Designation: E 1898 – 02

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

1. Scope

1.1 This test method covers the determination of silver in the range of 50 μg/g to 1000 μg/g by acid dissolution of the silver and measurement by atomic absorption spectrophotometry. Copper concentrates are internationally traded within the following concentration ranges:

Element	Unit	Concentration 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 *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:*
D 1193 Specification for Reagent Water[2]

E 29 Practice For Using Significant Digits in Test Data to Determine Conformance With Specifications[3]
E 50 Practices for Apparatus, Reagents and Safety Precautions for Chemical Analysis of Metals[3]
E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[3]
E 663 Practice for Flame Atomic Absorption Analysis[4]
E 882 Guide for Accountability and Quality Control in the Chemical Analysis of Metals[3]
E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry[3]
E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method[4]
E 1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods[3]

3. Terminology

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

4. Summary of Test Method

4.1 The analyst has the option of either digesting the sample in nitric and hydrochloric acids or nitric and perchloric acids, depending on their preference and equipment availability. The filtered solutions are aspirated into an air-acetylene flame of an atomic absorption spectrophotometer. 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.

5.2 This test method is intended to be a referee method for the determination of silver in copper concentrates. It is assumed that all who use this procedure will be trained analysts

capable of performing common laboratory procedures 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 E 882.

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 Spectrophotometer*, 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 to 4.0 μg/mL.

8. Reagents and Materials

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.[5] 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D 1193.

8.3 *Silver Standard Solution A* (1 mL = 1 mg Ag)—Dissolve 1000 g of silver metal (purity: 99.99 %, minimum) in 50 mL of nitric acid (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.

8.4 *Silver Standard Solution B* (1 mL = 10 μg Ag)—Pipet 10 mL of Silver Standard Solution A into a 1-L volumetric flask containing about 500 mL of water and 250 mL of hydrochloric acid. 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.

9. Hazards

9.1 For precautions to be observed in the use of certain reagents and equipment in this test method, refer to Practices E 50.

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. The laboratory sample must be pulverized, if necessary, so that 100 % passes a No. 100 (150 μm) sieve.

NOTE 2—Verify the adequacy of grind on a separate sub-sample. Do not pass the laboratory sample through the No. 100 sieve.

11. Calibration and Standardization

11.1 *Calibration Solutions*—By means of pipets, transfer 0, 5, 10, 20, 30, and 40 mL of Silver Standard Solution B 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 Ag/mL, respectively.

11.2 *Photometry*:

11.2.1 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.

11.2.2 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 11.1 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.

11.2.3 Aspirate the silver solution used in 11.2.2 to ensure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviation, *s*, of the readings, as follows:

$$s = 0.40\,(A-B) \tag{1}$$

where:
A = highest of the six values found, and
B = lowest of the six values found.[7]

11.2.4 Using water as a zero reference, and beginning with the solution to which no addition of silver was made in 11.1, 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 11.1 differs from the average of the six values in 11.2.3 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 11.2.1-11.2.4.

11.2.5 *Calibration Curve*—Plot the average net absorbance values versus micrograms of silver per millilitre on rectangular coordinate paper. Test for linearity as described in Guide E 1024.

12. Procedure

12.1 *Test Solution*:

12.1.1 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.

12.1.2 *Nitric and Hydrochloric Acid Decomposition*:

12.1.2.1 Place each test sample in a beaker as in 12.1.1. Add 35 mL HNO_3 (1+1), cover with a watchglass, 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 watchglass and beaker with HC1 (1+3) and filter through a dry high-wet strength, medium-porosity filter paper[7] into a clean volumetric flask, as shown in 12.1.1. Wash the paper eight times with HC1 (1+3) and discard the paper. Dilute to volume with HC1 (1+3) and mix.

NOTE 3—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.

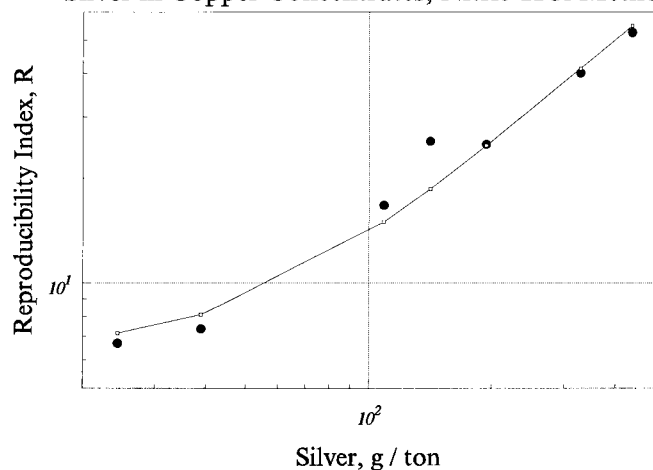## Silver in Copper Concentrates, Nitric-HCl Method

FIG. 1 Nitric-Hydrochloric Acid

12.1.3 *Nitric and Perchloric Acid Decomposition*:

12.1.3.1 Place each test sample in a beaker as in 12.1.1. Add 35 mL HNO_3 (1+1), cover with a watchglass, 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 4). Evaporate to dense white fumes. Continue fuming to near dryness.

NOTE 4—Handle perchloric acid in accordance with practices E 50 as follows:
Perchloric acid can be used safely, but only under carefully prescribed conditions. Dilute perchloric acid 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 perchloric acid oxidations and the procedures should be followed *exactly* as written. Specially designed hoods are specified for handling perchloric acid fumes and any hood in which perchloric acid may be fumed should not be used for other operations that permit easily oxidizable material to collect in the ducts or blower.

12.1.3.2 Cool slightly and dissolve salts in 35 mL HC1 (1+3). Heat to boiling. Allow to cool again. Rinse watchglass and beaker with HC1 (1+3) and filter through a dry, high wet-strength, medium- porosity filter paper[7] into a volumetric flask as shown in 12.1.1. Wash the paper eight times with HC1 (1+3) and discard the paper. Dilute to volume with HC1 (1+3) and mix (see Note 3).

12.2 Prepare a reagent blank by treating the same amount of all reagents as directed in 12.1.2 or 12.1.3. Use reagents from the same lots for blank and test solutions.

12.3 *Photometry*—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. Calculation

13.1 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 concentration of silver as follows:

$$\text{Silver, μg/g} = C\,(A - B)/D \tag{2}$$

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, and
D = weight of dry sample in final volume, g.

13.2 Average the test results for the triplicate test sample portions and round the results in accordance with Practice E 29, to the nearest μg/g.

14. Precision and Bias [7]

14.1 *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 E 1763 as a function of silver content:

$$\text{Nitric} - \text{Hydrochloric Acid: } R = \sqrt{6.49^2 + (0.1239\,C_{Ag})^2} \tag{3}$$

$$\text{Perchloric Acid: } R = \sqrt{5.30^2 + (0.1402\,C_{Ag})^2} \tag{4}$$

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.

14.2 *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

TABLE 1 Statistical Data, Nitric-Hydrochloric Acid Method

Test Material	Number of Laboratories	Silver found, µg/g	Min SD (S_M, Practice E 1601)	Reproducibility SD (S_R, Practice E 1601)	Reproducibility Index (R, Practice E 1601)	$R_{rel\ \%}$
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.

TABLE 2 Statistical Data, Perchloric Acid Method

Test Material	Number of Laboratories[A]	Silver found, µg/g	Min SD (S_M, Practice E 1601)	Reproducibility SD (S_R, Practice E 1601)	Reproducibility Index (R, Practice E 1601)	$R_{rel\ \%}$
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.
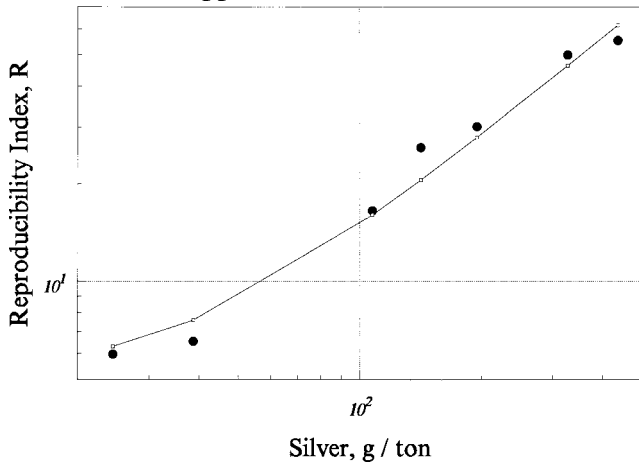
Silver in Copper Concentrates, Perchloric Method

FIG. 2 Perchloric Acid

TABLE 3 Predicted Reproducibility Index, R

Nitric-Hydrochloric Acid		Perchloric Acid	
Silver, µg/g	R	Silver, 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

bias in the method. The bias, however is less than the reproducibility (R) for the method. It is recommended that the 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.

15. Keywords

15.1 copper concentrates; silver content

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