



Standard Test Method for Platinum in Reforming Catalysts by Wet Chemistry¹

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1. Scope

1.1 This test method covers the determination of platinum in nonzeolitic, fresh reforming catalysts containing platinum as the only precious metal, in the range of concentration of 0.200 to 0.700 weight %.

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

E288 Specification for Laboratory Glass Volumetric Flasks

E456 Terminology Relating to Quality and Statistics

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

2.2 *U.S. Federal Specification:*

NNN-P-395C Tolerance for Class A Pipets³

3. Summary of Test Method

3.1 The ground alumina based reforming catalyst is dissolved using dilute hydrochloric acid. Stannous chloride is added to convert the platinum in solution to a yellowish-orange-colored platinum stannous hydrochloride complex. The absorbance of the resulting solution is measured comparatively at 403 nm by spectrophotometry and the platinum content is calculated from a previously determined value for the absorptivity.

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

4. Significance and Use

4.1 This test method provides a means of determining the platinum content of fresh reforming catalysts where the platinum is supported on an all alumina substrate.⁴

4.2 This test method is not intended to cover samples containing metals other than platinum. Palladium, rhenium, and rhodium in particular interfere with the spectrophotometric determination of platinum.

5. Apparatus

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

5.2 *Beakers*, 250-mL, tall form and 600-mL.

5.3 *Cells*, spectrophotometer, 1.0 cm, matched.

5.4 *Crucibles*, platinum, or porcelain, 50-mL.

5.5 *Desiccator*, vacuum.

5.6 *Filter Paper*, fine, ashless, slow filtering, 12.5 cm or equivalent.

5.7 *Flasks*, volumetric, conforming to tolerances specified by Specification E288, 500-mL and 1000-mL.

5.8 *Funnel*, filtering, fluted bowl, 65 mm top diameter, 150 mm stem.

5.9 *Graduated Cylinders*, 10-mL, 25-mL, 50-mL, 250-mL.

5.10 *Pipets*, conforming to tolerances specified by Federal Specification NNN-P-395C, 5-mL, 10-mL, 15-mL.

5.11 *Muffle Furnace*, capable of $1000 \pm 25^\circ\text{C}$.

5.12 *Spectrophotometer*, capable of measuring absorbance values between 200 to 800 nm with a photometric repeatability of ± 0.002 absolute at 1.0 absolute.

5.13 *Watch Glass*, flat, 100 mm.

5.14 *Watch Glass*, ribbed, 65 mm.

5.15 *Wash Bottle*, polyethylene, 500-mL.

5.16 *Weighing Vial*, 25 by 40 mm.

6. Reagents

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,

⁴ This test method can be extended to spent reforming catalyst by isolating the platinum by the methods described in *Analytical Chemistry*, Vol 32, No. 6, May 1960, p. 646, "Assay Procedure for Platinum in Reforming Catalysts."

where such specifications are available. 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.⁵

6.2 *Purity of Water*—Unless otherwise indicated, all references to water used as a reagent mean deionized or distilled water conforming to Specification D1193.

6.3 *Aluminum Chloride Solution*—Dissolve 453.6 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in water and dilute to a litre with water.

6.4 *Aqua Regia*—Mix three parts concentrated hydrochloric acid with one part concentrated nitric acid.

6.5 *Formic Acid (HCOOH)*.

6.6 *Hydrochloric Acid (HCl)*, concentrated, specific gravity 1.19.

6.7 *Hydrochloric Acid (HCl) Solution*, 18 to 19 volume % or 6 N. Dilute 500 mL of concentrated hydrochloric acid to a litre with water.

6.8 *Hydrochloric Acid (HCl)*, 3.7 volume % or 1.2 N. Dilute 100 mL of concentrated hydrochloric acid to a litre with water.

6.9 *Hydrogen Peroxide (H₂O₂)*, or chlorine gas.

6.10 *Nitric Acid (HNO₃)*, concentrated specific gravity 1.42.

6.11 *Platinum Wire*, 99.99 % platinum purity.

6.12 *Standard Platinum Solutions*, approximately 1 mg platinum per mL. Weigh approximately 1 g \pm 0.1 mg of platinum wire into a 250-mL tall form beaker. Add 7 mL of concentrated nitric acid, 21 mL of concentrated hydrochloric acid, cover the beaker using a ribbed watch glass and heat the contents at 85°C. Add additional acid until all of the platinum is dissolved. Evaporate the resulting chloroplatinic acid solution to a moist salt. Dissolve this material in 20 mL of 6 N hydrochloric acid solution and evaporate to dryness at 85°C. Wash the watch glass and sides of the beaker with about 20 mL of 6 N hydrochloric acid solution and evaporate to dryness again. Cool, wash the watch glass and sides of the beaker with about 20 mL of 6 N hydrochloric acid and dissolve the residue in the beaker. Add a few drops of formic acid to the sample to reduce any remaining nitric acid. Transfer this solution quantitatively to a 1000-mL volumetric flask. Add an additional 300 mL of concentrated hydrochloric acid, dilute to volume with water and mix thoroughly. Allow the solution to cool to room temperature and readjust carefully to volume with water and mix. This stock solution contains approximately 1000 ppm of platinum and provides suitable aliquots for platinum standards. Transfer aliquots of 5 mL, 10 mL, and 15 mL, respectively, to 3 clean 500-mL volumetric flasks. Add 175 mL of concentrated hydrochloric acid, and 30 mL of stannous chloride solution to the 500-mL flask. Add sufficient aluminum chloride solution, (approximately 15 mL), to bring the standard to the same stoichiometric aluminum level as the unknown. Add distilled water to bring the solution just to the neck of the flask, which

permits mixing of all components. Prior to taking a portion for a spectrophotometric reading, allow the solution to come to room temperature, add additional distilled water to adjust to the volumetric mark and mix the solution thoroughly.

6.13 *Stannous Chloride Reagent*—Dissolve 280 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 500 mL of concentrated hydrochloric acid with warming on a hot plate. Dilute to 1000 mL with water and mix thoroughly. Filter this solution if it is cloudy. This solution should be prepared fresh daily.

6.14 *Water*, distilled, reagent.⁵

7. Procedure

7.1 *Calcination*—The platinum level in reforming catalysts is normally reported on a volatile-free basis. The loss on ignition (LOI) determination (1000°C) is carried out separately, but weighed out at the same time as the ground sample for digestion. Due to the hygroscopic nature of the sample, weigh by difference from a weighing vial. Weigh in triplicate 3 g \pm 0.1-mg samples of reforming catalyst in platinum or porcelain crucibles, place in a muffle furnace at 1000° \pm 25°C, and keep at this temperature for 3 h. Remove the crucible from the muffle and transfer to a desiccator, cool, and weigh 1 h after removal from the muffle. The desiccant to be loaded in the desiccator is freshly regenerated Type 4A molecular sieves.

7.2 *Digestion*—Weigh a ground portion of catalyst into a 600-mL beaker to contain 6 to 8 mg platinum (for example, a 0.5 weight % platinum catalyst requires 1.2 to 1.6 g \pm 0.1 mg). After weighing, perform a digestion in a 600-mL beaker containing 150 mL of 6 N hydrochloric acid at 90°C. Add 1 to 2 mL of H₂O₂ or pass chlorine through the solution for 20 min to accelerate the reaction. Cover with a watch glass. After several hours heating at 85°C, only a trace of residue (Al_2O_3) remains. Dilute this solution and filter into a 500-mL flask, and wash the paper with hot water. Ignite the filter paper and redigest the residue in a few millilitres of aqua regia, evaporate to dryness, redissolve in 6 N HCl, evaporate to dryness, redissolve in 6 N HCl, and filter into the main solution. This solution is now ready to complex with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

NOTE 1—Filtration is necessary, since the very minute trace of alumina that remains insoluble approaches the colloidal state and interferes in the spectrophotometric measurement. The insoluble material settles on standing 20 h, but any disturbance of the solution redistributes it. In a nephelometric test the filtered solution, after complexing with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, should show a clarity similar to that of the standard solution.

7.3 *Color Development of Platinum Solution*—Complex the test sample contained in the 500-mL flask with 30 mL of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution and add sufficient additional concentrated HCl so that the flask contains 175 mL of HCl to equal that used in the platinum standard in 6.12. Adjust the solution to the volumetric mark with distilled water and mix. Run the set of three standard solutions prepared in 6.12 with the sample solutions. These standards provide the factor to be applied to the absorbance readings of the sample solutions. In turn, the milligrams and percentages of platinum are obtained. The readings should be taken the day following color development. With a typical set of readings the cells are first filled with a reference solution containing an exact mixture of the reagents omitting only platinum. Adjust the instrument to the zero base line. Determine absorbance with a spectrophotometer at 403

⁵ *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.

nm. It is recommended that a standard be measured and then a test sample, alternating through the measurements until the absorbance has been obtained for all solutions.

8. Calculation of Results

8.1 Derive from the measurements of the standards an average factor in terms of milligrams of platinum per absorbance unit. Then, use this factor to convert the absorbance values for the test sample into milligrams of platinum. Calculate the platinum concentration of the test sample in percent as follows:

$$(A/B \times 10) \quad (1)$$

where:

A = milligrams of platinum found in the sample, and

B = weight of volatile-free sample, g.

9. Precision and Bias

9.1 *Test Program*—An interlaboratory study was conducted in which the weight % platinum (volatile-free basis) was measured in one test material in seven separate laboratories.

Practice E691, modified for nonuniform data sets, was followed for the data reduction. Analysis details are in the research report.⁶

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)	95 % Repeatability Interval (Within Laboratory)	95 % Reproducibility Interval (between laboratories)
0.578 weight %	0.005 weight % (0.93 PCT of mean)	0.013 weight % (2.31 PCT of mean)

9.3 *Bias*—The test method described is without known bias since there are no reference standards available for comparison.

10. Keywords

10.1 platinum; precious-metal; reforming catalyst; spectrophotometric

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report D32-1035.

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