard solutions are stable for two months.

7.2 *Weighing*—Prepare a carefully riffled, finely ground sample of ambient-equilibrated catalyst. For example, the sample could be thinly spread on filter paper and exposed to room conditions for 16 h. The test method requires 7 to 10 g of sample. Samples for LOI and analysis shall be weighed at the same time.

7.2.1 For determination of percent loss on ignition at 1000°C, ignite a porcelain crucible with lid at 1000°C for at least 30 min, place in desiccator to cool and weigh to nearest 0.1 mg. Transfer approximately 2.0 g of ambient-equilibrated sample to the crucible and weigh to the nearest 0.1 mg with the lid in place. Duplicate loss on ignition measurements are required to determine the average LOI noted in the final calculations.

7.2.2 For determination of palladium, transfer in triplicate 0.75 to 0.85 g of sample, weighed to the nearest 0.1 mg, into a 100-mL TFE-fluorocarbon beaker.

7.3 *Loss on Ignition:*

7.3.1 Place the porcelain crucible containing the test sample in a muffle furnace maintained at 450°C and heat for at least 30 min.

7.3.2 Transfer the crucible to a muffle furnace maintained at 1000°C and heat for 1.5 h to constant weight.

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[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.3.3 Remove the crucible from the furnace, place in desiccator to cool, and weigh to nearest 0.1 mg.

7.3.4 Calculate weight percent loss on ignition at 1000°C as follows:

$$\text{Weight \% } LOI = \frac{(I - F)}{I} \times 100 \tag{1}$$

where:

I = initial sample weight, and
F = final sample weight.

7.4 *Preparation of Test Sample for Atomic Absorption:*

7.4.1 Cautiously add 30 mL of sulfuric acid (3M) mixture to the test sample in the TFE-fluorocarbon beaker. Add 10 mL of concentrated hydrofluoric acid.

7.4.2 Cover the beakers with TFE-fluorocarbon lids and digest the samples on a hot plate at medium heat until all solid material is in solution and light fumes are evolved.

7.4.3 Allow the solutions to cool. Dilute to 70 mL with distilled water. Add 10 mL of aqua regia. Boil gently for a few minutes.

7.4.4 Allow the solutions to cool. Transfer quantitatively to 500 mL volumetric flasks. Add 5 mL of the lanthanum chloride solution.

7.4.5 Dilute to volume when solutions have cooled to room temperature.

7.4.6 Analyze the sample with an atomic absorption spectrophotometer in the absorbance mode at 247.6 nm using air-acetylene flame with background correction.

7.4.7 Bracket the sample reading between appropriate calibration standards.

NOTE 6—Make certain that samples and standards are on the linear portion of the calibration curve. If a sample falls on the nonlinear portion of the curve, make appropriate dilution and matrix adjustments. Check zero setting before each standard and sample reading using the 0 mg/L standard.

8. Calculation of Results

8.1 Calculate the weight percent of palladium in the test sample on a 1000°C ignited basis as follows:

8.1.1 *Method 1*—Plot the absorbance of the standards versus the concentration of palladium in the standards. Determine the concentration of palladium in the sample using the calibration curve.

8.1.2 *Method 2*—The concentration of palladium in the sample solutions may be calculated as follows:

$$CS = \frac{(AS - AL) \times (CH - CL)}{(AH - AL)} + CL \tag{2}$$

where:

CS = mg/L of palladium in sample solution,
AS = absorbance of the sample,
AL = absorbance of lower standard,
AH = absorbance of higher standard,
CL = mg/L of palladium in the lower standard, and
CH = mg/L of palladium in the higher standard.

8.1.3 The concentration of palladium in the sample is calculated as follows:

$$\text{Palladium, \%} = \frac{CS}{\left[1.00 - \frac{\%\, LOI}{100}\right] \times W \times 20} \tag{3}$$

where:

CS = mg/L of palladium in sample solution,
W = grams of sample, and
LOI = average of duplicate loss on ignitions.

9. Precision and Bias[5]

9.1 *Test Program*—An interlaboratory study was conducted in which the weight % palladium (volatile free basis) was measured in one separate test material in eight separate laboratories. Practice E691, modified for non-uniform data sets, was followed for the data reduction. Analysis details are in the research report.

9.2 *Precision*—Pairs of test results obtained by a procedure similar to that described in the study are expected to differ in absolute value by less than 2.772 S, where 2.772 S is the 95 % probability interval limit on the difference between two test results, and S is the appropriate estimate of standard deviation. Definitions and usage are given in Terminology E456 and Practice E177, respectively.

Test Result (Consensus Mean) weight %	95 % Repeatability Interval (Within Laboratory) weight %	95 % Reproducibility Interval (Between Laboratories) weight %
0.5406	0.005 (0.95 % of mean)	0.021 (3.94 % of mean)

9.3 *Bias*—This test method is without known bias.

10. Keywords

10.1 atomic absorption; molecular sieve; molecular sieve catalyst; palladium

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D32-1034.

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