METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY-- DETERMINATION OF LOW-LEVEL SILVER BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	*By*	*To obtain*
gram (g)	0.03527	ounce, avoirdupois
microliter (μL)	2.64×10^{-7}	gallon
milliliter (mL)	2.64×10^{-4}	gallon

Degree Celsius (^{o}C) may be converted to degree Fahrenheit (^{o}F) by using the following equation:

$$^{o}F = 9/5\ (^{o}C) + 32$$

The following water-quality terms also are used in this report:

microgram per liter	(μg/L)
microsiemens per centimeter at 25 degrees Celsius	(μS/cm)

Other abbreviations are as follows:

ASTM	American Society for Testing and Materials
APDC	ammonium pyrrolidine dithiocarbamate
FEP	fluorinated ethylene propylene
HGA	heated graphite atomizer
LIS	low ionic strength
MIBK	methyl isobutyl ketone
nm	nanometer
NWQL	National Water Quality Laboratory
RSD	relative standard deviation
sp gr	specific gravity
SRWS	Standard Reference Water Sample
STPF	stabilized temperature platform furnace
THGA	transverse heated graphite atomizer

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ABSTRACT

Increased awareness of the quality of water in the United States has led to the development of a method for determining low levels (0.2-5.0 micrograms per liter) of silver in water samples. Use of graphite furnace atomic absorption spectrophotometry provides a sensitive, precise, and accurate method for determining low-level silver in samples of low ionic-strength water (specific conductance less than 100 microsiemens per centimeter), precipitation water, and natural water.

The minimum detection limit for low-level silver is 0.2 µg/L (microgram per liter). Precision data were collected for natural-water samples and SRWS (Standard Reference Water Samples). The overall percent relative standard deviation for natural-water samples with silver concentrations greater than 0.2 µg/L was less than 40 percent throughout the analytical range. For the SRWS with concentrations greater than 0.2 µg/L, the overall percent relative standard deviation was less than 25 percent throughout the analytical range.

The accuracy of the results was determined by spiking six natural-water samples with different known concentrations of the silver standard. The recoveries ranged from 61 to 119 percent at the 0.5-µg/L spike level. At the 1.25-µg/L spike level, the recoveries ranged from 92 to 106 percent. For the high spike level at 3.0 µg/L, the recoveries ranged from 65 to 113 percent.

The measured concentrations of silver obtained from known samples were within the Branch of Quality Assurance accepted limits of 1 1/2 standard deviations based on the SRWS program for Inter-Laboratory studies.

INTRODUCTION

The National Water Quality Laboratory (NWQL) has not had an approved method for determining low-level silver (0.2-5.0 µg/L) using graphite furnace atomic absorption spectrophotometry. The previous calibration technique used to analyze samples was the nonapproved method of standard additions. Because of the time and expense needed to analyze one sample, the method of standard additions is no longer practical. Using the method of standard additions, one

sample requires 50 minutes for analysis as compared to 10 minutes for the new method. Often with the method of standard additions, the analyst is unable to monitor the linear correlation coefficient of the curve because a new correlation coefficient is calculated for every sample; this problem also complicates the ability of the analyst to validate data. In general, the correlation coefficients were about 0.990 for the method of standard additions, while correlation coefficients are about 0.999 for the new method. A comparison of two SRWS showed that the standard deviations were 0.66 and 2.08 for the method of standard additions, while the same SRWS gave standard deviations of 0.37 and 0.70 with the new method.

Modern graphite-furnace atomizer technology reduces problems caused by limited sample size, interferences of chemicals, and dilution by gases such as in flame atomic absorption. Modern graphite furnace atomic absorption spectrophotometric technology uses a simultaneous background correction approach for high background absorption, which will cause erroneously high analytical results; one common type of background correction is the Zeeman effect (Slavin, 1984, p. 1-6). The graphite furnace atomic absorption spectrophotometric systems have improved sensitivity and low detection limits, which are beneficial to the determination of small concentrations of silver in water samples.

To analyze samples using graphite furnace atomic absorption spectrophotometry, the analyst places a sample volume in a graphite tube on a pyrolytic platform. This platform allows the sample to be heated to a thermal equilibrium prior to atomization. The thermal equilibrium reduces the effects caused by unequal heating and the samples' matrix on the analyte signal. There are two different ways to achieve the thermal equilibrium. The conventional heated graphite atomizer (HGA) heats the tube from the ends, whereas the transverse heated graphite atomizer (THGA) heats longitudinally along the axis of the tube, which allows for shorter equilibrium times and more uniform heating.

Various instrument conditions of the graphite furnace need to be optimized to obtain the optimal analytical results. These optimized conditions are known as the stabilized temperature platform furnace (STPF) conditions and will vary depending on the individual graphite furnace. The following characteristics need to be optimized to determine the most likely STPF conditions, according to Slavin and others (1983): peak area, fast electronics and sampling frequency, background correction, atomization temperature of the tube and platform, use of matrix modifier, maximum-power heating, and gas stop during atomization.

Once the STPF conditions are set, the sample is dried without spattering to reduce irregular or double peaks. The sample then is charred to remove as much of the matrix as possible before the atomization so as to decrease possible chemical interferences and high background signals.

During atomization the sample is completely volatilized for the analyte element. This process of vaporization and dissociation frees the analyte atoms and makes them available for absorption of the energy emitting from the lamp source. Because of particles or molecular species that scatter or absorb the energy emitted from the lamp source, a background correction is necessary to avoid erroneous analytical results. One type of background correction, known as the Zeeman effect, involves applying a strong external magnetic field to split the atomic spectral line. When the strong magnetic field is off, both the analyte and background lines are measured. When the strong magnetic field is on, the absorption line is split and shifted, and only the background is measured. The background measurement signal is subtracted from the sum of the background and analyte measurement signal, giving only an analyte absorption signal (Method D3919) (American Society for Testing and Materials, 1991).

This report describes a method for determining low-level silver developed by the U.S. Geological Survey (USGS) for use in the Survey's NWQL. The combined use of STPF conditions and Zeeman effect of background correction for graphite furnace atomic absorption spectrophotometry will allow the accurate and stable measurement of external standards and samples without using the method of standard additions. The method supplements other methods of the USGS for determination of inorganic substances in water that are described by Fishman and Friedman (1989):

I-2725-93 (silver, atomic absorption spectrophotometry, graphite furnace, LIS).

The method was implemented in the NWQL in May 1991.

This report provides a description of all aspects of the method from application through reporting of results. Precision and accuracy data are presented.

ANALYTICAL METHOD

Parameter and Code:
Silver, atomic absorption spectrophotometry, graphite furnace, LIS, I-2725-93

1. Application and scope

    1.1   This method is used to determine silver in samples of low ionic-strength water (specific conductivity less than 100 μS/cm), precipitation water, and natural water, which have been been filtered and acidified. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.2 to 5.0 μg/L.

    1.2   The analytical range and detection limits can be increased or decreased by varying the volume of sample injected or by diluting the sample. Purification of reagents and use of ASTM Type I reagent water (Method D1193) (American Society for Testing and Materials, 1991) is essential for obtaining low detection limits.

2. Summary of method

    2.1   Silver is determined by atomic absorption spectrophotometry in conjunction with a graphite furnace atomizer containing a pyrolytically coated graphite tube with a graphite platform (Hinderberger and others, 1981). 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 maximum-power heating. The absorption signal generated during atomization is recorded and compared to a standard curve produced with four standard solutions.

    2.2   Silver may be analyzed on the HGA or THGA instruments; the only differences are listed in sections 4.1.2 and 5.3.

3. Interferences

    3.1   Interferences in low ionic-strength samples, such as precipitation, normally are low. In addition, the use of the graphite platform reduces the effects of many interferences.

    3.2   Do not use matrix modifier with palladium; it may have elevated levels of silver which will cause high blank absorbencies.

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3.3   Precipitation samples usually contain small (<5 µg/L) concentrations of silver. Special precautionary measures need to be used during both sample collection and laboratory determination to prevent contamination.

4.   Apparatus

4.1   *Atomic absorption spectrophotometer*, for use at 328.1 nm and equipped with Zeeman background correction, a graphite furnace with temperature programmer, an automatic sample injector, and a computer that controls all operations, including integration of peak areas, temperature ramping times, and controlled gas flow capabilities during atomization of the sample.

4.1.1   Refer to the manufacturer's manual to optimize instrumental performance. The analytical range reported in paragraph 1.1 is for a 20-µL sample with 5 µL of matrix modifier.

4.1.2   *Graphite furnace*, capable of reaching temperature sufficient to atomize the element of interest. Warning: Dial settings frequently are inaccurate, and newly conditioned furnaces need to be temperature-calibrated.

4.1.2.1   *Conventional heated graphite atomizer* (HGA) that heats the tube from the ends.

4.1.2.2   *Transverse heated graphite atomizer* (THGA) that heats longitudinally along the axis of the tube.

4.1.3   *Graphite tubes and platforms*, pyrolytically coated.

4.2   *Labware*. Many trace metals at small concentrations absorb rapidly to glassware. To preclude this absorption, fluorinated ethylene propylene (FEP) or Teflon[1] labware may be used. All silver standards need to be stored in dark bottles because of their sensitivity to light. Polystyrene disposable cups are satisfactory for analyzing samples after they are cleaned with a silver-free surfactant and soaked in 10-percent HNO_3.

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

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[1]The use of trade and firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

5. Reagents

5.1 *Silver standard solution I*, 1.00 mL = 100 µg Ag. Dissolve 0.100 g Ag powder, Ultrex or equivalent, in 100 mL of concentrated HNO_3 (sp gr 1.41). Keep silver in solution and dilute to 1,000 mL with Type I reagent water. Store in amber bottle. This standard is stable for one year.

5.2 *Silver standard solution II*, 1.0 mL = 5 µg Ag. Take 50.0 mL of silver standard solution I and 95 mL of concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL (NOTE 1). Make immediately prior to preparing the working solutions at the time of analysis.

NOTE 1. Use acidified Type I reagent water (paragraph 5.6) to make all dilutions. Standard solution II needs to be stored in amber-sealed Teflon or FEP containers. Each container needs to be rinsed twice with a small volume of solution before filling.

5.3 *Matrix modifier solution*, $NH_4H_2PO_4$.

5.3.1 For HGA, add 40.0 g $NH_4H_2PO_4$ to 950 mL Type I reagent water, mix, and dilute to 1,000 mL. The concentration was used to achieve the proper characteristic mass.

5.3.2 For THGA, add 10.0 g $NH_4H_2PO_4$ to 950 mL Type I reagent water, mix, and dilute to 1,000 mL. The concentration was used to achieve the proper characteristic mass.

5.3.3 Analyze 20 µL of matrix modifier for silver concentration. If the silver reading is greater than 0.005 absorbance-second, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extract with methyl isobutyl ketone (MIBK) (NOTE 2). Analyze 20 µL of the purified solution. Repeat extraction until the silver level is reduced to the acceptable level (<0.2 µg/L). CAUTION: Do not add acid to the purified matrix modifier solution because the acid may have silver in it.

NOTE 2. To purify matrix modifier solution, pour the solution into a container. Add 0.25 g APDC for each liter of solution. While stirring adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent. Transfer portions of the solution to a separatory funnel, add 100 mL MIBK per liter of solution, and shake vigorously for at least 5 minutes. Frequently vent the funnel in a hood. Collect the extract in the FEP container. Repeat the extraction with 50 mL MIBK per liter of solution.

Because MIBK can dissolve some plastic autosampler cups, boil the solution for at least 10 minutes in a silicone-treated or acid-rinsed beaker covered with a watchglass to remove MIBK.

    5.4 *Silver working solutions.* Prepare the silver working solutions immediately prior to the time of analysis by diluting the appropriate quantity of solution II to 250 mL with Type I reagent water. Preserve with 25 mL of concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, before bringing to volume. Verify that the solutions achieve the characteristic mass before using. Store in amber bottles. The preparations for working solutions are listed in table 1.

Table 1.--*Preparations for working solutions*

[μg/L, micrograms per liter; μL, microliters]

Concentration of silver solution (μg/L)	Solution II quantities used (μL)
5.0	250.0
3.0	150.0
2.0	100.0
1.0	50.0

    5.5 *Nitric acid, concentrated,* ultrapure (sp gr 1.41). J.T. Baker Ultrex HNO_3 is adequately pure; however, each lot needs to be checked for contamination. Analyze acidified Type I reagent water for silver. Add 100 mL of concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by greater than 0.001 absorbance-second.

    5.6 *Water, acidified,* Type I reagent. Add 100 mL of ultrapure concentrated HNO_3 (sp gr 1.41) to each liter of water.

    5.7 *Water,* Type I reagent.

6. Procedure

    6.1 Systematically clean and rinse work areas with Type I water on a regular schedule. Use a clean environment during sample transfers. Ideally, the autosampler and the graphite furnace need to be in a dust- and analyte-free environment.

6.2   Soak the autosampler cups at least 30 minutes in a silver-free surfactant using an ultrasonic cleaner. Then soak and rinse in 10-percent HNO_3 until the cups are used; use cups within 48 hours of cleaning.

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

6.4   In sequence, inject 20-μL aliquots of blank and working solutions plus 5 μL of modifier each and analyze. Analyze the blank and working solutions twice from large concentration to small concentration. Generally, the curve needs to be linear (correlation coefficient of 0.999 or better) up to a peak-absorbance (peak-height) value of 0.40 absorbance-second.

6.5   Similarly, inject and analyze each sample twice (duplicate injections). Every tenth sample cup should contain either a working solution or a reference material.

6.6   Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, or platform. A major variation usually indicates autosampler malfunction.

7.   Calculations

Determine the micrograms per liter of silver in each sample from the digital display or the 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 factors.

8.   Reporting of results

Report concentrations of silver, dissolved, as follows: Less than 1.0 μg/L, nearest 0.1 μg/L; 1.0 μg/L and larger, two significant figures.

9.   Precision

Single-operator precision was determined on different water samples using 11 or 14 replicates for several days (tables 2 and 3).

Table 2.--*Precision of silver determination for water samples at 2.5 percent weight per volume of $NH_4H_2PO_4$ with heated graphite atomizer*

[μg/L, micrograms per liter]

Number of replicates = 11

Mean (μg/L)	Relative standard deviation (percent)
0.045	128
.18	35.4
1.15	13.9
1.63	34.1

Table 3.--*Precision of silver determination for water samples at 0.6 percent weight per volume of $NH_4H_2PO_4$ with transverse heated graphite atomizer*

[μg/L, micrograms per liter]

Number of replicates = 14

Mean (μg/L)	Relative standard deviation (percent)
1.23	9.4
3.13	7.0
4.51	10.8
5.64	8.9

DISCUSSION OF RESULTS

Precision

Single-operator precision for dissolved silver was determined on natural-water samples and on USGS Standard Reference Water Samples (SRWS), and the samples were used to determine the precision of silver by graphite furnace atomic absorption spectrophotometry. Even though several samples had mean concentrations less than the detection limit of 0.2 μg/L, the concentrations were used since most of the natural-water samples have silver concentrations less than

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0.2 µg/L. The precision for natural-water samples, which is expressed in percent relative standard deviation (RSD), is listed in tables 4 and 5. Eleven or fourteen replicate analyses were performed on each sample for several days. The correlation coefficients for standard curves, which were generated during this precision determination, ranged from 0.9988 to 0.9996 for the analyses. A standard calibration curve from the HGA is shown in figure 1. Additional data on precision were obtained for two SRWS (table 6).

Table 4.--*Precision of silver determination for natural-water samples at 2.5 percent weight per volume of NH₄H₂PO₄ with heated graphite atomizer*

[µg/L, micrograms per liter]

Sample number	Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
1	11	0.045	0.058	128
2	11	.18	.064	35.4
3	11	1.15	.160	13.9
4	11	1.63	.555	34.1

Table 5.--*Precision of silver determination for natural-water samples and Standard Reference Water Samples at 0.6 percent weight per volume of NH₄H₂PO₄ with transverse heated graphite atomizer*

[µg/L, micrograms per liter]

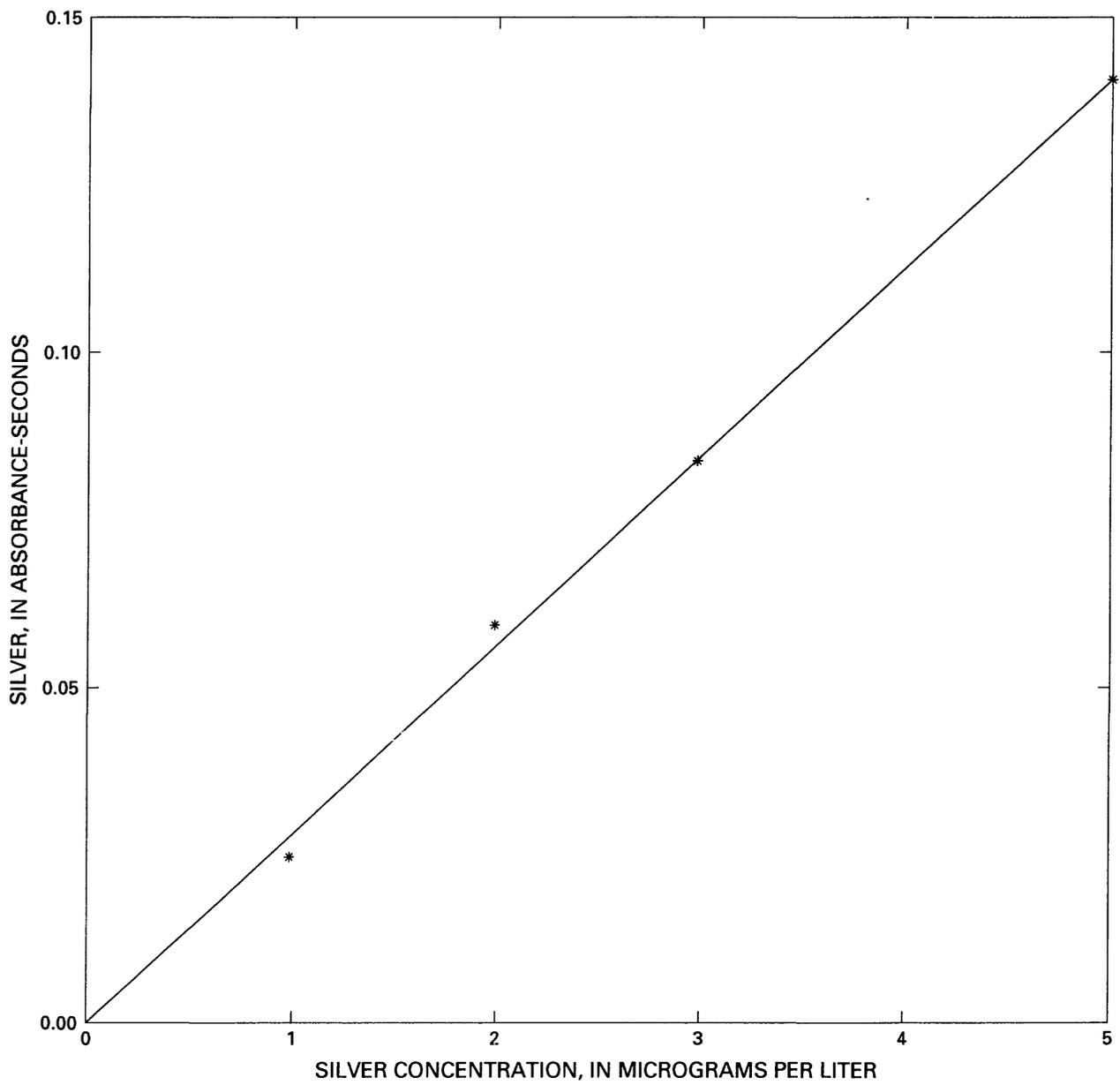| Sample number	Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
5	14	1.23	0.12	9.4
6	14	3.13	.22	7.0
7	14	4.51	.49	10.8
8	14	5.64	.51	8.9

Figure 1.—Standard calibration curve for silver.

Table 6.--*Precision of silver determination for Standard Reference Water Samples at 2.5 percent weight per volume of NH₄H₂PO₄ with heated graphite atomizer*

[SRWS, Standard Reference Water Samples; μg/L, micrograms per liter]

SRWS	Number of replicates	Mean value (μg/L)	Standard deviation of mean (μg/L)	Relative standard deviation (percent)	Most probable value (μg/L)	Calculated standard deviation (μg/L)
101	22	5.45	1.30	23.8	4.9	1.1
109	22	2.61	.49	18.9	2.1	1.1

Accuracy

Four natural-water samples were spiked at two different concentrations. These results are listed in tables 7 and 8. At less than the detection limit, the method obtained recoveries at 60 percent on the HGA and at 105 percent on the THGA. Near the detection limit, recoveries were 86 and 163 percent on the HGA. The second sample on the HGA did not perform as expected because at the 0.5-μg/L spike, recovery was lower than expected; and at the 3.0-μg/L spike, recovery was higher than expected. At greater than the detection limit, recoveries were between 90 and 120 percent on both the HGA and THGA.

Table 7.--*Silver recovery data for natural-water samples at 2.5 percent weight per volume of NH₄H₂PO₄ with heated graphite atomizer*

[μg/L, micrograms per liter]

Number of replicates = 11

Sample number	Present (μg/L)	Added (μg/L)	Standard deviation (μg/L)	Average found (μg/L)	Average recovery (percent)
1	0.045	0.5	0.10	0.35	61
2	.18	.5	.06	.61	86
3	1.15	.5	.22	1.67	102
4	1.63	.5	.57	2.22	119
1	.045	3.0	.45	2.01	65
2	.18	3.0	1.03	5.08	163
3	1.15	3.0	.53	4.06	96
4	1.63	3.0	1.11	5.04	113

Table 8.--*Silver recovery data for natural-water samples at 0.6 percent weight per volume of NH₄H₂PO₄ with transverse heated graphite atomizer*

[μg/L, micrograms per liter]

Number of replicates = 14

Sample number	Present (μg/L)	Added (μg/L)	Standard deviation (μg/L)	Average found (μg/L)	Average recovery (percent)
9	0	1.25	0.09	1.31	105.6
10	.03	1.25	.52	1.33	104.5
11	2.00	1.25	.73	3.14	93.6
12	4.51	1.25	.23	5.69	92.3

Detection Limit

Detection limits were analyzed to determine the calculated limit for each instrument (U.S. Environmental Protection Agency, 1990). The calculated detection limit may vary slightly because it is dependent on instrument conditions and often is less than the reported detection limit. A single operator analyzed a 0.6-μg/L Ag check standard on 10 different analyses for each instrument. The mean and standard deviation were calculated for the check standard. The standard deviation then was multiplied by the appropriate Student's T value at 99-percent confidence level to obtain the calculated detection limit. The calculated detection limit was 0.12 μg/L on the HGA and 0.09 μg/L on the THGA.

CONCLUSION

From the data presented, the determination of low-level silver by the graphite furnace atomic absorption spectrophotometric technique is superior to analyzing samples of water by the nonapproved method of standard additions. The new method has a detection limit of 0.2 μg/L. A comparison of two SRWS showed that standard deviations with the new method were 0.37 and 0.70. Finally, the new method gave a correlation coefficient of 0.999, and a blank sample measured less than 0.1 μg/L. The new method has a much shorter analysis time than the method of standard additions, saving the analyst 40 minutes per sample, a considerable savings in cost. For samples with concentrations

greater than the detection limits for both the HGA and THGA, the precision data generated are within the accepted guidelines. This new method is suitable for determining low-level silver in samples of low ionic-strength water, precipitation water, and natural water.

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