METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF ANTIMONY BY AUTOMATED-HYDRIDE ATOMIC ABSORPTION SPECTROPHOTOMETRY

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
centimeter (cm)	0.01	meter
gram (g)	0.03527	ounce, avoirdupois
liter (L)	0.2642	gallon
meter (m)	39.37	inch
microgram (μg)	0.000001	gram
micrometer (μm)	0.001	millimeter
milliliter (mL)	0.001	liter
millimeter (mm)	0.1	centimeter
nanometer (nm)	0.001	micrometer
pound per square inch (lb/in^2)	6.895	kilopascal

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

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

The following units of measurement and terms also are used in this report:

gram per liter	(g/L)
microgram per liter	(μg/L)
milliliter per minute	(mL/min)
millivolts	(mV)
molarity	(*M*)
normality	(*N*)

Other abbreviations are as follows:

AAS	atomic absorption spectrophotometry
ASTM	American Society for Testing and Materials
ICP	inductively coupled plasma
MDL	method detection limit
MPV	most probable value
NPDES	National Pollutant Discharge Elimination System
NWQL	National Water Quality Laboratory
SRWS	Standard Reference Water Sample
USGS	U.S. Geological Survey

METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF ANTIMONY BY AUTOMATED-HYDRIDE ATOMIC ABSORPTION SPECTROPHOTOMETRY

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ABSTRACT

The analysis of natural-water samples for antimony by automated-hydride atomic absorption spectrophotometry is described. Samples are prepared for analysis by addition of potassium persulfate and hydrochloric acid followed by an autoclave digestion. After the digestion, potassium iodide and sodium borohydride are added automatically. Antimony hydride (stibine) gas is generated, then swept into a heated quartz cell for determination by atomic absorption spectrophotometry.

Precision and accuracy data are presented. Results obtained on Standard Reference Water Samples agree with means established by interlaboratory studies. Spike recoveries for actual samples range from 90 to 114 percent. Replicate analyses of water samples of varying matrices give relative standard deviations from 3 to 10 percent.

INTRODUCTION

Antimony is a metallic element occasionally found in low concentrations in natural water. It is often used in the semiconductor industry and can serve as a tracer element in hydrogeologic systems for gold deposits, or as a pollution indicator. Determination of antimony also is required by the U.S. Environmental Protection Agency for National Pollutant Discharge Elimination System (NPDES) permits.

Determination of antimony by conventional air-acetylene flame atomic absorption spectrophotometry (AAS) is particularly difficult. The resonance wavelength of antimony is in the low ultraviolet region of the spectrum, where absorbance from the acetylene in the flame can occur. Analysis of stibine (antimony hydride or H_3Sb) in a heated quartz cell, after hydride generation AAS, removes these interferences and provides lower detection limits than either flame AAS or inductively coupled plasma atomic emission spectrophotometry.

In hydride generation AAS, the gaseous hydride is chemically produced by adding sodium borohydride to the sample (Andreae and others, 1981, p. 1766-1771). The gas is carried by a nitrogen purge into a heated quartz cell. When the stibine gas is atomized in the cell, a peak absorbance signal is produced with the height being proportional to the amount of analyte in the sample.

Water samples received by the National Water Quality Laboratory (NWQL) for analysis of metals are preserved to a pH of less than two using nitric acid to prevent loss of metals from solution. Digestion of the sample with potassium persulfate with heat under pressure decomposes any organically bound antimony. A subsequent reduction step, the addition of potassium iodide to the sample, guarantees that all of the antimony is present in the +3 valence state. Following the valence-state adjustment, sodium borohydride ($NaBH_4$) and hydrochloric acid (HCl) are added to produce stibine. The stibine is swept, using an inert gas purge, through a gas-liquid separator into a heated ($800^\circ C$) quartz cell. There, the stibine molecules are decomposed to atomic vapor, and an absorbance signal is produced proportional to the antimony concentration in the sample.

This report describes a method for determining antimony in samples of natural water containing at least 1 μg/L using automated-hydride AAS. The method supplements other methods of the U.S. Geological Survey (USGS) for determination of inorganic substances in water that are described by Fishman and Friedman (1989). This method was implemented in the NWQL in 1979.

ANALYTICAL METHOD

Parameters and Codes:
Antimony, dissolved, I-2055 (µg/L as Sb): 01095
Antimony, suspended recoverable, I-7055 (µg/L as Sb): 01096
Antimony, whole water recoverable I-4055 (µg/L as Sb): 01097

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 1 µg/L of antimony. Samples containing antimony concentrations greater than 20 µg/L need to be diluted.

1.2 Suspended recoverable antimony is calculated by subtracting dissolved antimony from whole water recoverable antimony.

1.3 Whole water recoverable antimony in samples of water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking, and a suitable portion of sample has been rapidly withdrawn from the mixture.

2. Summary of method

Organic antimony-containing compounds are decomposed by a potassium persulfate and hydrochloric acid digestion. The resultant decomposition products, along with inorganic antimony originally present, react with potassium iodide, hydrochloric acid, and finally with sodium borohydride to form stibine. The stibine is stripped from solution with the aid of nitrogen and then reduced to antimony atoms in a tube furnace placed in the optical path of an atomic absorption spectrophotometer at 217.6 nm.

3. Interferences

3.1 A number of ions, especially transition metal cations, interfere with borohydride reductions. In most natural water, concentrations of metal cations are several orders of magnitude below the levels causing interference (Andreae and others, 1981).

3.2 Absence of interferences from selenium and arsenic (which also form gaseous hydrides) was verified at concentrations of 100 µg/L. Higher concentrations were not tested.

4. Apparatus

4.1   *Atomic absorption spectrophotometer* and recorder.

4.2   Refer to manufacturer's manual to optimize instrument for the following:

    Grating...Ultraviolet
    Wavelength...217.6 nm
    Source (electrodeless discharge lamp)..........Antimony

4.3   *Autotransformer, variable*; Superior[1] powerstat type 3 PN1010 or equivalent.

4.4   *Pyrometer,* portable, 0 to 1,200°C; Thermolyne Model PM-20700 or equivalent.

4.5   *Gas-liquid separator*, Pyrex, packed with 3- to 5-mm Pyrex beads (fig. 1). Cooling of the condensing column to 4°C is required. The nitrogen gas flow rate is adjusted for maximum sensitivity by analyzing a series of identical standards. An optimum flow rate usually ranges from 100 to 150 mL/min.

4.6   *Tube furnace,* quartz, 10-mm inside diameter x 100-mm length with a quartz eyelet at each end of the tube to anchor nickel-chrome wire and tube fused to the center with a 2-mm inside diameter quartz tube. Wrap the tube furnace with approximately 5.5 m (18 ft) of 26-gage nickel-chrome wire and cover with an insulating ceramic fiber cloth. Mount lengthwise in the optical path of the atomic absorption spectrophotometer.

4.7   *Technicon AutoAnalyzer II,* consisting of sampler with a manifold and a proportioning pump (fig. 2).

5. Reagents

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

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

Liquid stream inlet
(3-millimeter
inside diameter)

Nitrogen inlet
(0.50-millimeter
inside diameter)

Tube furnace

20 millimeters

Ball and socket joint

Rubber stopper
(Number 0)

15-millimeter
inside diameter

Stripping column

Glass beads

Condensing column

Hydride

200 millimeters

300 millimeters

150 millimeters

5-millimeter
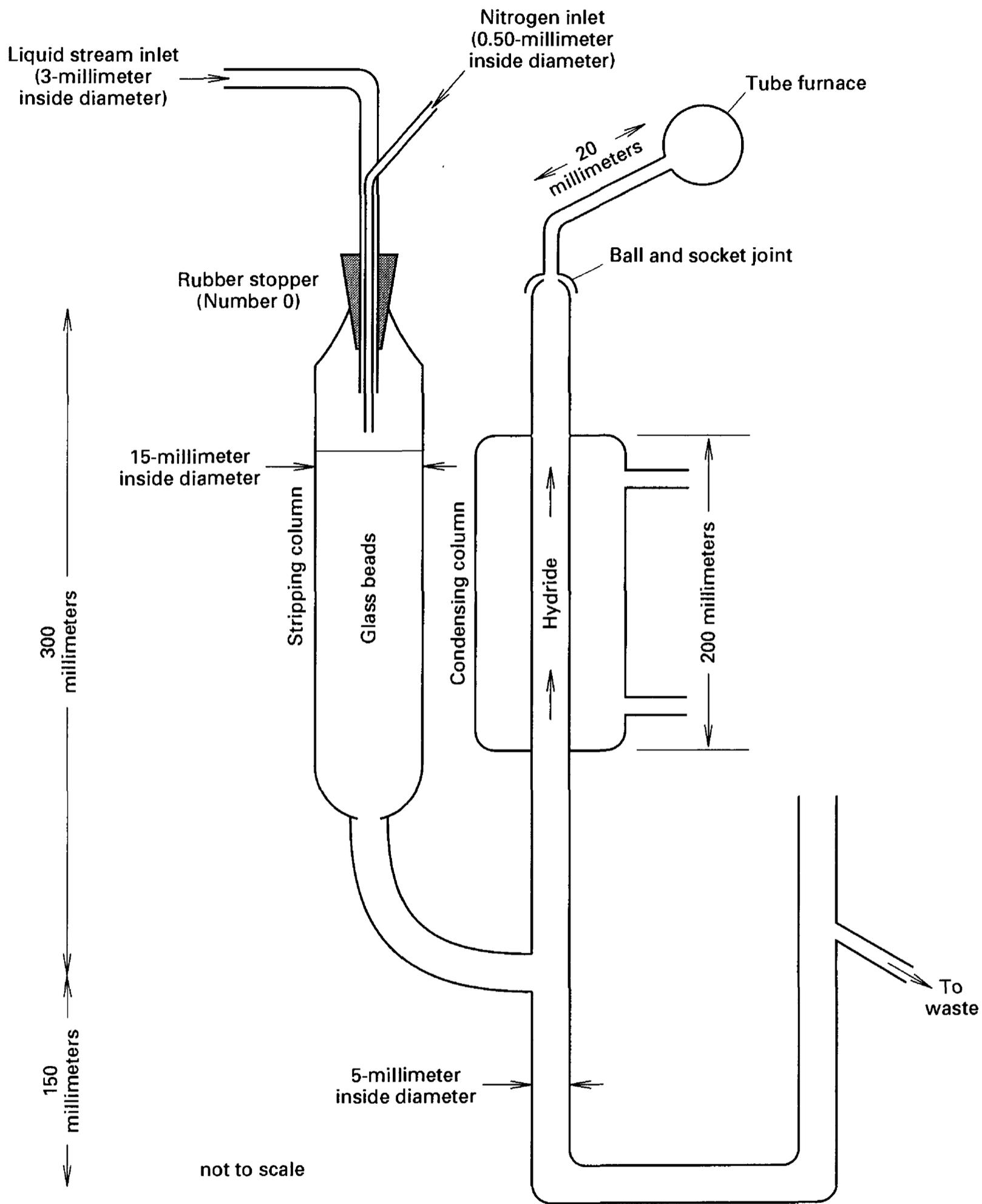inside diameter

To waste

not to scale

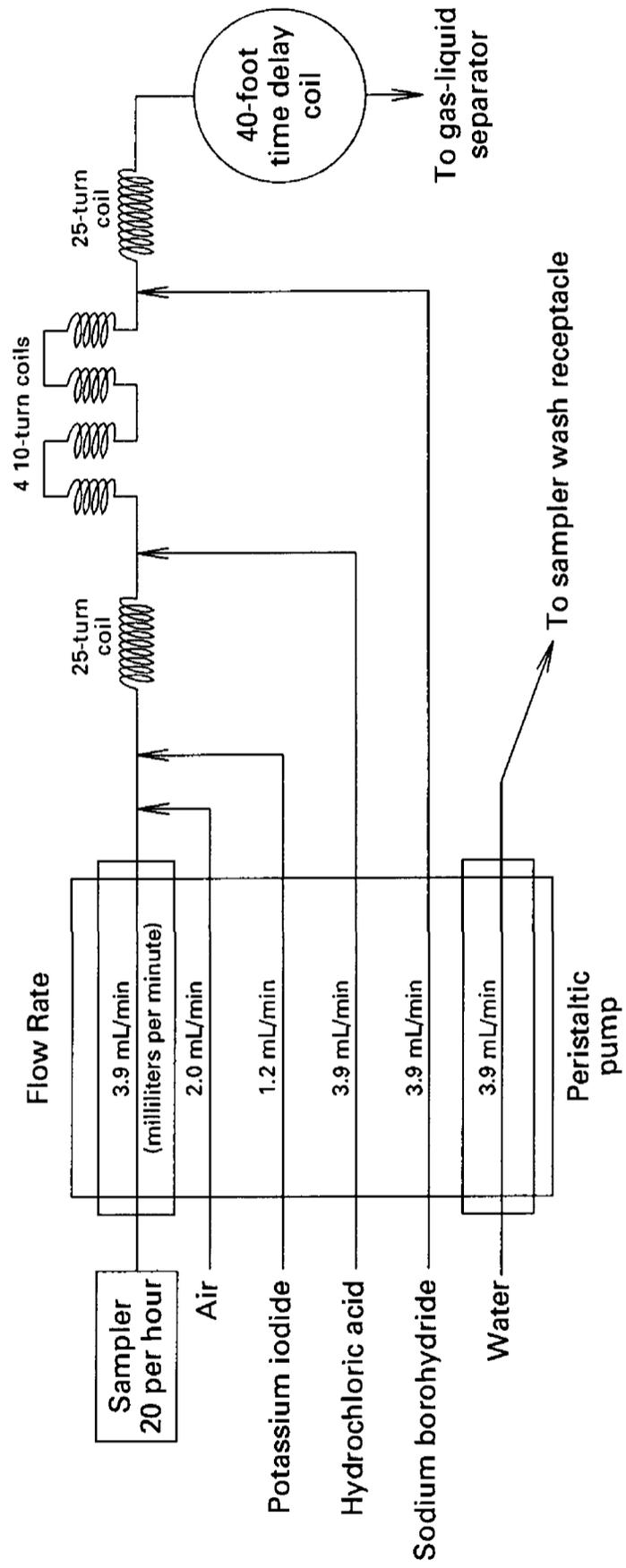Figure 1.—Gas-liquid separator and quartz tube furnace.

Figure 2.—Antimony manifold.

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5.2   *Antimony standard solution I*, 1.00 mL = 100 µg Sb. Dissolve 0.100 g Sb metal (99.999 percent) in a minimum amount of aqua regia made from ultrapure acids. Add water to increase rate of dissolution, and dilute to 1,000 mL with water. As an alternative, a commercially prepared standard solution may be used and diluted accordingly.

5.3   *Antimony standard solution II*, 1.00 mL = 10.0 µg Sb. Dilute 50.0 mL antimony standard solution I to 500.0 mL with water.

5.4   *Antimony standard solution III*, 1.00 mL = 1.0 µg Sb. Dilute 50.0 mL antimony standard solution II to 500.0 mL with water.

5.5   *Antimony working standards.* Prepare a blank and 1,000 mL each of a series of antimony working standards by appropriate dilution of antimony standard solution III with water. Each standard should also contain 0.4 percent concentrated HNO_3 by volume.

Antimony standard solution III (mL)	Antimony concentration (µg/L)
1	1
3	3
5	5
10	10
20	20

5.6   *Hydrochloric acid, 12M*, concentrated (specific gravity 1.19).

NOTE: All chemicals are reagent grade purity unless otherwise specified.

5.7   *Hydrochloric acid, 6M.* Add 500 mL concentrated HCl (specific gravity 1.19) to water, and dilute to 1 L.

5.8   *Potassium persulfate solution*, 18 g/L. Dissolve 18 g $K_2S_2O_8$ in water, and dilute to 1 L.

5.9   *Potassium iodide solution*, 100 g/L. Dissolve 100 g KI in water, and dilute to 1 L.

5.10   *Sodium borohydride solution*, 5 g/L. Dissolve 5 g $NaBH_4$ and 40 g NaOH in water, and dilute to 1 L.

6. Procedure

6.1   Pipet a volume of well-mixed sample containing less than 0.400 µg Sb (20 mL maximum) into a 20- x 150-mm borosilicate test tube.

6.2   Pipet 20-mL blanks, standard reference materials, and a complete set of standard solutions containing from 1 to 20 µg/L antimony into 20- x 150-mm test tubes.

6.3   Add 3.0 mL $K_2S_2O_8$ solution and 1.0 mL of concentrated HCl to each test tube. Cover tubes with plastic caps, and autoclave at 11 lb/in^2 at 115°C for 20 minutes.

6.4   Set up analytical manifold as shown in figure 2.

6.5   Using a variable autotransformer, apply voltage as needed to the tube furnace to maintain a constant temperature of 800°C. Calibrate the tube furnace temperature using a portable pyrometer with the thermocouple placed in the middle of the tube.

6.6   Feed all reagents through the system, using water in the sample line.

6.7   Condition the tube furnace by running two aliquots of a 40-µg/L undigested standard, followed by six aliquots of a 20-µg/L undigested standard.

6.8   With a 10-mV recorder, 20 µg/L of antimony will give a peak approximately 60 percent of full scale. If the sensitivity drops by 30 percent or more, replace the tube furnace or treat it by swabbing the furnace with hydrofluoric acid, followed by water rinses. (CAUTION: Follow appropriate laboratory safety procedures when using hydrofluoric acid.)

6.9   Set up sample tray to be analyzed. Place digested standards in tray after beginning with a blank sample. Place individual digested standards, blanks, or Standard Reference Water Samples of varying concentrations about every eight positions; then fill the remainder of the tray with unknown digested samples.

6.10   Remove the sample line from the wash solution when the baseline stabilizes, and begin the analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak against its respective antimony concentration. This curve may be generated using an appropriate computer program. A second-order polynomial function ($y=ax^2+bx+c$) usually provides improved concentration estimates than does the more conventional linear model ($y=mx+b$).

7.2 Determine the concentration of dissolved or whole water recoverable antimony in each sample by comparing its peak height to the analytical curve. Any baseline drift is taken into account when computing the height of a sample or standard peak.

7.3 To determine the concentration of suspended recoverable antimony, subtract concentration of dissolved antimony from the concentration of whole water recoverable antimony.

8. Reporting of results

Report antimony, dissolved (01095), whole water recoverable (01097), and suspended recoverable (01096), concentrations as follows: concentrations less than 10 μg/L are reported to the nearest microgram per liter; results greater than or equal to 10 μg/L are reported to two significant figures.

9. Precision

9.1 Precision expressed in terms of percent relative standard deviation for dissolved antimony for 20 replicate analyses, by one operator, is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
1.6	0.33	20.7
3.4	.35	10.3
4.6	.58	12.5
10.3	1.05	10.2

9.2   Precision expressed in terms of percent relative standard deviation for whole water recoverable antimony for eight replicate analyses, by one operator, is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
1.4	0.29	20.9
1.5	.12	8.3
2.0	.28	14.1
12.0	.37	3.1

DISCUSSION OF RESULTS

Precision and Bias

U.S. Geological Survey Standard Reference Water Samples (SRWS) were used to evaluate the precision of the method for determining antimony by automated-hydride atomic absorption spectrophotometry. Precision data for seven different SRWS's are listed in table 1. Replicate analyses were performed on each sample over a period of several days. An indication of the bias of the method, as well as antimony values determined by interlaboratory studies, are also listed in table 1.

Table 1.--*Precision and bias of antimony method*

[NWQL, National Water Quality Laboratory; SRWS, Standard Reference Water Sample of the Branch of Quality Assurance; AAS, atomic absorption spectrophotometry; µg/L, micrograms per liter; n, number of replicates; --, no data]

SRWS	NWQL automated-hydride AAS				Interlaboratory SRWS program		
	Mean (µg/L)	n	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
93	1.7	16	0.4	23.5	1.2	0.5	41.7
97	12.5	21	.7	5.2	11.3	2.0	17.7
99	4.1	18	.6	13.7	3.4	1.4	41.2
101	10.6	20	1.1	10.2	10.4	1.4	13.5
103	9.4	18	1.0	10.2	9.4	.5	5.3
105	5.4	18	.7	13.7	4.6	[1]4.4	--
107	12.0	21	.8	6.8	10.1	[1]2.5	--

[1]Pseudosigma values--USGS Branch of Quality Assurance changed statistical reporting methods.

The automated-hydride AAS means generally agree with the means obtained by interlaboratory analysis, and the results all fall within one standard deviation of the interlaboratory mean value. The percent relative standard deviations range from 5 to 24 percent. These data also are shown in figure 3. In addition, the precision of the automated technique is substantially better than the manual method (13-50 percent relative standard deviation) as reported by Fishman and Friedman (1989, p. 69).

The Student's t-test indicated a statistically significant difference at the 95-percent level between the interlaboratory means and the hydride AAS means for several of the SRWS. Those differences may be attributed to the one-laboratory, one-operator, one-method operation for the automated-hydride system compared to the multiple laboratory, multiple operator, multiple methods (flame AAS, ICP, and manual hydride) used in determining the interlaboratory most probable value (MPV). The differences between the automated-hydride values and interlaboratory MPVs become much less significant when considering the precision of the method and the reporting limit (nearest microgram per liter for values less than 10 µg/L, and two significant figures for values at or greater than 10 µg/L).
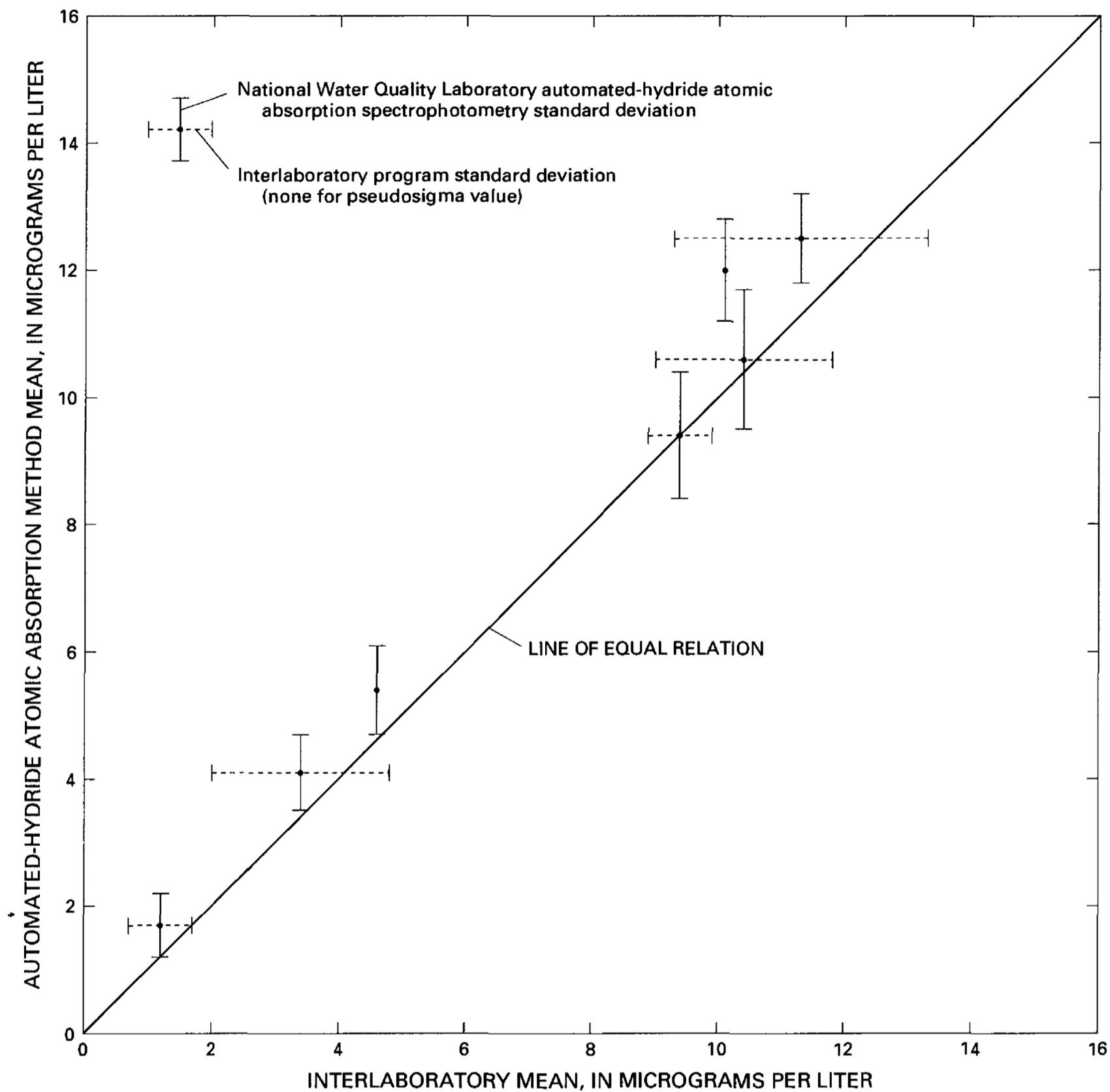
Figure 3.--Relation between antimony mean concentrations determined by automated-hydride atomic absorption spectrophotometry and inter-laboratory means for several Standard Reference Water Samples.

Spike Recovery

To further determine the accuracy of this method, 17 natural-water samples and blanks were spiked with known concentrations of antimony, then prepared and analyzed according to the automated-hydride AAS method. The results from the spike study are listed in table 2. Recoveries ranged from 90 to 114 percent.

The spike recovery studies on the 17 blanks and samples were repeated four times to give another measure of the precision of the method. Replicate data are listed in table 2, indicating percent relative standard deviations in the 3- to 10-percent range, depending on concentration.

Replicate samples also were prepared and analyzed on four separate days to give an additional measure of method repeatability on actual sample matrices. These data are listed in table 3 and shown in figure 4. Again, for actual samples with varying antimony concentrations (dissolved and whole water recoverable), the percent relative standard deviations range from 3 to 10 percent. For samples near the detection limit of 1 μg/L, the precision decreases, with percent relative standard deviations in the 20- to 50-percent range.

Table 2.--*Recovery of antimony in surface-water samples*

[μg/L, micrograms per liter]

Sample number	Mean results, in μg/L			Percent recovery	Standard deviation (μg/L)	Relative standard deviation (percent)
	Present	Added	Found			
Blank	0	5	5.0	100	0.29	5.8
Blank	0	5	5.1	102	.2	3.9
Blank	0	10	10.6	106	.62	5.9
Blank	0	5	5.7	114	.36	6.3
1	.2	10	10.7	105	.35	3.3
2	.5	10	11.6	110	.78	6.7
3	.7	10	9.9	93	.36	3.6
4	1.2	10	12.8	114	.71	5.6
5	1.7	5	6.9	103	.28	4.1
6	1.8	10	12.3	104	.45	3.6
7	2.7	10	12.6	99	.81	6.4
8	3.7	5	9.9	114	.54	5.4
9	4.7	10	13.2	90	1.32	10.0
10	5.4	10	14.9	97	1.21	8.1
11	5.8	10	15.0	95	.96	6.4
12	10.7	5	16.4	104	.84	5.1
13	12.3	5	16.4	95	.87	5.0

Table 3.--*Sample replication listing mean, standard deviation, and relative standard deviation for four separate analyses*

[μg/L, micrograms per liter]

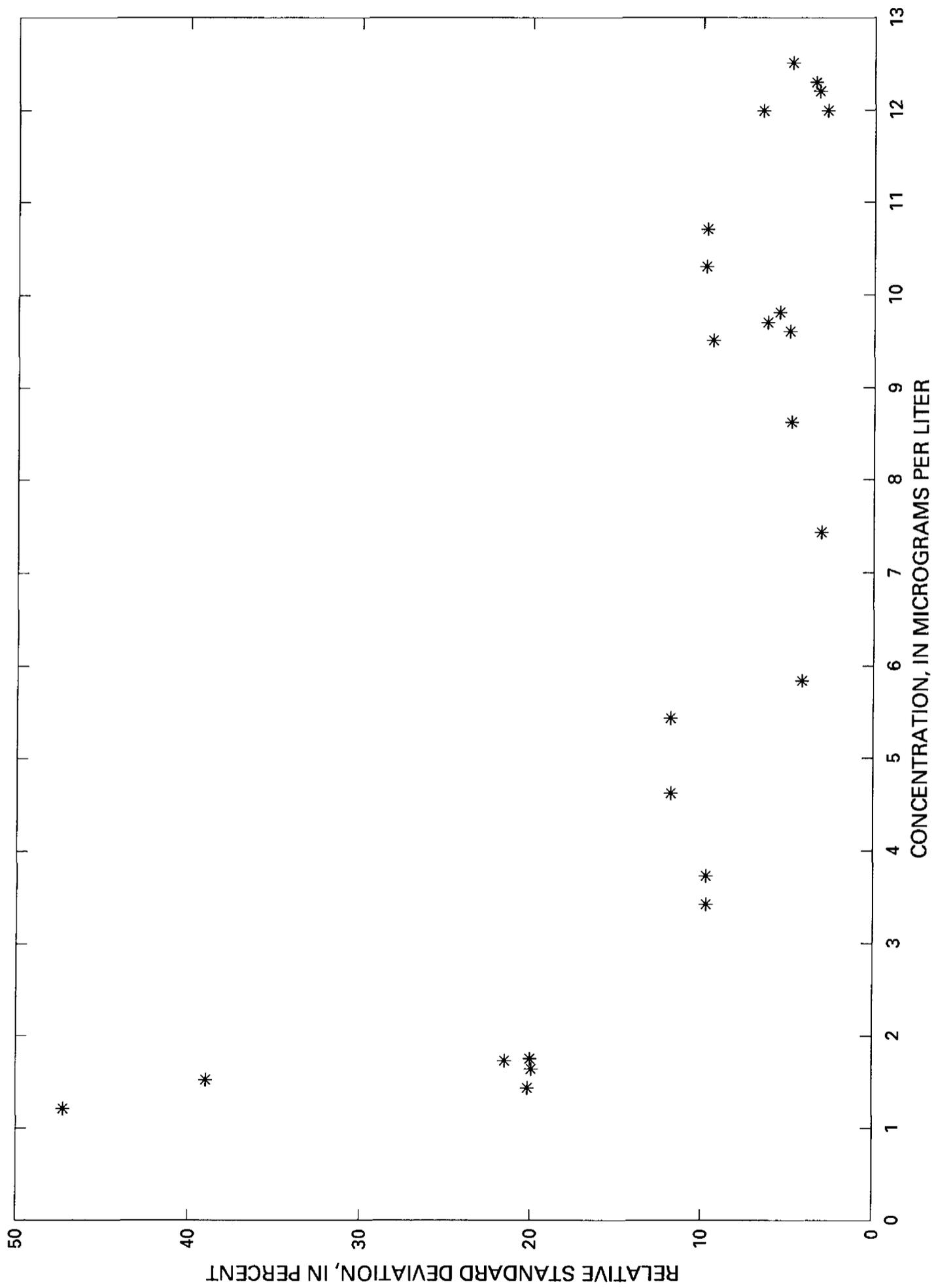| Sample number	Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
1	1.2	0.55	47.4
2	12.2	.43	3.5
3	5.8	.27	4.6
4	1.7	.38	22.3
5	1.5	.58	39.4
6	7.4	.25	3.4
7	9.7	.64	6.6
8	9.6	.51	5.3
9	8.6	.45	5.2
10	9.8	.57	5.8
11	12.3	.46	3.7
12	1.4	.29	20.9
13	12.0	.37	3.1

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Figure 4.--Antimony precision.

Detection Limit

   The method detection limit (MDL), using the procedure from the U.S. Environmental Protection Agency (1992, p. 565-567), is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. The theoretical detection limit was determined to be 0.71 µg/L, on the basis of three times the standard deviation of multiple blank determinations. An antimony standard was prepared with a concentration of 3 µg/L (approximately three times the theoretical detection limit). This standard then was analyzed ten times nonconsecutively. A mean and standard deviation were calculated from the data listed in table 4 to determine the MDL. According to the U.S. Environmental Protection Agency (1992, p. 565-567), the MDL was calculated to be 0.42 µg/L. A reporting limit of 1 µg/L was chosen as appropriate for this analysis.

Table 4.--*Determination of the antimony method detection limit*
[µg/L, micrograms per liter]

Replicate number	Concentration (µg/L)
1	2.8
2	2.8
3	2.9
4	2.9
5	2.7
6	2.7
7	3.0
8	2.8
9	2.9
10	3.2

Mean (µg/L)	= 2.87
Standard deviation (µg/L)	= 0.149
Number of points	= 10
Degrees of freedom	= 9
t value (99 percent confidence)	= 2.821
Method detection limit	= 0.42

CONCLUSIONS

The automated-hydride atomic absorption spectrophotometric method for antimony gives reproducible and accurate results for natural-water samples. The precision and bias are equal to or better than a manually operated antimony-hydride system. The automated system also provides the operator with ease of analysis and minimizes errors from incorrect or variable reagent additions that might occur during manual-hydride AAS analysis.

REFERENCES

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 36, 45, and 434.

Andreae, M.O., Asmodé, J.F., Foster, P., and Van't dack, L., 1981, Determination of antimony(III), antimony(V), and methylantimony species in natural waters by atomic absorption spectrometry with hydride generation: Analytical Chemistry, v. 53, no. 12, p. 1766-1771.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

U.S. Environmental Protection Agency, 1992, Primary drinking-water regulations, maximum contaminant levels (Appendix B to part 136, National primary drinking-water regulations): U.S. Code of Federal Regulations, Title 40, parts 100-149, revised as of July 1, 1992, p. 565-567.