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THE USE OF PALLADIUM AS A MATRIX MODIFIER FOR  
LEAD USING GRAPHITE FURNACE ATOMIC  
ABSORPTION TECHNIQUES

THESIS

BY

XI GONG

1997



TEXAS SOUTHERN UNIVERSITY



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**THE USE OF PALLADIUM AS A MATRIX MODIFIER FOR LEAD USING  
GRAPHITE FURNACE ATOMIC ABSORPTION TECHNIQUES**

THESIS

Presented in Partial Fulfillment of the Requirements for  
the Degree Master of Science in the Graduate School  
of Texas Southern University

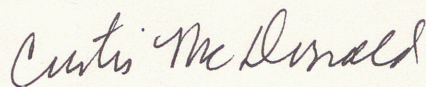
By

Xi Gong, B.S.

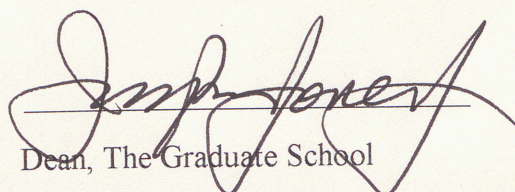
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1997

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# THE USE OF PALLADIUM AS A MATRIX MODIFIER FOR LEAD USING GRAPHITE FURNACE ATOMIC ABSORPTION TECHNIQUES

By

Xi Gong, M.S.

Texas Southern University, 1997

Professor Curtis W. McDonald, Advisor

Graphite Furnace Atomic Absorption Spectrometry (GFAAS) has been widely used as an analytical technique for trace level lead concentration determinations in a variety of applications such as blood, urine and soil. Based on a large amount of research on trace level lead analysis, this study targeted the development of a method for the determination of trace level lead with palladium as the matrix modifier using the graphite furnace atomic absorption spectrometer. The most important factors that affect lead absorbance signals are ashing temperature, atomization temperature and modifier concentration.

A variable condition for trace level lead analysis by GFAAS has been selected and discussed through experiments. In this study, lead absorbance with and without a palladium modifier was obtained by varying ashing or atomization temperatures while keeping other variables constant. The study of these variables generated some very interesting results. With a palladium as matrix modifier, ashing temperature can be used up to 800°C. This is desirable because a high ashing temperature will free lead from bulk matrix. Atomization temperatures can be chosen from 1200°C to 1900°C with a minimum impact of lead absorption.



## CHAPTER 1

### INTRODUCTION

Atomic absorption spectroscopy involves the study and measurement of the absorption of radiant energy by free atoms. The data obtained by studying this absorption provide spectroscopic and analytical information. The spectroscopic information includes the measurement of atomic energy levels, the determination of oscillator strengths, the population of atoms in various energy levels, atomic lifetimes, and so forth. The analytical information revealed includes qualitative and quantitative determination of elements, particularly the metallic elements of the periodic table. The analytical process involves the conversion of molecules or ions into free atoms and the measurement of absorption of radiation by these free atoms. The comparison of solutions of chemical compounds to free atoms involves areas of physics and chemistry.

The history of atomic absorption and the history of atomic emission are intimately interwoven. The story begins with the description of the visible spectrum by Isaac Newton. This early work generated studies on the interpretation of the physical properties of atoms. For about 100 years, the studies written entirely focused on the emission of radiation from atoms. In 1802 Wallaston reported the presence of dark bands in the radiation from the sun (1). At first it was thought that the absence of these atomic lines in the sun's spectrum indicated lack of this radiation and therefore of the relevant elements on the sun's surface. Later, Fraunhofer in 1814 and Bunsen in



1823 designated the origin of many of dark bands and measured the position of several hundred of them (2,3). Foucault in 1849 passed sunlight through a flame containing sodium vapor, expecting the dark sodium (Fraunhofer) lines to become more intense, indicating atomic absorption (4). Because the elements in the sun's spectrum were absent, Kirchhoff in 1859 deduced that the dark lines in the sun's spectra were caused by the absorption of atomic vapors rather than the lack of atomic emission (5). He termed these dark lines "reversed spectra." Forty years later, Kirchhoff and Bunsen showed that the wavelengths from one of the dark lines corresponded exactly with the yellow emission line obtained from excited sodium vapor (6). As a result of extensive studies, Bunsen and Kirchhoff established the fundamental principles: (i) every element when sufficiently excited in the gaseous state yields its own characteristic spectrum consequently, (ii) And the presence of the vapor of an element can be inferred with certainty by spectrum analysis when its characteristic lines are present (7). Based on this work, Kirchhoff further developed the important relationship that any species that can be excited to emit radiation at a particular wavelength can absorb at that wavelength (8). This pronouncement showed the fundamental relationship between emission and absorption spectra. For many years, the study was confined to the interpretation of the spectra in solar and interstellar atmospheres and the elucidation of those elements that were present in the atmospheres. By 1930, the fields of emission spectroscopy, including arc and spark emission, were well established but were used primarily for qualitative analysis. Practical difficulties were encountered with the absorption processes including the use of a photographic plate and the necessity of using high resolution systems. However, this was changed in 1953 by Alan Walsh and confirmed by Alkemade and Melatz in 1955 (9,10)



include Walsh's contributions to the field of atomic Absorption were significant (11).

(i) He used the hollow cathode as a light source, thus greatly reducing the resolution required for successful analyses. (ii) Photomultipliers were now available, and their use eliminated the problems associated with measuring small amounts of absorption with a photographic plate that necessitated the detection and measurement of minute changes in the darkness of this line. (iii) He introduced modulation into the system, which permitted the detector to distinguish between absorption by the atoms and emission by the atoms at the same wavelength. (iv) He utilized a flame as an atomization system. As an analytical tool, the aforementioned contributions were all major and vital to the development of atomic absorption. Although Dr. Walsh had shown the potential of the technique in Atomic Absorption, he had not unequivocally demonstrated its analytical usefulness. After subsequent discussions with several instrument companies, the instrument manufacturers remained unimpressed. However, Perkin Elmer models 290 and 303 came on the market in 1957, and the rest is history.

Analytical chemists are constantly pushing back the frontiers, and there is always a drive to obtain more sensitive procedures. The flame atomizer has been used extensively for many years and has proven capable of analyzing a great many samples submitted for routine analysis. Much research and development time has been devoted to exploiting the flame atomizer to its limit. In particular, three kinds of samples are handled well by this technique: (i) the analysis of high solid-containing samples such as seawater, urine, or blood; (ii) the determination of trace metals in samples available only in limited quantities such as clinical samples; and (iii) the determination of trace metal pollutants in gases, in particular, the atmosphere. Previously, these analyses



included pretreatment of the sample by either selective precipitation, selective extraction, or treating gas samples with a suitable scrubbing agent.

In the case of air pollution analyses, typical concentrations of metals in air may be  $1 \mu\text{g}/\text{m}^3$ . If one cubic meter of air were scrubbed and the metal extracted completely, then  $1 \mu\text{g}$  of that metal would be available for analysis. This in itself is a challenge, as is scrubbing a cubic meter of air, which may take several hours if it is to be done efficiently. With this background, carbon atomization methods of analysis were developed. Because of L'vov's work, it was recognized that they were capable of very high analytical sensitivity (12). At first glance, it seemed relatively easy to translate this into a highly precise and reliable quantitative method of analyses, and extensive research was put into its development.

The function of the atomizer is amply described by West as follows: "The basic requirements of the ideal atom reservoir are an efficient and rapid production of free atoms with the minimum background noise, a high level of reproducibility and a minimal memory effect and a minimal dilution of the atoms" (13). In practice, the development process enhanced the development and use of the flame atomizer.

### **Matrix Modifiers**

Matrix modification, as it is known today, may be defined as "the process of chemical alteration of the desired analyte, sample matrix, or graphite surface" (14). This complication has apparently led the International Union of Pure and Applied Chemistry (IUPAC) to recommend the generic term "chemical modification," which may be a better term to use. The goal of matrix modification, along with the other



components of the stabilized temperature platform furnace ( STPF ) technique, is to free the analysis from matrix effects and allow the determination of the lowest possible trace levels of analytes. The first publications in which matrix modifiers were used appeared in the literature in 1973. Machata and Binder reported the use of lanthanum, strontium, aluminum, and cesium in the determination of lead and thallium in blood and urine. The best results were obtained with lanthanum. The addition of 1 % lanthanum increased the peak absorbance sensitivity more than thallium (15). The same year, Matousek and Brodie used  $\text{H}_3\text{PO}_4$  for the determination of lead in air particulate samples. They found that without the  $\text{H}_3\text{PO}_4$ , multiple peaks were obtained. With the wall sampling technique used during this time, the volatilization of the various lead compounds was directly coupled with the heating of the tube wall (16). Thus, the residence time of the individual lead atoms depended upon the temperature at which volatilization occurred. The only possible solution to this problem would be to convert all the lead in the sample to a single form and to use a standard prepared in the same form. Around 1977, the basic building block concepts of matrix modification were in place. Matrix modifiers were used either to convert numerous forms of analyte to a single form or to cause temporal separation of matrix and analyte volatilization.

In the mid-1980s, Schlemmer and Welz considered whether a single modifier or modifier combination might be able to replace a number of the modifiers currently recommended (17). Such a universal or ideal matrix modifier would have the following characteristics: (i) It would increase the thermal stability of a number of elements to a minimum of about  $1000^\circ\text{C}$ . At this temperature, many matrix materials may be removed during the pyrolysis step. (ii) It must be available in high purity, free of contamination by the analytes to be determined. (iii) It must be an element that is



not routinely determined in the furnace. (iv) The modifier should not markedly reduce tube or platform life. (v) The modifier should not produce excessive or structured background (18). None of the modifiers in use in 1983 met all of these requirements. Ammonium phosphate, which was recommended for silver, cadmium, lead, and tin, was difficult to obtain in high purity. Solvent extraction was often required to remove contaminants. Nickel is very effective for the stabilization of arsenic.

Improvements were slowly made to the instrumentation and procedures used for graphite furnace determination. Better quality pyrolytically coated tubes became available. Rapid digital signal processing was offered in most instruments. Zeeman background correction became available. This evolution of the aforementioned techniques was hastened by the introduction of the STPF ( Stabilized-Temperature Platform Furnace ) concept by Slavin and co-workers in 1981. The STPF concept is proposed by Slavin who anticipated the combination of the latest hardware advances available, along with the platform atomization and peak area integration (19). It has now been demonstrated that the STPF concept is very effective in removing many of the previous problems with furnace analyses.

For a physic-chemical phenomenon to be useful as the basis of an analytical technique, it is generally necessary that the magnitude of what is measured to be linearly related to some simple function of concentration or amount of the determinant species in the sample or analysis. As most samples for analysis will be either solids or liquids, a very important step in performing analyses by atomic absorption spectrometry is based on the equation  $A=KLN$ , A is the absorbance, K is a constant, L is the path length in the absorbing medium, and N is the total number of atoms per unit volume. This equation is used to convert the elements to be determined into atomic vapor.



Although there are many ways of generating such vapor from solids or liquids, for a variety of practical reasons only two such methods are used in analytical AAS (Atomic Absorption Spectrophotometer). These are the combustion flame, into which the sample is introduced as a finely-dispersed aerosol solution, and the electrically heated furnace, into which the sample is mainly introduced as a solution or as a solid. For a limited range of elements, there is a third method in use, namely, the direct generation and separation of a chemical vapor from the solution phase with subsequent atomization, where a variety of atomizer devices can be used. A detailed discussion of atomization mechanisms is beyond the scope of this thesis. There are several texts available (20,21).

### **Interferences in Atomic Absorption Analysis**

Interferences encountered in AAS can be separated into the following categories: spectral, flame emission, chemical, matrix, nonspecific scattered Ionization. The majority of difficulties that analysts can expect to encounter arises from chemical, matrix, light-scattering and ionization interferences. Spectral interference is rarely encountered in atomic absorption spectrometry. Spectra interferences in the past were experienced typically if, in a given solution, element A was being determined in the presence of element B. If the source contained both elements and the absorption lines of these could not be resolved by the monochromes, element B would then cause an interference. In some early hollow-cathode lamps this was a well-known phenomenon. However, if we used an alternative absorption line, the probability of the two lines coinciding again would be extremely remote. Most of the interferences



have now disappeared due to improvements in the purification techniques of the cathodes.

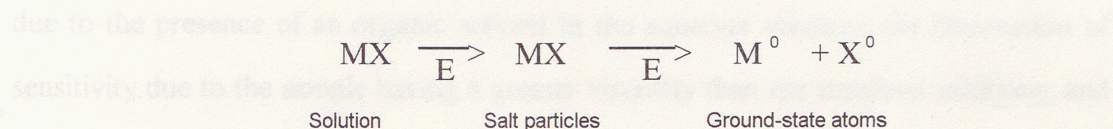
Emission interference was common in many early instruments which were accessories to UV/Visible spectrophotometers. They operated in most instances on a d.c. system. The interference was caused by the emission of element at the same wavelength as its absorption. All modern instruments use a.c. systems, which are of course "blind" to the continuous emission from the flame. However, if the intensity of the emission is high, the "noise" associated with the determination will increase since the noise of a photomultiplier detector varies with the square root of the radiation falling upon it. This effect can be reduced by either increasing the source current or by closing down the slit; both methods resulting in an increase in the signal-to-noise ratio.

Chemical interference is by far the most frequently encountered interference in AAS. Basically, a chemical interference can be defined as anything that prevents or suppresses the formation of ground state gaseous atoms in the flame. A common example is the interference produced by aluminium, silicon and phosphorus in the determination of magnesium, calcium, strontium, barium and many other metals. The interference is due to the formation of aluminous, silicates and phosphates which, in many instances, are refractory in the analytical flame being used. In order to overcome this type of interference, two techniques may be emphasized; both release the element under investigation. The first relies upon the application of chemistry in the knowledge that a compound may be added which will lead to the release of the element of interest through the formation of a preferential complex. Thus, a chelate such as EDTA can be added to complex the cation, thus preventing its association with an anion that could lead to the formation of a refractory compound.

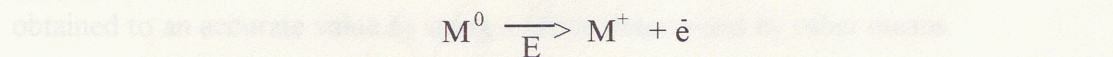


Alternatively, a reagent can be added that will preferentially form a compound with the interfering anion, again leading to the "release" of the cation; for example, the addition of lanthanum chloride to solutions of calcium containing the phosphate anion. The calcium is "released" due to the preferential formation of lanthanum phosphate.

Secondly, many chemical interferences may be overcome by using the higher temperatures of a nitrous oxide-acetylene flame, which will simply thermally decompose the sample. To understand ionization interferences, it is necessary to appreciate what is occurring in the flame during the aspiration of sample. The flame is being used as a source of energy to convert elements present in the solution mist, created by the nebulized, into ground-state atoms.



Many determinations require the use of the nitrous oxide-acetylene flame and it is usually under these conditions that ionization interferences occur. They arise from the energetic nature of the flame which, in addition to producing ground-state atoms, also excites some atoms to such an extent that one or more electrons are lost and ionization occurs.

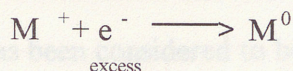


This effect will obviously be greatest with elements having low ionization potentials, such as the alkali and alkaline earth metals, e.g. barium is approximately 80% ionized in the nitrous oxide flame. Since the ground state, therefore, becomes depopulated, the sensitivity will decrease.

An equally important effect arises when an easily ionized element is being determined in the presence of another. There will be an enhancement of sensitivity effectively decreased, there will be a decrease in the effective signal. This non-



compared with pure aqueous standards. This arises from the presence of excess free electrons which suppress further ionization.



This effectively increases the population of ground-state atoms. In practical applications some use may be made of this phenomenon. By adding an excess of a readily ionized salt to samples and standards, an increase in sensitivity may be achieved. Potassium chloride is usually chosen for this purpose because of its high purity, low ionization potential and lack of visible emission in the flame.

Matrix interference is a general term covering: (i) Enhancement of sensitivities due to the presence of an organic solvent in the aqueous solution; (ii) Depression of sensitivity due to the sample having a greater viscosity than the standard solutions; and (iii) Depression of the result due to a high salt content.

These interferences can be readily overcome by using one of the following techniques: (i) The method of standard additions; (ii) Matching the matrix of the standards with the sample; (iii) Remove the cation to be determined from the interfering matrix by solvent or ion exchange; and (iv) Relating the erroneous value obtained to an accurate value by using a factor determined by other means.

Non-specific interference effect causes an enhancement of an analytical result due to the solution containing a high concentration of dissolved salts or a less extent stable absorbing molecules. The first effect is due to the presence of dried and semi-dried salt particles in the flame which scatter and absorb the incident radiation from the source, while the second effect is associated either broadband absorption from thermally stable matrix species. Since the intensity of the transmitted radiation will be effectively decreased, there will be an increase in the absorption signal. This non-



specific effect is wavelength dependent and is more pronounced at shorter wavelengths. It is most significant below 250 nm.

Palladium was first introduced as a matrix modifier for the determination of lead by Shan and Ni (22). It has been considered to be a universal matrix modifier for lead and a number of other metallic elements by Schemmer and Welz (17). These investigators did not study the role of the ashing and atomization temperatures on the ability of Pd to serve as a matrix modifier. This thesis research project is to study the utilization of palladium as a matrix modifier for the determination of lead in various solution media. Of specific concern is to study the role of ash and atomization temperature of the method for determining lead.

### Reagents and Materials

All standard solution and modifiers were prepared by diluting appropriate reagents with highest available purity in purified water with 1% nitric acid. High purity water was obtained by using a Milli-Q Plus System with a Milli-RS System (Millipore). Certified 1000 mg/L lead atomic absorption standard was purchased from Fisher Scientific Co. to use as standard solution. Certified 1000 mg/L palladium atomic absorption standard was purchased from Sigma Chemical Company, St. Louis, MO, to use as modifier. All working solutions were stored and measured in plastic ware which were soaked for at least two days and cleaned with detergent and rinsed thoroughly with high-purity water. The gas-grade argon gas used to purge the atomizers.



## CHAPTER 2

### EXPERIMENTAL METHODS AND PROCEDURES

#### Apparatus

A Perkin-Elmer Zeeman 4110 ZL Atomic Absorption Spectrophotometer equipped with an HGA-600 atomizer, an AS-60 autosampler and a PR-100 printer were used for most experiments. The spectrometer was interfaced to a personal computer (PC) in order to program the analysis procedure, operate the spectrometer and store absorption signals.

#### Reagents and Materials

All standard solution and modifiers were prepared by diluting appropriate reagents with highest available purity in purified water with 1% nitric acid. High purity water was obtained by using a Milli-Q Plus System with a Milli-RO6 System (Millipore). Certified 1000 mg/L lead atomic absorption standard was purchased from Fisher Scientific Co. to use as standard solution. Certified 1000 mg/L palladium atomic absorption standard was purchased from Sigma Chemical Company, St. Louis, MO, to use as modifier. All working solutions were stored and measured in plastic ware which were soaked for at least two days and cleaned with detergent and rinsed thoroughly with high-purity water. The plus-grade argon gas used to purge the atomizers.



Pyrolytic coated graphite tubes with built-in pyrolytic graphite platforms were used in the HGA-600 instruments. All graphite parts were supplied by Boden-seewerk Perkin-Elmer (Uberlingen, Germany).

### **Tube Conditioning**

New graphite tubes should be conditioned prior to analytical use by heated cleaning. The conditioning process removes impurities on the tube surface and in the tube material. It contributes to the general stabilization of the graphite. To condition the tube, use the program listed in Table 1. A gas flow of 250 ml./min. should be used for all steps and a read command set in step number 9. The tube is sufficiently conditioned when a blank value for the furnace program becomes constant.



## Procedure

TABLE 1

Furnace Program to Condition a Graphite Tube

Step#	Temperature ( $^{\circ}\text{C}$ )	Ramp Time (Sec)	Hold Time (Sec)
1	2200	60	2
2	20	1	20
3	2200	10	10
4	20	1	20
5	2300	10	10
6	20	1	20
7	2400	10	10
8	20	1	20
9	2500	1	5



## **Procedure**

The conditions and procedures outlined below were followed. The standard furnace temperature program is described in Table 2. Ashing and atomization temperature studies were performed by changing the ashing and atomization steps in Table 2. Lead measurement was made at wavelength 283.3 nm.

Sample insertion in the furnace was performed by using the AS-60 programmable sample dispenser. The sample dispenser picked up separate aliquot of sample, modifier and diluter (when called for) into the capillary then deposited the entire volume into the furnace. A total volume of 20  $\mu\text{L}$  was deposited. A 200  $\mu\text{g/L}$  of lead standard as stock solution was prepared from 1000 ppm standard purchased. A 5 mg/L of palladium as modifier stock solution was prepared from 1000 ppm standard. All solutions were acidified to final  $\text{HNO}_3$  concentrations of 1 % V/V.

## **Graphite Furnace Conditions**

The graphite furnace condition are shown in Table 2. It involves five steps. Basically, it includes drying, ashing, atomization and cleaning out steps. The primary purpose of the ashing step is to eliminate bulk materials associated with lead interference. During this step, the temperature is increased as high as possible to volatilize matrix components but below the temperature at which analyte loss would occur. The purpose of the atomization step is to produce an atomic vapor of the analyte elements, thereby allowing atomic absorption to be measured. The temperature in this step is increased to the point where dissociation of volatilized molecular species occurs.



## CHAPTER 3

TABLE 2

## Graphite Furnace Parameter

## Effect of Ashing Temperature

Step#	Function	Temperature ( $^{\circ}\text{C}$ )	Ramp Time (Sec)	Hold Time (Sec)	Internal Flow ( ml/min)	Read Step
1	dry	110	1	20	250	
2	dry	130	5	30	250	
3	char	400-900	10	20	250	
4	atomization	1200-1900	0	5	0	*
5	clean out	2450	1	3	250	



## CHAPTER 3

### RESULTS AND DISCUSSION

#### Effect of Ashing Temperature

The ashing temperature affects the absorbance significantly. The ashing temperatures range from 500°C to 600°C are generally recommended by most GFAAS methods. Table 3 shows the results of lead absorbance by varying ashing temperatures without the modifier when atomization temperature keeps constant. Table 4 shows the results of lead absorbance by varying ashing temperature with 15 ng palladium as modifier when atomization temperature is constant. Fig. 1 shows the peak area absorbance as a function of ashing temperature of 1 ng lead with and without 15 ng palladium modifier. Fig. 2 shows the peak area absorbance as a function of ashing temperature of 2 ng lead with and without 15 ng palladium modifier. Fig. 3 shows the peak area absorbance as a function of ashing temperature of 3 ng lead with and without 15 ng palladium modifier. These figures show that lead can only be pyrolyzed up to 600°C in the absence of modifier without significant volatilization lost. Adding palladium as modifier increases the ashing temperature to 800°C.



TABLE 3

The Ashing Temperatures Affect Lead Absorbance

Ashing Temp. (°C)	Absorbance			
	Lead (Pb)			Modifier
	1 ng	2 ng	3 ng	
400	0.1132	0.2246	0.3374	None
500	0.1147	0.2312	0.3473	None
600	0.1120	0.2291	0.3667	None
700	0.0875	0.1615	0.2322	None
800	0.0110	0.0172	0.0193	None
900	0.0022	0.0027	0.0032	None



TABLE 4

Results of Absorbance After Adding Modifier Palladium

Ashing Temp. (°C)	Absorbance			
	Lead (Pb)			Modifier
	1 ng	2 ng	3 ng	Pd (ng)
400	0.1121	0.2258	0.3355	15
500	0.1114	0.2235	0.3313	15
600	0.1104	0.2211	0.3289	15
700	0.1086	0.2171	0.3222	15
800	0.1036	0.1993	0.2914	15
900	0.0777	0.1555	0.2220	15
1000	0.0359	0.0895	0.1212	15
1100	0.0141	0.0334	0.0991	15



FIGURE 1

Peak Area Absorbance as a Function of Ashing Temperature

for the 1 ng Lead with and Without Palladium

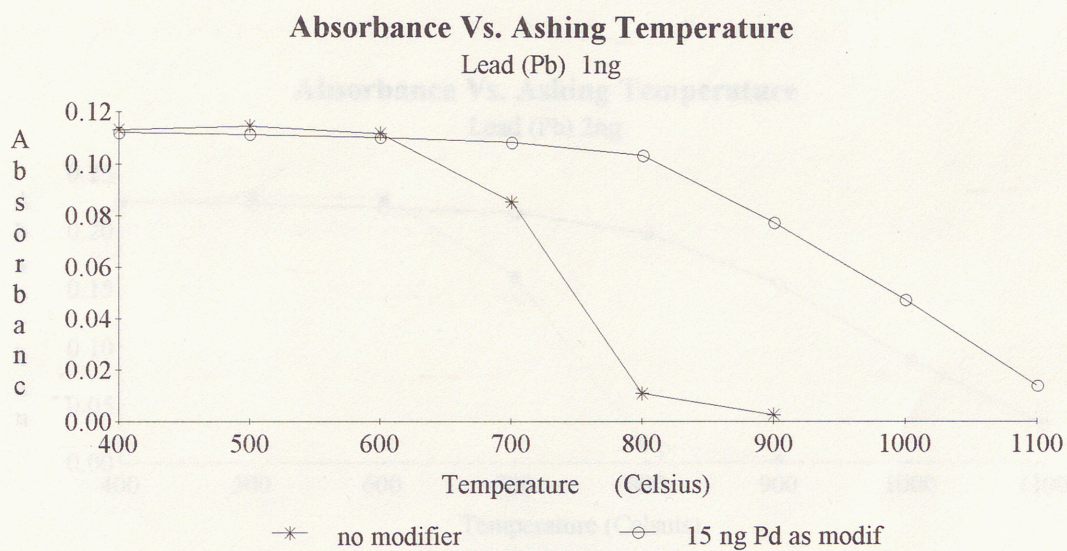
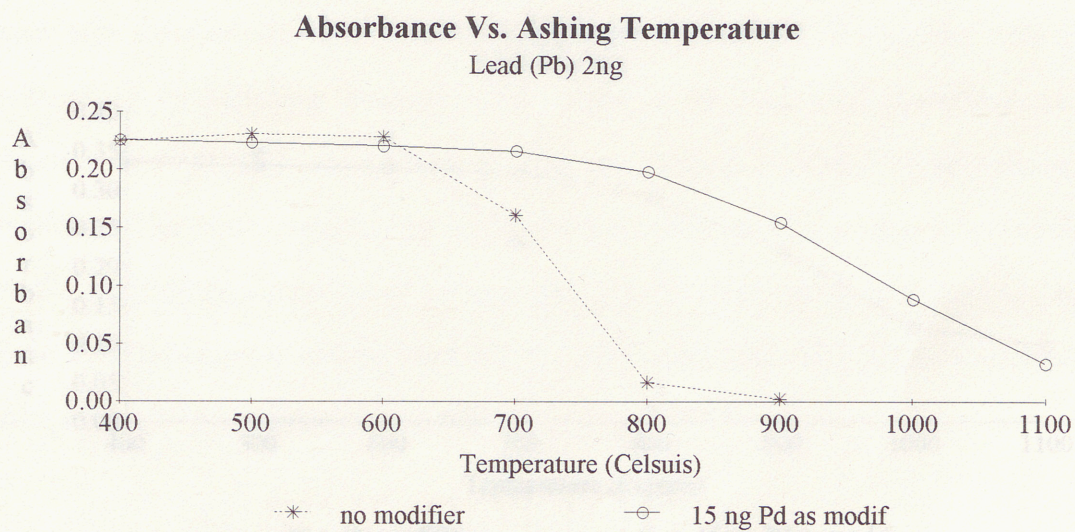




FIGURE 2

Peak Area Absorbance as a Function of Ashing Temperature  
for the 2 ng Lead with and Without Palladium





### Effect of Atomization Temperature

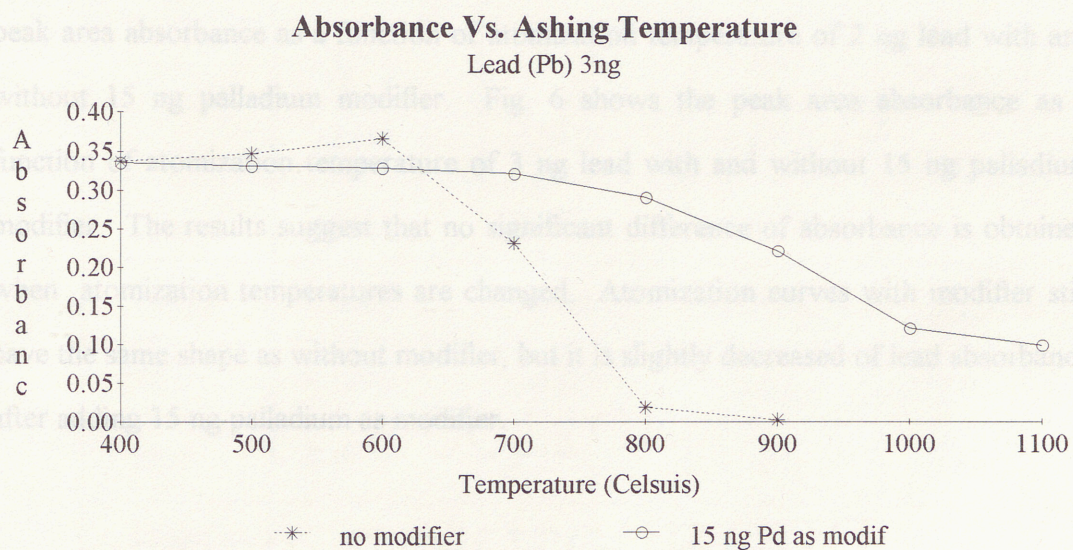
For 1 ng to 3 ng mass of lead, there were no significant differences in the integrated absorbance sensitivities for 15 ng palladium modifier. Tables 5 and Table 6 present the experimental data. Table 5 shows the results of lead absorbance by varying

### Peak Area Absorbance as a Function of Ashing Temperature

for the 3 ng Lead with and Without Palladium

temperature with 15 ng palladium as modifier when ashing temperature keeps constant. Fig. 4 shows the peak area absorbance as a function of atomization temperature of 1 ng lead with and without 15 ng palladium modifier. Fig. 5 shows the

peak area absorbance as a function of atomization temperature of 2 ng lead with and without 15 ng palladium modifier. Fig. 6 shows the peak area absorbance as a function of atomization temperature of 3 ng lead with and without 15 ng palladium modifier.





### **Effect of Atomization Temperature**

For 1 ng to 3 ng mass of lead, there were no significant differences in the integrated absorbance sensitivities for lead when using palladium modifier. Tables 5 and Table 6 present the experimental data. Table 5 shows the results of lead absorbance by varying atomization temperatures without the modifier when ashing temperature keeps constant. Table 6 shows the results of lead absorbance by varying atomization temperature with 15 ng palladium as modifier when ashing temperature keeps constant. Fig. 4 shows the peak area absorbance as a function of atomization temperature of 1 ng lead with and without 15 ng palladium modifier. Fig. 5 shows the peak area absorbance as a function of atomization temperature of 2 ng lead with and without 15 ng palladium modifier. Fig. 6 shows the peak area absorbance as a function of atomization temperature of 3 ng lead with and without 15 ng palladium modifier. The results suggest that no significant difference of absorbance is obtained when atomization temperatures are changed. Atomization curves with modifier still have the same shape as without modifier, but it is slightly decreased of lead absorbance after adding 15 ng palladium as modifier.

1800	0.1249	0.2354	0.3523	None
1900	0.1217	0.2268	0.3385	None



TABLE 5

The Atomization Temperatures Affect Lead Absorbance

Atomization Temp. (°C)	Absorbance			
	Lead (Pb)			Modifier
	1 ng	2 ng	3 ng	
1200	0.1438	0.2965	0.4416	None
1300	0.1500	0.3031	0.4479	None
1400	0.1448	0.2912	0.4393	None
1500	0.1407	0.2779	0.4253	None
1600	0.1325	0.2648	0.4062	None
1700	0.1285	0.2525	0.3936	None
1800	0.1249	0.2354	0.3521	None
1900	0.1217	0.2268	0.3385	None



TABLE 6

Results of Lead Absorbance with Modifier  
in the Condition of Changing Atomization Temperature

Atomization Temp. (°C)	Absorbance			
	Lead (Pb)			Modifier
	1 ng	2 ng	3 ng	Pd (ng)
1200	0.1005	0.2061	0.3110	15
1300	0.1036	0.2123	0.3167	15
1400	0.1008	0.2121	0.3173	15
1500	0.0986	0.1979	0.2876	15
1600	0.0945	0.1880	0.2781	15
1700	0.0940	0.1901	0.2779	15
1800	0.0942	0.1913	0.2777	15
1900	0.0931	0.1836	0.2685	15



FIGURE 4

Peak Area Absorbance as a Function of Atomization Temperature  
for the 1 ng Lead with and Without Palladium

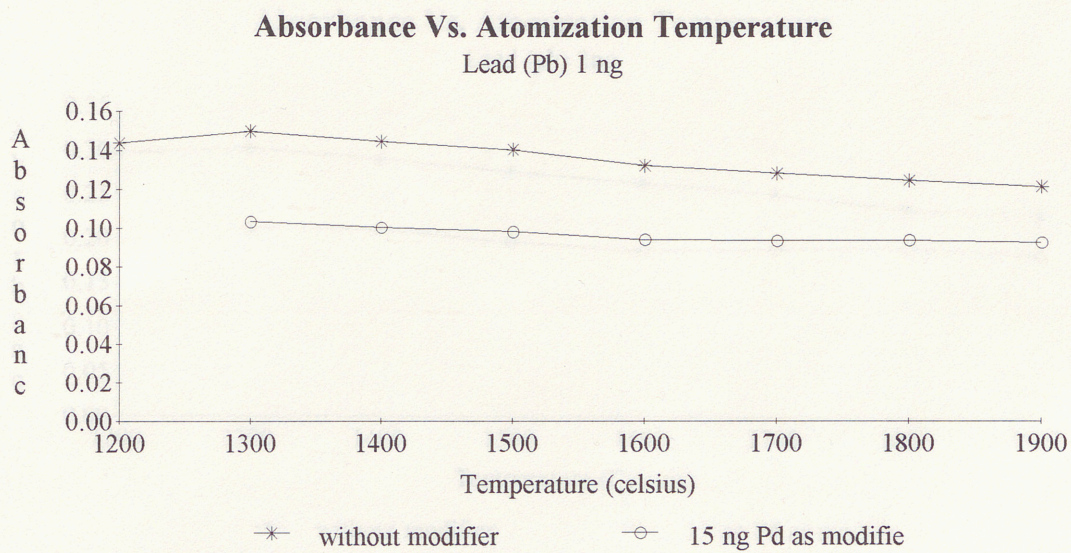
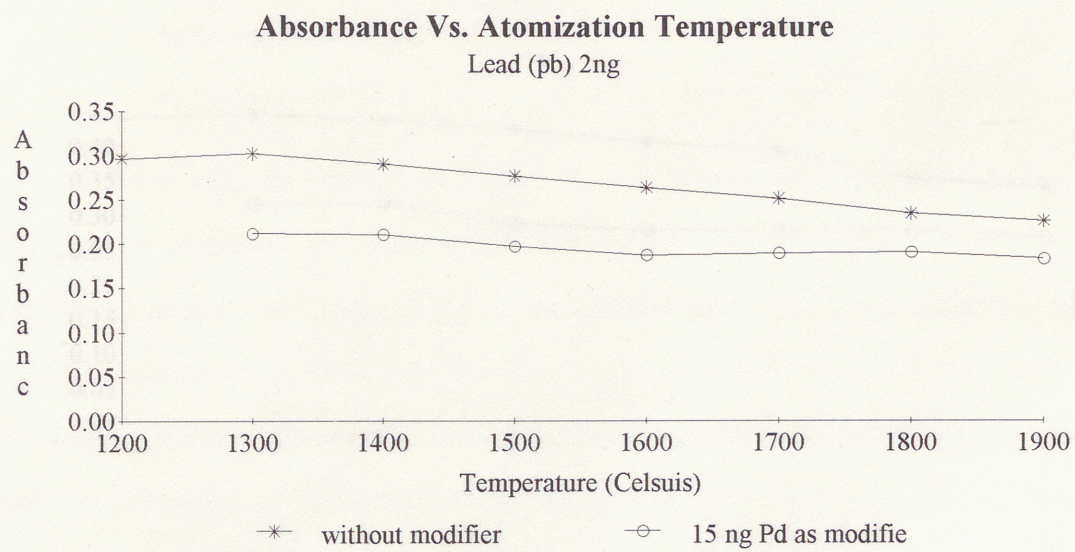




FIGURE 5

Peak Area Absorbance as a Function of Atomization Temperature  
for the 2 ng Lead with and Without Palladium





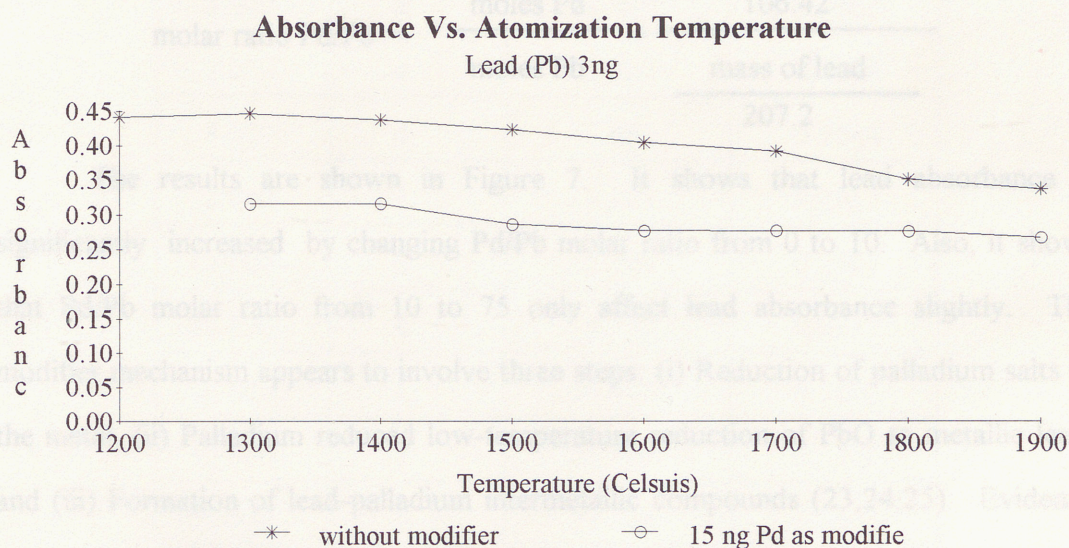
### Effect of Palladium Concentration on Absorbance Signal Response

Table 7 shows the effects of various modifier masses on the integrated area absorbance for lead. This experiment was designed to study the effect on the lead absorbance signal caused by an increase in mass of the palladium modifier. The amount of Pb was kept constant at 4 ng and the palladium masses were varied from 1 to 150 ng.

FIGURE 6

Peak Area Absorbance as a Function of Atomization Temperature

for the 3 ng Lead with and without Palladium





### **Effect of Palladium Concentration on Absorbance Signal Response**

Table 7 shows the effects of various modifier masses on the integrated area absorbance for lead. This experiment was designed to study the effect on the lead absorbance signal caused by an increase in the amount of the palladium modifier. The amount of Pb was kept constant at 4 ng and the palladium masses were varied from 1 to 150 ng. The ashing temperature and atomization temperature were kept constant at 800°C and 1700°C respectively. Apply the following equation to obtain the ratio of moles of Pd to moles of Pb.

$$\text{molar ratio Pd/Pb} = \frac{\text{moles Pd}}{\text{moles Pb}} = \frac{\frac{\text{mass of palladium}}{106.42}}{\frac{\text{mass of lead}}{207.2}}$$

The results are shown in Figure 7. It shows that lead absorbance is significantly increased by changing Pd/Pb molar ratio from 0 to 10. Also, it shows that Pd/Pb molar ratio from 10 to 75 only affect lead absorbance slightly. The modifier mechanism appears to involve three steps: (i) Reduction of palladium salts to the metal, (ii) Palladium reduced low-temperature reduction of PbO to metallic lead, and (iii) Formation of lead-palladium intermetallic compounds (23,24,25). Evidence for the latter is Pb-Pd bond formation revealed by X-ray photoelectron spectroscopy and X-ray diffraction identification of the intermetallic compounds Pd<sub>3</sub>Pb and Pb<sub>3</sub>Pd<sub>2</sub> (26,27). Since two intermetallic compounds are formed, it is hard to determine the percentages of these two compounds. The results suggest that excess palladium must be used to ensure the increased lead absorbance signal.



FIGURE 6

Molar Ratio of Palladium TABLE 7 Test the Lead Absorbance

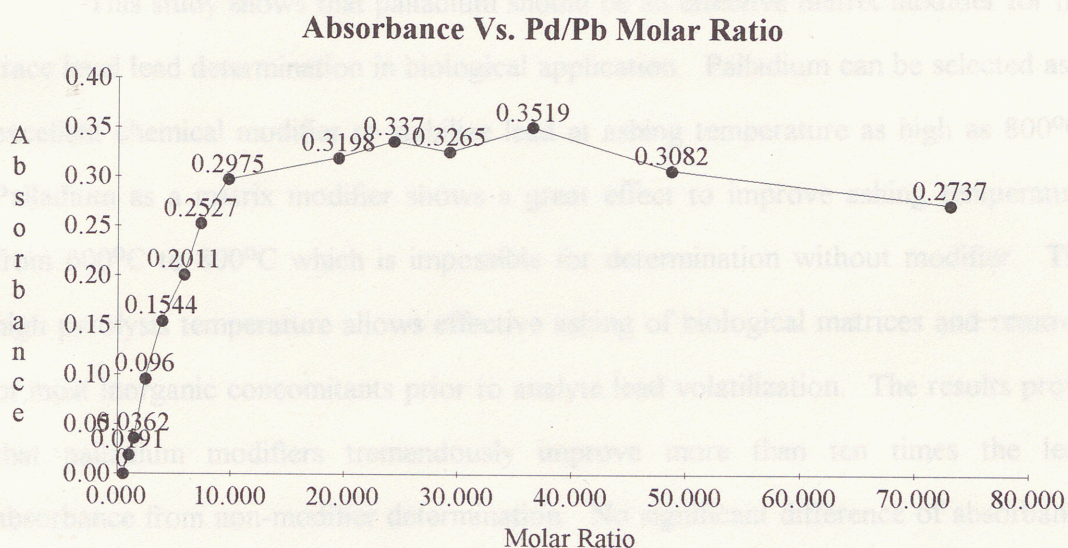
Modifier Concentration Affects Lead Absorbance

Palladium Pd (ng)	Lead Pb (ng)	Molar Ratio ( Pd:Pb)	Absorbance
1.000	4	0.487	0.0000
2.000	4	0.974	0.0191
3.000	4	1.460	0.0362
5.000	4	2.434	0.0960
8.000	4	3.894	0.1544
12.000	4	5.841	0.2011
15.000	4	7.301	0.2527
20.000	4	9.735	0.2975
40.000	4	19.470	0.3198
50.000	4	24.338	0.3370
60.000	4	29.205	0.3265
75.000	4	36.506	0.3519
100.000	4	48.675	0.3082
150.000	4	73.013	0.2737



FIGURE 6

Molar Ratio of Palladium to Lead Affect the Lead Absorbance





## CHAPTER 4

### CONCLUSION AND RECOMMENDATIONS

This study shows that palladium should be an effective matrix modifier for the trace level lead determination in biological application. Palladium can be selected as a excellent chemical modifier to stabilize lead at ashing temperature as high as 800°C. Palladium as a matrix modifier shows a great effect to improve ashing temperature from 600°C to 800°C which is impossible for determination without modifier. The high pyrolysis temperature allows effective ashing of biological matrices and removal of most inorganic concomitants prior to analyte lead volatilization. The results prove that palladium modifiers tremendously improve more than ten times the lead absorbance from non-modifier determination. No significant difference of absorbance was obtained when atomization temperatures were varied from 1200°C to 1900°C, and ashing temperature was a constant at 800°C.

Another critical factor affecting lead absorbance is palladium matrix modifier concentration. The strong dependency of the analyte signal on the mass of Pd agrees the formation of two intermetallic compounds, and the study indicates that the excess palladium matrix modifiers are needed in order to obtain the maximal absorbance signal (26,27). This study shows that lead absorbance increases when palladium to lead molar ratio is increasing up to a certain point. The lead absorbance signal changes significantly when the molar ratios of palladium chemical modifier to lead



concentration are under ten, but lead absorbances have only a slight change once the molar ratio is over ten.

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