Designation: E 378 – 97

Standard Test Method for Spectrographic Analysis of Silver by the Powder Technique[1]

This standard is issued under the fixed designation E 378; 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 spectrographic analysis of silver for the following elements in the ranges indicated:

Element	Concentration Range, %
Copper	0.0001 to 0.1
Lead	0.0001 to 0.05
Zinc	0.001 to 0.01
Bismuth	0.0001 to 0.01
Palladium	0.001 to 0.005
Chromium	0.0001 to 0.005
Iron	0.0001 to 0.005
Nickel	0.0001 to 0.005
Manganese	0.0001 to 0.005
Tin	0.0001 to 0.005

1.2 This test method is designed for the analysis of commercial and high-purity silver samples in the form of needles, chips, cast bars, or sheet stock.

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:*

B 413 Specification for Refined Silver[2]

E 50 Practices for Apparatus, Reagents and Safety Precautions for Chemical Analysis of Metals[3]

E 115 Practice for Photographic Processing in Optical Emission Spectrographic Analysis[3]

E 116 Practice for Photographic Photometry in Spectrochemical Analysis[3]

E 130 Practice for Designation of Shapes and Sizes of Graphite Electrodes[3]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[3]

E 409 Practice For Description and Performance of the Microphotometer[4]

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E 135.

4. Summary of Test Method

4.1 Samples and standards are prepared in the form of dry silver nitrate powder and packed into the craters of specially shaped graphite cup electrodes. The spectra are produced using dc arc excitation and recorded photographically. Intensity ratios of selected pairs of analytical lines and internal standard lines are determined photometrically. Concentrations are read from an analytical curve relating log intensity ratio to log concentration.

5. Significance and Use

5.1 Refined silver is marketed on purity. This test method is suitable for analysis of refined silver for compliance with Specification B 413.

6. Apparatus

6.1 *Excitation Source* providing a 12-A dc arc.

6.2 *Spectrograph* having 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 2500 to 3500 Å. An instrument having a reciprocal linear dispersion of 5 to 10 Å/mm in the first order satisfies these conditions.

6.3 *Photographic Processing Equipment* providing development, fixing, washing, and drying operations and conforming to the requirements of Practice E 115.

6.4 *Microphotometer* conforming to criteria of Practice E 409.

6.5 *Calculating Board* to convert microphotometer readings to log intensity ratios and concentrations.

7. Reagents and Materials

7.1 *Purity and Concentration of Reagents*—The purity and concentration of the chemical reagents used in preparing the

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[1] This test method is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.03 on Precious Metals.

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[2] *Annual Book of ASTM Standards*, Vol 02.04.

[3] *Annual Book of ASTM Standards*, Vol 03.05.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

standards and samples shall conform to the requirements prescribed in Practices E 50.

7.2 *Electrodes*—The sample electrode shall be high-purity Type S-4 and the counter electrode high-purity Type C-1 as described in Practice E 130.

7.3 *Silver Nitrate, High-Purity*. [5]

NOTE 1—Detection limits will be affected by the amount of impurity elements contained in the silver nitrate.

7.4 *Metals and Metal Salts*[3]—Bismuth, copper, iron, lead, nickel, palladium, and zinc as metals; chromium as chromium nitrate; manganese as manganese sulfate monohydrate; and tin as sodium stannate.

7.5 *Photographic Emulsion*. [6]

7.6 *Photographic Processing Solutions*— The formulas for photographic processing solutions are given in Practice E 115.

8. Preparation of Standards

8.1 *Silver Nitrate Stock Solution (1 mL = 1 g Ag)*—Dissolve 315.0 g of high-purity silver nitrate ($AgNO_3$) in 150 mL of water in a 200-mL volumetric flask and dilute to volume.

8.2 *Element Stock Solutions (1 mL = 0.5 mg of each element)*—Dissolve 100 mg of each metal in 10 mL of nitric acid (HNO_3, 1 + 1); dissolve 770 mg of chromium nitrate [$Cr(NO_3)_2 \cdot 9\,H_2O$] and 308 mg of manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$) in 10 mL of water; combine element solutions in a 200-mL volumetric flask and dilute with water to volume.

8.2.1 *Diluted Stock Solution*—Make dilutions of the element stock solutions with water to contain 0.05 mg and 0.005 mg of each element.

8.2.2 *Tin Stock Solution (1 mL = 0.5 mg Sn)*—Dissolve 225 mg of sodium stannate ($NaSnO_3 \cdot 3H_2O$) in water in a 200-mL volumetric flask and dilute to volume.

NOTE 2—Prepare the tin stock solution as well as any diluted stock solutions just prior to use to prevent precipitation or plating of elements.

8.3 *Working Standards*—Place 20-mL aliquots of the silver nitrate solution in 200-mL TFE-fluorocarbon evaporating dishes. Add measured amounts of the element solutions to prepare a series of standards containing impurity concentrations to cover the ranges designated in the Scope. Appropriate increments of concentration for the standards are 1, 2.5, 5, and 10. Evaporate each standard to dryness on a steam bath (Note 3). Bake for 2 h at 110°C. Grind the salt residue to a fine powder and store in tightly capped polyethylene containers.

NOTE 3—As the drying process progresses, break up the crystals with a TFE-fluorocarbon spatula and keep them pushed down in the dish to prevent the crystals from creeping.

9. Preparation of Samples

9.1 Transfer 1.0 g of the silver metal to an evaporating dish, add 5 mL of HNO_3 (3 + 1) and heat gently until dissolved. Evaporate to dryness, cool and grind the total silver nitrate residue to a fine powder. Store in a 110°C oven for a minimum of 2 h or until ready to sample.

TABLE 1 Analytical and Internal Standard Lines

Element	Analytical Line, Å	Concentration Range,
Copper	3247.54	0.0001 to 0.005
	2961.16	0.005 to 0.1
Lead	2833.06	0.0001 to 0.005
	2873.32	0.001 to 0.05
Zinc	3345.02	0.001 to 0.01
Bismuth	3067.72	0.0001 to 0.005
	2897.98	0.001 to 0.01
Palladium	3242.70	0.001 to 0.005
Chromium	3021.56	0.0001 to 0.005
	2835.63	
Iron	3021.07	0.0001 to 0.005
	2999.51	0.001 to 0.005
Nickel	3002.49	0.0001 to 0.005
	3050.82	
Manganese	2801.06	0.0001 to 0.005
	2798.27	
Tin	2839.99	0.0001 to 0.005
	2863.33	
Silver	3099.12	internal standard

10. Preparation of Apparatus

10.1 *Electrode System*—Firmly pack the dried silver nitrate powder level full into the crater of a preformed graphite electrode Type S-4 and insert in the lower electrode holder as the anode. Insert a Type C-1 counter electrode in the upper electrode holder as the cathode. Adjust the analytical gap to 3 mm.

11. Calibration

11.1 *Emulsion Calibration*—Calibrate the emulsion in accordance with Practice E 116.

11.2 *Preparation of Analytical Curves*— Convert the percent transmittances of the analytical lines and the internal standard line to intensity ratios using the emulsion calibration curve. Plot log intensity ratio versus log concentration to obtain the analytical curve.

12. Procedure for Excitation and Exposure

12.1 Produce and record the spectra according to the following conditions:

12.1.1 *Electrical Parameters*:

Current (d-c), A	12.0

12.1.2 *Exposure Conditions*:

Spectral region, Å	to include 2500 to 3500
Slit width, µm	50

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[5] For sources of high-purity metals and salts see *Report on Available Standard Samples and Related Materials for Spectrochemical Analysis, ASTM DS 2*, ASTM, 1964.

[6] Kodak Spectrum Analysis No. 1 film or plate or equivalent has been found satisfactory.

Preburn period, s	0
Exposure period, s	30

12.1.3 *Exposure Index*—The transmittance of the Ag 3099.12 Å line shall be approximately 40 %. Use a rotating sector or step filters as needed to obtain transmittances of the analytical lines between 10 and 90 %.

12.1.4 *Replicate Exposures*—Make duplicate exposures for each sample. Make quadruplicate exposures for each standard.

13. Photographic Processing

13.1 Process the emulsion in accordance with Practice E 115.

14. Photometry

14.1 With a microphotometer measure the transmittance of the analytical line pairs shown in Table 1. Correct the measurement for background when the transmittance of the background is below 95 % transmittance. Any background correction must be applied to spectra of both the calibration curve and the sample.

15. Calculation

15.1 Calculate the log intensity ratio for each analytical line pair from the emulsion calibration curve. Determine concentrations from the analytical curves.

TABLE 2 Summary of Cooperative Test Data7[7]

	Sample 1		Sample 2		Sample 3		Sample 4[A]	
Sample	Average Concentration, %[B]	Relative Standard Deviation[C]	Average concentration, %[B]	Relative Standard Deviation[C]	Average Concentration, %[B]	Relative Standard Deviation[C]	Average Concentration, %[B]	Relative Standard Deviation[C]
Copper	0.0697	8.4	0.0159	20.9	0.0023	18.9	0.0006	22.6
Lead	0.0161	8.5	0.0095	8.8	0.0014	10.6	0.0008	13.3
Zinc	0.0135	9.3	0.0146	11.2	0.0013	18.2	...	...
Bismuth	0.0036	7.0	0.0011	6.1	0.0005	6.4	0.0001	...
Palladium	0.0036	19.8	0.0021	19.9	0.0019	11.1	...	...
Chromium	0.0002	15.0	0.0002	11.9	0.0002	16.5	...	...
Iron	0.0021	14.9	0.0024	12.3	0.0012	18.9	0.0006	23.2
Nickel	0.0041	9.9	0.0015	11.9	0.0002	18.3	...	...
Manganese	0.0006	5.7	0.0004	12.3	0.0001	7.9	...	...
Tin	0.0027	8.5	0.0024	13.5	0.0001	25.9	...	...

[A] Average relative standard deviation is given only for elements reported by all five testing laboratories. The concentration of the elements not reported is below the concentration range designated in the Scope.

[B] Each value represents the average from five laboratories, each laboratory making determinations on each of four days.

[C] The Relative Standard Deviation, *RSD*, is calculated as follows:

$$RSD\ x = (100/\bar{X})\sqrt{\Sigma d^2/(n-1)}$$

where:

$\bar{X}$ = average concentration.

d = difference of the determinations from the mean, and

n = number of determinations.

16. Precision and Bias

16.1 *Precision*—The precision of the test method is summarized in Table 2.

16.2 *Bias*—The accuracy of the test method approaches the precision. Supporting data are on file at ASTM Headquarters.[7]

17. Keywords

17.1 DC arc; optical emission; silver (impurities in); silver powder technique; spectrographic analysis

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[7] Supporting data, based on the results of cooperative tests, have been filed at ASTM Headquarters. Request: RR E02-72.

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