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Stability of Low Concentration Calibration Standards for Graphite Furnace Atomic Absorption Spectrophotometry

by D. A. Bass and L. B. TenKate

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STABILITY OF LOW CONCENTRATION CALIBRATION STANDARDS FOR GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

by

Dean A. Bass and Lynn B. TenKate

Analytical Chemistry Laboratory

Chemical Technology Division

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

STABILITY OF LOW CONCENTRATION CALIBRATION STANDARDS FOR GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

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ABSTRACT

Graphite furnace atomic absorption spectrophotometry (GFAAS) is used for determination of ultra-trace metals in environmentally important samples. In the generation of GFAAS calibration curves for many environmental applications, low concentration calibration standards must be prepared daily, as required by the Statement of Work (SOW) for the U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP). This results in significant time and work for the analyst and significant cost to the Analytical Chemistry Laboratory (ACL) for chemicals and waste management. While EPA SW 846 is less prescriptive than the CLP SOW, ACL has been following the CLP guidelines because in-house criteria regarding the stability of GFAAS standards have not been established.

A study was conducted to determine the stability of GFAAS standards for analytes commonly used in the ACL (single and mixed) as a function of time. Data were collected over nine months. The results show that GFAAS standards for Sb, Pb, Se, Ag, and Tl are stable for a longer period of time than currently assumed by the CLP SOW. Reducing the frequency of preparing these standards will increase efficiency, decrease the handling of hazardous

substances, decrease the quantity of hazardous waste generated, and decrease the quantity of hazardous substances to be ordered and stocked by the laboratory. These benefits will improve GFAAS analysis quality, reduce costs, enhance safety, and lower environmental concerns.

I. INTRODUCTION

Graphite furnace atomic absorption spectrophotometry (GFAAS) is used for determination of ultra-trace metals in environmentally important samples. To perform these analyses, low concentration standards must be prepared. The stability of these standards is of concern. The CLP SOW[1] requires that calibration standards be prepared daily. This results in significant time and work for the analyst and significant costs for chemicals and waste management. In addition, if these standards are incorrectly prepared or mishandled, costly reruns and additional standard preparations may be required. Eliminating unnecessary standard preparation will increase the analysis efficiency.

Other researchers have investigated the lifetimes of metal solution standards. Puchelt and Noltner[2] determined the stability of low concentration standards using inductively coupled plasma - mass spectrometry (ICP-MS). Huff et al.[3] have studied standards in the 0.2 to 10 µg/mL concentration range using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). These authors found standards stable in excess of one year when stored in the appropriate acids.

We initiated a study to determine the stability of analyte concentration in standards typically used in GFAAS. Data collected over a nine-month period provided results for:

1. Effect of analytes commonly used in the ACL on standard concentration stability. Analytes studied were Sb, Pb, Se, Ag and Tl.
2. Effect of acid concentration on standard concentration stability. Standards were prepared in acid concentrations ranging from 0 to 5 percent.
3. Effect of mixed standards on standard concentration stability.
4. Effect of analyte concentration on standard concentration stability.

This study shows that GFAAS standards for Sb, Pb, Se, Ag, and Tl are stable for a longer period of time than currently assumed by the CLP SOW.[1] The ability to use standards for a longer period will mean a savings of time and money, use of less acids and toxic standards, and a minimization of hazardous waste.

II. EXPERIMENTAL

A. Apparatus

The GFAAS measurements were performed on a Perkin-Elmer 5100 Atomic Absorption Spectrometer equipped with Zeeman background correction, a PE AS-60 auto-sampler, an Epson Equity III Plus personal computer, and an Epson EX-800 printer. GEM Version 5.0 software provided instrument control, calculations, and data storage. Pyro-coated graphite furnace tubes (Perkin-Elmer) with L'vov platforms were used for all analytical runs and were replaced as required. Electrode-less discharge lamps (Perkin-Elmer) were used for Sb, Se, and Tl. Thermo Jarrel Ash hollow cathode lamps were used for Pb and Ag.

B. Reagents

1. Acids

Instra-Analyzed HNO_3 (J. T. Baker, Inc.) was used in blanks, standards, and test solution preparations. All preparations and dilutions were made with purified water having a specific conductance of approximately 0.5 $\mu\Omega^{-1}$.

2. Standards and Test Solutions

For clarification in the report, "standards" refer to solutions used to calibrate the AA system, and "test solutions" refer to solutions to be monitored to determine analyte solution stability. The calibration standard 100X (100 times the desired concentration) stock solutions and continuing calibration verification standard (CCV) were prepared from Instra-Analyzed Atomic Spectral Standards (J. T. Baker, Inc.) and a Custom Grade Thallium Standard (Inorganic Ventures, Inc.). The test solutions and initial calibration verification (ICV) standard (100X stock solutions) were prepared from standard reference materials of the

National Institute of Standards and Technology (NIST). Test solutions, calibration standards, and ICV and CCV solutions were prepared by making serial dilutions of the 100X stock solutions and adjusting to the appropriate acidity. Table 1 summarizes the test solutions prepared. Each cell in Table 1 represents a single test solution, except those under "Mixed Solution." Each column below "Mixed Solution" represents a single test solution. The second mixed solution was made two weeks after the first. The analyte concentrations for both solutions are given in Table 1.

3. Matrix Modifiers

The matrix modifiers used were those employed for routine GFAAS analytical work in ACL. Table 2 summarizes the concentrations of matrix modifiers and modifier preparation.

C. Procedures

A furnace temperature program was developed for each element. These programs are detailed in Tables 3 to 7. Gas flow rates were set at 300 mL/min for all stages of the furnace control program except during atomization. Gas flow was stopped during atomization. An autosampler program was set up for each element. Appropriate calibration standards, ICVs, CCVs, blanks, test solutions, diluents, and matrix modifiers were loaded into the autosampler tray.

Fresh calibration standards, ICVs, and CCVs were prepared from the appropriate 100X dilution every 24 h during instrument runs. A calibration was performed using a blank and three standards for each element before it was measured. Linear calibration fits were used for all elements except antimony, which used a quadratic calibration fit.

All standards, blanks, test solutions, ICVs, and CCVs were run in duplicate, and the average is reported in Sec. III, Results and Discussion. If the relative standard deviation (RSD) between replicates was greater than 20%, the duplicate sequence was automatically repeated. An ICV value outside ±10% of the known value automatically caused a recalibration and remeasurement of the ICV. A CCV value outside ±10% of the known value automatically caused a recalibration and remeasurement of the previous ten test solutions.

For the test solutions, an initial run concentration of ±10% of the known concentration was considered to validate the preparation. Duplicate test solutions (see Table 1) were prepared two weeks after the initial preparation to verify observed changes, if any, in test solution concentrations.

III. RESULTS AND DISCUSSION

Several factors can affect the lifetime (i.e., concentration stability) of standards used in GFAAS. Analyte concentration can decrease because of factors such as precipitation of the analyte from the solution and chemical or physical adsorption of the analyte on the container walls. Factors that can increase analyte concentrations include solution evaporation and extraction of analyte from the container material itself or from material adsorbed on the container walls. The extraction of metals from the container walls is not expected for the analytes studied here. The effect of evaporation of water from standard solutions was studied by Huff et al.,[3] who weighed their test solutions to monitor evaporation. They concluded that the effect of evaporation on the lifetime of properly stored standard solutions was negligible during normal laboratory use.

Regardless of the mechanism of standard degradation, the end results of interest are changes in concentration as a function of time. Of particular interest are general trends in the concentrations as a function of time. Figure 1 shows three possible trends in the data. Plots A and C represent changes in the concentration or degradation of the standard, and Plot B represents the expected result in a stable solution.

When the lifetimes of analytical standards are discussed, the primary concern is the period of time in which their concentration remains stable. For GFAAS, variation in the results of 0.5 to 5% is typical,[4] but ±10% accuracy of calibration check standards is considered acceptable.[1] We therefore established that changes greater then 10% indicate standard concentration degradation. While RSDs on duplicate injections of greater than 20% were automatically remeasured, test solutions and CCVs with RSDs greater than 10% and test solutions with changes greater than 10% were further evaluated to determine their validity.

For example, a data point was not used if the following conditions were met:

1. A given measurement for a test solution was more than ±10% of the expected value,
2. All or most of the test solutions in the same analytical sequence exceeded ±10%, or the reproducibility of the duplicate injections was greater than expected (10%), and
3. On subsequent measurements the test solution was within 10% of the expected value.

An individual erroneous measurement can exceed the ±10% criterion and does not necessarily indicate that the standard has degraded. Trends, as shown in Fig. 1 (Plots A and C), will be used as an indication of standard degradation.

A. Effect of Analyte Concentration

This study looks specifically at test solutions containing analytes in the 5 to 240 µg/L concentration range, as shown in Table 8. The concentrations were varied for each analyte and were at the level used in GFAAS measurements in the ACL. Huff et al.[3] have shown high concentration standards (0.2-10 µg/mL) to be stable for six months, which was the duration of their study. However, lower concentration standards, as those used in GFAAS, might be more susceptible to the degradation mechanisms. For example, the adsorption of the analyte on the container wall, or the extraction of the analyte from the container may occur in a fixed amount. This fixed amount would greatly affect the lower concentration standards. On the basis of equilibrium considerations precipitation of the analyte would more likely affect high concentration standards and the mixed-analyte standards.

Figure 2 shows the antimony concentrations over the 9-month testing period. The legend shows the initial antimony concentration for test solutions used. In the Fig. 2 legend, Sb2 refers to the second test solution prepared at a later date. Degradation of the solutions (as in Fig. 1, plots A and C) is not observed from these data. All trends follow the "B" stability curve, as shown in Fig. 1, indicating the solutions were stable through the time of this study.

Figures 3 to 6 show concentration stability for Pb, Se, Ag, and Tl, respectively. Similarly to Fig. 2, Pb2, Se2, Ag2, and Tl2 indicate a second test solution prepared at a later date. In all cases, the trends indicate that the test solutions were stable through the time studied. Of particular interest is the silver test solution, which is known to be light sensitive. No special steps were taken to protect the silver test solution from light, yet it remained stable.

B. Effect of Acid Concentration

The importance of acidifying samples and standards to maintain stability for metal determinations is well known. Methods often require samples to be in acid concentrations ranging from a few tenths of a percent to five percent or even more. These concentrations assure that the analytes remain in a stable solution form and do not precipitate. Table 9 shows the concentrations of nitric acid used in this part of the study. The purchased solution and 100X stock solutions used to prepare the test solutions also contained 2% nitric acid. After dilution of these stock solutions, the resulting nitric acid concentration is 0.02%, plus the percent additional acid added to each test solution.

Figures 7 to 11 show the effect of acid concentration on the stability of Sb, Pb, Se, Ag, and Tl solutions, respectively. The designation "0.5%(2)" refers to the second test solution at 0.5% acid concentration, prepared at a later date. The trends indicating degradation (Fig. 1, Plots A and C) in test solution concentration are not present for any of the analytes at any of the acid concentrations. As before, this is of particular interest for silver, which is light sensitive. No precaution was taken to prevent the exposure of the test solution to light. Also of interest are the 0% acid-added test solutions, which are below the acid concentrations that would be used in the laboratory and are expected to be least stable. It appears that low acid concentrations do not greatly degrade analyte lifetimes.

C. Effect of Mixed-Analyte Solutions

Often, in GFAAS and other atomic spectroscopy techniques, multielement standards are prepared and used for instrument calibration. This portion of the study looks at the effect of other analytes in the test solution on the lifetime of the analyte of interest. Table 10 shows the initial concentration of each analyte present in the two mixed test solutions. The test solutions were prepared in 1% nitric acid. Mixed-analyte solutions could have shorter lifetimes if, for example, the analytes reacted with each other and precipitated from solution. Also, the As and Sb stock standards were in 50% HCl. After dilution, the resulting chloride concentration was 150 ppm for test solution 1 and 85 ppm for test solution 2. These chlorides could react with the other analytes and precipitate as metal chlorides.

Figures 12 and 13 show the stability results for the mixed-analyte test solutions. Again, the analyte concentrations were stable throughout the time of the study. Thus, the analytes did not interact with each other and the chlorides did not react with the other analytes.

IV. CONCLUSIONS

The results showed test solutions to be stable throughout the nine months of this study. We primarily looked at situations typically used in analytical operations. However, we also examined conditions that are not typically used due to concern for degradation of the standard lifetimes. These conditions included long-term storage of silver-containing test solutions in containers or areas not designed to protect them from room light. Another adverse condition included the addition of no acid to some of the test solutions. (The addition of acid is required by the EPA to increase the stability of the standard.) For the test solutions in which no acid was added, the acid concentration was approximately 0.02%, resulting from the contribution of the 100X stock solutions, which are in 2% nitric acid. This is significantly below the EPA recommendation of approximately 2% nitric acid. Even in these controlled, non-recommended conditions, the test solutions remained stable.

These results indicate that standards do not need to be prepared fresh daily for GFAAS calibrations. Reducing the frequency of preparing these standards will reduce the chances of preparation errors, increase efficiency, decrease the handling of hazardous substances, decrease the quantity of hazardous waste generated, and decrease the quantity of hazardous substances to be ordered and stocked by the laboratory. These benefits will improve analysis quality, lower costs, enhance safety and reduce environmental concerns in the Analytical Chemistry Laboratory.

ACKNOWLEDGMENTS

This work was supported by an Analytical Development Fund from the ACL. The authors wish to thank Irene M. Fox and Peter C. Lindahl for their assistance in this project.

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Table 1. Composition of Test Solutions

	Concentration (µg/L)							
	Acid						**Mixed Solution**	
	0%	**0.5%**	**1.0%**			**5.0%**	**Sol.1**	**Sol.2**
Se	25	25[a]	5[a]	25[a]	50	25	50	25
Pb	25	25[a]	5[a]	25[a]	50	25	50	25
Ag	25	25[a]	10[a]	25[a]	50	25	50	25
Tl	25	25	10[a]	25[a]	50	25	50	25
Sb	120	120[a]	60[a]	120[a]	240	120	240	120

[a] A second solution was prepared two weeks after the first.

Table 2. Composition of Matrix Modifiers

Element	Matrix Modifier	Preparation
Se, Sb	0.02% Ni; 0.01% Mg; 0.02% Pd	10 mL 0.2% (w/v)$Ni(NO_3)_2$-$6H_2O$ 10 mL 0.1% (w/v)Mg as NO_3 10 mL 0.2% (w/v)Pd as NO_3 dilute to 100 mL with 1% nitric acid
Pb, Ag	1.6% $(NH_4)_2HPO_4$; 0.01% Al; 0.02% Pd	4 mL 40% (w/v)$(NH_4)_2HPO_4$ 10 mL 0.2% (w/v)Pd as NO_3 10 mL 0.1% (w/v)Al as Cl dilute to 100 mL with 1% nitric acid
Tl	2% H_2SO_4; 0.02% Pd	2 mL H_2SO_4 (conc.) 10 mL 0.2% (w/v)Pd as NO_3 dilute to 100 mL with 1% nitric acid

Table 3. Furnace Temperature Program for Antimony

Step	Stage	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Gas Flow (mL/min)
1	Dry[a]	110	1	10	300
2	Dry[a]	120	25	2	300
3	Dry[a]	150	15	3	300
4	Ash	700	12	2	300
5	Ash	1000	3	2	300
6	Cool-down	20	1	15	300
7	Atomization	2400	0	5	0
8	Clean	2650	1	5	300

[a] Initial drying conditions. Drying conditions were adjusted as needed.

Table 4. Furnace Temperature Program for Lead

Step	Stage	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Gas Flow (mL/min)
1	Dry[a]	140	1	1	300
2	Dry[a]	120	20	1	300
3	Dry[a]	130	20	1	300
4	Ash	400	15	1	300
5	Ash	800	3	2	300
6	Cool-down	20	1	15	300
7	Atomization	1800	0	4	0
8	Clean	2500	1	5	300

[a] Initial drying conditions. Drying conditions were adjusted as needed.

Table 5. Furnace Temperature Program for Selenium

Step	Stage	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Gas Flow (mL/min)
1	Dry[a]	140	1	1	300
2	Dry[a]	120	20	1	300
3	Dry[a]	130	20	1	300
4	Ash	400	15	1	300
5	Ash	1000	3	2	300
6	Cool-down	20	1	10	300
7	Atomization	2300	0	5	0
8	Clean	2500	1	5	300

[a] Initial drying conditions. Drying conditions were adjusted as needed.

Table 6. Furnace Temperature Program for Silver

Step	Stage	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Gas Flow (mL/min)
1	Dry[a]	140	1	1	300
2	Dry[a]	120	20	1	300
3	Dry[a]	130	20	3	300
4	Ash	500	10	2	300
5	Ash	1000	3	2	300
6	Cool-down	20	1	15	300
7	Atomization	1700	0	4	0
8	Clean	2500	1	5	300

[a] Initial drying conditions. Drying conditions were adjusted as needed.

Table 7. Furnace Temperature Program for Thallium

Step	Stage	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Gas Flow (mL/min)
1	Dry[a]	110	1	10	300
2	Dry[a]	120	25	10	300
3	Dry[a]	150	25	1	300
4	Ash	500	10	1	300
5	Ash	1000	3	2	300
6	Cool-down	20	1	15	300
7	Atomization	2300	0	5	0
8	Clean	2500	1	5	300

[a] Initial drying conditions. Drying conditions were adjusted as needed.

Table 8. Analyte Concentrations in Test Solutions

Analyte	**Concentration (µg/L)**				
Se	5	5	25	25	50
Pb	5	5	25	25	50
Ag	10	10	25	25	50
Tl	10	10	25	25	50
Sb	60	60	120	120	240

Table 9. Acid Concentrations in Test Solutions

Analyte	Concentration (µg/L)	Nitric Acid (%)[a]			
Sb	120	0	0.5	1	5
Pb	25	0	0.5	1	5
Se	25	0	0.5	1	5
Ag	25	0	0.5	1	5
Tl	25	0	0.5	1	5

[a] Represents the amount of nitric acid added.

Table 10. Initial Analyte Concentrations in Mixed Test Solutions (µg/L)

Element	Test Solution 1	Test Solution 2
Sb	240	120
As[a]	75	50
Pb	50	25
Se	50	25
Ag	50	25
Tl	50	25

[a] Present in the standard, but not measured in the study.

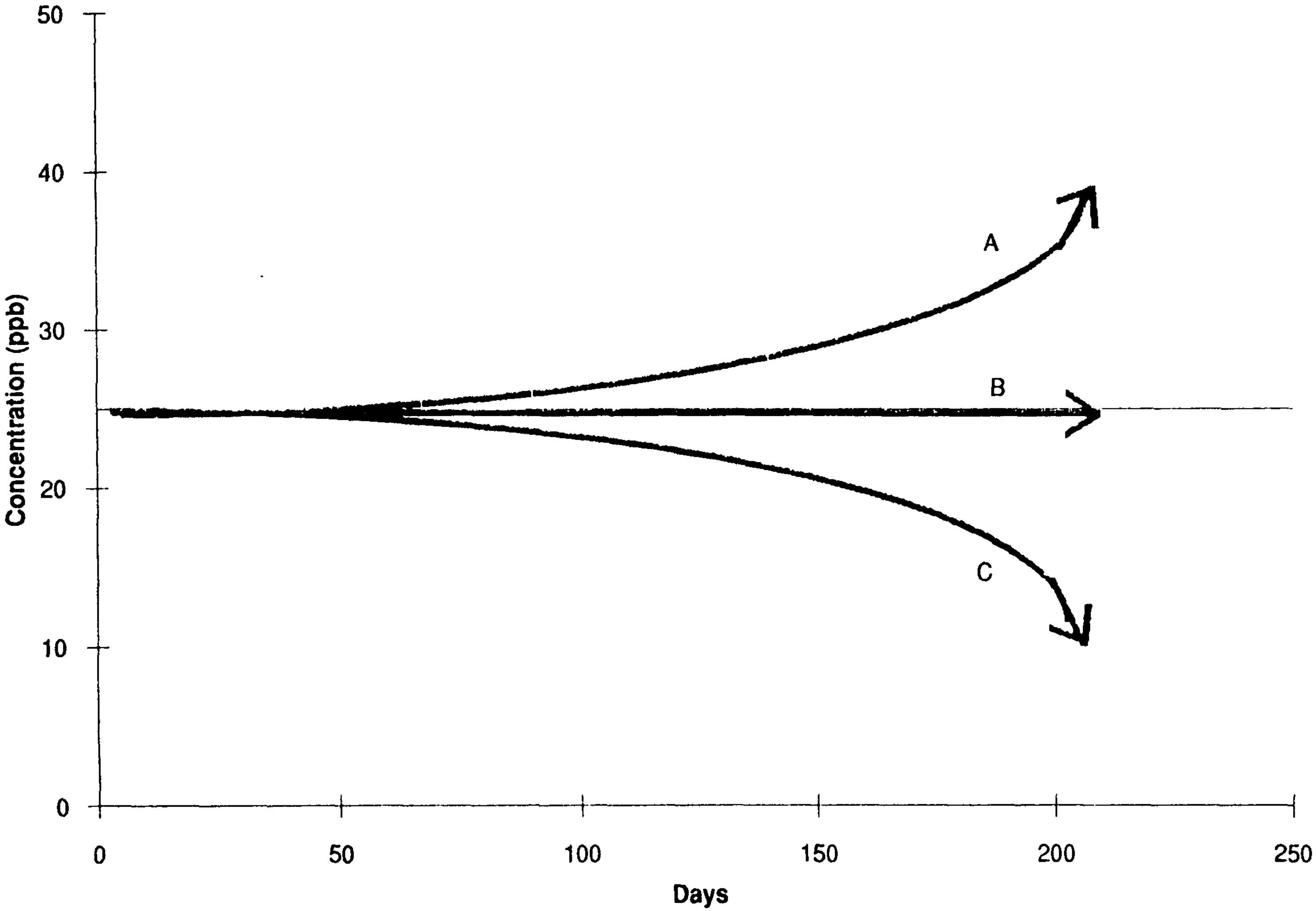

Fig. 1. Example of Possible Trends in Concentrations of Standards as a Function of Time

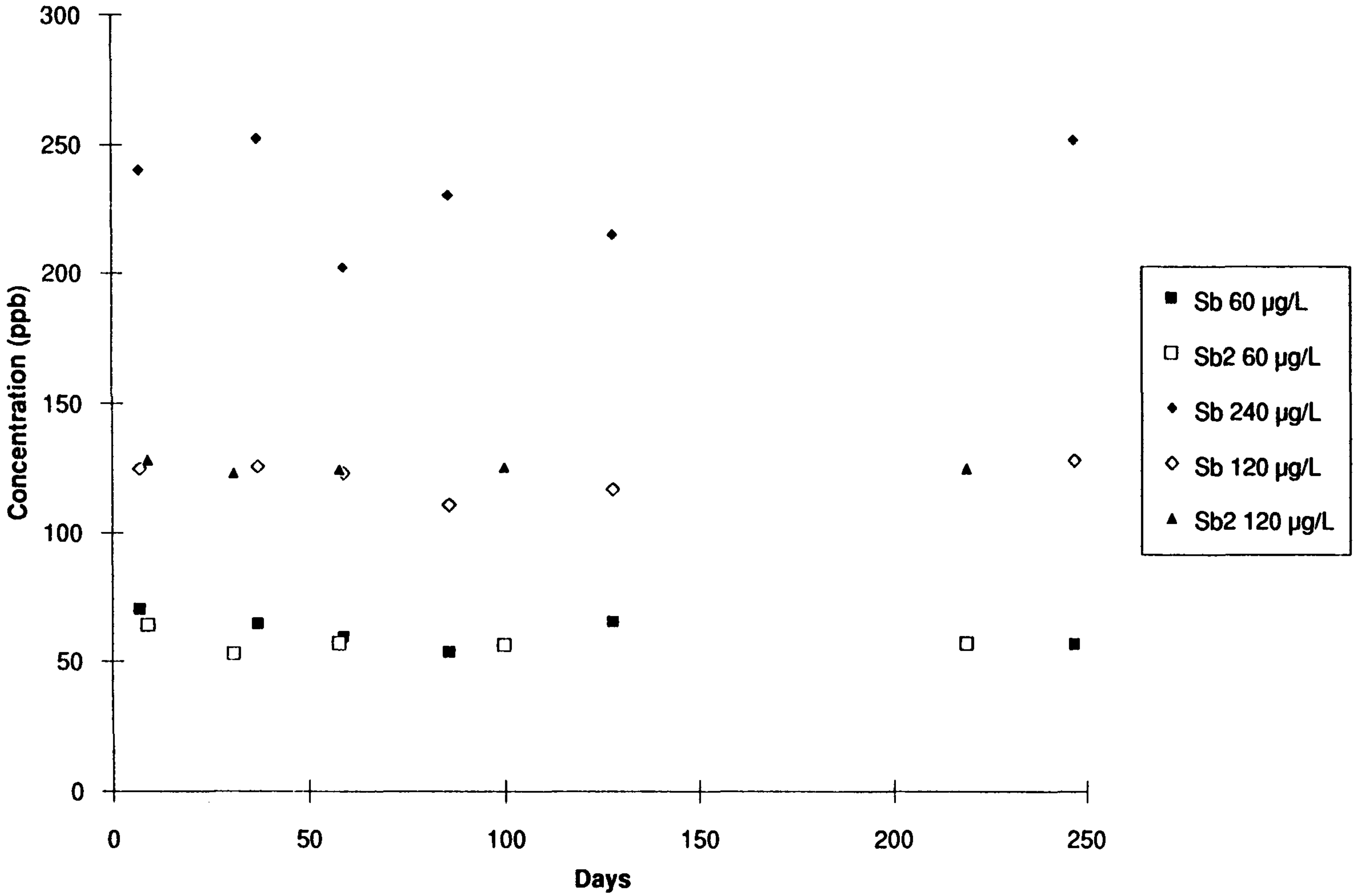

Fig. 2. Antimony Concentrations as a Function of Time

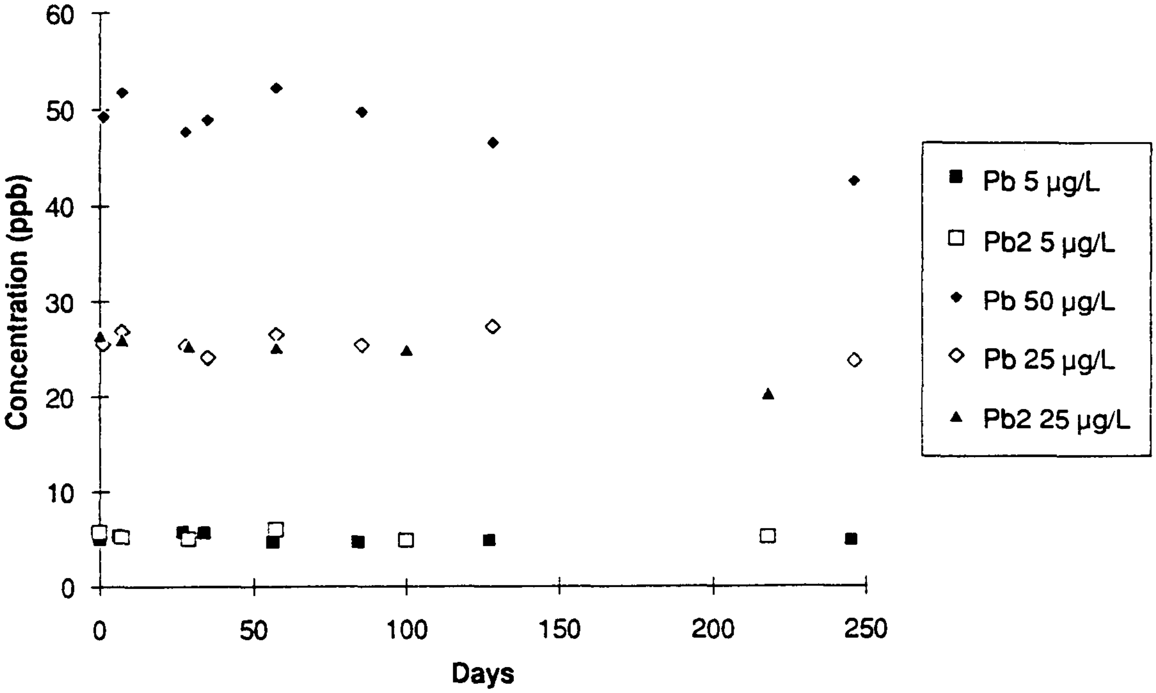

Fig. 3. Lead Concentrations as a Function of Time

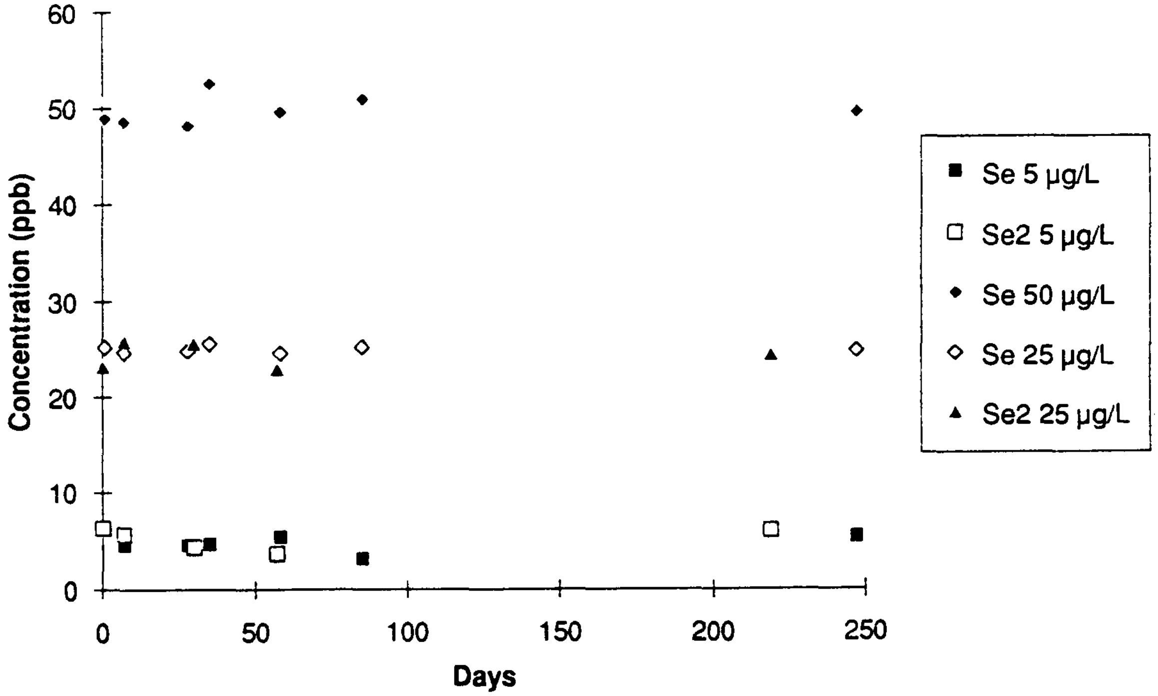

Fig 4. Selenium Concentrations as a Function of Time

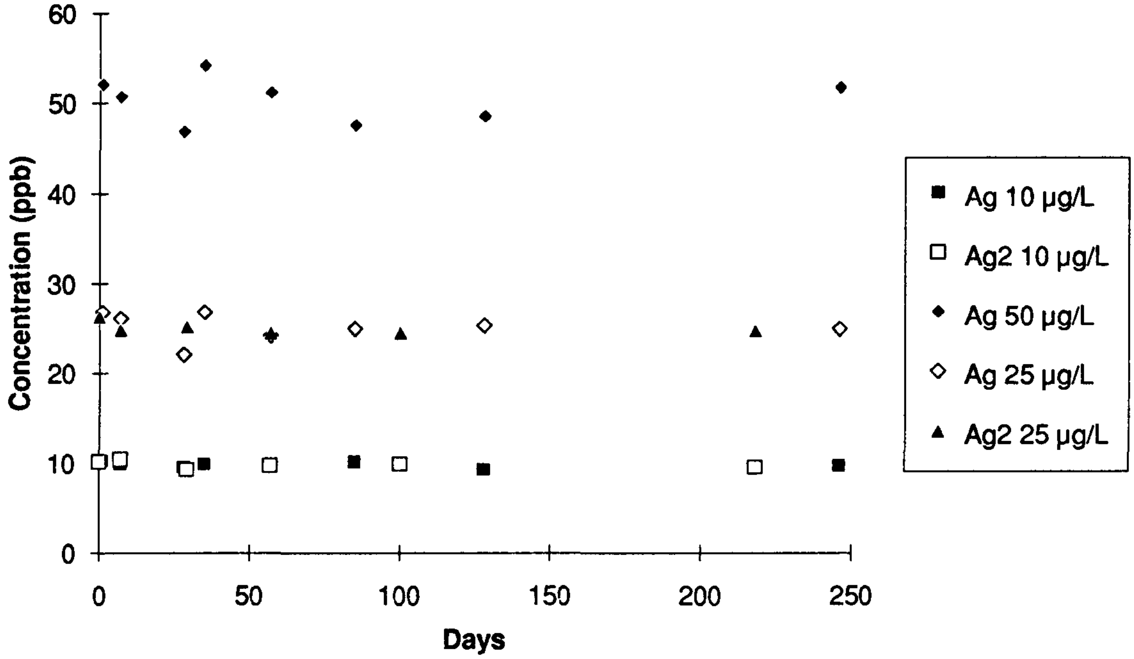

Fig. 5. Silver Concentrations as a Function of Time

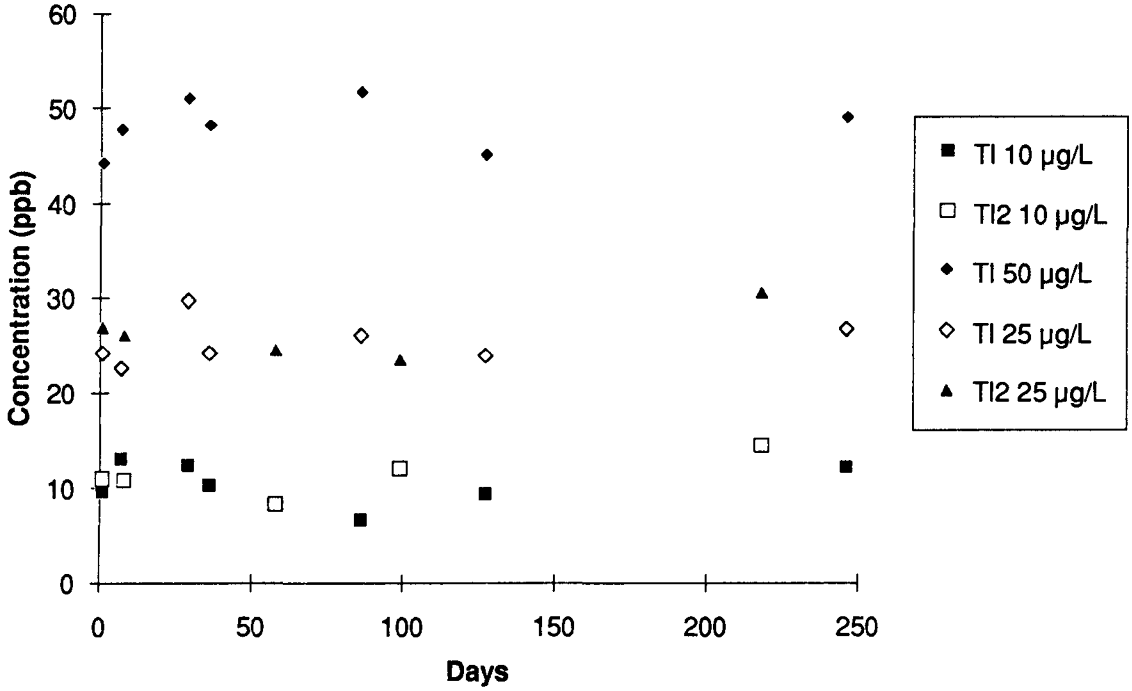

Fig. 6. Thallium Concentrations as a Function of Time

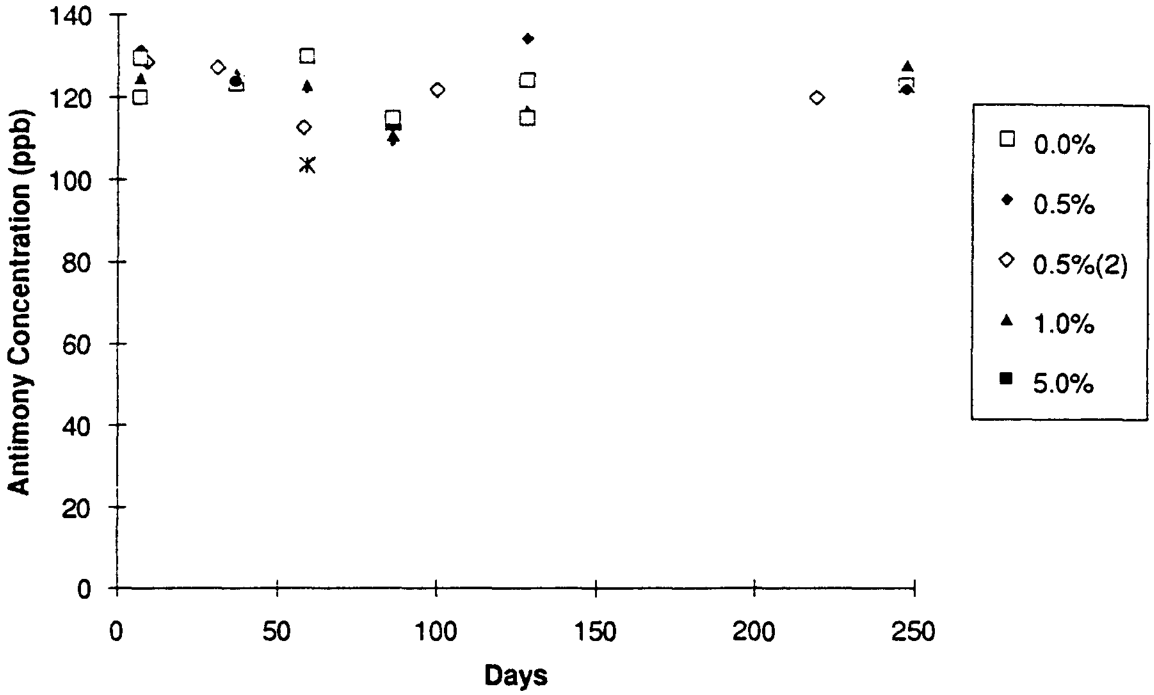

Fig. 7. Antimony Concentrations as a Function of Time in Various Acid Concentrations

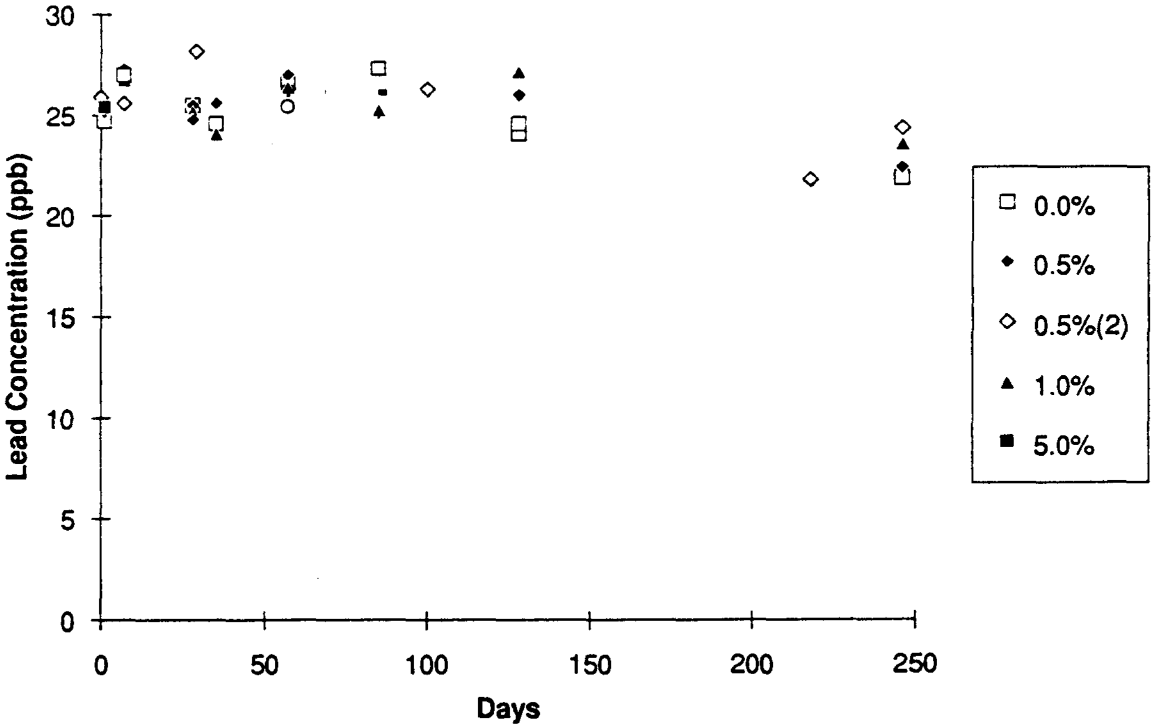

Fig. 8. Lead Concentrations as a Function of Time in Various Acid Concentrations

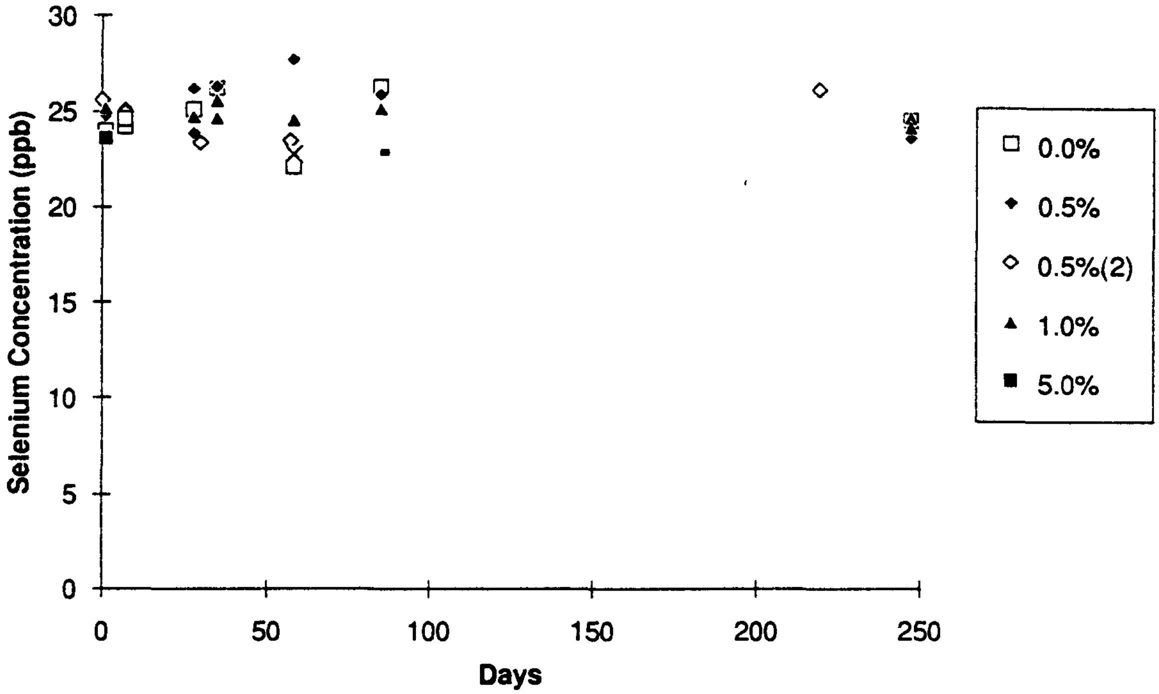

Fig. 9. Selenium Concentrations as a Function of Time in Various Acid Concentrations

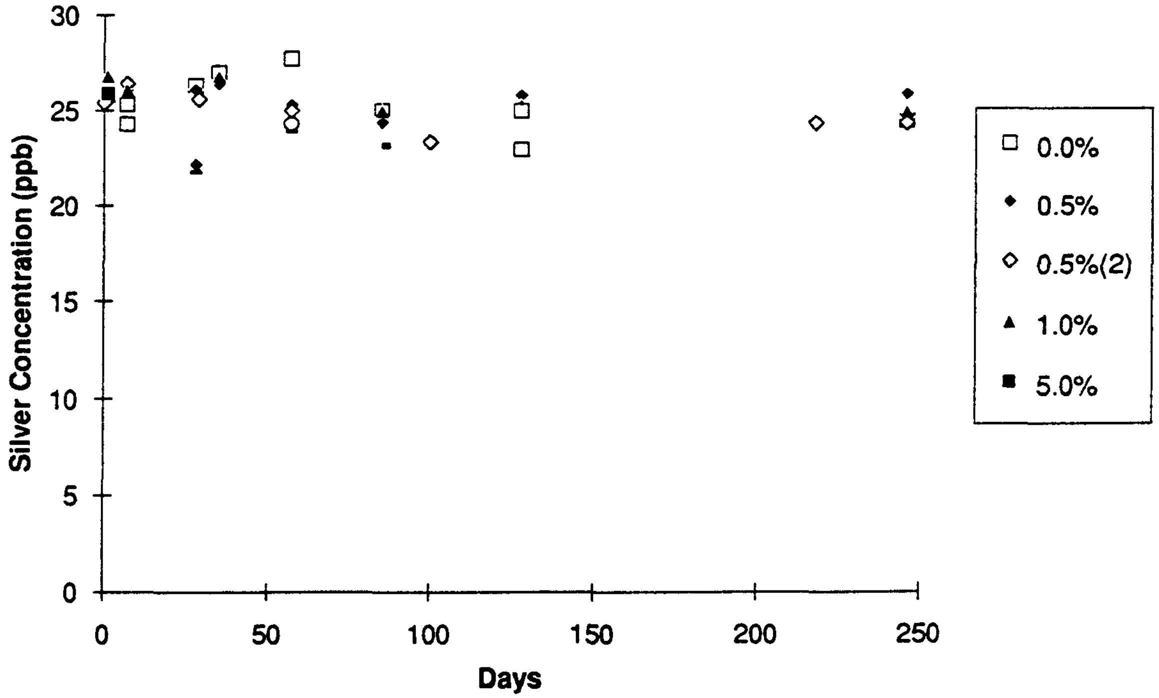

Fig. 10. Silver Concentrations as a Function of Time in Various Acid Concentrations

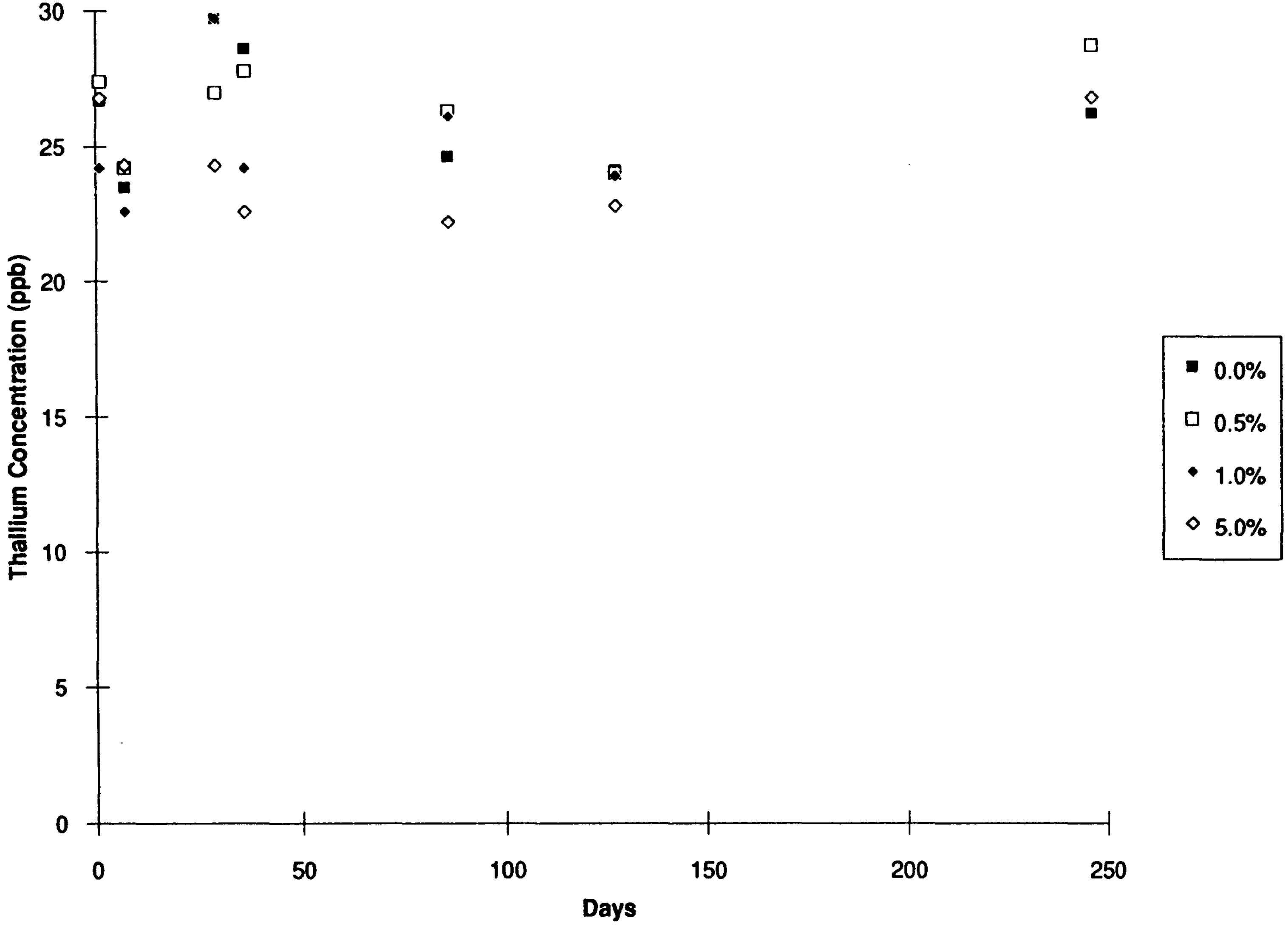

Fig. 11. Thallium Concentrations as a Function of Time in Various Acid Concentrations

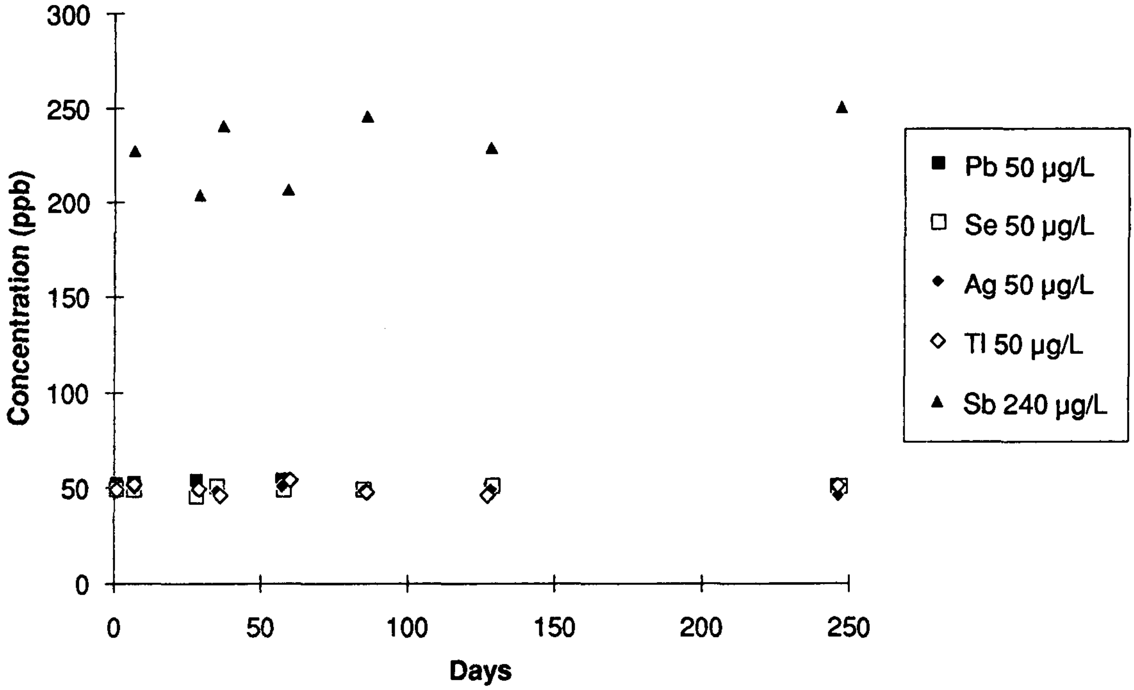

Fig. 12. Analyte Concentrations as a Function of Time in a Multielement Solution

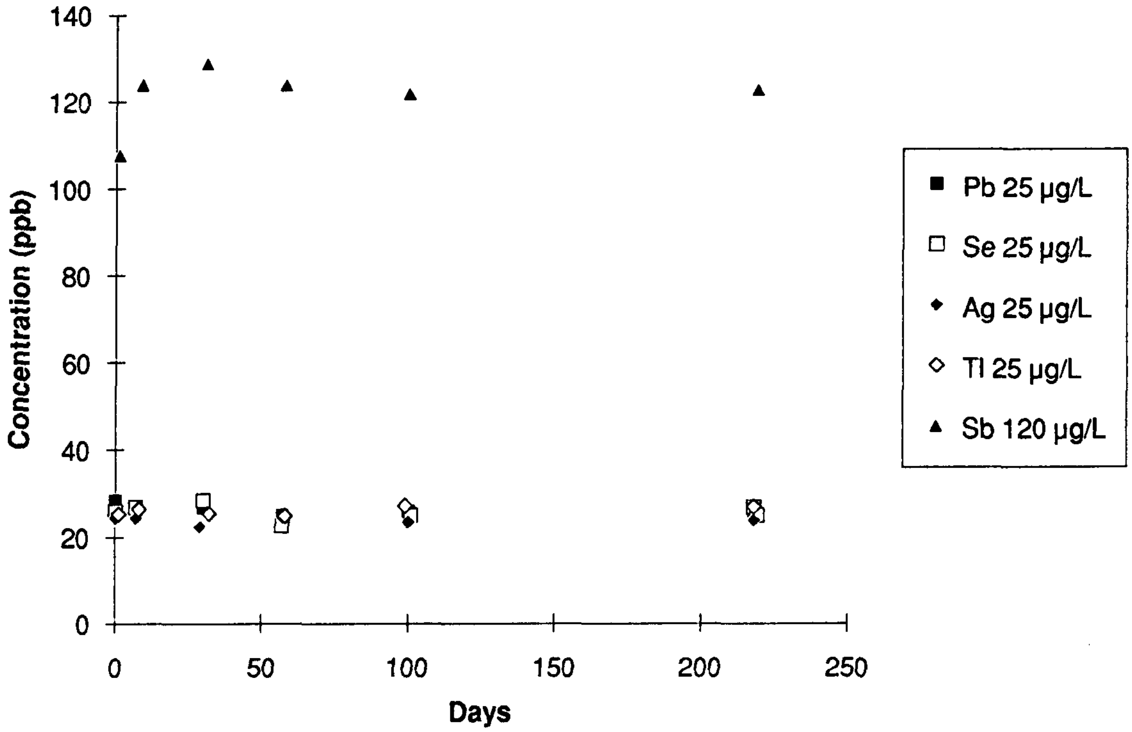

Fig. 13. Analyte Concentrations as a Function of Time in a Multielement Solution

Appendix A.

Data

Table A-1. Antimony Data (µg/L)

Conc. Sb (µg/L) Acid (%)	**60** **1**	**120** **1**	**240** **1**	**120** **0**	**120** **0.5**	**120** **5**	**60** **1**	**120** **1**	**120** **0.5**	**240** **comb**	**120** **comb**
Prep. Date	4/13	4/13	4/13	4/13	4/13	4/13	5/11	5/11	5/11	4/13	5/11
Analysis Date											
20-Apr	70.2	125	240	120	132	130				228	
20-May	64.6	126	252	124	125	124	63.9	129	129	241	124
11-Jun	59.5	123	202	130	122	104	52.8	124	127	207	129
8-Jul	53.5	111	230	115	110	113	56.9	125	113	246	124
19-Aug	65.2	117	215	124	134	115	56.2	126	122	229	122
16-Dec	56.8	128	252	123	122	128	56.9	125	120	251	123

Table A-2. Lead Data (µg/L)

Conc. Pb (µg/L) Acid (%)	**5** **1**	**25** **1**	**50** **1**	**25** **0**	**25** **0.5**	**25** **5**	**5** **1**	**25** **1**	**25** **0.5**	**50** **comb**	**25** **comb**
Prep. Date	4/14	4/13	4/13	4/13	4/13	4/13	5/11	5/11	5/11	4/13	5/11
Analysis Date											
14-Apr	4.9	25.4	49.3	24.7	25.2	25.4				52	
20-Apr	5.4	26.8	51.8	27	27.3	27				52.7	
11-May	5.7	25.2	47.7	25.5	25.5	24.8	5.7	26.4	25.9	53.8	28.4
18-May	5.6	24	49	24.6	25.6	24.1	5.2	26	25.6	51.6	26.4
9-Jun	4.6	26.4	52.2	26.6	27	25.4	4.9	25.2	28.2	54.3	
10-Jun											26.7
7-Jul	4.6	25.3	49.7	27.3	25.1	26.1	6	25.1	26.3	49.4	24.8
19-Aug	4.8	27.2	46.5	24.1	26	24.6	4.8	24.8	26.3	49.9	25.8
15-Dec	4.8	23.6	42.5	21.9	22.4	24.4	5.1	20.3	21.8	48	24.9

Table A-3. Selenium Data (µg/L)

Conc. Se (µg/L)	**5**	**25**	**50**	**25**	**25**	**25**	**5**	**25**	**25**	**50**	**25**
Acid (%)	**1**	**1**	**1**	**0**	**0.5**	**5**	**1**	**1**	**0.5**	**comb**	**comb**
Prep. Date	4/13	4/13	4/13	4/13	4/13	4/13	5/11	5/11	5/11	4/13	5/11
Analysis Date											
14-Apr	6.1	25.2	48.9	24	24.8	23.6				49.3	
20-Apr	4.5	24.7	48.5	24.2	25.2	24.6				49.2	
11-May	4.5	24.8	48.1	25.1	26.2	23.9	6.3	23.3	25.6	45.6	25.9
18-May	4.6	25.6	52.5	26.2	26.3	24.7	5.6	25.9	25	50.7	26.8
10-Jun	5.4	24.6	49.6	22.1	27.7	22.8	4.3	25.7	23.4	48.8	28.4
7-Jul	3.1	25.2	50.9	26.3	25.9	22.9	3.6	23	23.5	49	22.8
20-Aug										51	24.8
15-Dec										50.9	26.8
16-Dec	5.4	24.8	49.5	24.6	23.7	24.3	5.9	24.4	26.2	50.4	25

Table A-4. Silver Data (µg/L)

Conc. Ag (µg/L)	**10**	**25**	**50**	**25**	**25**	**25**	**10**	**25**	**25**	**50**	**25**
Acid (%)	**1**	**1**	**1**	**0**	**0.5**	**5**	**1**	**1**	**0.5**	**comb**	**comb**
Prep. Date	4/13	4/13	4/13	4/13	4/13	4/13	5/11	5/11	5/11	4/13	5/11
Analysis Date											
14-Apr	10.3	26.8	52	25.8	25.8	25.9				50	
20-Apr	9.9	26.1	50.7	24.3	26	25.3				49.9	
11-May	9.6	22.1	46.8	26.3	26.1	22.2	10.2	26.4	25.4	49.1	24.3
18-May	9.9	26.8	54.1	27	26.4	26.8	10.4	24.9	26.4	48.3	24.3
9-Jun	9.9	24.2	51.1	27.7	25.3	24.3	9.3	25.2	25.6	50.8	22.4
7-Jul	10.2	25	47.5	25	24.4	23.2	9.7	24.5	25	48.3	24.6
19-Aug	9.3	25.3	48.5	23	25.8	25	9.9	24.5	23.4	49.2	23.4
15-Dec	9.8	25	51.7	24.5	25.9	24.4	9.6	24.8	24.4	46	23.8

Table A-5. Thallium Data (µg/L)

Conc. Tl (µg/L)	**10**	**25**	**50**	**25**	**25**	**25**	**10**	**25**	**50**	**25**
Acid (%)	**1**	**1**	**1**	**0**	**0.5**	**5**	**1**	**1**	**comb**	**comb**
Prep. Date	4/13	4/13	4/13	4/13	4/13	4/13	5/11	5/11	4/13	5/11
Analysis Date										
14-Apr	9.6	24.2	44.2	26.7	27.4	26.8			49	
20-Apr	13.1	22.6	47.8	23.5	24.2	24.3			51.8	
12-May	12.4	29.7	51	29.7	27	24.3	11	27	49.5	25.2
19-May	10.3	24.2	48.2	28.6	27.8	22.6	10.8	26.2	46.2	26.4
12-Jun									54.1	25.4
8-Jul	6.6	26.1	51.7	24.6	26.3	22.2	8.3	24.6	47.6	24.9
18-Aug	9.4	23.9	45.1	24.1	24	22.8	12.1	23.6	46.2	27
15-Dec	12.2	26.8	49.1	26.2	28.7	26.8	14.5	30.6	51	26.9

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