

# Methods for Environmental Samples

## Application Note

### Atomic Absorption

#### Author

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#### Introduction

The United States Environmental Protection Agency (EPA) requires the determination of important trace elements in a variety of environmental samples. Graphite furnace atomic absorption methods are recommended for some elements including As, Se, Cd, Pb, Tl, Sb, Ag, Be and Cr. Graphite furnace analyses can be difficult due to chemical and spectral interferences. Quantification in atomic absorption requires that for a given analyte mass the signal be identical in the reference standard and in the sample. Chemical interferences occur when sample matrix constituents alter the atomization efficiency of the analyte element resulting in a matrix dependent analyte signal. Chemical (or matrix) interferences can be minimized by the use of platform atomization techniques and appropriate matrix modifiers.

The platform technique involves the use of a graphite platform which is inserted into the graphite furnace tube. The sample is deposited on the platform instead of the furnace wall, and during atomization the platform temperature lags the furnace wall temperature by several hundred degrees. Under these conditions, the analyte compounds are not vaporized until the furnace wall and gaseous environment have approached a steady-state temperature. This minimizes chemical interferences.

The addition of a matrix modifier can be used to alter the volatility of either the analyte element or a bulk matrix component. The matrix modifier is added to the sample prior to atomization. It can decrease the volatility of the analyte element or increase the volatility of a sample matrix component. Many important environmental elements are relatively volatile (Cd, Pb, As and Se). These elements could be prematurely lost in the graphite furnace temperature cycle resulting in inaccurate quantification. With the addition of an appropriate matrix modifier these elements can be stabilized to higher temperatures. This can greatly reduce matrix interferences.



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Non-specific absorption (background) and spectral interferences can also affect the accuracy of graphite furnace analyses. Non-specific absorption is a false signal due to either molecular absorption and/or light scattering. It can be corrected for by accurate simultaneous background correction systems (Deuterium or Zeeman). Spectral interferences can occasionally occur. For example, low level selenium determinations in the presence of high levels of iron can be difficult with deuterium background correction due to spectral interferences. The use of Zeeman background correction is superior for some types of samples and is recommended by EPA for the determination of As and Se.

This study outlines graphite furnace (GFAAS) methodology for Agilent SpectrAA Zeeman atomic absorption spectrometers. The important environmental elements As, Se, Cd, Pb, Tl, Sb, Ag, Be and Cr are included. Techniques such as Zeeman background correction, platform atomization, matrix modification and peak area signal measurement were utilized in order to reduce interferences. Results from the analysis of real samples will be discussed.

## Methodology

Table 1 lists the Superfund contract required detection limits (CRDLs) required by the EPA. Quality assurance requirements of the contract lab program specify that one atomic absorption standard must be at the CRDL. A blank and at least three calibration standards must cover an appropriate concentration range. Table 1 lists the standard calibration ranges used in this study. In the case of As, Se, Pb, Tl, Sb and Ag, the lowest calibration standard was the specified CRDL. Because of the high sensitivity of the GFAAS technique, calibration standards for Cd, Be and Cr were established with one or more standards below the CRDL. In all cases, one calibration standard was at the contract required detection limit. Appropriate sample dilutions can be used to obtain sample concentration levels in the range of the calibration standards. In this study four calibration standards were prepared utilizing the dilution capabilities of the GTA-96 programmable sample dispenser. (For As, the four standards were premixed and a constant volume was injected). Platform atomization was used for all determinations except for Cr which required wall atomization. Peak area absorbance measurements were utilized for all elements.

Table 1. Elements Determined by GFAAS — Concentration Ranges

Element	Contract required detection limit (µg/L) (CRDL)	Calibration ranges (µg/L)(this study)
Antimony	60	60–240
Arsenic	10	10–100
Beryllium	5	1–10
Cadmium	5	0.5–5
Chromium	10	5–50
Lead	5	5–50
Selenium	5	5–50
Silver	10	10–100
Thallium	10	10–100

EPA approved matrix modifiers were used for the appropriate elements\*\*. The modifier solutions that were used in this study are listed in Table 2.

Table 2. Matrix Modifiers

Element	Matrix modifier
Antimony	3% NH <sub>4</sub> NO <sub>3</sub>
Arsenic	1000 mg/L Ni in 5% HNO <sub>3</sub>
Cadmium	1% NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>
Lead	1% H <sub>3</sub> PO <sub>4</sub>
Selenium	1000 mg/L Ni in 5% HNO <sub>3</sub>
Thaallium	1000 mg/L Pd*

\* Requires the addition of a reducing agent for consistent performance.

Palladium is an EPA recommended modifier for the determination of thallium, however, its effectiveness as a modifier is influenced by its chemical form.

The results of a study using different palladium forms illustrate the important factors for palladium matrix modification in the analyses of real samples. These results are discussed in the following section under thallium.

\*\* The modifiers used in this study are approved by the EPA in SW-846/Test Methods for Evaluating Solid Waste.

## Furnace Methodology

The following section presents the furnace programs used in this study. Calibration results and the calibration graph are also shown for most elements. The Hot Inject capability of the GTA-96 was utilized for most of the temperature programs. This allowed the dry portion of the temperature program to be very short (10–30 seconds). Most of the temperature programs were under 1.5 minutes. This resulted in high sample throughput. Long term studies were done with real samples and the results will be discussed in the next section of this publication.

### Selenium

A Photron Super Lamp was used. The matrix modifier was 1000 mg/L Ni in 5% HNO<sub>3</sub>. Calibration standards of 5.0, 10.0, 15.0 and 50.0 µg/L Se were auto-mixed from a master standard of 50.0 µg/L. The graphite furnace method, calibration results and calibration graph are shown in Figure 1. Figures are appended to the end of this paper.

### Arsenic

A Photron Super Lamp was used. The matrix modifier was 1000 mg/L Ni in 5% HNO<sub>3</sub>. Calibration standards of 10.0, 10.0, 50.0 and 100.0 µg/L As were premixed. The graphite furnace method, calibration results and calibration graph are shown in Figure 2. Pre-mixed standards resulted in a more linear calibration graph. Auto-mixing 2 µL to 28 µL total volume for the lowest standard often resulted in calibration graphs that curved upward. It is believed this is due to incomplete mixing with the modifier solution. This upward curvature was only seen for arsenic and selenium with standard volumes under 5 µL. Pre-mixed standards appear to give better results for these two elements if very low volumes (< 5 µL) are used for the low standards. All other elements in this study gave excellent results with auto-mixed standards.

### Lead

The matrix modifier used for the Pb study was 1% phosphoric acid. Calibration standards of 5.0, 12.5, 25.0 and 50.0 µg/L Pb were prepared from a master standard of 50 µg/L. The auto-mixing capabilities of the GTA-96 PSD were utilized. The graphite furnace method, calibration results and calibration graph are shown in Figure 3. The excellent precision permitted the use of only two replicates, further speeding up the analysis.

### Cadmium

The matrix modifier for the cadmium study was 1.0% NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. Calibration standards of 0.50, 1.25, 2.50 and 5.00 µg/L Cd were prepared from a master standard of 5.00 µg/L. The auto-mixing capabilities of the sampler were utilized. The graphite furnace method, calibration results and calibration graph are shown in Figure 4.

### Antimony

For antimony, utilization of the alternate resonance line of 231.2 nm and a SBW of 0.5 nm resulted in better stability and less curvature than the primary resonance line of 217.6 nm. The sensitivity was more than adequate to meet the required CRDL. The matrix modifier was 3% NH<sub>4</sub>NO<sub>3</sub>. Calibration standards of 60, 120, 180 and 240 µg/L Sb were auto-mixed from a master standard of 240 µg/L. The graphite furnace method, calibration results and calibration graph are shown in Figure 5.

### Beryllium

Beryllium did not require a matrix modifier. Calibration standards of 1.0, 2.0, 5.0 and 10.0 µg/L Be were auto-mixed from a master standard of 10 µg/L. The graphite furnace method, calibration results and calibration graph are shown in Figure 6.

### Chromium

Chromium required wall atomization. Calibration standards of 20.0, 20.0, 50.0 and 100.0 µg/L Cr were auto-mixed from a master standard of 100.0 µg/L. A matrix modifier was not required. The graphite furnace method and calibration graph are shown in Figure 7.

### Silver

Silver did not require a matrix modifier. Calibration standards of 20.0, 20.0, 50.0 and 100.0 µg/L Ag were auto-mixed from a master standard of 200.0 µg/L. To reduce sensitivity, 0.3 L/min inert gas was introduced during the atomization steps. The graphite furnace method and calibration graph are shown in Figure 8.

## Thallium

The matrix modifier chosen for the thallium method was 1000 mg/L Pd plus 2% citric acid. Calibration standards of 10.0, 20.0, 50.0 and 100.0 µg/L Tl were auto-mixed from a master standard of 100.0 µg/L Tl. The graphite furnace method, calibration results and calibration graph are shown in Figure 9.

The key to successfully using palladium as a matrix modifier is to combine it with a reducing agent. A study was done to compare the performance of mixed palladium modifiers in several environmental samples. These included brackish water and soil digest samples. Platform atomization was used to conduct spike recovery studies. The results of this study are shown in Table 3.

Table 3. Pd Modifier Comparison — Spike Recovery Study

	Pd(NO <sub>3</sub> ) <sub>2</sub> no reducing agent	Pd(NO <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> acid	PdCl <sub>2</sub> + 2% citric	PdCl <sub>2</sub> + 2% hydroxyl- amine HCL
D.I. H <sub>2</sub> O 1% HNO <sub>3</sub>	104%	98%	98%	99%
#9 Brackish H <sub>2</sub> O	17%	93%	90%	86%
31247-17	21%	46%	105%	53%
31247-28	38%	81%	105%	86%
31247-32	16%	100%	98%	91%
31247-46	49%	76%	102%	35%

Commercially available solutions of palladium are typically PdCl<sub>2</sub>. By itself, PdCl<sub>2</sub> is a very poor matrix modifier even for the determination of thallium in simple water samples. PdNO<sub>3</sub> is the preferred form of palladium, however if the sample contains high levels of chlorides, recoveries will be poor. If a reducing agent is added both PdNO<sub>3</sub> and PdCl<sub>2</sub> will result in more consistent recoveries. Any of a variety of reducing agents can be used, including a pre-mixed gas of 5% H<sub>2</sub> in 95% argon, hydroxylamine HCl, ascorbic acid, citric acid, et. al. Hydroxylamine HCl may give poor results if the sample contains very high levels of nitric acid. In this particular study, PdCl<sub>2</sub> plus 2% citric acid gave excellent recoveries for all the samples investigated. Citric acid can be added directly to the palladium solution. There was no problem using the more commonly available PdCl<sub>2</sub> solution.

## Results

For several of the elements, accuracy and long term stability of the furnace methodology were investigated by repeated analysis of check standards and real samples.

## Selenium

Accuracy and stability results for the selenium method are reported in Table 4. A blank, check standard, two digested soil samples (31247-32 and 31247-28) and one water sample (31247-32) were analyzed repeatedly (20 times). The results obtained in this study closely matched the expected or "reported" concentrations. The overall precision of repeated analyses is listed, as well as the average individual precisions of three replicate absorbance readings. All results were obtained versus one direct calibration. Standard Additions was not necessary for accurate results

Table 4. Selenium Results

Sample	No. times analyzed	$\bar{x} \pm \sigma$ µg/L	Average RSD%	Reported concentration µg/L	Average individual RSD% (3 replicates)
Blank	21	0.0 ± 0.3	—	0.0	—
Check std	20	24.3 ± 0.4	1.6%	25.0	1.1%
31247-17	20	6.0 ± 0.3	5.0%	5.6	7.2%
31247-28*	20	42.3 ± 1.1	2.6%	428.0	1.5%
31247-32	20	1.2 ± 0.3	25.0%	1.6	46.8%

\* Sample diluted 1:10

## Arsenic

A similar study was carried out using the arsenic methodology. The results are reported in Table 5. A blank, check standard, an EPA trace metal standard, three soil digest samples (31247-17, 31247-28, and 31247-46) and three water samples (31247-32, NSHL T-3, and NSHL T-4) were analyzed repeatedly. The concentration results obtained in this study closely matched the 'reported' concentrations. Standard Additional calibration was not necessary as direct calibration provided excellent results.

Table 5. Arsenic Results

Sample	No. times analyzed	$\bar{x} \pm \sigma$ µg/L	Average RSD%	Reported concentration µg/L	Average individual RSD% (3 replicates)
Blank	10	0.3 ± 0.5	—	0.0	—
Check std	11	19.5 ± 0.8	4.1%	20.0	1.4%
EPA TM1	10	27.4 ± 0.9	3.3%	26.7 ± 3.6	0.9%
31247-17	11	10.1 ± 0.5	5.0%	10.0	2.1%
31247-28	12	9.4 ± 0.6	6.4%	9.2	2.9%
31247-32	10	49.2 ± 1.3	2.6%	53.8	0.6%
31247-46	10	4 ± 0.5	6.8%	7.0	2.8%
NSHL T-3	8	104.0 ± 3.0	2.9%	105.0 ± 22.0	0.6%
NSHL T-4	8	32.6 ± 1.7	5.2	30.0 ± 5.0	1.6%

## Lead

The results obtained from a similar study of the lead methodology are reported in Table 6. A blank, check standard, an EPA trace metal standard and two water samples (NSHL T-3 and NSHL T-4) were analyzed repeatedly. Again, the concentration results from this study closely matched the Reported concentration values. The mean relative standard deviation of repeated analyses and the average individual relative standard deviation are also listed. These results were obtained with direct calibration. Standard Additions calibration was not necessary.

Table 6. Lead Results

Sample	No. times analyzed	$\times \pm \sigma$ $\mu\text{g/L}$	Average RSD%	Reported concentration $\mu\text{g/L}$	Average individual RSD% (3 replicates)
Blank	9	$1.0 \pm 0.3$	–	0.0	–
Check std	9	$19.5 \pm 0.8$	4.1%	20.0	1.4%
EPA TM1	7	$40.5 \pm 0.7$	1.7%	$42.7 \pm 15.0$	0.8%
NSHL T-3	7	$16.3 \pm 0.4$	2.5%	(14.0 – 20.0)	1.5%
NSHL T-4	4	$24.6 \pm 0.3$	1.2%	$26.7 \pm 8.0$	0.9%

## Cadmium

Accuracy and stability of results for the cadmium method are listed in Table 7. A blank, a check standard, an EPA trace metal standard, and two water samples (NSHL T-3 and NSHL T-4) were analyzed repeatedly. The concentrations of cadmium obtained in this study closely matched the “reported” concentration. The mean relative standard deviation of repeated analysis and the average individual relative standard deviation are listed. Accurate results were obtained without Standard Additions.

Table 7. Cadmium Results

Sample	No. times analyzed	$\times \pm \sigma$ $\mu\text{g/L}$	Average RSD%	Reported concentration $\mu\text{g/L}$	Average individual RSD% (3 replicates)
Blank	1	0.07	–	0.0	–
Check std	5	$4.99 \pm 0.09$	1.7%	5.00	0.5%
EPA TM1	13	$8.63 \pm 0.10$	1.2%	$9.10 \pm 1.0$	0.9%
NSHL T-3	13	$4.44 \pm 0.04$	0.9%	$4.98 \pm 0.8$	1.0%
NSHL T-4	13	$5.05 \pm 0.09$	1.8%	$5.20 \pm 1.1$	0.7%

## Antimony

A similar study was carried out using the antimony methodology. The results are reported in Table 8. A blank, two check standards, and two digested soil samples were analyzed

repeatedly. The antimony calibration was established with standard concentrations of 60–240  $\mu\text{g/L}$  Sb using the less sensitive 231.2 nm resonance line. Sensitivity was more than adequate to meet contract requirements. If necessary, precisions for samples of less than 10  $\mu\text{g/L}$  Sb could be improved by using the more sensitive primary resonance line (217.6nm). “Reported” concentration values were not available for the soil digest samples 31247–17 and 31247–28. Recovery studies were done on these samples. Recoveries were 101% and 99% respectively. This confirmed that there was no interference from the sample matrix.

Table 8. Antimony Results

Sample	No. times analyzed	$\times \pm \sigma$ $\mu\text{g/L}$	Average RSD%	Reported concentration $\mu\text{g/L}$	Average individual RSD% (3 replicates)
Blank	6	$0.0 \pm 0.5$	–	–	–
Check std 1	6	$49.4 \pm 1.7$	3.4%	50.0	1.2%
Check std 2	4	$124.0 \pm 4.0$	3.2%	125.0	0.8%
31247-17	5	$8.6 \pm 1.3$	15.1%	n/a	10.7%
31247-28	5	$10.0 \pm 1.2$	12.0%	n/a	5.1

## Beryllium

A similar study was carried out using the beryllium methodology and the results are listed in Table 9. A blank, check standard, an EPA trace metal standard and three digested soil samples (31247-17, 31246-28 and 31247-46) were analyzed repeatedly. Reported concentration values were not available for the digested soil and water samples. Standard Additions calibration was utilized to determine the accuracy of the direct method. The standard Additions results are reported in Table 9.

Table 9. Beryllium Results

Sample	No. times analyzed	$\times \pm \sigma$ $\mu\text{g/L}$	Average RSD%	Reported concentration $\mu\text{g/L}$	Average individual RSD% (3 replicates)
Blank	4	$0.15 \pm 0.06$	–	0.0	–
Check std	8	$9.9 \pm 0.4$	4.0%	10.0	2.8%
EPA TM1*	13	$30.5 \pm 0.9$	2.9%	29.0	2.4%
31247-17	3	$1.3 \pm 0.2$	15.4%	1.4**	11.2%
31247-28	3	$1.5 \pm 0.2$	8.3%	2.7**	5.7%
31247-46	3	$1.5 \pm 0.2$	13.3%	1.7**	6.8%

\* EPA TM1 was diluted 1:4 and all other samples were diluted 1:2 with the PSD-96 to fall within the Be calibration range.

\*\* By Standard Additions

## **Conclusion**

The graphite furnace methodology presented in this study was developed following EPA recommendations. Varian SpectrAA-300/400 Zeeman spectrometer systems were utilized. Nine important environmental elements were investigated (As, Se, Cd, Pb, Tl, Sb, Ag, Be, and Cr). Methods used to reduce interferences included matrix modifiers, pyrolytic graphite platforms, peak area absorbance measurements and Zeeman background correction. Difficult, real samples were analyzed repeatedly to demonstrate long term stability and accuracy. The Hot Inject capability reduced analysis time. A typical single analysis cycle was less than two minutes. Time consuming Standard Additions calibration was not necessary for the accurate determination of any of the elements in this study. Excellent results were obtained for all elements using the GFAAS methodology presented.

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OPERATOR Cindy Beach  
 DATE 2/10/88  
 BATCH ENSECO-Final Run  
 PROGRAM 11 Se Super Lamp

INSTRUMENT MODE ABSORBANCE  
 CALIBRATION MODE CONCENTRATION  
 MEASUREMENT MODE PEAK AREA  
 LAMP POSITION 4  
 LAMP CURRENT (mA) 15  
 SLIT WIDTH (nm) 1.0  
 SLIT HEIGHT NORMAL  
 WAVELENGTH (nm) 196.0  
 SAMPLE INTRODUCTION SAMPLER AUTOMIXING  
 TIME CONSTANT 0.05  
 MEASUREMENT TIME (sec) 1.0  
 REPLICATES 4  
 BACKGROUND CORRECTION DN  
 MAXIMUM ABSORBANCE 1.20

FURNACE PARAMETERS					
STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	220	15.0	3.0	NORMAL	NO
2	220	5.0	3.0	NORMAL	NO
3	500	10.0	3.0	NORMAL	NO
4	900	15.0	3.0	NORMAL	NO
5	900	10.0	3.0	NORMAL	NO
6	2200	0.7	0.0	NORMAL	YES
7	2200	2.7	0.0	NORMAL	YES
8	2400	2.0	3.0	NORMAL	NO
9	40	12.8	3.0	NORMAL	NO

SAMPLER PARAMETERS			
VOLUMES (μL)			
	SOLUTION	BLANK	MODIFIER
BLANK	--	20	0
STANDARD 1	2	18	0
STANDARD 2	4	16	0
STANDARD 3	10	10	0
STANDARD 4	20	0	0
SAMPLE	20	0	0

RECALIBRATION RATE 0  
 RESLOPE RATE 0

MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO  
 TEMPERATURE 135  
 INJECT RATE 10

SAMPLE	CONC ug/L	%RSD	MEAN ABS	READINGS			
BLANK	0.0		0.005	0.006	0.005	0.005	0.004
STANDARD 1	5.0	5.0	0.016	0.017	0.016	0.015	0.017
STANDARD 2	10.0	7.3	0.033	0.031	0.035	0.031	0.035
STANDARD 3	25.0	2.6	0.095	0.093	0.094	0.098	0.096
STANDARD 4	50.0	1.2	0.200	0.200	0.196	0.201	0.202

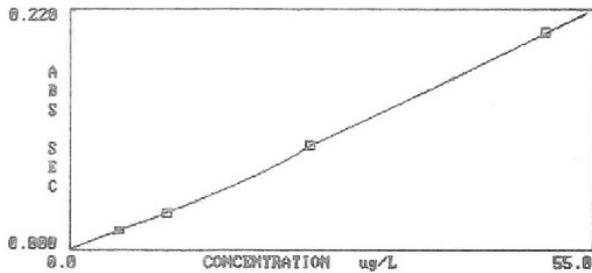


Figure 1. The graphite furnace method, calibration results and calibration graph for selenium.

OPERATOR Cindy Beach  
 DATE 3/14/88  
 BATCH As final run  
 PROGRAM 9 As Digested Samples

INSTRUMENT MODE ABSORBANCE  
 CALIBRATION MODE CONCENTRATION  
 MEASUREMENT MODE PEAK AREA  
 LAMP POSITION 4  
 LAMP CURRENT (mA) 8  
 SLIT WIDTH (nm) 0.5  
 SLIT HEIGHT NORMAL  
 WAVELENGTH (nm) 193.7  
 SAMPLE INTRODUCTION SAMPLER PREMIXED  
 TIME CONSTANT 0.05  
 MEASUREMENT TIME (sec) 2.0  
 REPLICATES 3  
 BACKGROUND CORRECTION ON  
 MAXIMUM ABSORBANCE 0.95

FURNACE PARAMETERS					
STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	350	20.0	3.0	NORMAL	NO
2	600	15.0	3.0	NORMAL	NO
3	1100	10.0	3.0	NORMAL	NO
4	1100	10.0	3.0	NORMAL	NO
5	1100	1.0	0.0	NORMAL	NO
6	2400	0.7	0.0	NORMAL	YES
7	2400	2.7	0.0	NORMAL	YES
8	2400	2.0	3.0	NORMAL	NO

SAMPLER PARAMETERS			
	VOLUMES (μL)		MODIFIER
	SOLUTION	BLANK	
BLANK	--	20	8
STANDARD 1	20	0	8
STANDARD 2	20	0	8
STANDARD 3	20	0	8
STANDARD 4	20	0	8
SAMPLE	20	0	8

RECALIBRATION RATE 0  
 RESLOPE RATE 0  
 MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO  
 TEMPERATURE 150  
 INJECT RATE 7

SAMPLE	CONC ug/L	%RSD	MEAN ABS	READINGS		
BLANK	0.0		-0.001	-0.001	-0.002	-0.000
STANDARD 1	10.0	1.0	0.050	0.049	0.050	0.051
STANDARD 2	20.0	0.9	0.107	0.106	0.107	0.107
STANDARD 3	50.0	1.2	0.262	0.259	0.265	0.260
STANDARD 4	100.0	0.3	0.499	0.501	0.498	0.499

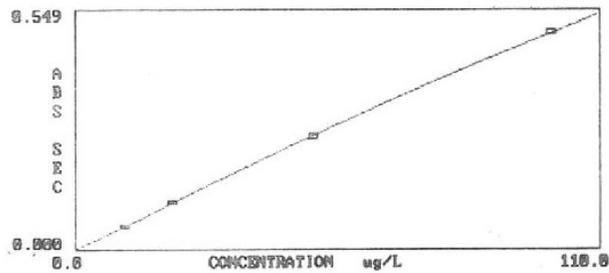


Figure 2. The graphite furnace method, calibration results and calibration graph for arsenic.

OPERATOR Cindy Beach  
 DATE 4/18/88  
 BATCH Final Pb run (5-50 ppb)  
 PROGRAM 60 Pb EPA Methods

INSTRUMENT MODE ABSORBANCE  
 CALIBRATION MODE CONCENTRATION  
 MEASUREMENT MODE PEAK AREA  
 LAMP POSITION 3  
 LAMP CURRENT (mA) 5  
 SLIT WIDTH (nm) 0.5  
 SLIT HEIGHT NORMAL  
 WAVELENGTH (nm) 283.3  
 SAMPLE INTRODUCTION SAMPLER AUTOMIXING  
 TIME CONSTANT 0.05  
 MEASUREMENT TIME (sec) 1.0  
 REPLICATES 2  
 BACKGROUND CORRECTION ON  
 MAXIMUM ABSORBANCE 1.40

FURNACE PARAMETERS					
STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	450	10.0	2.0	NORMAL	NO
2	600	15.0	2.0	NORMAL	NO
3	600	20.0	2.0	NORMAL	NO
4	600	1.0	0.0	NORMAL	NO
5	2200	0.8	0.0	NORMAL	YES
6	2200	2.7	0.0	NORMAL	YES
7	2200	2.0	2.0	NORMAL	NO

SAMPLER PARAMETERS			
	VOLUMES (μL)		
	SOLUTION	BLANK	MODIFIER
BLANK	--	20	3
STANDARD 1	2	18	3
STANDARD 2	5	15	3
STANDARD 3	10	10	3
STANDARD 4	20	0	3
SAMPLE	20	0	3

RECALIBRATION RATE 0  
 RESLOPE RATE 0  
 MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO  
 TEMPERATURE 150  
 INJECT RATE 5

SAMPLE	CONC ppb	%RSD	MEAN ABS	READINGS	
BLANK	0.0		-0.001	-0.002	-0.001
STANDARD 1	5.0	15.6	0.024	0.026	0.021
STANDARD 2	12.5	2.0	0.066	0.067	0.065
STANDARD 3	25.0	0.9	0.132	0.131	0.133
STANDARD 4	50.0	0.5	0.251	0.250	0.251

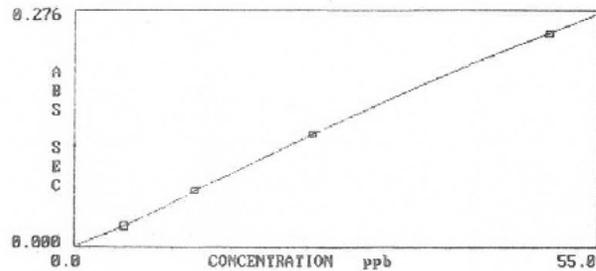


Figure 3. The graphite furnace method, calibration results and calibration graph for lead.

OPERATOR Cindy Beach  
 DATE 3/22/88  
 BATCH Cd EPA Method  
 PROGRAM 3 Cd EPA Method

INSTRUMENT MODE ABSORBANCE  
 CALIBRATION MODE CONCENTRATION  
 MEASUREMENT MODE PEAK AREA  
 LAMP POSITION 1  
 LAMP CURRENT (mA) 4  
 SLIT WIDTH (nm) 0.5  
 SLIT HEIGHT NORMAL  
 WAVELENGTH (nm) 228.8  
 SAMPLE INTRODUCTION SAMPLER AUTOMIXING  
 TIME CONSTANT 0.05  
 MEASUREMENT TIME (sec) 1.0  
 REPLICATES 2  
 BACKGROUND CORRECTION ON  
 MAXIMUM ABSORBANCE 0.70

STEP NO.	TEMPERATURE (C)	FURNACE PARAMETERS		GAS TYPE	READ COMMAND
		TIME (sec)	GAS FLOW (L/min)		
1	350	20.0	3.0	NORMAL	NO
2	500	15.0	3.0	NORMAL	NO
3	500	10.0	3.0	NORMAL	NO
4	500	1.0	0.0	NORMAL	NO
5	2000	0.8	0.0	NORMAL	YES
6	2000	2.0	0.0	NORMAL	YES
7	2200	2.0	3.0	NORMAL	NO

	SAMPLER PARAMETERS		MODIFIER
	SOLUTION VOLUMES (rL)	BLANK	
BLANK	--	20	5
STANDARD 1	2	18	5
STANDARD 2	5	15	5
STANDARD 3	10	10	5
STANDARD 4	20	0	5
SAMPLE	10	10	5

RECALIBRATION RATE 0  
 RESLOPE RATE 0  
 MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO  
 TEMPERATURE 150  
 INJECT RATE 7

VOLUME CORRECTION APPLIED

SAMPLE	CDNC ug/L	%RSD	MEAN ABS	READINGS	
BLANK	0.00		0.009	0.008	0.010
STANDARD 1	0.50	12.6	0.045	0.048	0.041
STANDARD 2	1.25	2.1	0.121	0.119	0.123
STANDARD 3	2.50	1.0	0.245	0.247	0.243
STANDARD 4	5.00	2.0	0.437*	0.431*	0.443*

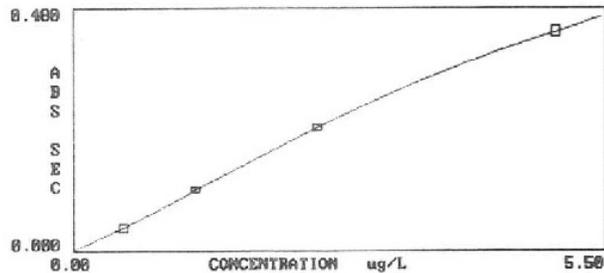


Figure 4. The graphite furnace method, calibration results and calibration graph for cadium.

OPERATOR Cindy Beach  
 DATE 4/28/88  
 BATCH Antimony  
 PROGRAM 46 Sb EPA project-2nd

INSTRUMENT MODE ABSORBANCE  
 CALIBRATION MODE CONCENTRATION  
 MEASUREMENT MODE PEAK AREA  
 LAMP POSITION 2  
 LAMP CURRENT (mA) 10  
 SLIT WIDTH (nm) 0.5  
 SLIT HEIGHT NORMAL  
 WAVELENGTH (nm) 231.2  
 SAMPLE INTRODUCTION SAMPLER AUTOMIXING  
 TIME CONSTANT 0.10  
 MEASUREMENT TIME (sec) 1.0  
 REPLICATES 3  
 BACKGROUND CORRECTION DN  
 MAXIMUM ABSORBANCE 1.40

STEP NO.	FURNACE PARAMETERS				GAS TYPE	READ COMMAND
	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)			
1	200	25.0	3.0		NORMAL	NO
2	350	20.0	3.0		NORMAL	NO
3	900	15.0	3.0		NORMAL	NO
4	900	10.0	3.0		NORMAL	NO
5	900	1.0	0.0		NORMAL	NO
6	2100	0.8	0.0		NORMAL	YES
7	2100	2.0	0.0		NORMAL	YES
8	2400	2.0	3.0		NORMAL	NO
9	40	12.3	3.0		NORMAL	NO

	SAMPLER PARAMETERS VOLUMES (μL)		
	SOLUTION	BLANK	MODIFIER
BLANK	--	20	8
STANDARD 1	5	15	8
STANDARD 2	10	10	8
STANDARD 3	15	5	8
STANDARD 4	20	0	8
SAMPLE	20		8

RECALIBRATION RATE 0  
 RESLOPE RATE 0  
 MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO  
 TEMPERATURE 145  
 INJECT RATE 7

SAMPLE	CONC	ZRSD	MEAN ABS	READINGS		
BLANK	0.0		-0.001	0.002	-0.003	-0.003
STANDARD 1	60.0	1.9	0.275	0.270	0.276	0.280
STANDARD 2	120.0	1.4	0.551	0.549	0.560	0.545
STANDARD 3	180.0	0.4	0.805	0.807	0.802	0.807
STANDARD 4	240.0	1.2	1.014	1.003	1.028	1.013

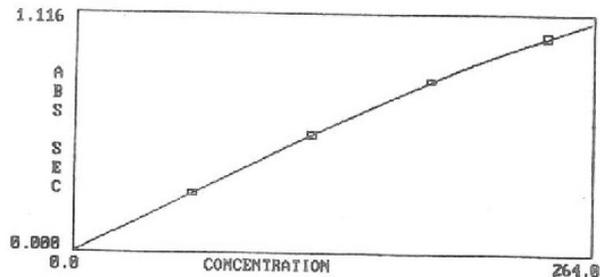


Figure 5. The graphite furnace method, calibration results and calibration graph for antimony.

OPERATOR Cindy Beech  
 DATE 5/17/88  
 BATCH Be  
 PROGRAM B3 Be EPA work

INSTRUMENT MODE ABSORBANCE  
 CALIBRATION MODE CONCENTRATION  
 MEASUREMENT MODE PEAK AREA  
 LAMP POSITION 1  
 LAMP CURRENT (mA) 5  
 SLIT WIDTH (nm) 1.0  
 SLIT HEIGHT NORMAL  
 WAVELENGTH (nm) 234.9  
 SAMPLE INTRODUCTION SAMPLER AUTOMIXING  
 TIME CONSTANT 0.05  
 MEASUREMENT TIME (sec) 1.0  
 REPLICATES 2  
 BACKGROUND CORRECTION ON  
 MAXIMUM ABSORBANCE 0.70

FURNACE PARAMETERS					
STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	240	30.0	3.0	NORMAL	NO
2	1200	15.0	3.0	NORMAL	NO
3	1200	10.0	3.0	NORMAL	NO
4	1200	1.0	0.0	NORMAL	NO
5	2400	0.6	0.0	NORMAL	YES
6	2400	4.0	0.0	NORMAL	YES
7	2600	2.0	3.0	NORMAL	NO

SAMPLER PARAMETERS		
VOLUMES (μL)		
	SOLUTION	BLANK
BLANK	--	20
STANDARD 1	2	18
STANDARD 2	4	16
STANDARD 3	10	10
STANDARD 4	20	0
SAMPLE	10	10

RECALIBRATION RATE 0  
 RESLOPE RATE 0  
 MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO  
 TEMPERATURE 135  
 INJECT RATE 7

SAMPLE	CONC (ug/L)	WFO	MEAN ABS	STDEV	REPLIKES
BLANK	0.0		0.007	0.008	0.006
STANDARD 1	1.0	4.3	0.069	0.067	0.071
STANDARD 2	2.0	1.1	0.140	0.139	0.141
STANDARD 3	5.0	1.6	0.346	0.350	0.342
STANDARD 4	10.0	0.9	0.664	0.660	0.668

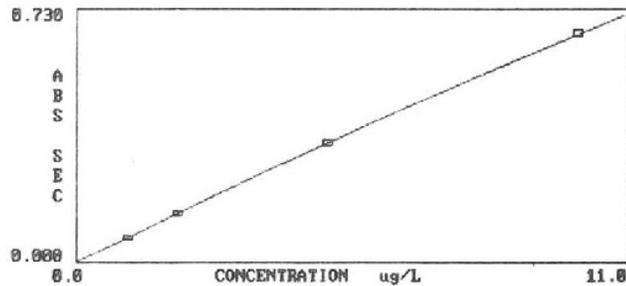


Figure 6. The graphite furnace method, calibration results and calibration graph for beryllium.

OPERATOR Cindy Beach  
 DATE 12/21/87  
 BATCH CHROMIUM

PROGRAM 26 Cr EPA Project

INSTRUMENT MODE ABSORBANCE  
 CALIBRATION MODE CONCENTRATION  
 MEASUREMENT MODE PEAK AREA  
 LAMP POSITION 6  
 LAMP CURRENT (mA) 7  
 SLIT WIDTH (nm) 0.2  
 SLIT HEIGHT REDUCED  
 WAVELENGTH (nm) 357.9  
 SAMPLE INTRODUCTION SAMPLER AUTOMIXING  
 TIME CONSTANT 0.05  
 MEASUREMENT TIME (sec) 1.0  
 REPLICATES 2  
 BACKGROUND CORRECTION DN  
 MAXIMUM ABSORBANCE 2.00

STEP NO.	FURNACE PARAMETERS			GAS TYPE	READ COMMAND
	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)		
1	85	5.0	3.0	NORMAL	NO
2	95	60.0	3.0	NORMAL	NO
3	120	10.0	3.0	NORMAL	NO
4	1000	10.0	3.0	NORMAL	NO
5	1000	10.0	3.0	NORMAL	NO
6	1000	1.0	0.0	NORMAL	NO
7	2600	0.8	0.0	NORMAL	YES
8	2600	2.0	0.0	NORMAL	YES
9	2600	2.0	3.0	NORMAL	NO

	SAMPLER PARAMETERS		MODIFIER
	SOLUTION VOLUMES (uL)	BLANK	
BLANK	--	20	
STANDARD 1	2	18	
STANDARD 2	4	16	
STANDARD 3	10	10	
STANDARD 4	20	0	
SAMPLE	20		

RECALIBRATION RATE 0  
 RESLOPE RATE 0

MULTIPLE INJECT NO HOT INJECT NO PRE INJECT NO

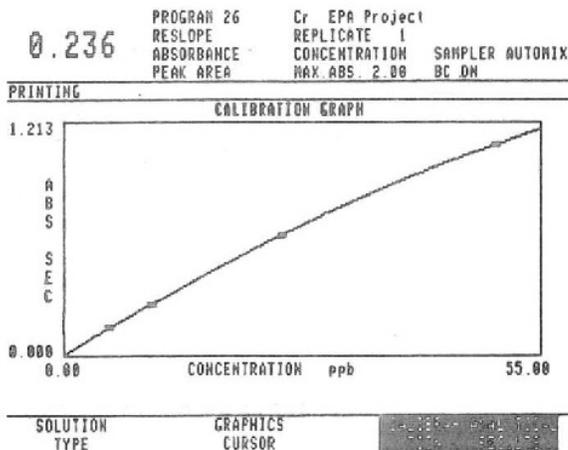


Figure 7. The graphite furnace method, calibration results and calibration graph for chromium.

OPERATOR Cindy Beach  
 DATE 12/30/87  
 BATCH SILVER  
 PROGRAM 20 Ag EPA PROJECT

INSTRUMENT MODE ABSORBANCE  
 CALIBRATION MODE CONCENTRATION  
 MEASUREMENT MODE PEAK AREA  
 LAMP POSITION 8  
 LAMP CURRENT (mA) 4  
 SLIT WIDTH (nm) 0.5  
 SLIT HEIGHT NORMAL  
 WAVELENGTH (nm) 328.1  
 SAMPLE INTRODUCTION SAMPLER AUTOMIXING  
 TIME CONSTANT 0.05  
 MEASUREMENT TIME (sec) 1.0  
 REPLICATES 2  
 BACKGROUND CORRECTION ON  
 MAXIMUM ABSORBANCE 1.30

FURNACE PARAMETERS					
STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	140	5.0	3.0	NORMAL	NO
2	220	50.0	3.0	NORMAL	NO
3	600	10.0	3.0	NORMAL	NO
4	600	20.0	3.0	NORMAL	NO
5	600	1.0	0.3	NORMAL	NO
6	2300	0.9	0.3	NORMAL	YES
7	2300	2.0	0.3	NORMAL	YES
8	2300	2.0	3.0	NORMAL	NO
9	40	12.0	3.0	NORMAL	NO

SAMPLER PARAMETERS			
VOLUMES (uL)			
	SOLUTION	BLANK	MODIFIER
BLANK	---	20	
STANDARD 1	2	18	
STANDARD 2	4	16	
STANDARD 3	10	10	
STANDARD 4	20	0	
SAMPLE	20	0	

RECALIBRATION RATE 10  
 RESLOPE RATE 0

MULTIPLE INJECT NO HOT INJECT NO PRE INJECT NO

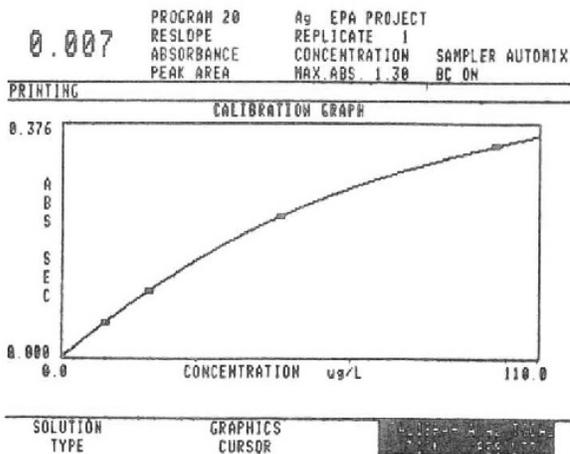


Figure 8. The graphite furnace method, calibration results and calibration graph for silver.

OPERATOR Cindy Beach  
 DATE 5/9/88  
 BATCH Final thallium run  
 PROGRAM 62 T1 EPA methods - Pd

INSTRUMENT MODE ABSORBANCE  
 CALIBRATION MODE CONCENTRATION  
 MEASUREMENT MODE PEAK AREA  
 LAMP POSITION 2  
 LAMP CURRENT (mA) 10  
 SLIT WIDTH (nm) 0.5  
 SLIT HEIGHT NORMAL  
 WAVELENGTH (nm) 276.8  
 SAMPLE INTRODUCTION SAMPLER AUTOMIXING  
 TIME CONSTANT 0.05  
 MEASUREMENT TIME (sec) 1.0  
 REPLICATES 2  
 BACKGROUND CORRECTION ON  
 MAXIMUM ABSORBANCE 0.55

FURNACE PARAMETERS					
STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	250	20.0	3.0	NORMAL	NO
2	1000	20.0	3.0	NORMAL	NO
3	1000	10.0	3.0	NORMAL	NO
4	1000	1.0	0.0	NORMAL	NO
5	2400	0.7	0.0	NORMAL	YES
6	2400	2.0	0.0	NORMAL	YES
7	2400	2.0	3.0	NORMAL	NO
8	40	11.8	3.0	NORMAL	NO

SAMPLER PARAMETERS			
VOLUMES (fL)			
	SOLUTION	BLANK	MODIFIER
BLANK	--	20	8
STANDARD 1	2	18	8
STANDARD 2	4	16	8
STANDARD 3	10	10	8
STANDARD 4	20	0	8
SAMPLE	10	10	8

RECALIBRATION RATE 0  
 RESLOPE RATE 0  
 MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO  
 TEMPERATURE 145  
 INJECT RATE 7

SAMPLE	CONC	%RSD	MEAN ABS	READINGS	
BLANK	0.0		0.006	0.006	0.005
STANDARD 1	10.0	6.1	0.032	0.033	0.030
STANDARD 2	20.0	0.5	0.060	0.060	0.059
STANDARD 3	50.0	0.6	0.137	0.136	0.138
STANDARD 4	100.0	0.4	0.240	0.239	0.241

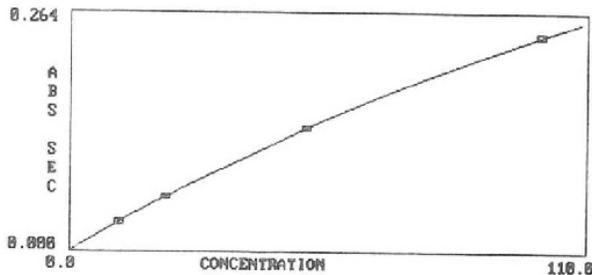


Figure 9. The graphite furnace method, calibration results and calibration graph for thallium.

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