Designation: D 3610 – 00 (Reapproved 2004)

Standard Test Method for Total Cobalt in Alumina-Base Cobalt-Molybdenum Catalyst by Potentiometric Titration Method[1]

This standard is issued under the fixed designation D 3610; 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 cobalt (expressed as the oxide) in fresh cobalt-molybdenum catalyst, in the range of 0.5 to 10 % cobalt oxide.

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 Water[2]

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[3]

3. Summary of Test Method

3.1 The sample is decomposed by adding water and sulfuric acid and then heating until completely dissolved. The cold solution is diluted with water and transferred to a 250-mL volumetric flask. An aliquot of this solution containing between 10 and 30 mg of cobalt is transferred to a 250-mL beaker containing measured volumes of potassium ferricyanide and ammonium citrate solutions, ammonia, and petroleum ether. The excess of ferricyanide is then back-titrated with a standard cobalt solution.

4. Significance and Use

4.1 This test method sets forth a procedure by which catalyst samples may be compared either on an interlaboratory or intralaboratory basis. It is anticipated that catalyst producers and users will find this test method to be of value.

5. Interferences

5.1 None of the elements normally found in fresh cobalt-molybdenum catalysts interferes with this method. (Elements such as nickel, phosphorus, silicon, aluminum, and molybdenum do not interfere; elements such as iron, chromium, vanadium, and manganese do interfere).

6. Apparatus

6.1 *Analytical Balance and Weights*—The balance used to weigh the sample shall have a precision of 0.1 mg. Analytical weights shall be of precision grade or calibrated against a set of certified standard weights.

6.2 *Buret*—The 50-mL buret used to deliver the standard potassium ferricyanide and standard cobalt solutions shall be of precision grade and shall be read to 0.01 mL by interpolation.

6.3 *Glassware*—Beakers used in the analysis of the sample shall be of chemical-resistant glass and free of etched surfaces. Before using, all glassware shall be cleaned in hot dilute hydrochloric acid and thoroughly rinsed with water.

6.4 *Potentiometric Titration Apparatus*—Apparatus No. 3B of Practices E 50, or equivalent.

6.5 *Hot Plate*—Capable of maintaining surface temperature of at least 300°C.

7. Reagents

7.1 *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.

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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] Withdrawn.

[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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type IV.

7.3 *Ammonium Citrate Solution* (680 g/L)—Dissolve 680 g of diammonium hydrogen citrate $(NH_4)_2HC_6H_5O_7$ in 750 mL of water and dilute to 1 L.

7.4 *Ammonium Hydroxide* (sp. gr. 0.90)—Concentrated ammonium hydroxide (NH_4OH).

7.5 *Cobalt Standard Solution* (1 mL = 1.494 mg of CoO)—Dissolve 5.80 g of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ in 500 mL of water, transfer to a 1-L volumetric flask, dilute to volume, and mix. Since cobalt nitrate may not always be stoichiometric, its content may be checked versus high-purity cobalt metal (99.9 % purity).

7.6 *Petroleum Ether*, b.p. 60 to 110°C.

7.7 *Potassium Ferricyanide Solution* (1 mL ~ 1.494 mg of CoO):

7.7.1 Dissolve 6.58 g of potassium ferricyanide $K_3Fe(CN)_6$ in water and dilute to 1 L. Store the solution in a dark-colored bottle. Standardize the solution just before use as follows: Transfer from a 50-mL buret approximately 25 mL of $K_3Fe(CN)_6$ solution to a 250-mL beaker. Record the interpolated buret reading to the nearest 0.01 mL. Add 25 mL of ammonium citrate solution, 90 mL of concentrated ammonia, and stir. Cool to 5 to 10°C and maintain this temperature during the titration. Cover the solution with a layer of 10 mL of petroleum ether. Transfer the beaker to a potentiometric titration apparatus. While stirring, titrate the $K_3Fe(CN)_6$ solution with cobalt standard solution (1 mL = 1.494-mg CoO) using a 50-mL buret. Titrate at a fairly rapid rate until the end point is approached and then add the titrant in one drop increments through the end point. After the addition of each increment, record the buret reading and voltage when equilibrium is reached. Estimate the buret reading at the end point to the nearest 0.01 mL by interpolation.

7.7.2 Calculate the cobalt oxide equivalent as follows:

$$\text{CoO equivalent, mg/mL} = (X \times Y)/Z \qquad (1)$$

where:

X = millilitres of cobalt standard solution required to titrate the potassium ferricyanide solution,

Y = milligrams of CoO per millilitre of standard solution, and

Z = millilitres of potassium ferricyanide solution.

Triplicate values should be obtained for the cobalt oxide equivalent. The values obtained should check within 1 to 2 parts per thousand.

7.8 *Sulfuric Acid* (sp. gr. 1.84)—Concentrated sulfuric acid (H_2SO_4).

8. Sample Preparation

8.1 Pulverize the analytical sample to pass a No. 100 (150-µm) sieve. Ignite the pulverized sample for 30 min at 550°C in a muffle furnace. Allow to cool in a desiccator.

9. Procedure

9.1 Transfer a 4.5-g sample, weighed to the nearest 1 mg, to a 250-mL beaker. Moisten with 25 mL of water, add slowly 40 mL of concentrated sulfuric acid, and stir. Cover the beaker and heat, using a hot plate or a Bunsen burner, until the sample is completely decomposed. (Silica, if present, will not dissolve.) Allow to cool and dilute to about 200 mL with distilled water. Allow to cool, transfer into a 250-mL volumetric flask, dilute to volume, and mix.

9.2 Prepare in a 250-mL beaker a mixture of the following: 25.0 mL of ferricyanide solution measured to the nearest 0.01 mL, 25 mL of ammonium citrate solution, and 90 mL of concentrated ammonia. Stir the mixture and cover with 10 mL of petroleum ether.

9.3 Cool to 5 to 10°C, transfer the beaker to a potentiometric titration apparatus, and maintain the 5 to 10°C temperature during the titration.

9.4 While stirring, transfer, using a pipet, from the 250-mL volumetric flask an aliquot containing between 10 and 30 mg of CoO.

9.5 Using a 50-mL buret, titrate the excess $K_3Fe(CN)_6$ with the cobalt solution (1 mL = 1.494-mg CoO) at a fairly rapid rate until the end point is approached, and then add the titrant in one-drop increments through the end point.

NOTE 1—For a successful titration, the sample solution must be added to the excess $K_3Fe(CN)_6$ solution and not vice versa.

9.6 After the addition of each increment, record the buret reading and voltage when equilibrium is reached. Estimate the buret reading at the end point to the nearest 0.01-mL interpolation.

10. Calculation

10.1 Calculate the percentage of cobalt oxide as follows:

$$\text{Cobalt oxide, \%} = [(AB - CD)/E] \times 100 \qquad (2)$$

where:

A = millilitres of standard potassium ferricyanide solution,

B = cobalt oxide equivalent of the standard potassium ferricyanide solution,

C = millilitres of cobalt standard solution,

D = concentration of cobalt standard solution (mg CoO/mL), and

E = milligrams of sample used.

TABLE 1 Statistical Information

Test Sample	CoO Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1. SN-4318 (nominal 3 % CoO, 15 % MoO_3)	3.72	0.17 % CoO	0.22 % CoO
2. SN-4319 (nominal 6 % CoO, 12 % MoO_3)	5.58	0.12 % CoO	0.19 % CoO

11. Precision [5]

11.1 Seven laboratories participated in supplying data under the conditions outlined in Practice E 173. Statistical data calculated in accordance with this procedure are presented in Table 1.

12. Keywords

12.1 alumina-base catalysts; cobalt; molybdenum; potentiometric

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D32-1001.

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