The Reduction of Matrix Interferences Utilizing the Platform in Graphite Furnace AAS

Application Note

Atomic Absorption

Author

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Introduction

Graphite furnace techniques are characterized by excellent analytical sensitivity and are the methods of choice for the determination of trace elements in various environmental, biological, and clinical samples. However, they can be plagued by matrix interferences which complicate methods development and sample analysis. This is particularly true for the determination of volatile elements in complex matrices.

Graphite furnace interferences can be conveniently classified as chemical interferences, those that affect the production of analyte atoms, and spectral interferences arising from the temporal overlay of the signals from non-specific absorption and the analyte peak. Chemical interferences encountered in the graphite furnace include vapor phase and condensed phase interferences. With the application of the graphite platform technique proposed by L'vov [1], chemical interferences and spectral interferences can be reduced, particularly in the determination of volatile elements in difficult matrices.

The graphite platform is placed in the graphite tube and sample atomization takes place from the platform rather than the tube wall. The temperature of the platform lags behind the temperature of the tube wall and gaseous environment. This temperature lag causes delayed sample vaporization and analyte atomization which can reduce chemical and background interferences. Delayed sample vaporization will often reduce vapor phase interferences since the higher gas phase temperature experienced discourages formation of volatile compounds. The use of the platform can also help to reduce background absorption through increased dissociation of molecular species at the higher gas phase temperature achieved in the furnace prior to sample vaporization.

In this study, several samples with difficult matrices were analyzed. These included a refractory solid (MgO), high purity copper, and a biological fluid (whole blood). The elements determined, including As, Pb, and Sn, were relatively volatile. Comparisons were made between wall atomization and platform atomization using HP-86 computer graphics displays of atomic as well as background absorbance peaks. The potential benefits of platform atomization were investigated. It was hoped that with platform atomization, chemical interferences would be sufficiently reduced to eliminate time-consuming standard additions typically required for accurate analysis of difficult matrices by wall atomization. This study was carried out using an Agilent GTA-95 graphite furnace with programmable sample dispenser and Agilent AA-975 and AA-875 spectrometers.

Determination of As and Pb in MgO

The first sample studied was a refractory material, MgO. The fine white powder was dissolved in nitric acid and diluted to a final concentration of 1 gram/100 mL (1% MgO) in 4% $HN0_3$. The difficulties with this sample were due to its refractory nature. With a boiling point of 3600 °C, it is never totally removed from the graphite furnace. Arsenic was to be determined at the $\leq$ 3.0 µg/g level in the original sample. Using wall atomization, the background level was relatively low with the 1300 °C ash that could be used with nickel nitrate matrix modifier. This sample matrix produced problems after a number of injections. White flakes of MgO tended to build up at the ends of the graphite tube. This caused higher levels of background as well as baseline shifts which prevented accurate analysis. Shown in Figure 1 is a comparison between the atomic and background peaks for the first injection and the 20th injection using wall atomization. (Background absorbance is indicated by the thinner line.) The build-up problem became so acute soon after the 20th injection that the furnace had to be opened and cleaned.

One of the first things which is apparent when using platform atomization is the temporal shift as shown in Figure 2. The atomization peak appearance time was delayed until after 1 second. In Figure 1 (wall atomization), the peak appearance time was approximately 0.5 seconds. The background absorbance was reduced and a sharper atomization 2.9 µg/g As and 0.8 µg/g Pb. Standard addition peak produced a larger absorbance value in both peak determinations were unnecessary for accurate results, height and area. However, the real advantage of the and for this type of sample, minimizing the number of graphite platform was long term stability. The problems caused by the low volatility of MgO were minimized. Through the twentieth injection there was no significant increase in background and no visible build-up of MgO flakes which had caused baseline problems using wall atomization. The GTA-95 furnace parameters used for platform atomization are listed in Table 1. The first four steps constitute the dry stage and were carefully optimized for best precision. An ash temperature of 1300 °C was used along with an atomization temperature of 2800 °C. The atomization ramp rate was 1250 °C/second. The sample volume and matrix modifier volume are also listed in Table 1.

Pb was also determined in the MgO samples. The levels of Pb were quite low. Therefore, the most sensitive 217.0 nm resonance line was used. As indicated in Figure 3, the atomization peak appeared between two background peaks when wail atomization was used. The same build-up and background problems previously encountered for As occurred, so no long term study was done with wall atomization.

Using platform atomization, the Pb peak was delayed as shown in Figure 4. The first background peak seen with wall atomization was not present and the second background peak was reduced. There was also an increase in the peak height measurement. But again, as with the As determination, the real advantage was long term stability. The absorbance measurements of the fiftieth injection closely matched those of the first injection. Further study indicated that soon after the sixtieth injection, it was necessary to clean the MgO from the ends of the graphite furnace. As previously shown, however, baseline shifts and MgO build-up problems were encountered after only 20 injections with wall atomization. Table 2 lists the GTA-95 parameters for the Pb determinations in MgO using the graphite platform. An ash temperature of 900 °C was used. The maximum ramp rate of 2000 °C/second was used to the atomization temperature of 2800 °C. Platform atomization of the MgO samples offered definite advantages over wall atomization. The higher gas phase temperature produced more efficient removal of the refractory MgO from the furnace, therefore reducing the build-up of MgO flakes.

Table 3 lists the results of As and Pb determinations for three MgO samples. The results are reported in µg/g in the original MgO material. The two numbers listed for each of the three samples are two independent sample preparations. (All were dissolved in HNO_3 and diluted to 1 gram/100 mL.) The best precisions were obtained in peak height. The average precisions (RSD) listed are based on two injections of each sample. Peak area was not used for the lead due to quite low absorbance values which did not exhibit the excellent precision of the peak height measurements. The values obtained for sample number 3 correlated well with the expected values of 2.9 µg/g As and 0.8 µg/g Pb. Standard addition determinations were unnecessary for accurate results, and for this type of sample, minimizing the number of injections reduces the build-up of MgO flakes.

Determination of Sn in High Purity Copper

A second type of analysis investigated was the determination of low levels of tin in high purity copper. The calibration curves shown in Figure 5 were derived from Sn standards in 1000 µg/g Cu in 2% HNO_3. There was a marked improvement in sensitivity when the graphite platform was used, apparent with peak area as well as peak height absorbance measurements (triangles indicate peak area and circles indicate peak height. The thick lines are calibrations by platform atomization and the thin lines are calibrations by wall atomization).

In this study three NBS Cu samples were analyzed. The copper was dissolved in concentrated HNO_3 and diluted to a final concentration of 1% copper in 4% HNO_3. One of the NBS samples contained a relatively high concentration of Sn (65 µg/g). After sample preparation, the sample presented to the furnace contained 650 µg/L Sn. An additional 5X dilution was made and the Sn concentration was determined by direct calibration with standards containing an equal amount of copper. Wall atomization calibrations by both peak height and peak area gave excellent results without standard additions.

However, the other NBS standards contained very low levels of tin. One contained 1.5 µg/g Sn and the other 0.8 µg/g Sn. After sample preparation, the solution presented to the furnace contained 15 and 8 µg/L Sn respectively in 1% copper solution. Dilution was not feasible and the 1% copper matrix did appear to cause problems. Figure 6 illustrates wall atomization of a 25 µL volume of the NBS Cu sample containing 1.5 µg/g Sn (at the 235.5 nm resonance line). No reasonable analyte absorbance peak was obtained and the background peak shown in Figure 6 was greater than 1.0 absorbance. Interestingly, no atomization peak was obtained from the platform at this resonance line either. However, the background peak was lowered to approximately 0.6 absorbance and was shifted later in time.

The 235.5 nm resonance line is the most sensitive Sn line for flame atomization. The 286.3 nm line is about 60% more intense although approximately a third less sensitive (from Hollow Cathode Lamp Data, Varian Techtron). An investigation using this line for the Sn calibration standards (in the same copper matrix as shown previously in Figure 5), indicated that for graphite furnace determinations, the 286.3 nm line might be preferable. As shown in Figure 7 there was no significant sensitivity difference by either peak height or peak area measurements between the two wavelengths. The higher intensity of the 286.3 line resulted in less baseline noise. Also, it was expected that analysis of the copper at 286.3 would show less background absorbance. As illustrated in Figure 8, this was found to be true. The background peak was reduced from over 1.0 absorbance to 0.6 absorbance. With wall atomization, where no atomization peak was obtained at the 235.5 nm line, a measurable peak was obtained at the 286.3 nm line for the NBS Cu sample containing 1.5 µg/g Sn (15 µg/L Sn in the 1% solution). From this point on the 286.3 nm line was used.

When platform atomization is used, the background is further reduced to less than 0.3 absorbance for 25 µL of the 1% solution (Figure 9). There is also enhancement in both peak area and peak height absorbance. As expected, there was a shift in the atomization peak appearance time.

The platform furnace temperature parameters are listed in Table 4. An ash temperature of 1100 °C was used with maximum ramp rate to the atomization temperature of 2800 °C. With the optimization platform temperature program at the 286.3 nm line, the third NBS standard containing 0.8 µg/g Sn (8 µg/L Sn in the 1% Cu solution) produced reasonable absorbance peaks even for this very low level. This is illustrated in Figure 10. The detection limit in this difficult matrix was estimated at 1.0 µg/L Sn or 0.1 °g/g Sn in the original copper sample.

For the determination of the low level Sn concentration in the NBS Cu II and III samples, standards were prepared in a 1% solution of the NBS "O" sample. Direct calibration in both peak height and peak area produced excellent results as shown in Figure 11.

From this study, some comments on matrix modifiers for tin can be made. Various matrix modifiers have been reported in the literature including diammonium hydrogen citrate, trisodium citrate and EDTA [2]. Tin in most matrices will require some sort of matrix modification for stabilization and atomization as a single analyte peak. Although a thorough study of matrix modifiers was not undertaken, it was determined that copper itself is a good matrix modifer for tin. The addition of diammonium hydrogen citrate was determined to be unnecessary with the high levels of copper present and was found to be detrimental over long periods of time. The organics tended to cause build-up of carbonaceous material on the platform. An investigation into the potential of copper as a matrix modifier indicated that copper needs to be present at a minimum of 200 mg/L to be effective. Nickel has been reported in the literature as another modifier for tin [3]. It appears to be somewhat more effective than copper and a lower concentration can be used. But in this case, when a bulk matrix component acts as a matrix modifier, the most appropriate analytical method is to add that compound or element to the standards as was done for these determinations.

Figure 12 shows the effect of increasing the levels of copper on the platform atomization of 44 µg/L Sn. Two other concentrations were used, 1000 and 2000 mg/L Cu, but the change in peak appearance time and peak shape did not become obvious until higher levels of copper were used. A temporal shift of the Sn atomization peak is apparent with increasing levels of copper. Also the peak shapes are different from that normally encountered in graphite furnace analysis. The front of the peaks rise considerably slower with higher concentrations of copper, giving them a "reversed" appearance (i.e. a more gradual slope on the front rather than the back). It is assumed this is due to a physical interference or occlusion of the analyte Sn in the Cu matrix, particularly when the Cu matrix approaches the 1% level. It could be expected that this type of physical interference would be present with both wall atomization and platform atomization. Peak height absorbances decreased with increasing concentrations of copper, however the differences in peak area were not significant. The best technique would be to match the standard and sample with respect to copper concentration or to use peak area measurement.

Determination of Pb in Blood

The final analysis evaluated was the determination of Pb in whole blood. This analysis has been done routinely by graphite furnace. With a 1:1 dilution of the whole blood with 2% Triton X-100, standard additions calibration has been necessary to obtain accurate results when wall atomization is used [4].The analyte absorbance and background absorbance profiles using wall atomization of 10 µL volume of blood diluted 1:1 with 2% Triton X-100 are shown in Figure 13. The analyte peak appeared between two background peaks.

When the same sample was atomized from the platform, the first background peak disappeared and the second was reduced from approximately 1.2 absorbance to 0.9 absorbance as illustrated in Figure 14. The peak maximum occurred when the background was relatively low. The most sensitive resonance line for Pb (217.0 nm) was used. For normal levels of Pb in blood, the 283.3 secondary line would provide adequate sensitivity and the background would be further reduced. Depending on the Pb level to be determined, one could also further dilute the samples which would minimize potential dispensing difficulties.

The final parameters chosen for this study included the more sensitive 217.0nm Pb line because two of the samples analyzed contained quite low levels of Pb. The blood samples had been previously treated with sodium heparin. They were diluted 1:4 with 2% Triton X-100. The addition of 0.5% Triton X-100 to aqueous standards and blank improved dispensing characteristics. A volume of 15 µL was used. The platform furnace parameters are shown in Table 5. The first three steps constitute the dry stage and were carefully optimized for good reproducibility. An ash temperature of 650 °C was used with an atomization temperature of 2700 °C. The atomization ramp rate was reduced from the maximum (2000 °C/second) to 1580 °C/ second. This provided better separation between the analyte peak and background peak, and also improved precision.

A 4X dilution of blood analyzed by direct calibration against aqueous standards using the platform gave results that correlated well with results from an alternative method (solvent extraction, flame analysis). Results are listed in Table 6. Standard addition References calibrations were performed on the lower concentration samples as additional verification. Peak height absorbance measurements were used for all the furnace determinations.

Conclusion

Graphite platform atomization does offer distinct advantages over wall atomization in many instances. Used with effective temperature programs and other techniques such as matrix modification, platforms may allow the analyst to obtain excellent results in difficult analytical situations which present problems when wall atomization is used. In the work presented here, three sample matrices were studied. The benefits of graphite platform atomization included decreased background, improved long term stability, and minimized chemical interferences as indicated by the ability to accurately analyze these difficult samples using direct calibration rather than standard additions.

References

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3. W. Slavin, G. Carnrick, D. Manning, W. Pruszkowska, "Recent Experiences with the Stabilized Temperature Platform Furnace and Zeeman Background Correction", Atomic Spectrosc., 4 69(1983).
4. K. Brodie, M. Routh, "Trace Analysis of Lead in Blood, Aluminium and Manganese in Serum and Chromium in Urine by Graphite Furnace Atomic Absorption Spectrometry", Clinical Biochemistry, 17 19 (1984).

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Table 1. As in MgO Platform Atomization Furnace Operating Parameters

Step No.	Temperature °C.	Time Sec.	Gas Flow	Gas Type	Read Command
1	110	10	3.0	Normal	
2	250	70	3.0	Normal	
3	350	30	3.0	Normal	
4	600	10	3.0	Normal	
5	1300	5.0	3.0	Normal	
6	1300	10	3.0	Normal	
7	1300	1.0	.0	Normal	
8	2800	1.2	0	Normal	•
9	2800	2.0	.0	Normal	•
10	2800	2.0	3.0	Normal	

Sample Volume 20 µL 1% Solution Matrix Modifier 8 µL 500 mg/L Ni

Table 2. Pb in MgO Platform Atomization Furnace Operating Parameters

Step No.	Temperature °C.	Time Sec.	Gas Flow	Gas Type	Read Command
1	110	10	3.0	Normal	
2	250	70	3.0	Normal	
3	350	30	3.0	Normal	
4	600	20	3.0	Normal	
5	900	5.0	3.0	Normal	
6	900	10	3.0	Normal	
7	900	1.0	.0	Normal	
8	2800	1.0	0	Normal	•
9	2800	2.0	.0	Normal	•
10	2800	2.0	3.0	Normal	

Table 3 As and Pb in MgO Platform Result

As 20,40,60 µg/L		
	Height	Area
#1	1.5µg/g	1.6
	1.4	1.6
#2	2.4	2.3
	2.1	1.8
#3	3.0	2.8
(2.9µg/g)	2.9	2.8
$\bar{X}$ RSD	3.3%	5.1%

Pb 4,8,16 µg/L	
	Height
#1	1.2 µg/g
	1.2
#2	0.7
	0.7
#3	0.7
(0.8µg/g)	0.7
$\bar{X}$ RSD	2.0%

Table 4. Tin in NBS Copper Platform Furnace Opperating Parameters

Step No.	Temperature °C.	Time Sec.	Gas Flow	Gas Type	Read Command
1	90	10	3.0	Normal	
2	200	60	3.0	Normal	
3	320	40	3.0	Normal	
4	1100	5.0	3.0	Normal	
5	1100	10	3.0	Normal	
6	2800	.9	.0	Normal	•
7	2800	2.3	.0	Normal	•
8	2800	2.0	3.0	Normal	
9	50	13	3.0	Normal	
10					

Table 5. Pb in Blood Platform Atomization Furnace Operating Parameters

Step No.	Temperature °C.	Time Sec.	Gas Flow	Gas Type	Read Command
1	80	20	3.0	Normal	
2	250	60	3.0	Normal	
3	350	35	3.0	Normal	
4	650	15	3.0	Normal	
5	650	15	3.0	Normal	
6	650	1.0	.0	Normal	
7	2700	1.3	.0	Normal	•
8	2700	2.0	.0	Normal	•
9	2800	2.0	3.0	Normal	
10	40	13	3.0	Normal	

Table 6. Blood Lead Results

Direct Calibration Platform	Standard Additions	Alternate Method*
5.6 µg/dL	5.6 µg/dL	5.0 µg/dL
11	9.8	10
26		28

*Solvent extraction, flame analysis

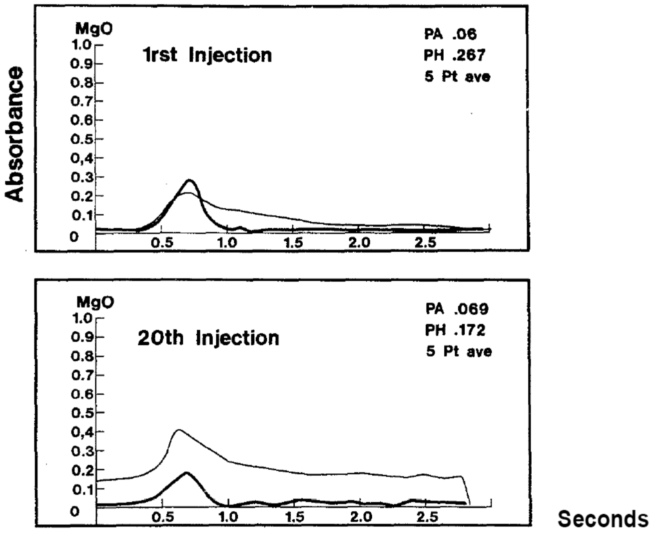


Figure 1. As in MgO wall atomization.

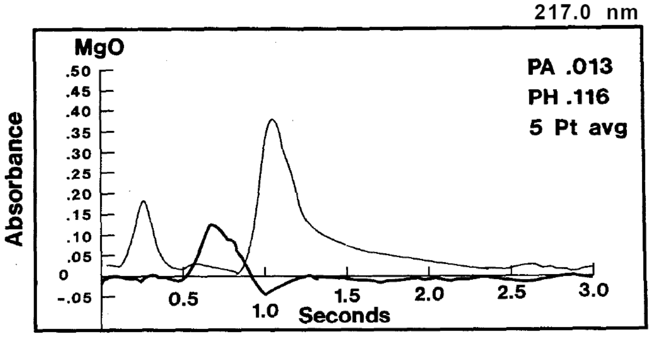


Figure 3. Pb in MgO wall atomization.

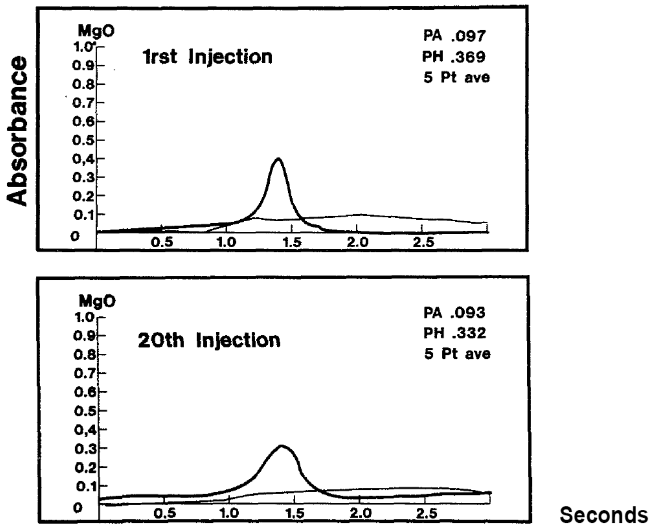


Figure 2. As in MgO platform atomization.

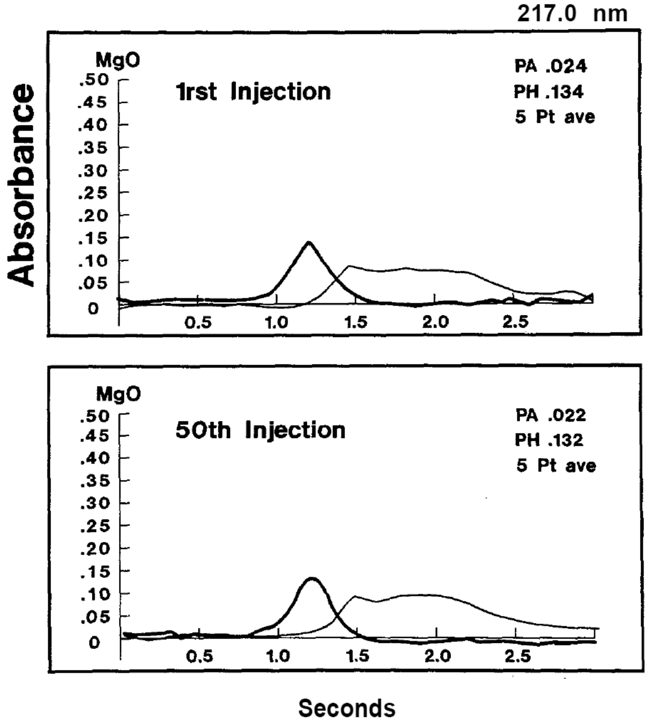


Figure 4. Pb in MgO platform atomization.

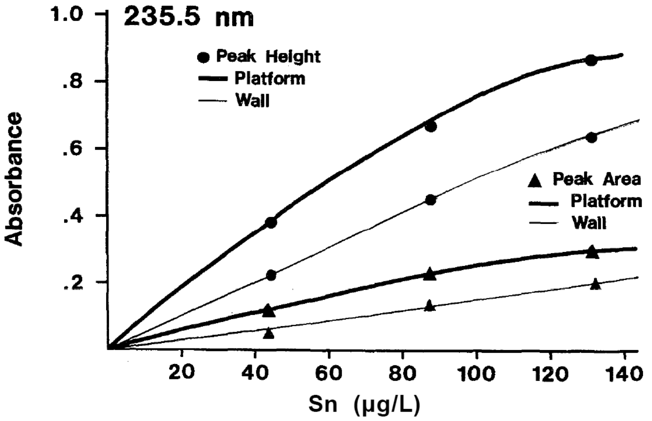


Figure 5. *Tin in copper calibration graphite platform versus wall atomization.*

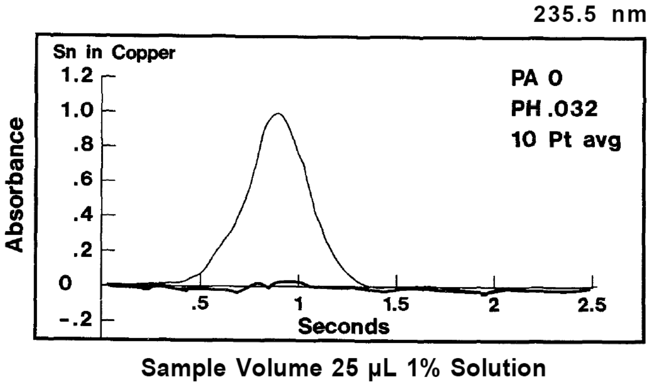


Figure 6. *NBS Cu II (1.5 µg/g Sn) wall atomization.*

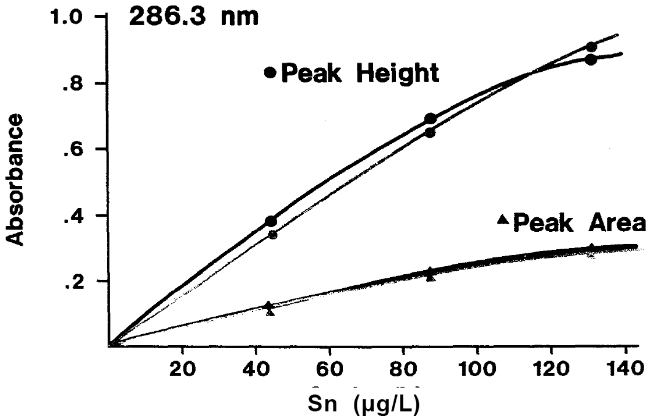


Figure 7. *Tin in copper calibration graphite platform.*

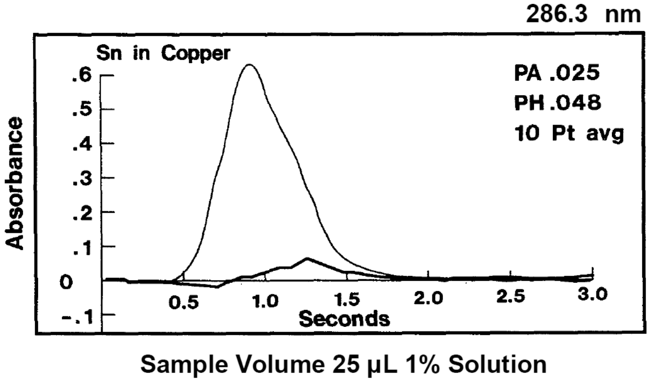


Figure 8. *NBS Cu II (1.5 µg/g Sn) wall atomization.*

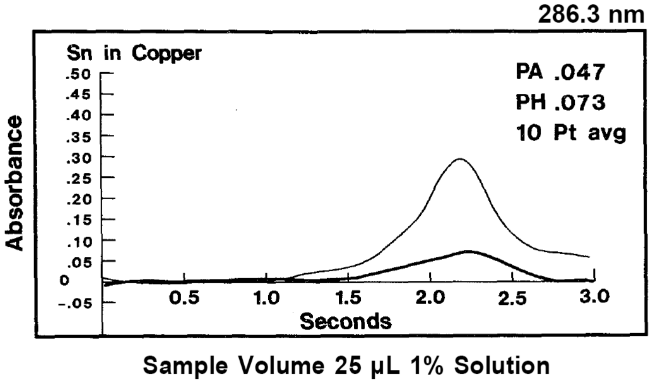


Figure 9. *NBS Cu II (1.5 µg/g Sn) platform atomization.*

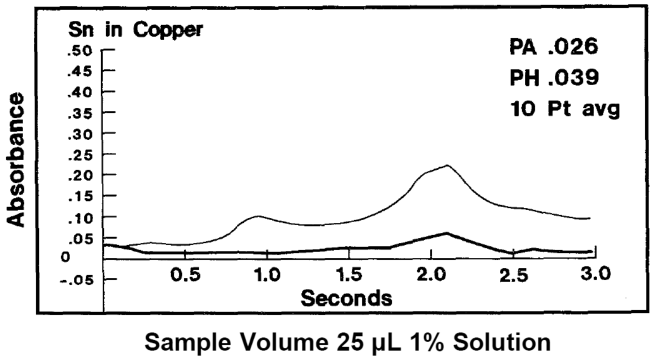


Figure 10. *NBS Cu III (0.8 µg/g Sn) platform atomization.*

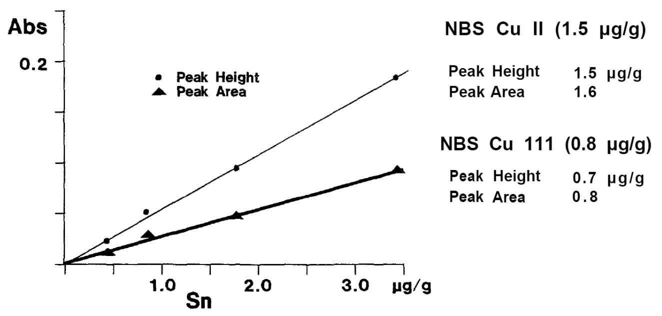


Figure 11. Results - Sn in NBS copper.

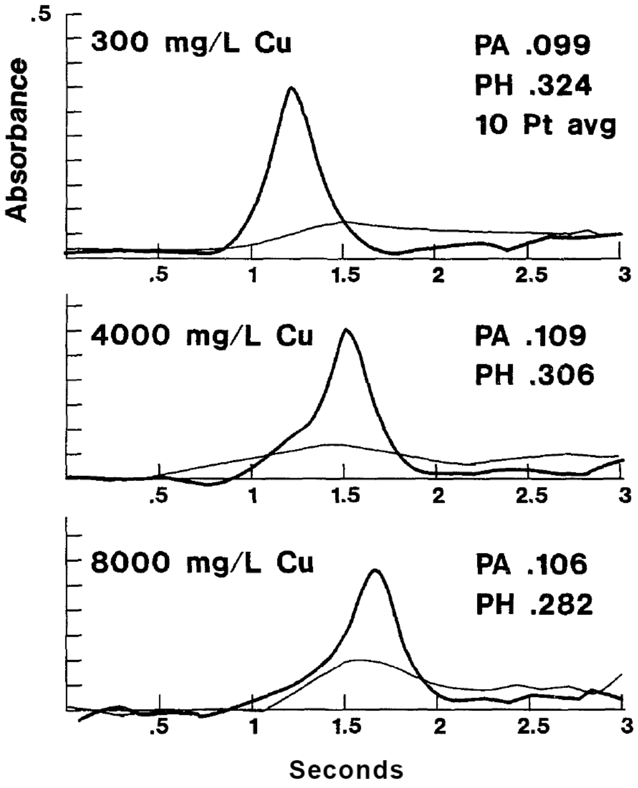
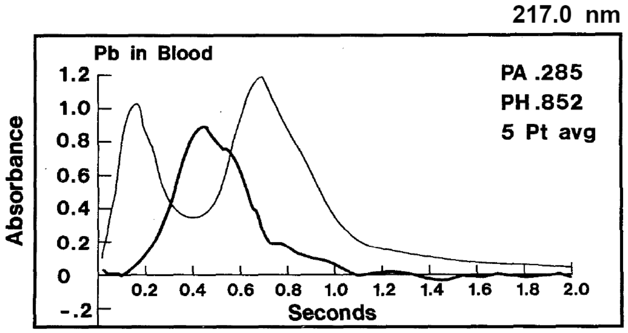
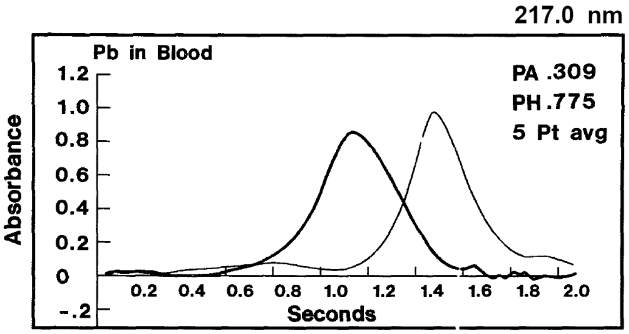


Figure 12. The effect of copper on tin atomization.



Sample Volume 10 µL Blood 1:1 with 2% Triton X-100

Figure 13. Pb in blood wall atomization.



Sample Volume 10 µL Blood 1:1 with 2% Triton X-100

Figure 14. Pb in blood platform atomization.

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Printed in the USA
November 1, 2010
AA054

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