



Standard Test Method for Platinum in Reforming Catalysts by Wet Chemistry¹

This standard is issued under the fixed designation D 4642; 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 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:

D 1193 Specification for Reagent Water²

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods³

E 288 Specification for Laboratory Glass Volumetric Flasks³

E 456 Terminology Relating to Quality and Statistics³

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method³

2.2 U.S. Federal Specification:

NNN-P-395C Tolerance for Class A Pipets⁴

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.

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.⁵

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 E 288, 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°C \pm 25°C.

5.12 *Spectrophotometer*, capable of measuring absorbance values between 200 to 800 nm with a photometric repeatability of \pm 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, where such specifications are available. Other grades may be

¹ This test method is under the jurisdiction of ASTM Committee D-32 on Catalysts and is the direct responsibility of Subcommittee D32.03 on Chemical Composition.

Current edition approved Jan. 15, 1992. Published March 1992. Originally published as D 4642 – 86. Last previous edition D 4642 – 92.

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ Available from Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS.

⁵ The 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."

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

6.2 *Purity of Water*—Unless otherwise indicated, all references to water used as a reagent mean deionized or distilled water conforming to Specification D 1193.

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* (H_2O_2), or chlorine gas.

6.10 *Nitric Acid* (HNO_3), 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 $1 \text{ g} \pm 0.1 \text{ mg}$ 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.²

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 $3 \text{ g} \pm 0.1\text{-mg}$ samples of reforming catalyst in platinum or porcelain crucibles, place in a muffle furnace at $1000^\circ \pm 25^\circ\text{C}$, 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 $1.2 \text{ to } 1.6 \text{ g} \pm 0.1 \text{ mg}$). 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 H_2O_2 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 nm. It is recommended that a standard be measured and then a test sample, alternating through the measurements until the

⁶ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeial Convention, Inc. (USPC), Rockville, MD."

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 E 691, modified for nonuniform data sets, was followed for the data reduction. Analysis details are in RR: D32-1035.

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 Practices E 456 and E 177, 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.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.