Designation: E1898 – 13

Standard Test Method for Determination of Silver in Copper Concentrates by Flame Atomic Absorption Spectrometry[1]

This standard is issued under the fixed designation E1898; 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 silver in the range of 13 µg/g to 500 µg/g by acid dissolution of the silver and measurement by atomic absorption spectrometry. Copper concentrates are internationally traded within the following content ranges:

Element	Unit	Content Range		
Aluminum	%	0.05	to	2.50
Antimony	%	0.0001	to	4.50
Arsenic	%	0.01	to	0.50
Barium	%	0.003	to	0.10
Bismuth	%	0.001	to	0.16
Cadmium	%	0.0005	to	0.04
Calcium	%	0.05	to	4.00
Carbon	%	0.10	to	0.90
Chlorine	%	0.001	to	0.006
Chromium	%	0.0001	to	0.10
Cobalt	%	0.0005	to	0.20
Copper	%	10.0	to	44.0
Fluorine	%	0.001	to	0.10
Gold	µg/g	1.40	to	100.0
Iron	%	12.0	to	30.0
Lead	%	0.01	to	1.40
Magnesium	%	0.02	to	2.00
Manganese	%	0.009	to	0.10
Mercury	µg/g	0.05	to	50.0
Molybdenum	%	0.002	to	0.25
Nickel	%	0.0001	to	0.08
Silicon	%	0.40	to	20.0
Silver	µg/g	18.0	to	8000
Sulfur	%	10.0	to	36.0
Tin	%	0.004	to	0.012
Zinc	%	0.005	to	4.30

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 its use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 The analyst has the option of either digesting the sample in HNO_3 and HCl or HNO_3 and $HClO_4$, depending on their preference and equipment availability. The filtered solutions are aspirated into an air-acetylene flame of an atomic absorption spectrometer. Spectral energy at approximately 328.1 nm from a silver hollow cathode lamp is passed through the flame and the absorbance is measured. This absorbance is compared with the absorbance of a series of standard calibration solutions.

5. Significance and Use

5.1 In the primary metallurgical processes used by the mineral processing industry for copper bearing ores, copper and silver associated with sulfide mineralization are concentrated by the process of flotation for recovery of the metals.

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[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

Current edition approved April 1, 2013. Published June 2013. Originally approved in 1997. Last previous edition approved in 2007 as E1898 - 07. DOI: 10.1520/E1898-13.

[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.

5.2 This test method is a comparative method and is intended to be a referee method for compliance with compositional specifications for metal content or to monitor processes.

5.3 It is assumed that all who use this method will be trained analysts capable of performing skillfully and safely. It is expected that work will be performed in a properly equipped laboratory and that proper waste disposal procedures will be followed. Appropriate quality control practices must be followed such as those described in Guide E882.

6. Interferences

6.1 Elements normally found in copper concentrates do not interfere. Use of instrumental background correction is required to compensate for non specific absorption interferences in the flame.

7. Apparatus

7.1 *Atomic Absorption Spectrometer,* capable of resolving the 328.1 nm silver line, equipped with an air-acetylene premix burner and a silver hollow cathode lamp. The performance of the instrument must be such that the response of silver absorbance is linear over the range of 0.5 µg/mL to 4.0 µg/mL.

8. Reagents and Materials

8.1 *Silver Calibration Solutions*—By means of pipets, transfer (0, 5, 10, 20, 30, and 40) mL of Silver Standard Solution B (8.3) into 100-mL volumetric flasks. Dilute to the mark with HC1 (1 + 3) and mix. These solutions are (0, 0.5, 1.0, 2.0, 3.0, and 4.0) µg /mL, respectively.

8.2 *Silver Standard Solution A* (1 mL = 1 mg Ag)—Dissolve 1000 g of silver metal (purity: 99.99 %, minimum) in 50 mL of HNO_3 (1+1). Dilute to about 100 mL and boil gently to expel the oxides of nitrogen. Cool and transfer to a 1-L volumetric flask. Dilute to the mark and mix. Solution must be clear, otherwise, discard it and repeat the preparation. Store in a dark bottle.

NOTE 1—All reagents must be free of chloride contamination.

8.2.1 A certified reference solution meeting these specifications may also be used.

8.3 *Silver Standard Solution B* (1 mL = 10 µg Ag)—Pipet 10 mL of Silver Standard Solution A (8.2) into a 1-L volumetric flask containing about 500 mL of water and 250 mL of HCl. Mix, cool, dilute to the mark, and remix. If turbid, discard the solution and repeat the preparation. Transfer to a dark bottle. Prepare immediately before use.

8.4 *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.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

8.5 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I or II of Specification D1193. Other reagent water types, Type III or Type IV, may be used if they do not cause silver precipitation or effect non-measurable change in the blank or sample.

9. Hazards

9.1 For precautions to be observed in the use of certain reagents and equipment in this test method, refer to Practices E50.

10. Sampling and Sample Preparation

10.1 The gross sample must be collected and prepared so that it is representative of the lot of copper concentrate to be analyzed.

NOTE 2—Gross samples may need to dried at low temperature in order to determine the mercury content without drying losses.

10.2 The laboratory sample must be ground, if necessary, so that 100 % passes a 150 µm sieve.

NOTE 3—Verify the adequacy of grind on a separate sub-sample. Do not pass the laboratory sample through the 150 µm sieve.

11. Preparation of Apparatus

11.1 Follow the instrument manufacturer's instructions to adjust the instrument for silver at 328.1 nm. Warm up the instrument with background correction applied in accordance with the manufacturer's instructions.

11.2 With the silver hollow cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 328.1 nm line.

11.3 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the silver solution with the highest concentration from the series prepared in 8.1 and adjust the burner, acetylene, and air flow rates to obtain maximum response. Whenever one or more of these parameters is changed, recalibration is necessary.

11.4 Aspirate the silver solution used in 11.3 to ensure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviation, s, of the readings, as follows:

$$s = 0.40\,(A - B) \qquad (1)$$

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[3] *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 *Reagent Chemicals and Standards*, by Joseph Rosin, D. Nostrand Co., Inc., New York, NY, and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

where:

A = highest of the six values found, and
B = lowest of the six values found.

NOTE 4—Can also be calculated as follows:

$$s = \sqrt{\frac{\Sigma(c-d)^2}{(e-1)}}$$

where:

c = individual absorbance readings,
d = mean of absorbance readings, and
e = number of readings (6).

11.5 Using water as a zero reference, and beginning with the solution to which no addition of silver was made in 8.1, aspirate each calibration solution in ascending order of concentration, and record its absorbance. If the value of the solution with the highest concentration used in 8.1 differs from the average of the six values in 11.4 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, take appropriate corrective measures, and repeat 11.2-11.5.

12. Calibration

12.1 Calibration Curve—Plot the average net absorbance values versus micrograms of silver per millilitre on rectangular coordinate paper or calibrate in accordance with the manufacturer's instructions.

12.2 Using water as a zero reference, aspirate calibration standards alternately until stable readings occur (within 2 %). Alternate readings: three samples, a standard, three samples and another standard, etc., until the absorbance for all samples and standards have been determined at least three times. (The absorbances should repeat within 2 %). Average all values for standards and samples. Plot curve of absorbance versus µg/mL silver in the standards. Read sample absorbance from the curve to obtain µg/mL values of the samples. Standards and blank must plot a straight line near zero absorbance on the graph.

13. Procedure

13.1 *Test Solution:*

13.1.1 Select three test samples for each concentrate and transfer an appropriate amount to tared weighing vessels. Dry at 105 °C in a drying oven for at least two hours to constant weight. Select final weights in accordance with the following:

Est. Ag, µg/g	Sample Wt., g	Wt. Tolerance, mg	Dil., mL
20-150	2.0	0.1	100
150-300	2.0	0.1	200
300-500	1.0	0.1	200
500-1000	1.0	0.1	500
1000-3000	1.0	0.1	1000

Transfer to a 250-mL beaker.

13.1.2 *HNO_3 and HCl Decomposition:*

13.1.2.1 Place each test sample in a beaker as in 13.1.1. Add 35 mL HNO_3 (1+1), cover with a watch glass, and heat gently until dissolution is complete. Add 10 mL HC1, slip cover aside, and evaporate to dryness. Dissolve the dry salts in 25 mL HC1 (1+3). Heat to boiling, then cool. Rinse watch glass and beaker with HC1 (1+3) and filter through a dry high-wet strength, medium-porosity filter paper[4] into a clean volumetric flask.. Wash the paper eight times with HC1 (1+3) and discard the paper. Dilute to volume with HC1 (1+3) and mix.

NOTE 5—Some copper concentrates may not be totally decomposed by these digestion methods. The user is advised to check any residue from the digestion procedure for residual silver.

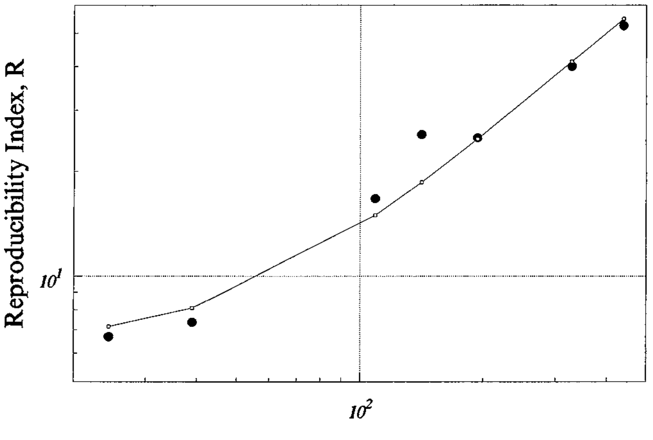

FIG. 1 Ag in Cu concentrates: HNO_3-HCl Method

13.1.3 *HNO_3 and $HClO_4$ Decomposition:*

13.1.3.1 Place each test sample in a beaker as in 13.1.1. Add 35 mL HNO_3 (1+1), cover with a watch glass, and heat gently until dissolution is complete and oxides of nitrogen are dispelled. Cautiously add 10 mL of $HClO_4$ and continue heating (see Note 6). Evaporate to dense white fumes. Continue fuming to near dryness.

NOTE 6—Handle $HClO_4$ in accordance with practices E50 as follows: $HClO_4$ can be used safely, but only under carefully prescribed conditions. Dilute $HClO_4$ has the same hazardous properties as other strong acids, but the concentrated acid, especially when it is hot, reacts rapidly and often with violently explosive force with oxidizable materials. Only well-established procedures should be employed for $HClO_4$ oxidations and the procedures should be followed *exactly* as written. Specially designed hoods are specified for handling $HClO_4$ fumes and any hood in which $HClO_4$ may be fumed should not be used for other operations that permit easily oxidizable material to collect in the ducts or blower.

13.1.3.2 Cool slightly and dissolve salts in 35 mL HC1 (1+3). Heat to boiling. Allow to cool again. Rinse watch glass and beaker with HC1 (1+3) and filter through a dry, high wet-strength, medium- porosity filter paper[4] into a volumetric flask. Wash the paper eight times with HC1 (1+3) and discard the paper. Dilute to volume with HCl (1+3) and mix.

13.2 Prepare a reagent blank by treating the same amount of all reagents as directed in 13.1.2 or 13.1.3. Use reagents from the same lots for blank and test solutions.

13.3 *Measurement*—Using water as a zero reference, aspirate calibration standards alternately until stable readings occur (within 2 %). Alternate readings: three samples, a standard, three samples and another standard, etc., until the absorbance for all samples and standards have been determined at least

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[4] Whatman No. 54 or No. 541 has been found suitable.

three times. (The absorbances should repeat within 2 %). Average all values for standards and samples. Plot curve of absorbance versus µg/mL silver in the standards. Read sample absorbance from the curve to obtain µg/mL values of the samples. Standards and blank must plot a straight line near zero absorbance on the graph.

14. Calculation

14.1 Convert the absorbance of the test sample solutions and the reagent blank solution to micrograms of silver per millilitre of the final dilution volume by means of the calibration curve. Calculate the content of silver as follows:

$$E = C(A - B)/D \qquad (2)$$

where:

A = µg of silver per mL in the final test solution,
B = µg of silver per mL in the final reagent blank,
C = final volume of test solution, mL,
D = weight of dry sample in final volume, g, and
E = silver content in the test sample, µg/g

14.2 Average the test results for the triplicate test sample portions and round the results in accordance with Practice E29, to the nearest µg/g, using the rounding method.

15. Precision and Bias[5]

15.1 *Precision*—Thirty-one laboratories cooperated in testing these methods and obtained the statistical information summarized in Table 1 and Table 2. The reproducibility index data fits the analytical error model of Guide E1763 as a function of silver content:

$$HNO_3 - HCl{:}R = \sqrt{6.49^2 + (0.1239\ C_{Ag})^2} \qquad (3)$$

$$HNO_3 - HClO_4{:}R = \sqrt{5.30^2 + (0.1402\ C_{Ag})^2} \qquad (4)$$

where:

C_{Ag} = content of silver, µg/g

These relationships are plotted in Fig. 1 and Fig. 2. The equations or Table 3 may be used to approximate the reproducibility index to be expected at various silver contents.

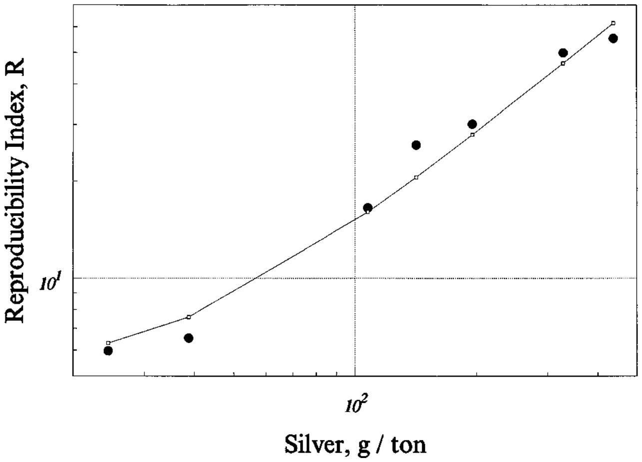

FIG. 2 Ag in Cu concentrates: HNO_3-$HClO_4$ Method

TABLE 3 Predicted Reproducibility Index, *R*

HNO_3-HCl		HNO_3-$HClO_4$	
Ag, µg/g	*R*	Ag, µg/g	*R*
15	6.75	15	5.70
30	7.48	30	6.77
60	9.87	60	9.94
120	16.2	120	17.6
250	31.6	250	35.4
500	62.3	500	70.3
1000	124	1000	140

15.2 *Bias*—The bias of the test method is indicated by the mean of interlaboratory results for sample 91-8 which is an accepted reference material, CANMET CCU-1a. The accepted reference value is 144.8 µg/g Ag and the mean of the interlaboratory study is 141 µg/g Ag, indicating a slightly low bias in the method. The bias, however is less than the reproducibility (R) for the method. It is recommended that the

TABLE 1 Statistical Data, HNO_3-HCl Method

Test Material	Number of Laboratories	Silver found, µg/g	Min SD (S_M, Practice E1601)	Reproducibility SD (S_R, Practice E1601)	Reproducibility Index (*R*, Practice E1601)	$R_{rel\ \%}$
91-7	29[A]	24.37	0.9664	2.3889	6.6889	27.44
91-5	31	39.02	1.1674	2.6286	7.360	18.86
91-4	31	108.8	2.486	5.974	16.726	15.37
91-8	25[B]	141.1	2.083	9.139	25.589	18.14
91-6	31	193.5	3.493	8.959	25.085	12.96
91-2	31	329.3	5.478	14.294	40.023	12.15
91-1	31	439.7	5.147	18.741	52.476	11.93
	Certified Silver, µg/g	Bias, µg/g	Material Identification (Source)		Description	
91-8	144.8	–4	CANMET CCU-1a		Copper concentrate	

[A] Results from two laboratories submitting fewer than three replicates not included.
[B] Results from six laboratories submitting fewer than three replicates not included.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1020.

TABLE 2 Statistical Data, HNO_3-$HClO_4$ Method

Test Material	Number of Laboratories[A]	Silver found, µg/g	Min SD (S_M, Practice E1601)	Reproducibility SD (S_R, Practice E1601)	Reproducibility Index (R, Practice E1601)	$R_{rel\ \%}$
91-7	30	24.41	0.8304	2.1351	5.9782	24.49
91-5	30	38.66	1.1694	2.3379	6.5461	16.93
91-4	30	107.7	2.039	5.889	16.489	15.31
91-8	18[B]	141.5	2.820	9.255	25.913	18.31
91-6	30	195.4	5.333	10.752	30.106	15.40
91-2	30	328.4	11.491	17.845	49.965	15.21
91-1	30	437.6	6.682	19.774	55.366	12.65
	Certified Silver, µg/g	Bias, µg/g	Material Identification (Source)		Description	
91-8	144.8	- 3	CANMET CCU-1a		Copper concentrate	

[A] Laboratory 13 submitted no data using the perchloric acid method.

[B] Results from 13 laboratories submitting fewer than three replicates not included.

user of the test method include accepted reference materials and compare the accepted values for the reference materials with the mean of the test results. When the mean of the test results is outside of the accepted range for the reference materials, the problem in the application of the method must be corrected before repeating the analysis.

16. Keywords

16.1 copper concentrates; flame atomic absorption spectrometry; silver content

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