# Standard Test Method for Nickel and Vanadium in FCC Equilibrium Catalysts by Hydrofluoric/Sulfuric Acid Decomposition and Atomic Spectroscopic Analysis[1]

This standard is issued under the fixed designation D1977; 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 nickel and vanadium in equilibrium catalysts where the vanadium and nickel concentrations are greater than 50 and 25 mg/kg, respectively.

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
D3766 Terminology Relating to Catalysts and Catalysis
E105 Practice for Probability Sampling Of Materials
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:*[3]

Federal Specification NNN-P-395C Tolerance for Class A Pipets

## 3. Terminology

3.1 *Definitions*—See Terminology D3766.

## 4. Summary of Test Method

4.1 The test specimen (as received) is decomposed with hydrofluoric and sulfuric acids. After complete volatilization of the hydrofluoric acid and cooling, the sulfate salts are diluted to the appropriate concentration range for analysis by flame atomic absorption, direct current plasma emission, or inductively coupled plasma emission spectroscopies. The instrument is calibrated with matrix-matched standards. Solutions of the test specimen are analyzed.

## 5. Significance and Use

5.1 This test method is a procedure by which catalyst samples may be compared on an inter- or intra-laboratory basis. Catalyst producers and user should find this test method to be of value.

## 6. Interferences

6.1 The enhancement of alumina in the samples are overcome by using matrix-matched standards. Any dilutions needed to achieve the working ranges for vanadium and nickel must contain the same $Al_2O_3$ (7800 ppm) concentration as the standards.

6.2 If using optical emission, consult tables showing interfering line near analyte lines; if significant overlap occurs, one must apply interelement correction or choose an alternate emission line.

## 7. Apparatus

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

7.2 *Hot Plate*, capable of maintaining 250 ± 10°C at surface.

7.3 *TFE Fluorocarbon Beaker*, 250 mL.

7.4 *Volumetric Flasks*, borosilicate glass, 50, 100, 250, 500, and 1000-mL capacity conforming to Specification E288.

7.5 *Pipettes*, borosilicate glass, 5, 10, and 25 mL, conforming to Federal Specification NNN-P-395C.

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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, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS.

7.6 *Bottles*, polyethylene, 100 and 1000 mL.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents 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 sufficient purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean type IV reagent water, as defined in Specification D1193.

8.3 *Required Reagents*:

8.3.1 *Hydrofluoric Acid* (HF), concentrated, 48 %.

8.3.2 *Sulfuric Acid*, ($H_2SO_4$), concentrated, 98 %.

8.3.3 *Sulfuric Acid*, 49 volume %, add slowly, while stirring, one part of concentrated $H_2SO_4$ (98 %) to one part of water, then cool.

8.3.4 *Hydrochloric Acid*, concentrated, 38 %.

8.3.5 *Hydrochloric Acid*, 19 volume %, add slowly, while stirring, one part of concentrated HCl (38 %) to one part of water, then cool.

8.3.6 *Nitric Acid ($HNO_3$)*, concentrated, 70 %.

8.3.7 *Reference Standard Solution*—1000 mg/L nickel (see Note 1).

NOTE 1—If emission spectrometry is to be used, standards must contain no interfering element(s) in concentration(s) great enough to yield an interference of more than 0.1% of the analytical response.

8.3.8 *Reference Standard Solution*—1000 mg/L vanadium (see Note 1).

8.3.9 *Aluminum Chloride*, reagent grade, $AlCl_3 \cdot 6H_2O$

8.3.10 *Aluminum Stock Solution*—39 000 mg/L $Al_2O_3$, dissolve 184.5 g of $AlCl_3 \cdot 6H_2O$ in water and dilute to 1 L and store in a polyethylene bottle.

8.3.11 *Hydrogen Peroxide*—3 % solution.

## 9. Sampling

9.1 The selection of a representative analytical sample from the bulk material is outside the scope of this test method. Parties using this test method for comparison purposes will have agreed on the selection of an analytical sample. If a sampling procedure is desired, Practice E105 is recommended.

## 10. Preparation of Standards

10.1 *Nickel*—Prepare standard solutions containing 0, 5.0, 20.0, and 50.0 mg/L Ni in a matrix of 7800 mg/L $Al_2O_3$ and 10 % hydrochloric acid by transferring 0, 5.0, 20.0, and 50.0 mL of the 1000-mg/L solution to 1000-mL volumetric flasks containing 200 mL of the 39 000-mg/L $Al_2O_3$ solution and 100 mL concentrated hydrochloric acid. Dilute solutions to volume with distilled water and store in polyethylene bottles.

10.2 *Vanadium*—Prepare standard solutions containing 0, 10.0, 25.0, 50.0 and 100.0 mg/L V in a matrix of 7800 mg/L $Al_2O_3$ and 10 % hydrochloric acid by transferring 0, 10.0, 25.0, 50.0, and 100.0 mL of the 1000-mg/L solution to 1000-mL volumetric flasks containing 200 mL of the 39 000-mg/L $Al_2O_3$ solution and 100 mL concentrated hydrochloric acid. Dilute solutions to volume with distilled water and store in polyethylene bottles.

## 11. Procedure

11.1 Weigh three test specimens of approximately 2.0 g each to the nearest 0.1 mg and transfer to 250-mL TFE-fluorocarbon beakers. A reagent blank should be carried along with each set of samples.

11.2 Add 10 mL 48 % sulfuric acid, 10 mL concentrated nitric acid, and 10 mL concentrated hydrofluoric acid.

11.3 Transfer beaker and contents to a hot plate (no hotter than 250°C to avoid melting the beaker) and evaporate to near dryness.

11.4 Remove beaker from hot plate and cool to ambient temperature.

11.5 Add 20 mL 19 % hydrochloric acid and 30 mL 3% hydrogen peroxide, cover with watch glass and return beaker to hot plate.

11.6 Heat solution to boiling and continue to boil until all the salts are dissolved.

11.7 After dissolution is complete, remove beaker from hot plate and cool to ambient temperature.

11.8 Wash watch glass, catching washings in the beaker, and transfer solution quantitatively to a 100-mL volumetric flask. Dilute to volume with water and mix well.

11.9 Using direct current argon plasma spectrometry (DCP), inductively coupled argon plasma spectrometry (ICP), or atomic absorption spectrophotometry (AAS), determine concentration of analytes in solutions of test specimens. If apparent concentration is greater than that of the most concentrated standard, perform an additional dilution so that result is bracketed by two or more standards.

## 12. Calculations

12.1 Calculate the concentration of nickel and vanadium as follows:

$$\text{mg/L metal} = \frac{C \times D}{S} \quad (1)$$

where:

$C$ = concentration of metal in solution, mg/kg,

$D$ = volume equivalent of dilution used for analysis; if solution 10.8 is used directly, D = 100 mL. If a further dilution is needed, $D = 100 \text{ mL} \times V_2/V_1$, where $V_1$ is the aliquot of solution 10.8 and $V_2$ is the volume to which it was diluted, and

$S$ = Sample mass.

## 13. Precision and Bias

13.1 *Test Program*—An interlaboratory study was conducted in which the named property was measured in three

[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.

separate test materials in eight separate laboratories. Practice E691, modified for non-uniform data sets, was followed for the data reduction period.

13.2 *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 Results for Ni (Consensus Mean) | 95 % Repeatability Interval (Within Laboratory) | 95 % Reproducibility Interval (Between Laboratories) |
|---|---|---|
| 208 mg/kg | 8 mg/kg (3.9 % of mean) | 14 mg/kg (6.7 % of mean) |
| 152 mg/kg | 5 mg/kg (3.3 % of mean) | 24 mg/kg (15.8 % of mean) |
| 437 mg/kg | 9 mg/kg (2.1 % of mean) | 31 mg/kg (7.1 % of mean) |

| Test Results for V (Consensus Mean) | 95 % Repeatability Interval (Within Laboratory) | 95 % Reproducibility Interval (Between Laboratories) |
|---|---|---|
| 1191 mg/kg | 43 mg/kg (3.6 % of mean) | 201 mg/kg (16.9 % of mean) |
| 1898 mg/kg | 72 mg/kg (3.8 % of mean) | 303 mg/kg (16.0 % of mean) |
| 3346 mg/kg | 82 mg/kg (2.4% of mean) | 531 mg/kg (15.9 % of mean) |

13.3 *Bias*—This test method described is without known bias since there is by definition no absolute standard for comparison.

## 14. Keywords

14.1 acid decomposition; atomic spectroscopy; ECAT; FCC equilibrium catalysts; nickel; vanadium