



# Standard Test Methods for Chemical and Spectrochemical Analysis of Nuclear-Grade Silver-Indium-Cadmium Alloys<sup>1</sup>

This standard is issued under the fixed designation C 760; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods cover procedures for the chemical and spectrochemical analysis of nuclear grade silver-indium-cadmium (Ag-In-Cd) alloys to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Silver, Indium, and Cadmium by a Titration Method	7-15
Trace Impurities by Carrier-Distillation Spectrochemical Method	16-22

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *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.* For specific hazard and precautionary statements, see Section 5 and Practices E 50.

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

**C 752** Specification for Nuclear-Grade Silver-Indium-Cadmium Alloy

**D 1193** Specification for Reagent Water

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

**E 115** Practice for Photographic Processing in Optical Emission Spectrographic Analysis<sup>3</sup>

2.2 *Other Document:*

NBS Circular 602<sup>4</sup>

## 3. Significance and Use

3.1 Silver-indium-cadmium alloy is used as a control material in nuclear reactors. In order to be suitable for this purpose, the material must meet the specifications for assay and impurity content. These test methods are designed to show whether or not a given material meets the specifications as given in Specification **C 752**.

3.1.1 An assay is performed to determine whether the material has the chemical composition specified.

3.1.2 The impurity content is determined to ensure that the maximum concentration limit of impurities is not exceeded.

## 4. Purity of Reagents

4.1 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,<sup>5</sup> 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.

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

## 5. Hazards

5.1 Proper precautions should be taken to prevent inhalation or ingestion of heavy element (silver, indium, or cadmium) powder or dust during handling.

5.2 Workers should observe precautions as specified in vendor-supplied Material Safety Data Sheets (MSDS).

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.03 on Neutron Absorber Materials Specifications.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Withdrawn.

<sup>4</sup> Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, <http://www.nist.gov>.

<sup>5</sup> "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 "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

## 6. Sampling

6.1 Suggestions for sampling this alloy are given in Specification **C 752**.

## SILVER, INDIUM, AND CADMIUM BY A TITRATION METHOD

### 7. Scope

7.1 This test method is applicable to the determination of silver, indium, and cadmium in alloys of approximately 80 % silver, 15 % indium, and 5 % cadmium used in nuclear reactor control rod applications. The titrimetric methods presented<sup>6,7</sup> will yield results with a bias of the order of 0.1 %.

### 8. Summary of Test Method

8.1 A weighed sample is dissolved in nitric acid and diluted to a known volume, and aliquots are removed for analysis. Silver is determined first by titrating with standardized sodium chloride solution to the potentiometric endpoint indicated by a chloride-selective ion electrode. Following the silver titration, the solution is boiled to coagulate the silver chloride. The pH is adjusted to 2.5 and the indium content is titrated with EDTA, using PAN (1-(2-pyridylazo)-2-naphthol) indicator. The pH is then raised to 6.0 and the cadmium is titrated with EDTA using the same indicator. The entire process requires approximately 20 min per aliquot, exclusive of sample weighing and dissolution.

### 9. Interferences

9.1 No interferences have been observed from any elements normally encountered as impurities in nuclear grade silver-indium-cadmium alloy over the concentration ranges expected.

### 10. Apparatus

10.1 *Burets*, precision, two, 25-mL capacity, preferably Schellbach type with TFE-fluorocarbon stopcock and automatic zero. They shall be certified or tested to conform with tolerances specified in NBS Circular 602.

10.2 *Reference Electrode*—Saturated calomel electrode.

10.3 *Glass pH Electrode*—Standard type.

10.4 *Chloride Specific Ion Electrode*.

10.5 *Expanded Scale pH/millivolt Meter*.

### 11. Reagents

11.1 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH<sub>4</sub>OH).

11.2 *Buffer Solution, pH4*—0.5 M sodium acetate—0.5 M acetic acid.

11.3 *Cadmium (Cd)*—Metal, >99.99 % pure.

11.4 *Ethylenediaminetetraacetate Dihydrate Disodium Salt (EDTA) Solution (0.01000 M)*—Weigh  $3.722 \pm 0.001$  g of EDTA into a small plastic beaker. Dissolve with water, transfer quantitatively to a 1-L volumetric flask, and make up to volume

with water. Transfer the solution to a plastic storage bottle. Do not allow the EDTA solution to stand in contact with glass containers.

11.5 *Indium (In)*—Metal, >99.99 % pure.

11.6 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO<sub>3</sub>).

11.7 *PAN Indicator Solution (0.1 % PAN in Methanol)*—Dissolve 100 mg of 1-(2-pyridylazo)-2-naphthol in 100 mL of methyl alcohol and mix until completely dissolved.

11.8 *Silver (Ag)*—Metal, >99.99 % pure.

11.9 *Sodium Chloride (NaCl)*.

11.10 *Sodium Chloride Solution (0.0500 M)*—Dry sodium chloride (NaCl) at 120°C, in a weighing bottle, to a constant weight and cool to room temperature in a desiccator. Weigh  $2.922 \pm 0.001$  g of the dried NaCl into a small plastic beaker. Dissolve in water, quantitatively transfer to a 1-L volumetric flask, and make up to volume with water.

### 12. Standardization

12.1 *Silver-Indium-Cadmium Calibration Standard*:

12.1.1 Clean approximately 8.0 g of silver metal, 1.5 g of indium metal, and 0.5 g of cadmium metal with an organic solvent and air dry.

12.1.2 Weigh each metal accurately and transfer to a 100-mL beaker.

12.1.3 Add sufficient water to cover the metal pieces and add HNO<sub>3</sub>(sp gr 1.42) dropwise until dissolution is complete.

12.1.4 Transfer quantitatively to a 100-mL volumetric flask and dilute to volume with water.

12.2 *Calibration of NaCl and EDTA Titrants*:

12.2.1 Pipet 10 mL of the calibration standard into a 100-mL volumetric flask and dilute to volume with water. (Retain this solution as a working standard.)

12.2.2 Pipet 10 mL of the diluted standard into a 100-mL beaker and adjust the volume to about 25 mL with water.

12.2.3 Adjust the pH to approximately 1 using NH<sub>4</sub>OH (sp gr 0.90).

12.2.4 Place a TFE-fluorocarbon-coated stirring bar in the solution and insert the chloride specific ion electrode and the reference electrode.

12.2.5 Stir at a moderate rate and titrate the silver with NaCl solution. Record millivolt readings versus volume added. Allow sufficient time for equilibrium readings to be attained.

12.2.6 The titration end point is taken as the termination of the rapidly rising segment of the millivolt versus volume titration curve.

12.2.7 Adjust to pH  $2.5 \pm 0.2$  by dropwise addition of acetate buffer solution (pH4).

12.2.8 Remove the electrodes and rinse thoroughly to avoid loss of indium and cadmium.

12.2.9 Heat the solution to boiling on a hotplate until the supernatant liquid is clear. Allow to cool.

12.2.10 Add 4 drops of PAN indicator solution. The solution should be deep purple.

12.2.11 Titrate the indium with standard EDTA solution to the sharp transition from purple to yellow. The volume used corresponds to the indium content.

12.2.12 Adjust to pH  $6 \pm 0.2$  with NH<sub>4</sub>OH (sp gr 0.90). The color of the solution will change back to purple.

<sup>6</sup> Cheng, K. L., "Complexometric Titration of Indium," *Analytical Chemistry*, Vol 27, 1955, p. 1582.

<sup>7</sup> Cheng, K. L., "Complexometric Titration of Copper and Other Metals in a Mixture," *Analytical Chemistry*, Vol 30, 1958, p. 243.

12.2.13 Titrate the purple solution with standard EDTA until the color again changes to yellow. The volume used corresponds to the cadmium content.

### 13. Procedure

13.1 Clean approximately 1.0 g of the sample with an organic solvent and air dry.

13.2 Weigh the cleaned sample accurately and transfer it to a 100-mL beaker.

13.3 Cover the sample with water and add HNO<sub>3</sub>(sp gr 1.42) dropwise until the sample is completely dissolved.

13.4 Transfer the solution quantitatively to a 100-mL volumetric flask and dilute to volume with water.

13.5 Proceed with the determination of silver, indium, and cadmium as described in 12.2.2-12.2.13.

### 14. Calculation

14.1 Symbols:

$S$  = sample weight, mg,

$D.F.$  = dilution factor = 0.1,

$F_S$  = calibration factor for silver, mg Ag/mL of titrant,

$F_I$  = calibration factor for indium, mg In/mL of titrant, and

$F_C$  = calibration factor for cadmium, mg Cd/mL of titrant.

14.2 Calibration Calculations:

$$F_S = \frac{\text{mg of Ag in calibration standard aliquot}}{\text{mL of standard NaCl solution added}} \quad (1)$$

$$F_I = \frac{\text{mg of In in calibration standard aliquot}}{\text{mL of standard EDTA solution added}} \quad (2)$$

$$F_C = \frac{\text{mg of Cd in calibration standard aliquot}}{\text{mL of standard EDTA solution added}} \quad (3)$$

14.3 Sample Calculations:

$$\text{Ag, \%} = \text{mL of NaCl titrant} \times F_S \times 10/S \quad (4)$$

$$\text{In, \%} = \text{mL of EDTA titrant} \times F_I \times 10/S \quad (5)$$

$$\text{Cd, \%} = \text{mL of EDTA titrant} \times F_C \times 10/S \quad (6)$$

### 15. Precision and Bias

15.1 Precision—The estimated standard deviation for a single measurement of each element is 0.03 % for silver, indium, and cadmium.

15.2 Bias—The estimated bias, measured using a known 80 % Ag-15 % In-5 % Cd alloy, is as follows: Ag, -0.02 %; In, +0.09 %; Cd, -0.03 %, absolute.

## TRACE IMPURITIES BY CARRIER-DISTILLATION SPECTROCHEMICAL METHOD

### 16. Scope

16.1 This test method is applicable to the determination of the trace impurities listed in 19.1 in silver-indium-cadmium alloys.

### 17. Summary of Test Method

17.1 The sample is cleaned, and a weighed quantity is dissolved in nitric acid. An equivalent weight of graphite is

added to the solution and it is evaporated to dryness at  $85 \pm 5^\circ\text{C}$ . The residue is moistened with a few drops of water and mixed until a slurry is obtained. A dilute hydrochloric acid solution is added and mixed well. The slurry is evaporated to dryness at  $85 \pm 5^\circ\text{C}$  in subdued light.

17.2 The dried sample mixture is blended with a barium fluoride-graphite carrier, weighed into graphite anode caps, and excited in a d-c arc. The spectrum is recorded photographically, and the spectral lines of interest are compared visually with standards exposed on the same plate.

### 18. Apparatus

18.1 Spectrograph—A spectrograph with sufficient resolving power and linear dispersion to separate the analytical lines from other lines in the spectrum of the sample in the spectral region from 220 to 400 nm is recommended. Instruments with a reciprocal linear dispersion of 0.3 nm/mm or less are satisfactory.

18.2 Excitation Source—A d-c arc source capable of sustaining a 12-A d-c arc.

18.3 Excitation Stand—Conventional type with adjustable water-cooled electrode holders.

18.4 Balance—A torsion-type balance with a capacity of 1.0 g and capable of weighing to the nearest 0.5 mg.

18.5 Pulverizer-Mixer—A mechanical mixer with a plastic vial and ball.

18.6 Comparator—Conventional type is satisfactory.

18.7 Photographic Processing Equipment—Photographic processing equipment conforming to the requirements of Practices E 115.

18.8 Steam Bath—Conventional type.

18.9 Drying Oven—Conventional type, stainless steel construction.

18.10 Beakers—25 or 50-mL capacity TFE-fluorocarbon construction.

18.11 Stirring Rods—TFE-fluorocarbon construction.

18.12 Venting Tool—See Fig. 1.

18.13 Electrodes—ASTM Types S-1, S-2, and C-1.

### 19. Reagents

19.1 Barium Fluoride (BaF<sub>2</sub>)—>99.90 % purity, < 10 μm particle size.

19.2 Barium Fluoride-Graphite Carrier—Homogenize 5 parts BaF<sub>2</sub> with 95 parts graphite in a plastic vial with a plastic ball on a mechanical mixer.

19.3 Cadmium—Cadmium metal, >99.99 % purity.

19.4 Graphite—Spectrographic grade, 200-mesh, nonpelletizing type.

19.5 Hydrochloric Acid (6 N)—Dilute 500-mL of redistilled hydrochloric acid (HCl, sp gr 1.19) to 1 L with double-distilled water.

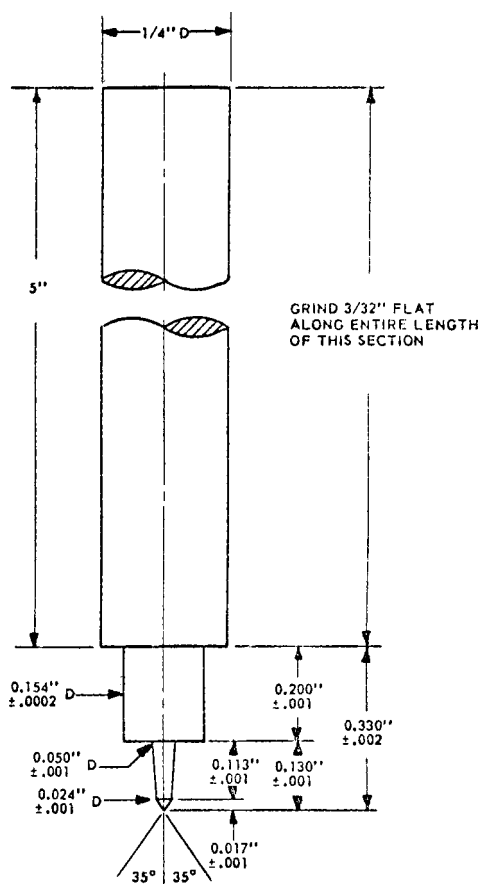
19.6 Indium—Indium metal, >99.99 % purity.

19.7 Nitric Acid (8 N)—Dilute 500 mL of redistilled nitric acid (HNO<sub>3</sub>, sp gr 1.42) to 1 L with double-distilled water.

19.8 Silver—Silver metal, >99.99 % purity.

### 20. Procedure

20.1 Preparation of Standards:



in.	Metric Equivalents		mm
	mm	in.	
0.001	0.03	0.154	3.91
0.002	0.05	0.200	5.08
0.017	0.43	0.330	8.38
0.024	0.61	3/32	2.4
0.050	1.27	1/4	6.4
0.113	2.87	5	127
0.130	3.30		

FIG. 1 Venting Tool

20.1.1 A minimum of four standards containing 1 to 1000 µg/g of each impurity element to be determined by blending known amounts of each impurity oxide or salt with a graphite matrix.<sup>8</sup>

20.1.2 Dissolve 20.00 g of silver metal, 3.75 g of indium metal, and 1.25 g of cadmium metal in 75-mL of 8 N HNO<sub>3</sub>. Cool and dilute to 200-mL in a volumetric flask with double-distilled water.

20.1.3 Pipet 2 mL of the Ag-In-Cd solution (see 20.1.2) into each of five TFE-fluorocarbon beakers (25-mL capacity). Weigh 250 ± 1 mg of graphite into the first beaker and 250 ± 1 mg of each graphite base standard (see 20.1.1) into the four remaining beakers, one standard in each of the beakers.

20.1.4 Thoroughly mix the graphite and the solution using a TFE-fluorocarbon stirring rod and carry through the sample preparation procedure starting with 20.2.5.

<sup>8</sup> G-Standards, commercially available from Spex Industries Inc., 3880 Park Ave., Edison, NJ 08820, have been found satisfactory.

20.2 Preparation of Samples:

20.2.1 Clean 0.5 to 1.0 g of sample with file, wash with organic solvent, and air dry.

20.2.2 Weigh the sample to the nearest 1 mg and transfer it to a 25-mL TFE-fluorocarbon beaker.

20.2.3 Add 5 mL of 8 N HNO<sub>3</sub> and let stand until the sample is completely dissolved.

20.2.4 Weigh an amount of graphite equivalent to the sample weight ± 1.0 mg and transfer it to the TFE-fluorocarbon beaker. Thoroughly mix using a TFE-fluorocarbon stirring rod.

20.2.5 Evaporate to dryness on a steam bath.

20.2.6 Cool the sample and add about 1 mL of double-distilled water and mix to a slurry with the TFE-fluorocarbon rod.

20.2.7 Add 3 mL of 6 N HCl and mix thoroughly with the TFE-fluorocarbon rod.

20.2.8 Evaporate to dryness in subdued light, or total darkness, on the steam bath.

20.2.9 Place the beaker in a drying oven, in total darkness, at 85 ± 5°C for 3 h.

20.2.10 Cool and pulverize the sample, in the TFE-fluorocarbon beaker, using the TFE-fluorocarbon stirring rod.

20.2.11 Use a mechanical mixer to blend 100 mg of sample with 100 mg of BaF<sub>2</sub>-graphite carrier in a plastic vial with a plastic ball for 30 s.

NOTE 1—The actual carrier is the mixture of BaF<sub>2</sub> and AgCl. The BaF<sub>2</sub>-graphite is not sufficient if the silver in the sample is not converted to AgCl.

20.2.12 Weigh duplicate 50-mg charges of samples and standards into ASTM Type S-2 anode caps.

20.2.13 Tap pack, vent the charge, and electrically excite under conditions listed below.

20.3 Spectrographic Procedure—Excitation and exposure conditions:

Discharge	d-c arc
Current, A	10 (shorted)
Electrode gap, mm	3
Preburn, s	5
Exposure, s	40
Slit width, µm	10
Wavelength range, nm	210 to 440, first order
Light transmission:	
Total filter	25 % T
Split field filter	100/10 % T
Emulsion	SA #1

20.4 Photographic Processing—Process the plates in accordance with Practice E 115.

21. Calculation

21.1 Visually compare the density of the sample impurity spectral line with the corresponding line in the standard spectrum. Estimate the impurity concentration using the lines listed in the following table.

Element	Analytical Lines		Concentration Range, µg/g
	Wavelength, nm		
Aluminum	256.80, 308.22		10 to 500
Arsenic	309.27, 234.98		50 to 500

Boron	249.68, 249.77	1 to 100	Titanium	334.90, 322.35	10 to 500
Beryllium	234.86	1 to 100	Vanadium	318.34, 318.40	5 to 100
Bismuth	306.77	1 to 100	Zinc	334.50, 330.26	10 to 500
Calcium	393.37, 422.67	50 to 1000	Zirconium	339.20, 334.82	100 to 1000
Cobalt	240.72, 304.40	1 to 100			
Chromium	283.56	10 to 1000			
Copper	324.75, 327.40	1 to 100			
Iron	283.56, 302.06	10 to 1000			
Magnesium	279.55, 280.27	10 to 500			
Manganese	279.83, 280.11	10 to 500			
Molybdenum	317.04, 313.26	10 to 500			
Sodium	330.23	50 to 500			
Nickel	305.08, 300.25	10 to 500			
Phosphorus	255.33	100 to 1000			
Lead	283.31, 261.42	5 to 100			
Silicon	251.61, 251.43	10 to 500			
Tin	284.00, 317.50	5 to 100			

## 22. Precision and Bias

**22.1 Precision**—When the sample plates are visually compared to the standard plates, experienced analysts can expect analytical results to vary within a factor of two; that is, 50 % to 200 % of the actual impurity element concentration.

**22.2 Bias**—Since there is no accepted reference material for determining bias in this test method, no statement on bias is being made.

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