

Silver, atomic absorption spectrophotometry, graphite furnace

Parameters and Codes:

Silver, dissolved, I-2724-89 ($\mu\text{g/L}$ as Ag): (01075)

Silver, whole water recoverable, I-4724-89 ($\mu\text{g/L}$ as Ag): (01077)

1. Application

1.1 This method is used to determine silver in samples of water and water-suspended sediment with a specific conductance not greater than $10,000 \mu\text{S/cm}$. With Zeeman background correction and a $20\text{-}\mu\text{L}$ sample, the method is applicable in the range from 1 to $10 \mu\text{g/L}$. Sample solutions that contain silver concentrations greater than $10 \mu\text{g/L}$ must be diluted or be analyzed by an alternate method. This method was implemented in the National Water Quality Laboratory in May 1989.

1.2 The analytical range and detection limit can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings.

1.3 Whole water recoverable silver in samples of water-suspended sediment must undergo preliminary digestion by method I-3485 before being determined.

2. Summary of method

Silver is determined by atomic absorption spectrophotometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). Whole water recoverable silver samples are evaporated to dryness and then brought back to volume with $0.1N \text{HNO}_3$ prior to introduction to the graphite furnace. A sample is placed on the graphite platform, and a matrix modifier is added. The sample then is evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal produced during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences for samples with specific conductances less than $10,000 \mu\text{S/cm}$ normally are small. In addition, the use of the graphite platform reduces the effects of many interferences.

3.2 Hydrochloric acid added to the water-suspended samples during the digestion process causes false silver signals. A concentration of $30 \mu\text{L HCl}$ per milliliter of water will cause false readings of 2 to $3 \mu\text{g/L}$ of silver.

Concentrations increase proportionately with increased additions of HCl. Evaporate digested samples to dryness to remove excess HCl.

3.3 Special precautionary measures to prevent contamination are used during sample collection and laboratory determination.

4. Apparatus

4.1 *Atomic absorption spectrophotometer*, for use at 328.1 nm and equipped with Zeeman background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer needs to have high-temperature ramping and controlled argon-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize operations and instrumental performance. A 20- μ L sample with a 10- μ g/L concentration of silver should yield a signal of approximately 0.59 absorbance-second. This absorbance signal is based on silver's characteristic mass of 1.5 pg for a signal of 0.0044 absorbance-second. A 20- μ L sample generally requires 30 seconds at 130°C to dry. Samples that have a complex matrix might require a longer drying or charring time. Peak shapes may be used to detect insufficient drying, charring, or atomization times or temperatures.

4.1.2 *Graphite furnace*, capable of reaching a temperature of 1,800°C sufficient to atomize silver. **Warning:** dial settings frequently are inaccurate, and newly conditioned furnaces need to be temperature-calibrated.

4.1.3 *Graphite tubes and platforms*, pyrolytically coated graphite tubes and platforms are suggested.

4.2 *Labware*. Many trace metals at small concentrations adsorb rapidly to glassware. To preclude this problem, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternatively, glassware, particularly flasks and pipets, can be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co.), according to the manufacturer's instructions. Check autosampler cups for contamination. Lancer polystyrene disposable cups are satisfactory after acid rinsing. Alternatively, reusable Teflon or FEP cups can be purchased.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen also can be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Matrix modifier solution*, 6.9 g/L $\text{NH}_4\text{H}_2\text{PO}_4$ and 1.005 g/L $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: Add 13.8 g $\text{NH}_4\text{H}_2\text{PO}_4$ to 950 mL water; mix and dilute to 1,000 mL. Add 2.01 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to 950 mL water; mix and dilute to 1,000 mL. Mix the two solutions together 1 + 1. Analyze 20 μL of matrix modifier to determine if silver contamination is present. If the silver reading is more than 0.005 absorbance-second, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) followed by extraction with methyl isobutyl ketone (MIBK) (NOTE 1). Analyze 20 μL of the purified solution. Repeat extractions until the silver level is reduced to the acceptable level. DO NOT ADD ACID TO THE PURIFIED MATRIX MODIFIER SOLUTION.

NOTE 1. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Add 10.0 g APDC to 1 L of water and mix well. Add 5.0 mL of the APDC solution to each 100.0 mL of matrix modifier. Shake vigorously for 10 minutes. Add 10 mL MIBK/100 mL of solution and shake vigorously for at least 10 minutes. Separate MIBK by draining through separatory funnel. Repeat process. Since some MIBK will remain in the solution, boil for 10 minutes in a silicone-treated or acid-rinsed container covered with a watch glass.

5.2 *Nitric acid*, concentrated, ultrapure (sp gr 1.41): J.T. Baker Ultrex brand HNO_3 is adequately pure; however, check each lot for contamination. Analyze acidified water (paragraph 5.9) for silver. Add 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-second.

5.3 *Nitric acid*, 0.1N: Add 6.4 mL ultrapure concentrated HNO_3 to water and dilute to 1 L.

5.4 *Silver standard solution I*, 1.00 mL = 1,000 μg Ag: A commercially prepared and certified silver standard can be used. An alternate method is to dissolve 1.0000 g silver wire in a minimum of dilute HNO_3 . Heat to increase rate of dissolution. Add 4 mL ultrapure concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with water.

5.5 *Silver standard solution II*, 1.00 mL = 10.0 μg Ag: Dilute 10.0 mL silver standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified water (paragraph 5.9) to make dilutions. Store all standards in sealed Teflon or FEP containers. Rinse each container twice with a small volume of standard solution before filling the storage container. Standard stored for 6 months in FEP containers yielded values equal to freshly prepared standards.

5.6 *Silver standard solution III*, 1.00 mL = 1.00 µg Ag: Dilute 100.0 mL silver standard solution II to 1,000 mL with acidified water. Prepare fresh monthly.

5.7 *Silver working solution IV*, 1.00 mL = 0.010 µg Ag: Dilute 10.0 mL silver standard solution III to 1,000 mL, with acidified water. Prepare fresh monthly.

5.8 *Silver working solution V*, 1.00 mL = 0.005 µg Ag: Dilute 5.0 mL silver standard solution III to 1,000 mL with acidified water. Prepare fresh monthly.

5.9 *Water, acidified*: Add 4 mL ultrapure concentrated HNO₃ (sp gr 1.41) to each liter of water.

5.10 *Water*: All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

6. Procedure

6.1 The autosampler and the graphite furnace need to be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1N HNO₃ solution.

6.3 For dissolved silver, proceed to paragraph 6.4. Follow instructions in paragraph 6.3.1 for whole water recoverable silver.

6.3.1 Pipet 1.0 mL of each digested sample into autosampler cups. Add 100 µL concentrated HNO₃ and 100 µL matrix modifier solution.

6.3.2 In a clean hood environment, allow samples to evaporate to dryness. Temperatures as great as 50°C can be used to speed the process.

6.3.3 Add 1.0 mL 0.1N HNO₃ and allow samples to sit overnight in a closed container to avoid evaporation. Proceed with paragraph 6.4 (except do not rinse sample cups).

6.4 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.5 In sequence, inject 20-μL aliquots of blank and a minimum of two standards (NOTE 3) in duplicate. Construct the analytical curve from the integrated peak areas (absorbance-seconds).

NOTE 3. The automatic sampler is programmed to inject 5.0 μL of matrix modifier along with blank, standards, and samples.

6.6 Similarly, inject and analyze the samples in duplicate. Every tenth sample cup needs to contain either a standard, blank, or a reference material.

6.7 Restandardize as required, although with the use of L'vov platforms, restandardization generally is not necessary. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, or platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of silver in each sample from the digital display of printer output. Dilute those samples containing concentrations of silver that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factor.

8. Report

Report concentrations of silver, dissolved (01075), and whole water recoverable (01077), as follows: less than 10 μg/L, the nearest 1 μg/L; 10 μg/L and greater, two significant figures.

9. Precision

9.1 Analysis of six samples for dissolved silver by a single operator is as follows:

<u>Number of replicates</u>	<u>Mean (µg/L)</u>	<u>Standard deviation (µg/L)</u>	<u>Relative standard deviation (percent)</u>
39	1.0	0.0	0.0
7	1.1	0.04	3.6
38	2.2	0.70	31.8
7	5.2	0.09	1.7
33	6.6	0.88	13.3
34	10.2	1.22	12.0

9.2 Analysis of three samples for whole water recoverable silver is as follows:

<u>Number of replicates</u>	<u>Mean (µg/L)</u>	<u>Standard deviation (µg/L)</u>	<u>Relative standard deviation (percent)</u>
7	1.2	0.16	13.3
11	2.0	0.71	35.5
10	6.2	0.50	8.1

9.3 The precision and bias for dissolved silver was tested on several standard reference water samples. A known amount of silver was added to each sample, and single operator precision and bias for the samples are as follows:

<u>Amount present (µg/L)</u>	<u>Number of replicates</u>	<u>Amount added (µg/L)</u>	<u>Found (µg/L) (NOTE 4)</u>	<u>Standard deviation (percent)</u>	<u>Relative standard deviation (percent)</u>	<u>Percent recovery</u>
2.1	6	4.5	4.2	0.4	0.9	93.3
2.1	6	1.6	1.5	0.1	3.1	98.8
2.2	6	3.1	3.0	0.8	2.6	96.8
5.9	6	3.3	2.8	0.4	13.7	84.8
6.1	6	5.5	5.1	0.2	4.3	92.7

NOTE 4. The amount originally present has been subtracted.

References

- American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 45-47.
- Hinderberger, E.J., Kasser, M.L., and Koirtyohann, S.R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1.