Designation: D4782 – 04

Standard Test Method for Palladium in Molecular Sieve Catalyst by Wet Chemistry[1]

This standard is issued under the fixed designation D4782; 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 *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

3. Summary of Test Method

3.1 The test sample is treated with hydrofluoric acid and evaporated to dryness to remove silica; the residue is fused with potassium pyrosulfate, and the cooled melt is dissolved in 4 % H_2SO_4. A measured excess of 0.01 N potassium iodide (KI) is added to precipitate palladium as palladium iodide (PdI_2). The precipitate is filtered and washed, and a small amount of sodium sulfite is added to the filtrate to reduce any free iodine to iodide. The excess iodide is titrated with 0.01 N $AgNO_3$ potentiometrically, using a silver electrode versus a calomel electrode. A second sample taken at the same time 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 metals other than palladium.

5. Apparatus

5.1 *pH Meter with Millivolt Scale* or automatic recording titrator.

5.2 *Silver-Sulfide Electrode.*

5.3 *Silver-Silver Chloride Double Junction* reference electrode with 10 % KNO_3 in the outer chamber.

5.4 *Fisher Burner.*

5.5 *Low-Temperature Muffle Furnace*, 450°C.

5.6 *High-Temperature Muffle Furnace*, 1000°C.

5.7 *Hot-Plate*, with sand bath as a preferred option.

5.8 *Magnetic Stirrer and TFE-Fluorocarbon-Coated Stirring Bars.*

5.9 *Burets*, 25-mL, with 0.1-mL graduations or an equivalent.

5.10 *Volumetric Flasks*, 1000-mL.

5.11 *High-Silica Beakers*, 400-mL, with disposable borosilicate beakers as an option. Alternatively, a petri dish can be used for the fusion step, with polypropylene beakers being used thereafter.

5.12 *Watch Glasses*, preferably ribbed, 87 mm.

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

5.14 *Weighing Papers.*

5.15 *Porcelain Crucibles*, [3] 10-mL.

5.16 *Graduated Cylinders*, 5-mL, 10-mL, 25-mL, 100-mL.

5.17 *Filter Paper*, Whatman No. 40, 11 cm.

5.18 *Funnel*, filter.

5.19 *Desiccator.*

5.20 *Crucible Cover*, porcelain.

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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] Alundum or other suitable materials may be used.

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 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 *Desiccant Molecular Sieve*, type 4A.

6.4 *Filter Paper Pulp*.

6.5 *Hydrofluoric acid* (HF), 48 %.

6.6 *Potassium Iodide Solution*, 0.01 *N*—Dissolve 1.66 g of potassium iodide (KI) in distilled water, dilute to 1000 mL, and mix well.

6.7 *Potassium Pyrosulfate* ($K_2S_2O_8$).

6.8 *Silver Nitrate Solution*, 0.01000 *N*—Dissolve 1.6989 g of silver nitrate ($AgNO_3$) in distilled water, dilute to 1000 mL, and mix well.

NOTE 1—The preparation of the $AgNO_3$ standard solution is a critical step. If any traces of chloride, organic matter or reducing agents are present in the water, more $AgNO_3$ will be used in the back-titration and the final result will be low. Standardization is recommended.

6.9 *Sodium Sulfite Solution*, 10 % Dissolve 10 g of anhydrous sodium sulfite (Na_2SO_3) in 100 mL of distilled water.

6.10 *Sulfuric Acid* (H_2SO_4) concentrated, sp gr 1.84.

6.11 *Sulfuric Acid, 48 % or 9 M*—Add slowly, stir one part concentrated H_2SO_4 (96 %) to one part water, then cool.

6.12 *Sulfuric Acid, 4 % or 0.72 M*—Dilute 80 mL of 48 % sulfuric acid to 1000 mL.

7. Procedure

7.1 *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.

7.1.1 For determination of percent loss on ignition at 1000°C, ignite a porcelain crucible 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 sample to the crucible and weigh to the nearest 0.1 mg.

7.1.2 For determination of palladium, transfer approximately 1.6 g of sample, weighed to the nearest 0.1 mg, into a 400-mL high-silica beaker.

7.2 *Loss on Ignition*:

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

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

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

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

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

where:

I = initial sample weight, and

F = final sample weight.

7.3 *Preparation of Test Sample for Titration*:

7.3.1 Cautiously add about 3 mL water to the high-silica beaker to disperse the test sample.

7.3.2 Add 12 mL hydrofluoric acid (HF) to effect dissolution and evaporate to dryness on the cooler areas of the sand bath to remove silicon dioxide (SiO_2).

7.3.3 Promptly remove the beaker from the sand bath, cover residue with 9 g of potassium pyrosulfate, and heat gently over a Fisher burner until all excess hydrofluoric acid (HF) is driven off. Heat over flame until clear fusion results. Tilt or swirl the beaker on cooling to prevent breakage.

7.3.4 Add 20 mL of 48 % H_2SO_4 and 15 mL of distilled water, cover and heat to boiling on sand bath to dissolve melt. Remove from the sand bath, dilute to 200 mL with boiling distilled water, and cool.

7.3.5 Place beaker on a magnetic stirrer, insert stirring bar and add a small wad of paper pulp. Add 5 mL of HF and stir sample a minimum of 5 min to complex the iron present and solubilize any remaining SiO_2.

7.3.6 Add exactly 20.00 mL of 0.01 N KI from a buret while stirring, and continue stirring for 5 min to coagulate the PdI_2.

7.3.7 Discontinue stirring, remove stirring bar and rinse into the beaker with distilled water.

7.3.8 Filter contents of beaker through 11 cm size Whatman No. 40 filter paper. A Buchner funnel can optionally be used for filtering. Add about 1 mL of 10 % sodium sulfite solution to filtrate. Wash the beaker four times and the filter paper five times with 4 % H_2SO_4.

7.4 *Titration*:

7.4.1 Perform the potentiometric titration with 0.01000 N $AgNO_3$ solution in accordance with the steps as follows:

7.4.1.1 Titrate quickly with 0.01000 *N* $AgNO_3$ solution to a predetermined millivolt reading (for example, using 1-mL increments to an electrode potential reading of about 200 mV), then add titrant in smaller increments of about 0.1 mL, obtaining scale readings after each addition.

NOTE 2—The point of maximum deflection per increment can be readily determined during the titration by noting the difference between consecutive scale readings. The difference will increase sharply near the end point and decrease sharply after the end point. The derivative function can also be used.

7.4.1.2 Record milliliters of $AgNO_3$ and millivolt readings on a graph or on a titration sheet like that shown in Fig. 1, and obtain the end point from the inflection point of the titration curve.

7.4.2 Determine the titer of the 0.01 *N* KI solution in accordance with the following steps:

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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.

Millilitres	E (millivolts)	$\Delta E/\Delta V$ mV/mL	$\Delta^2 E/\Delta V^2$ mV/mL

TITRATION RECORD

Sample ____________________

Solvent ____________________

Titrant ____________________

Normality ____________________

Ind. Elect. ____________________

Ref. Elect. ____________________

Miscellaneous ____________________

READING SHOULD NOT CHANGE BY
MORE THAN 6 MV PER MINUTE,
BEFORE NEXT ADDITION OF $AgNO_3$.

	Millivolts											
mL of 0.01 N Ag^+	30 s	1 min	2 min	3 min	4 min	5 min	6 min	7 min	8 min	9 min	10 min	11 min

FIG. 1 Titration Record

7.4.2.1 Add 5 mL HF to 250 mL of 4 % H_2SO_4 in a 400-mL high-silica beaker. Add exactly 20.00 mL of 0.01 N KI from a buret, introduce a stirring bar, and add about 1 mL of 10 % of Na_2SO_3 solution.

7.4.2.2 Titrate potentiometrically with 0.01000 N of $AgNO_3$ solution as described in 7.4.1, using a buret.

8. Calculation of Results

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

$$\text{Palladium, weight \%} = \frac{(T - V)N \times 0.0532 \times 100}{S \times \dfrac{(100 - \%\ LOI)}{(100)}} \quad (2)$$

where:

T = 0.01000 N $AgNO_3$, mL, used to titrate 20 mL of 0.01 N KI,

V = 0.01000 N $AgNO_3$, mL, used to titrate sample,

N = normality of 0.01000 N $AgNO_3$,

S = sample weight, g,

% LOI = loss on ignition weight percent, as determined in 7.2.4, and

0.0532 = milliequivalent weight of palladium.

9. Precision and Bias

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 twelve 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 E177, respectively.

Test Result (Consensus Mean) weight %	95 % Repeatability Interval (Within Laboratory) weight %	95 % Reproducibility Interval (Between Laboratories) weight %
0.5390	0.004 (0.78 % of mean)	0.024 (4.54 % of mean)

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

10. Keywords

10.1 catalyst; molecular sieve; palladium

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