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Rhodium a Potential Chemical Modifier for the Determination of Lead Using Graphite Furnace Atomic Absorption Spectrometric (GFAAS) Techniques

Prima Tatum

RHODIUM, A POTENTIAL CHEMICAL MODIFIER FOR THE DETERMINATION OF LEAD USING GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRIC (GFAAS) TECHNIQUES

THESIS

BY

PRIMA TATUM

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THESIS

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Chairperson, Thesis Committee

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Texas Southern University, 2000

Professor Curtis McDonald, Advisor

There are several ways to determine trace amounts of lead in biological samples. The use of matrix modifiers and auxiliary modifiers along with the Graphite Furnace Atomic Absorption Spectrometric technique is one of the ways to measure the levels of lead in blood and urine. This study is directed towards the use of rhodium as a matrix modifiers for the determination of lead using Graphite Furnace Atomic Absorption (GFAAS) technique. At a constant atomization temperatures, the ashing temperature has an effect on the lead absorbance signal.

The effect modifiers and an auxiliary modifier on the analysis of lead in blood using GFAAS have been investigated in this study. This research was conducted at varying ashing temperatures and at a constant atomization temperature. The results of this study produced some interesting results. The use of the rhodium and auxiliary modifier increased the absorbance signal at ashing temperatures ranging from 800°C -

1000°C. These high temperatures allowed for the matrix to be removed and the analyte to be measured accurately. The atomization temperature was constant at 1500°C.

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Chairperson, Thesis Committee — May 4, 2000 — Date

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Committee Member — May 4, 2000 — Date

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CHAPTER 1

INTRODUCTION

Atomic absorption spectroscopy involves the study and measurement of the absorption of optical radiation in the gaseous state. The data from this study provides a wide range of analytical and spectroscopic information on the sample being analyzed. The analytical process involves the breaking down of the analyte into atoms and the measurement of the amount of light absorbed by those atoms (3). The analytical data consist of both quantitative and qualitative information. An analysis of the data can provide information on the concentration of the analyte or the numbers of elements present in an unknown sample. The spectroscopic data can include the oscillation strength, atomic energy levels and the population of atoms in various energy levels, as well as other characteristics (3).

The history of absorption spectroscopy is considered to have its evolution with Newton's discovery of the solar spectrum in 1666. Newton's experiment was repeated by Wallaston and in 1802 reported a number of black lines that intersected the sun's spectrum (6). Further investigation was done and in 1823, Fraunhoffer was able to measure the wavelength of these black lines. Brewster in 1820 expressed the view that the Frauhoffer lines were due to the absorption process in the sun's atmosphere (6). In 1855, Bunsen performed an experiment introducing various salts in a flame by means of a platinum wire (26). The colored flames produced were viewed through a spectroscope, and he noted that the colors were linked to the element and compound in

which they were present. These bright lines were characteristic of a specific element. This discovery was the birth of emission spectroscopy. Kirchnoff, interested in Bunsen's findings, remeasured the wavelength of many of the Fraunhofer lines and compared them to the lines measurements found in the laboratory (26). He proved that they came from the same element, thus concluding that the elements found in the lab were also present in the sun (26). He explained the reversal appearance of the sun was due to the process of absorption as the emission rays passed through the cool outer layer of the sun's atmosphere. This caused the lines to show up dark against the bright background. He also concluded that absorption occurs only at the same wavelength as emission, and for all other wavelengths the gas is transparent. In 1955, two independent papers were published by Alkemade and Milatz and Walsh discussing the techniques used to measure the absorption of a sample and how the data is related to the concentration of the unknown in the sample (1, 31).

Atomic absorption spectrometry as an analytical tool made very little progress due to the absorption being measured was occurring over an extremely narrow part of the spectrum. It would require very high resolution to measure any significant absorption from a continuum lamp. In 1955, Walsh described the hollow cathode lamp line source that would alleviate that problem (31). A line source emits only at discrete wavelength. The spectral lines are narrower than the absorption lines being measured, thus the need for high resonance is not required.

Atomic absorption spectroscopy is a widely used technique for the determination of trace and major elements in a wide range of analyte types. In this technique there are two methods of atomization in which a sample can be atomized. They are flame

atomization and electrothermal atomization (25). Flame atomization is a process in which a sample of solution is broken down into small droplets by a flow of gaseous oxidants mixed with gaseous fuel, and carried into a flame where atomization occurs. Once the sample is carried into the flame the process for desolvation begins to take place. The aerosol is then volatilized into a molecule. The molecules are dissociated into atoms and the measurement is taken. Electrothermal atomization offers a greater sensitivity than that of the flame, due to the short amount of time required to atomize a sample (25). It also requires a smaller volume of the sample. In this method a few microliters of a sample are first evaporated at low temperature and then ashed at a somewhat higher temperature in a electrically heated graphite tube. Once the ashing is complete the current is rapidly increased to several hundred amperes, which causes the temperature to soar to about 2000°C – 3000°C; atomization of the entire sample occurs in a period of a few milliseconds. After atomization the absorbance of the analyte is then measured in the region immediately above the heated surface.

Chemical Modifiers

Electrothermal atomic absorption spectroscopy is also referred to as Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). It is an important tool for the trace element determination in the environmental and clinical fields. In this technique high temperatures are required for the ashing of the sample matrix and the atomization of the analyte. The temperature at which charring occurs can cause the analyte to evaporate prematurely. This early evaporation has an affect upon the absorbance of the analyte. In order to alleviate the problem, of loss of analyte in the pyrolysis process, chemical modifiers were introduced in the sample matrix. The purpose for the addition of

chemical modifiers is to free the analysis from the matrix effect and allow for the determination of trace levels of the analyte (5). Machata and Binder published one of the first papers using chemical modifiers in 1973 (15). They used lanthanum, strontium, aluminum, and cesium in the determination of lead and thallium in blood and urine. The best results were observed with the use of lanthanum. The peak absorbance sensitivity was increased more than thallium by the addition of 1% of lanthanum. The same year Machata and Binder were conducting their research, Matousek and Brodie used H_3PO_4 for the determination of lead in air samples (16). Multiple peaks were observed without the use of H_3PO_4. The year of 1977 was the beginning of the concept of chemical modifiers.

The use of chemical modifiers has become routine procedure during the determination of a wide range of elements in most materials when graphite furnace atomic absorption spectroscopy (GFAAS) is used. These chemical modifiers are selected so that a higher pyrolysis temperatures may be used for volatile analytes in order to reduce or eliminate both background absorption and gas-phase interference (22). A chemical modifier is a chemical that is added to the sample matrix that causes a change in its chemical characteristics. This modification process delays atomization and converts the analyte to a more thermally stable compound (5). Once the analyte is stable, higher temperature can be used and the interfering matrix component can be volatilized before atomization begins.

Although a chemical modifier can retard evaporation of the analyte until the matrix has charred away, it also may cause some problems in the analysis. The need for the use of higher atomization temperature may reduce the characteristic mass due to a

higher rate of diffusion from the tube. Characteristic mass is defined as the mass of the analyte that produces an integrated absorbance of 0.0044-sec (21). According to Frech and L'vov, the analyte may condense with a chemical modifier in cool regions of a graphite tube (8). Chemical modifiers also produce spectral interference.

A chemical modifier must possess a few traits that will not hinder the analysis of the analyte. An ideal chemical modifier must be available in high purity and must stabilize the analyte to a high pyrolysis temperature (3). It can not significantly reduce the life time of the graphite furnace nor cause spectral interferences. A good modifier would be applicable to a wide variety of elements and not contain an element in high concentration that may be determined at trace levels (3). Butcher and Sneedon says that some commonly used modifiers are magnesium nitrate, ammonium dihydrogen or diammonium hydrogen phosphate, nickel (nitrate), and palladium (nitrate) (3).

Several chemical have been suggested for the use as chemical modifiers for the determination of a wide variety of substances. Six of them are palladium(Pd), ruthenium(Ru), rhodium(Rh), iridium(Ir), platinum(Pt), and osmium(Os). These platinum metals have appeared to be efficient modifiers because they have the potential to be universal modifiers for the analysis of countless numbers of analytes says McDonald (17).

Palladium has been established as a universal modifier, but Schelmmer and Welz says that a mixture of palladium and magnesium nitrate can also be used as a universal modifier for the determination of various elements (23). McDonald state that the addition of a reducing agent to the palladium modifier was to in sure that the modifier is reduced to a metal early in the temperature program (18). A study of palladium in comparison

with rhodium and ruthenium with the addition of a reducing agent was conducted by Tsalev and Slaveykova (28). They stated that in the presence of an absorbic acid reductant, the pretreatment temperature of the three modifiers were similar or higher by +50°C to +250°C for most volatile analytes. Through most of the analysis ruthenium had the highest pretreatment temperature. Thus indicating that ruthenium mixed with absorbic acid is more efficient than that of palladium and absorbic acid for the analysis of As, Ge, In, P, Se, Te, and Tl.

The use of palladium as a chemical modifier in graphite furnace atomic absorption spectroscopy has been well recognized and proves to be an efficient collector for trapping of volatile hydrides. Palladium has been studied in a carbide-coated platform as a permanent modifier for hydride-forming elements in GFAAS. Tsalev, D'Ulivo, Lampugnani, Di Marco, and Zamboni state that there are certain advantages of a palladium coated graphite tube or platform (27). It has demonstrated (i) high trapping efficiency, (ii) relatively low collection temperatures, (iii) small modifier mass, (iv) improved GFAAS performance characteristics for volatile elements, resulting in better sensitivity, particularly in peak height measurements, and (v) more uniform and less critical parameters of thermal programming for different analytes, which greatly facilitates the multi-element sequestration and quantification (27).

Ruthenium is another platinum metal that has been suggested as a chemical modifier study of the performance of ruthenium was conducted by Littlejohn (13). Ruthenium was compared to palladium according to McDonald (18). The modifiers were reduced before the sample was injected. When hydrogen was used with 2 μg of palladium a charring temperature up to 1100°C was reached. Ruthenium produced a

higher sensitivity for the 0.5 ng of lead. The results for the preconditioning method were somewhat similar to that of the addition of the reductant. The charring temperature reached for palladium was 1100°C and for the ruthenium 1000°C. The sensitivity of ruthenium when compared with that of palladium was once again higher, according to McDonald (18).

Rhodium has also been suggested for the determination of elements. There is limited publication concerning the performance of rhodium as a chemical modifier. According to Tsalev and Slaveykova, it is less volatile than ruthenium and palladium with the addition of absorbic acid (28). Rhodium proved to be more efficient than palladium in elements such as As, In, P, Se, Te, and Ti (28).

Iridium is one of the platinum metals that has been suggested as a chemical modifier for the determination of various elements. A study was performed on thermally stabilized iridium on an integrated carbide-coated platform as a permanent modifier for hydride forming elements in GFAAS. This study, conducted by Tsalev, D'Ulivo, Lampugnani, Di Marco, and Zamboni, found that iridium is very strongly stabilized on carbide coated surfaces (27). They also stated that the volatilization losses started only at temperatures above 2050°C - 2100°C and cleanout temperatures can also be safely increased up to 2100°C - 2150°C. At these working temperatures Ir would be expected to be in its solid state. It would also appear to be bounded more strongly to the carbide-coated surface of the platform. Tsalev, D'Ulivo, Lampugnani, Di Marco, and Zamboni concluded that iridium is a more promising efficient thermal stabilizer for numerous volatile elements (27). They also noted that this statement is true if the pyrolysis, atomization, and cleanout temperatures are kept below 1400°C, 2050°C - 2100°C, and

2200°C respectively. Iridium was better stabilized on tungsten treated platforms than the zirconium treated platforms.

Lead Determination

Lead determination in biological materials has been widely studied. For the analysis of lead several techniques have been suggested. The technique of anodic stripping voltammetry/DPASV is one them (2). This analytical method provided excellent quantification capabilities and it is very useful as independent reliable method in comparative studies and in biological samples. There has been several application of this methods to biological materials. Another analytical tool is inductively coupled plasma-atomic emission spectrometry (ICP-AES) (2). This techniques offers multielement capabilities with limit of detection for the pneumatic nebulization, electrothermal vaporization, ultrasonic nebulization, and preconcentration levels to be 14 µg/L, 17 µg/L, 1 – 5 µg/L, and 0.5 - 0.6 µg/L, respectively. Inductively coupled plasma-mass spectrometry also has been suggested as a method of analysis. This technique has a much better limit of detection. It is valuable in metabolic, nutritional, occupational/environmental health studies of lead isotope ratios and speciation. The technique that is best used for the detection of lead is the graphite furnace atomic absorption spectroscopy. Along with this technique additives and chemical modifiers were used. Suitable additives for the GFAAS for lead are diluted HNO_3 and diluted H_3PO_4, organic acids and their ammonium salts, aqueous Triton X-100, and many others (2). Most of these chemicals are common dilutents and modifiers. They provide moderate stabilization and other beneficial effects.

Chemical modifiers have been instrumental in the determination of lead. "In the absence of the modifiers the pyrolysis temperatures for lead are confined only to 350°C - 550°C with aqueous solutions and 300°C - 400°C with dithiocarbomate extracts. The premature lose of analyte is due to the high volatility of many lead species" (2). When chemical modifiers were used lead was stabilized with in the temperature range of 600°C - 1200°C. The atomization temperatures should be increased to 1800°C - 2000°C in order for the atomization of the stabilized lead may take place. Many modifiers with single components and mixed components have been tested for the detection of lead (2).

Several types of modifiers have been used in the analysis of lead. Phosphate based modifiers have been proven to be very reactive toward lead (2). They are able to shift the pyrolysis temperatures up to 650°C - 900°C. Ammonium hydrogen phosphates are more efficient that orthophosphoric acid. The disadvantages of these modifiers are excessive background absorption and blank contributions. The over stabilization effect has been observed as high concentration of the modifiers. Nobel metals have also been used for the determination of lead. They are more efficient thermal stabilizers for very small masses of the analyte. Palladium has been deemed the preferential modifier over rhodium and ruthenium. Platinum shows the same performance as palladium, but it is less reactive and difficult to keep in solutions. Palladium gives much better in the presence of reductants in lead analysis (2).

The determination of lead has been a major concern of the Center for Disease Control (CDC). Lead poisoning is a common health problem in the United States. According to McDonald it is associated with industrialization, and the distribution of lead in the environment (17). Low levels of lead in the blood can have adverse effects. This

has been proven scientifically by the Center for Disease Control and Prevention (CDCP). Several techniques have been suggested for the determination of lead in blood samples. The most popular technique is Graphite Furnace Atomic Absorption Spectrometry. This technique has increased the sensitivity of the analysis to the parts per billion level. It has also decreased sample handling requirements and has excellent selectivity. The earliest blood lead analysis was reported by Fernandez (7). He diluted the blood with Triton-X, but did not add any modifier. The determination of lead is not as simple as Fernandez put it, because of the spectral and non-spectral interferences. In order to avoid these problems special procedures are to be followed. The use of chemical modification helps alleviate interferences in the determination of lead by GFAAS. The addition of the modifier to the sample permits the removal of inferents during charring by retarding the analyte atomization.

The most common non-spectral interference the lead experiences in the analyte volatilization. This due to lead forming halides. To overcome this problem (i) the use of ammonium nitrate, as chemical modifier, with the L'vov platform, (ii) the use of matrix modifiers in a pyrolytic graphite tube, and (iii) employing the mixture of modifiers with the L'vov platform and Zeeman effect background correction. According to Navarro, Granadillo, Parra, and Romero phosphate based matrix modifiers induce the formation of thermally stabilized lead phosphate species (20). These species retard the release of lead atoms in the gaseous phase. They also stated that lead can be determined in a halide matrix using ammonium phosphate as the chloride. This chloride could be pre-volatilized as ammonia chloride. Navarro, Granadillo, Parra, and Romero further stated that salts such as $NH_4H_2PO_4$ are the preferred matrix modifiers for lead, because they

control the volatility of the analyte and the concomitants (20). They also concluded that magnesium, as $Mg(NO_3)_2$, has also demonstrated to be a useful chemical modifier for the determination of lead because it permits charring at higher temperatures. Since Slavin showed the function of the adding Mg is to imbed the analyte in a matrix of magnesium oxide, delay volatilization of the analyte until the magnesium oxide is vaporized, and thus reducing the interference effect. Navarro, Granadillo, Parra, and Romero (20) concluded that a mixture of $NH_4H_2PO_4$ and $Mg(NO_3)_2$ should be sufficient to compensate for the interferences in GFAAS determination of lead (20).

Navarro, Granadillo, Parra, and Romero observed the loss of lead at lower charring temperature in the absence of a chemical modifier for their research of the determination of lead in whole blood by GFAAS with matrix modification (20). The integrated absorbance measured increased for $NH_4H_2PO_4$ concentrations. A further increase was noted with the mixture of $NH_4H_2PO_4$ and $Mg(NO_3)_2$ modifiers. A decrease in the integrated absorbance signals were obtained when an excessive amount of modifiers was used. This was due to the over stabilization of the analyte which delayed atomization of the lead says Navarro, Granadillo, Parra, and Romero (20).

The use of platinum metals as chemical modifiers has been suggested for the determination of lead. Palladium, ruthenium, rhodium, iridium, platinum, and osmium have been used in the analysis of various elements. Palladium is the most studied platinum metal, and has been established as a modifier that was utilized in several analysis by Schemmer and Welz (23). Platinum, rhodium and iridium also has been investigated as potential modifiers for the analysis of lead. A comparative study of each of the platinum metals role in the determination of lead has not been studied. Nor has the

affect of ashing temperatures on the ability of the six platinum metals to serve as chemical modifiers.

The purpose of this thesis research project was to study the use of rhodium as a chemical modifier for the determination of lead. Also, this research involved the study of how ashing temperatures affect this metal's ability to perform as modifiers.

CHAPTER 2

EXPERIMENTAL METHODS AND PROCEDURES

Apparatus

A Perkin-Elmer Zeeman 4100ZL Atomic Absorption Spectrophotometer equipped with an HGA Atomizer, an AS-72 autosampler and 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 solutions and modifiers were prepared by diluting appropriate reagents with the highest available purified water with 1 % nitric acid. The high purity water was obtained by using a Milli - Q Plus System with Milli - RO6 System (Millipore). Certified 1000 mg/L lead atomic absorption solution and certified 1000 mg/L rhodium atomic absorption standard were purchased from Sigma Chemical Company, St. Louis Mo. to use as modifiers and to make samples. All working solutions were stored and measured in plastic war which were soaked for at least two days and cleaned with detergents and rinsed thoroughly with high-purity water. The Plus-grade argon gas was 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-Sweewerk Perkin-Elmer (Uberlingen, Germany)

Tube Conditioning

New graphite tubes should be conditioned prior to analytical use by cleaning at high temperatures. The conditioning process removes impurities on the tube surface and in the tube materials. 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

The conditions and procedures outlined below were followed. The standard furnace temperature program is described in Table 2. Ashing temperature studies were performed by changing the temperature in the charring steps in Table 2. The atomization temperature was maintained at a constant temperature of 1500°C. Lead measurements were made at a wavelength of 283.3 nm.

The sample insertions into the furnace were performed by using the AS-72 programmable sample dispenser. The sample dispenser picked up separate aliquots of the sample, modifier, and diluter into the capillary then deposited the entire volume into the furnace. A total ranging from 12 µL to 19 µL was deposited. A 400-ppb lead standard was used as a stock solution. It was prepared from a 1000ppm standard. The pure stock solution of 1000 ppm of rhodium was utilized in the research. A 2 µL sample of the rhodium standard was used in the measurements. All solution were acidified to a final volume with HNO_3 that had a concentration of 1% v/v.

TABLE 1

Furnace Program to Condition Graphite Tube

Step #	Temperature (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

Graphite Furnace Conditions

The graphite furnace conditions are shown in Table 2. It involves five steps. These steps are drying, ashing, atomization, and cleanout. The primary purpose of the ashing step is to eliminate the bulk material associated with lead interference. During this step, the temperature is increased as high as possible to volatilize the matrix components. However, the temperature is kept below the temperature at which the analyte began to deteriorate. The purpose of the atomization step is to produce an atomic vapor of the analyte elements, therefore allowing atomic absorption to be measured. The temperature in this step is increased to the point where dissociation of the volatilized molecular species occurs.

TABLE 2

Graphite Furnace Parameter

Step #	Function	Temperature (°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	800 – 1200	10	20	250	
4	Atomization	1500	0	5	0	
5	Clean Out	2450	1	3	250	

CHAPTER 3

RESULTS AND DISCUSSION

Effects of Ashing Temperature

The absorbance of the lead sample was affected greatly by the ashing temperatures. The ashing temperatures ranged from 900°C - 1300°C; and the atomization temperature was kept constant at 1500°C. In figures 1 - 5 are the results for the lead samples that were analyzed without the presence of the modifier at the varying ashing temperatures. Figure 1 shows the absorbance peak of 5 µL of a 400-ppb solution measured at an ashing temperature of 900°C and an atomization temperature of 1500°C. Figure 2 exhibits a 5 µL sample that was measured at 1000°C and 1500°C. These temperatures are the ashing and atomization temperatures, respectively. Figures 3 - 5 also show the absorbance measurement for a 5 µL sample of lead. The parameters at which these measurements were taken are 1100°C, 1200°C, 1300°C, respectively. The atomization temperature remained at 1500°C. These figures show that as the ashing temperature increased the absorbance of lead decreased. Table 3 shows that the absorbance of the lead samples without the modifier. The ashing temperatures at which the lead concentration was measured in a significant amount varied from 900°C - 1100°C. At temperatures higher than 1100°C, a notable decrease in absorbance was observed. The introduction of a modifier to the lead sample proved to be a positive addition. The analysis of lead, in the presence of a modifier, was performed at ashing

temperatures ranging from 900°C - 1300°C. A 2 μL solution of rhodium modifier, with a concentration of 1000 ppm, was added to the 400 ppb Pb sample. The results for this study are shown in Figures 6 – 10 and a comparison of the absorbance signals is shown in Table 3. Figure 6 shows the absorbance signal for 5 μL of lead and 2 μL of Rh. The ashing and atomization temperatures were 900°C and 1500°C, respectively. As shown in Table 3 the signal increased with the presence of the modifier. The signal in Figure 6 increased by 0.54% when compared with the signal in Figure 1. Figure 7 shows the absorbance of 5 μL of lead and 2 μL of Rh at an ashing temperature of 1000°C and at an atomization temperature of 1500°C. An increased of 1.60% was also noted in the absorbance signal when compared with the signal in Figure 2. In Figures 8 - 10, a decrease in the absorbance was noted in comparison with the signals in Figures 3 - 5. A comparison of the absorbance signals is shown in Table 3. In Figure 8, the abosorbance decreased by 4.53%, and in figure 9 the absorbance decreased by 18.63%. The addition of the modifier increased the absorbance signal of the lead, however at ashing temperatures higher than 1000°C the signal began to decrease. The same pattern, followed by the absorbance signals of the lead in the absence of the chemical modifier, was also followed by the signals with the presence of the modifier. As the ashing temperatures increased the absorbance decreased. At temperatures higher than 1100°C, a great loss of analyte was noted.

TABLE 3

A Comparison of the Absorbance Signals

Temperature (°C)	Lead sample mean abs.	Lead sample + Rh mean abs.	Blood lead sample mean abs.	Blood lead sample + Rh mean abs.	Blood lead sample + Rh + H_3PO_4
800	*	*	0.0443	0.0611	0.0641
900	0.2398	0.2411	0.0399	0.0477	0.0593
1000	0.2393	0.2432	0.0316	0.0296	0.0379
1100	0.2326	0.2229	0.0131	0.0027	-0.0022
1200	0.0936	0.0789	*	*	*
1300	-0.0084	-0.0026	*	*	*

* Measurements were not taken at this temperature.

Figure 1. The Absorbance of 5 μL of Pb at an Ashing Temperature of 900°C

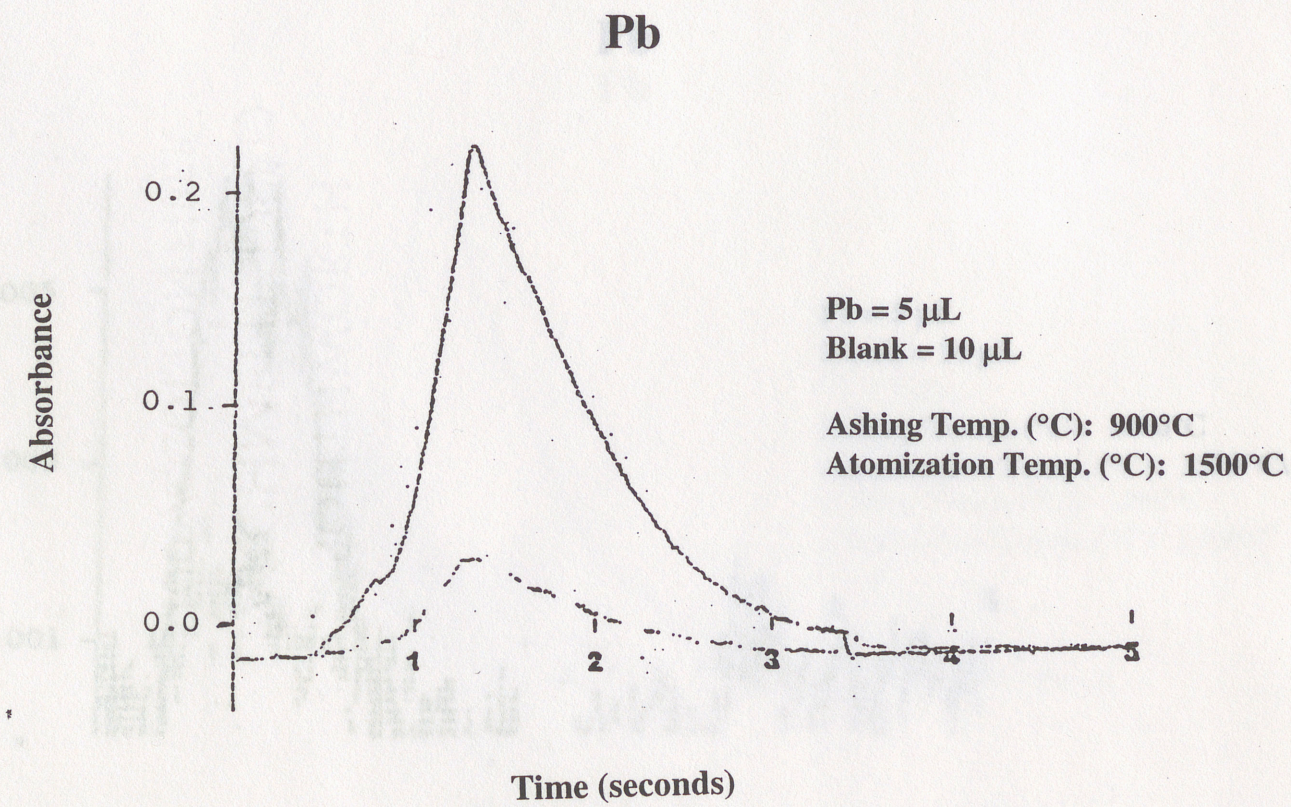


Figure 2. The Absorbance of 5 μL of Pb at an Ashing Temperature of 1000°C

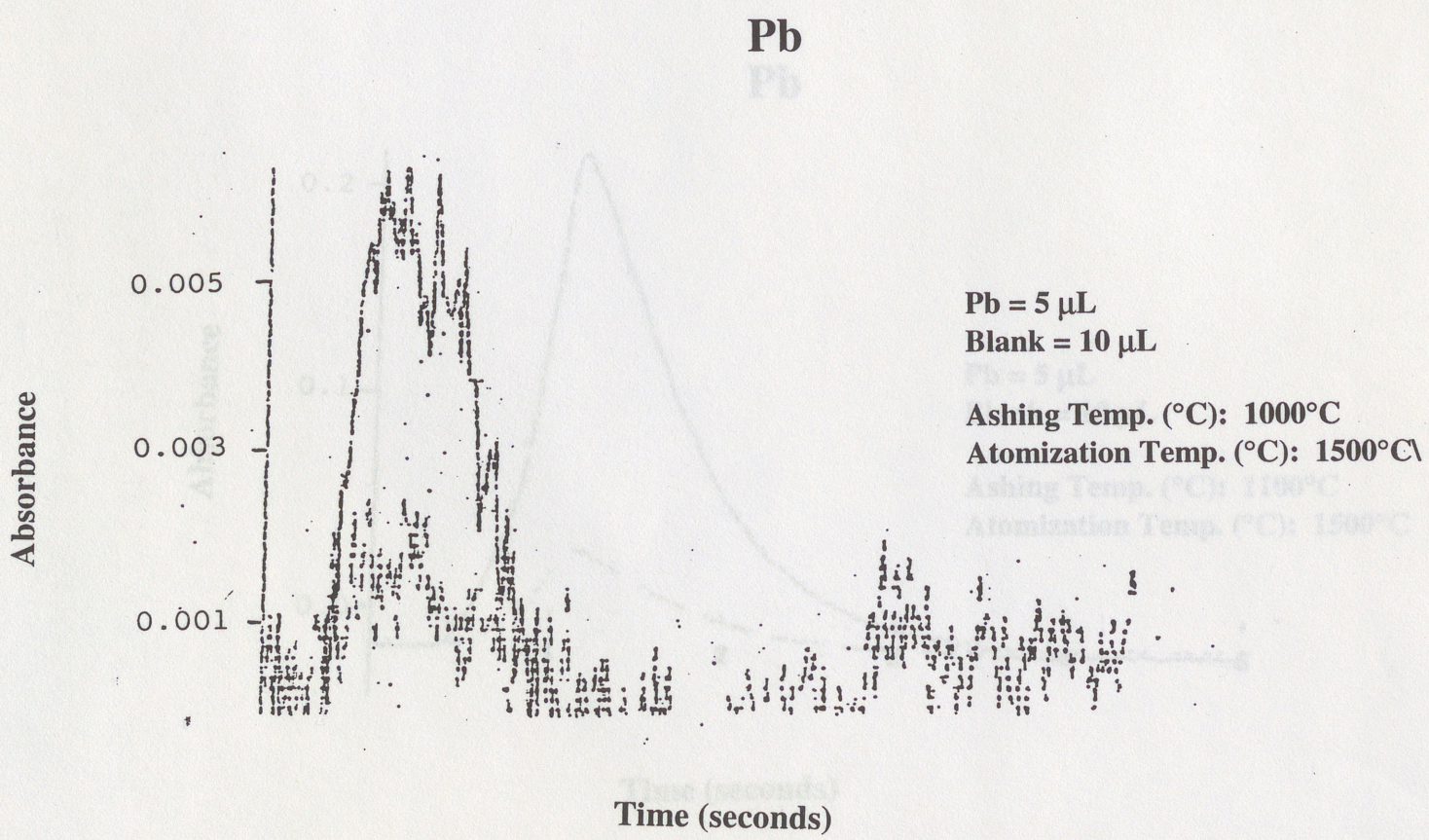


Figure 3. The Absorbance of 5 μL of Pb at an Ashing Temperature of 1100°C

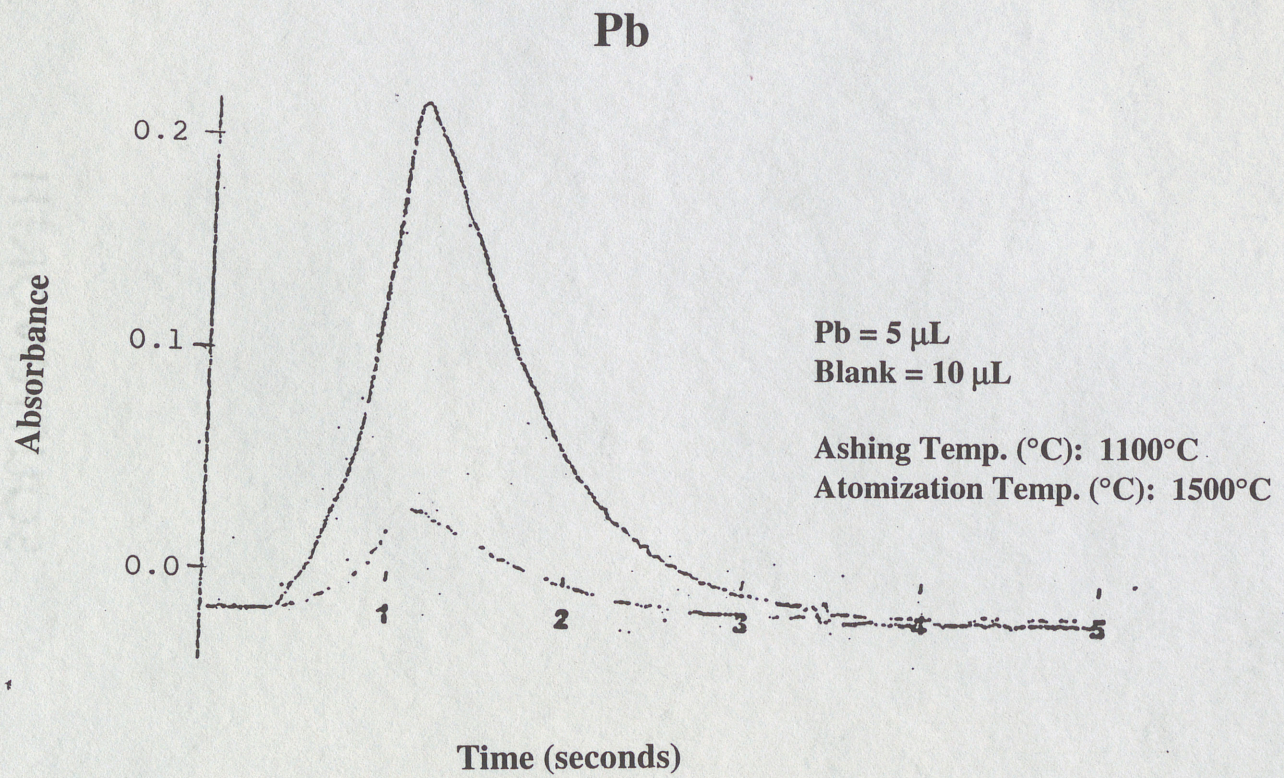


Figure 4. The Absorbance of 5 μL of Pb at an Ashing Temperature of 1200°C

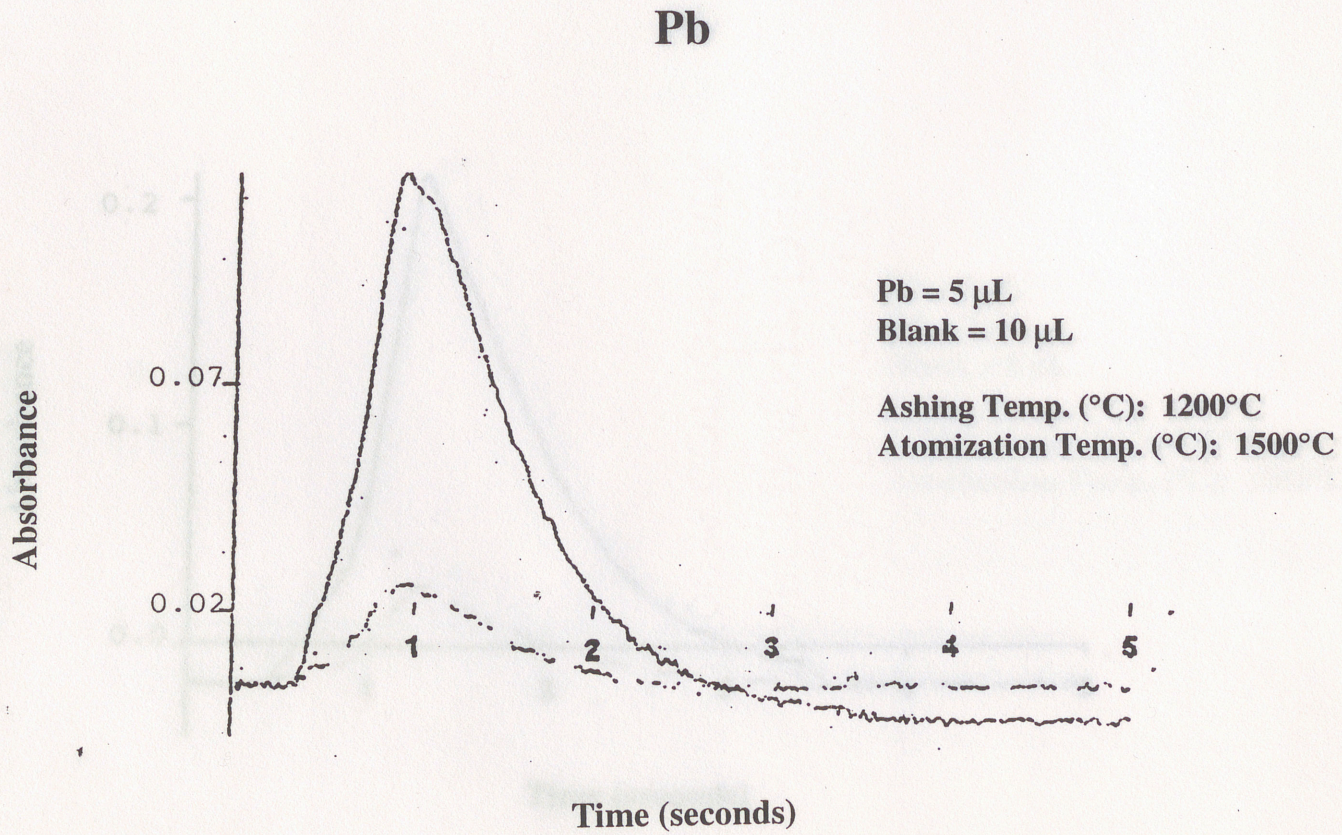


Figure 5. The Absorbance of 5 µL of Pb at an Ashing Temperature of 1300°C

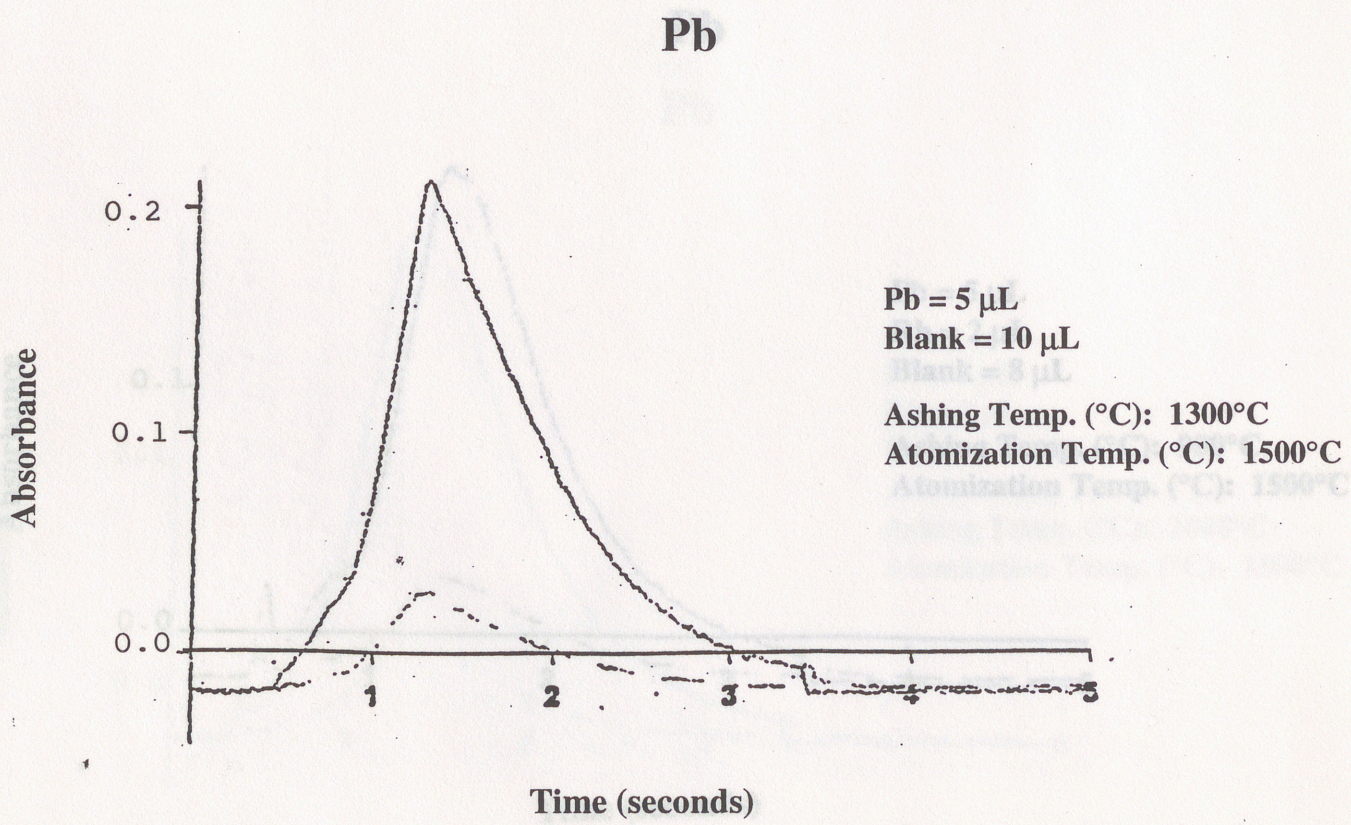


Figure 6. The Absorbance of 5 μL of Pb and 2 μL of Rh at an Ashing Temperature of 900°C

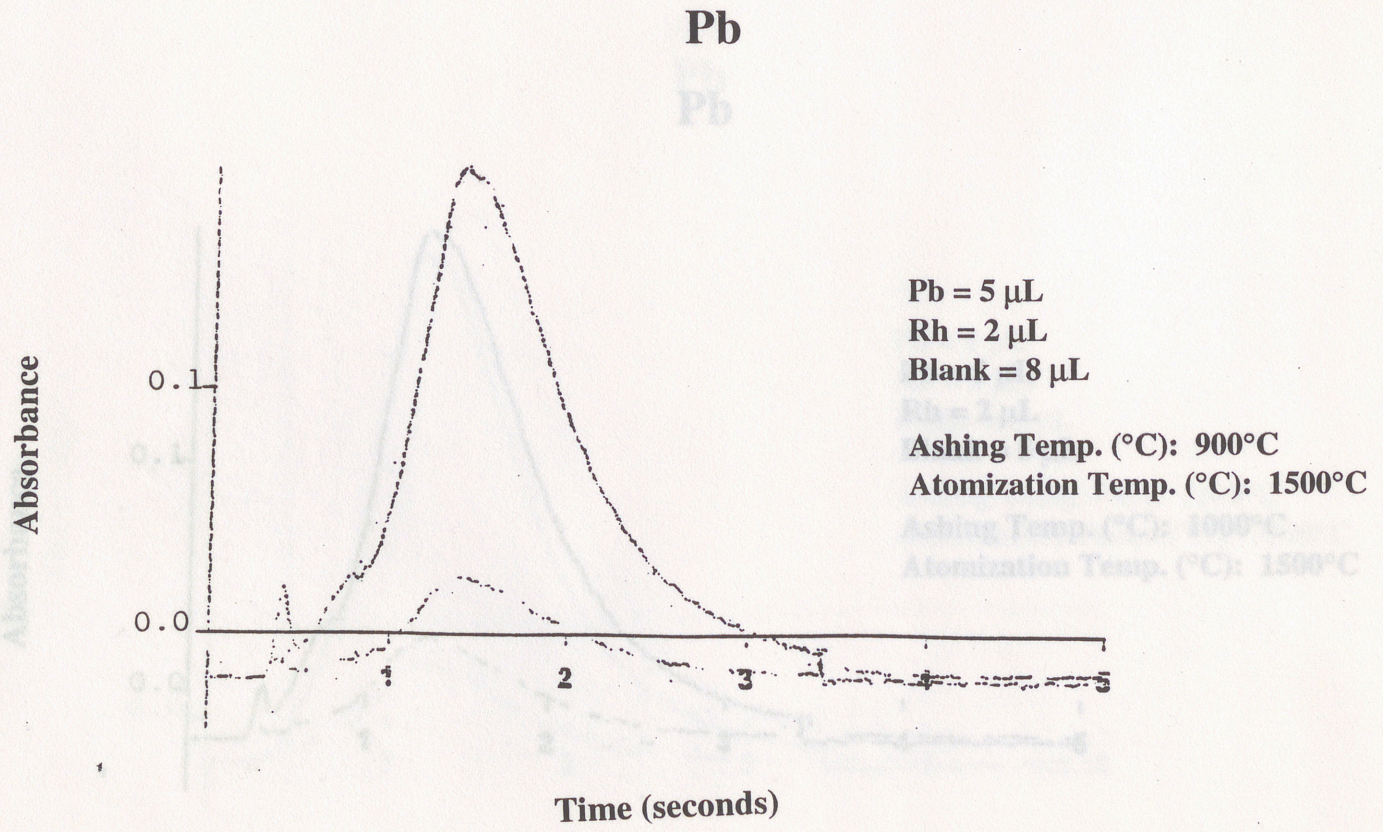


Figure 7. The Absorbance of 5 μL of Pb and 2 μL of Rh at an Ashing Temperature of 1000°C

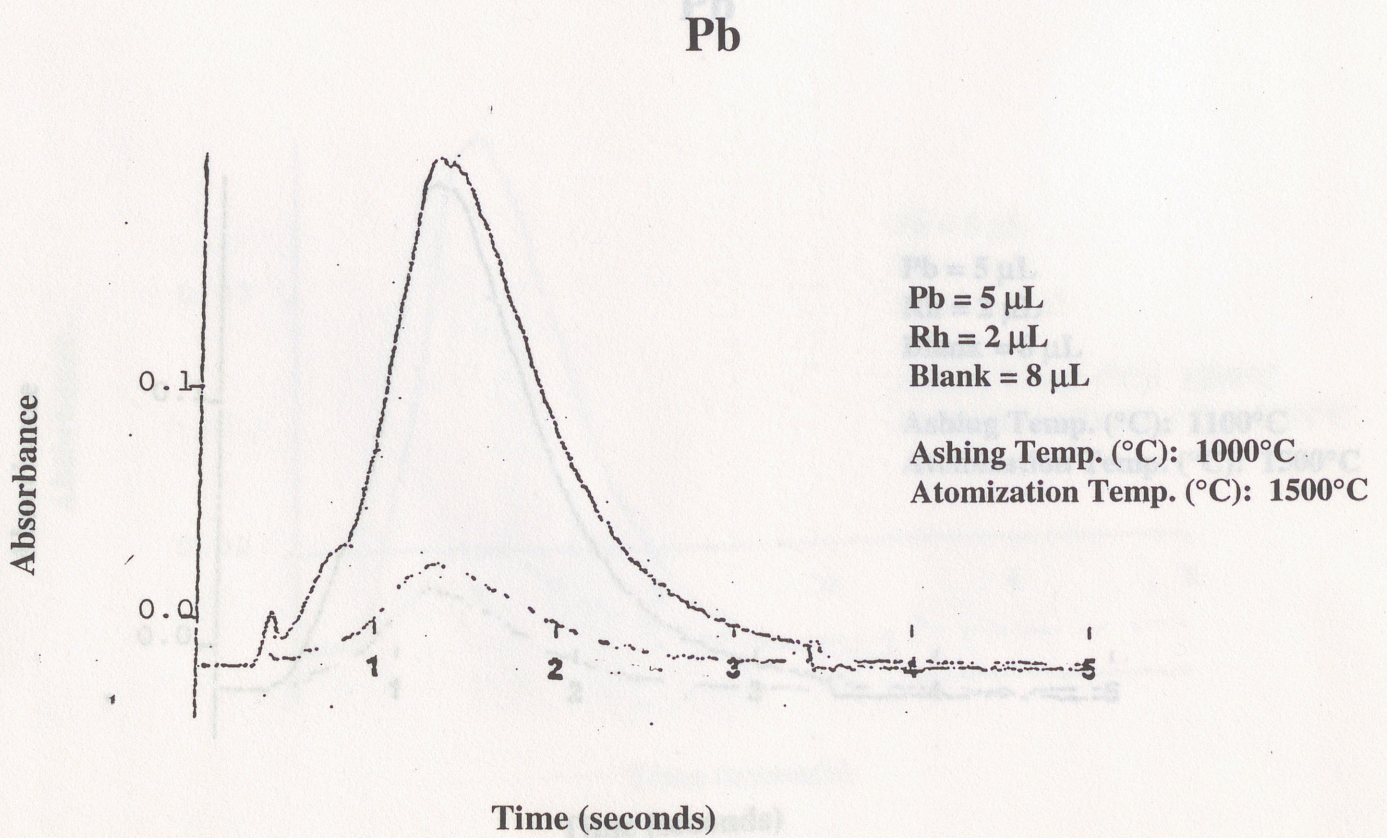


Figure 8. The Absorbance of 5 μL of Pb and 2 μL of Rh at an Ashing Temperature of 1100°C

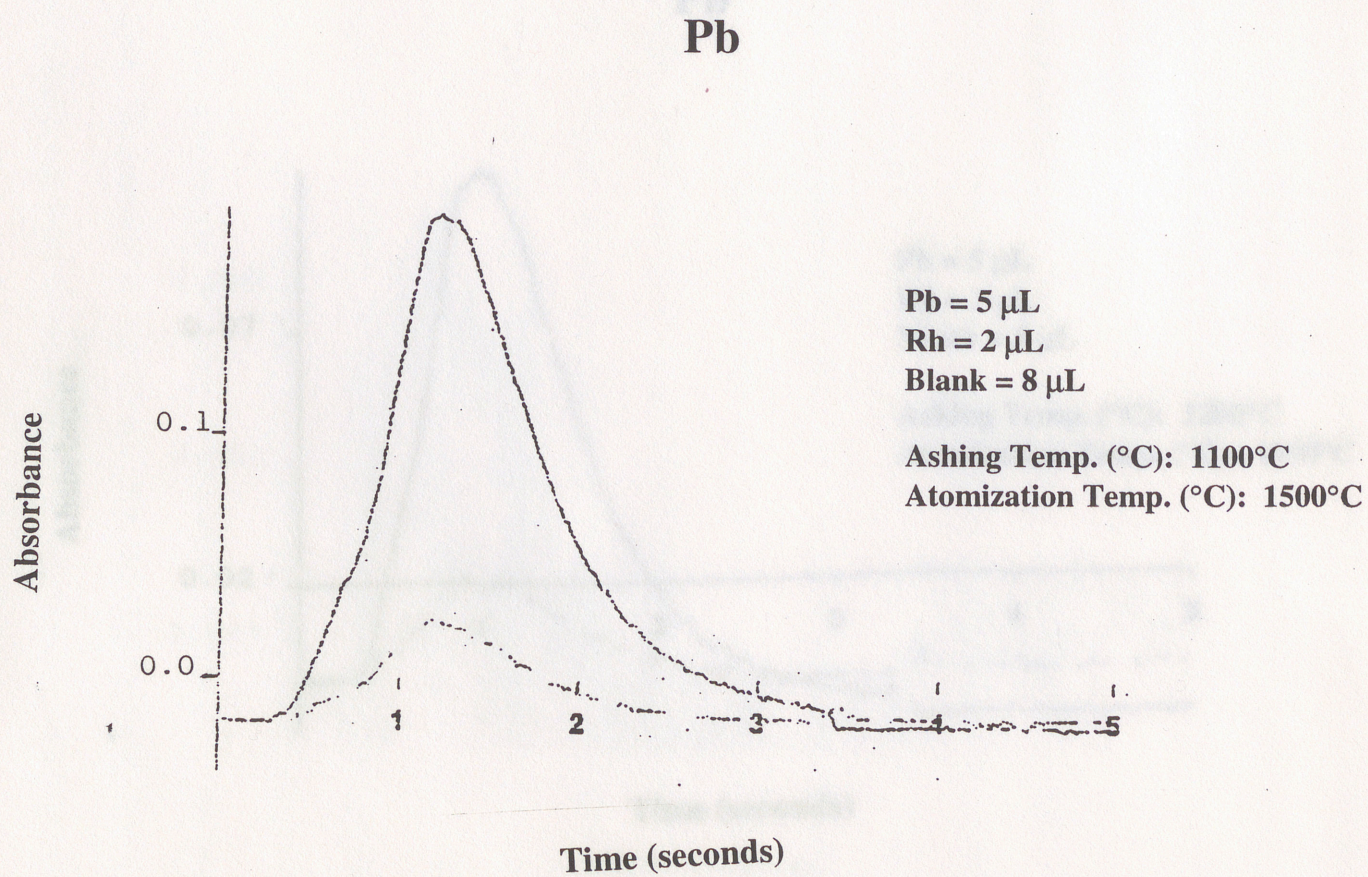


Figure 9. The Absorbance of 5 μL of Pb and 2 μL of Rh at an Ashing Temperature of 1200°C

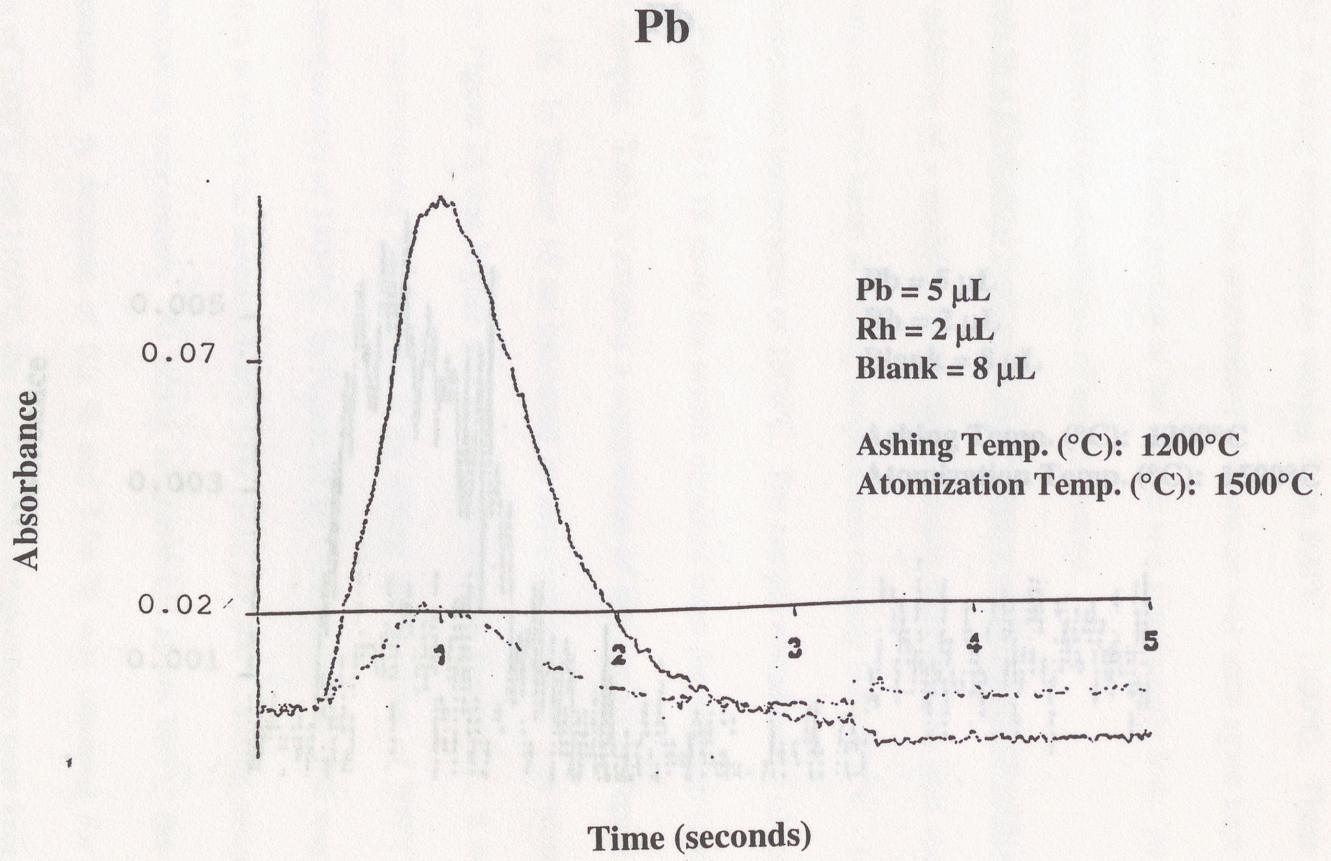
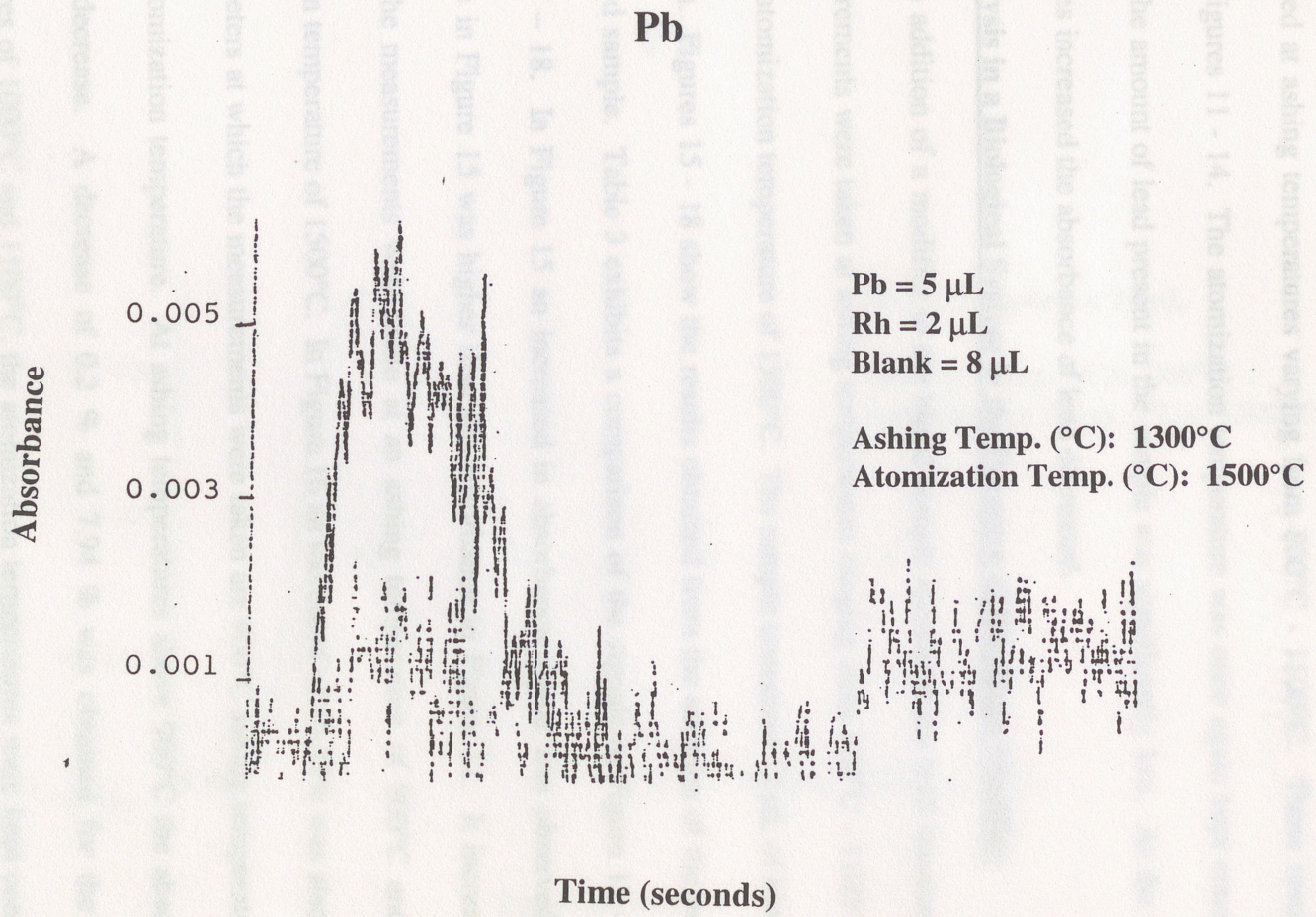


Figure 10. The Absorbance of 5 μL of Pb and 2 μL of Rh at an Ashing Temperature of 1300°C



Lead Analysis in a Biological System

The analysis of lead in blood samples were performed. A 12 μL sample of blood was analyzed at ashing temperatures varying from 800°C - 1100°C. These results are shown in Figures 11 - 14. The atomization temperature was once again kept constant at 1500°C. The amount of lead present in the sample was significantly low. As the ashing temperatures increased the absorbance of lead decreased.

Lead Analysis in a Biological System in the Presence of Rhodium Modifier

The addition of a modifier to the blood sample increased the lead measurement. The measurements were taken at ashing temperatures ranging from 800°C - 1100°C, and a constant atomization temperature of 1500°C. The sample contained 12 μL of blood and 2 μL of Rh. Figures 15 - 18 show the results obtained from the addition of the modifier to the blood sample. Table 3 exhibits a comparison of the signals in Figure 11 – 14 to Figures 15 – 18. In Figure 15 an increased in absorbance signal was observed. The absorbance in Figure 15 was higher than the absorbance in Figure 11. It increased by 27.5%. The measurements were taken at an ashing temperature of 800°C and at an atomization temperature of 1500°C. In Figure 16 an increased of 16.35% was also noted. The parameters at which the measurements were taken are 900°C ashing temperature and 1500°C atomization temperature. At ashing temperatures above 900°C the absorbance began to decrease. A decrease of 0.2 % and 7.94 % was obtained for the ashing temperatures of 1000°C and 1100°C, the atomization temperatures were kept constant at 1500°C. These results are shown in Figures 17 - 18. At 1100°C ashing temperature a loss of the analyte was noted.

Figure 11. The Absorbance of 12 μL of the Blood Sample at an Ashing Temperature of 800°C

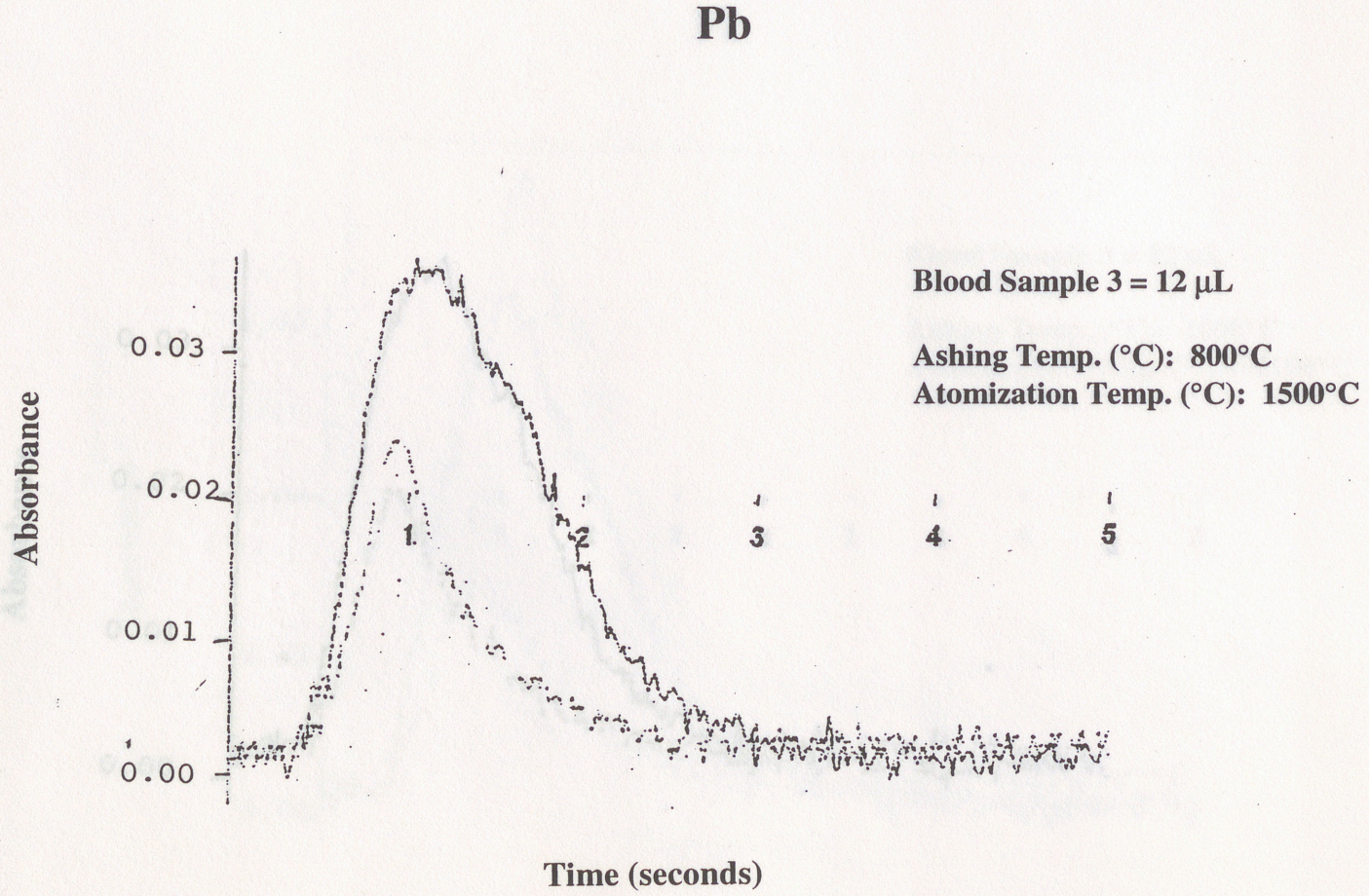


Figure 12. The Absorbance of 12 μL of the Blood Sample at an Ashing Temperature of 900°C

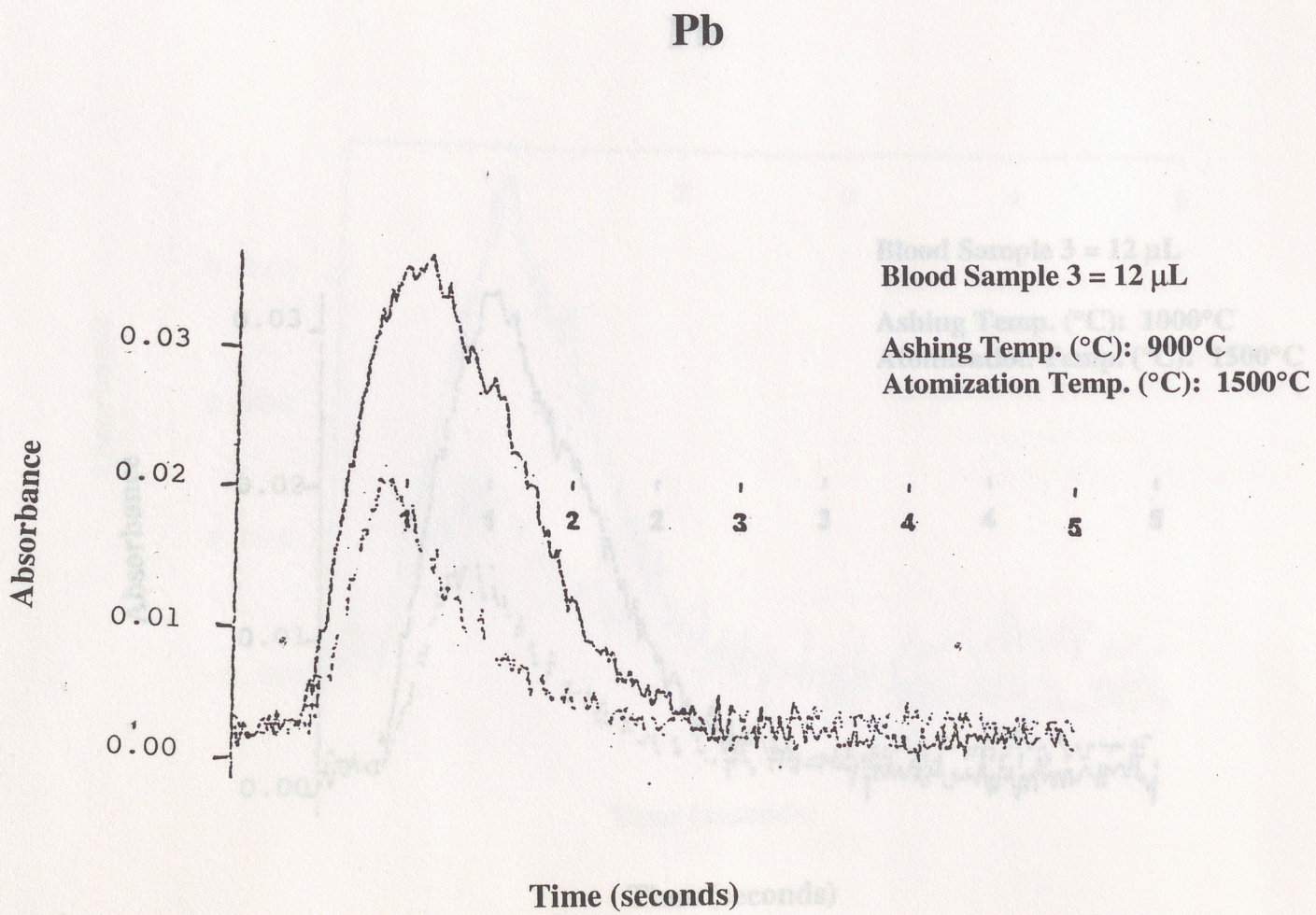


Figure 13. The Absorbance of 12 μL of the Blood Sample at an Ashing Temperature of 1000°C

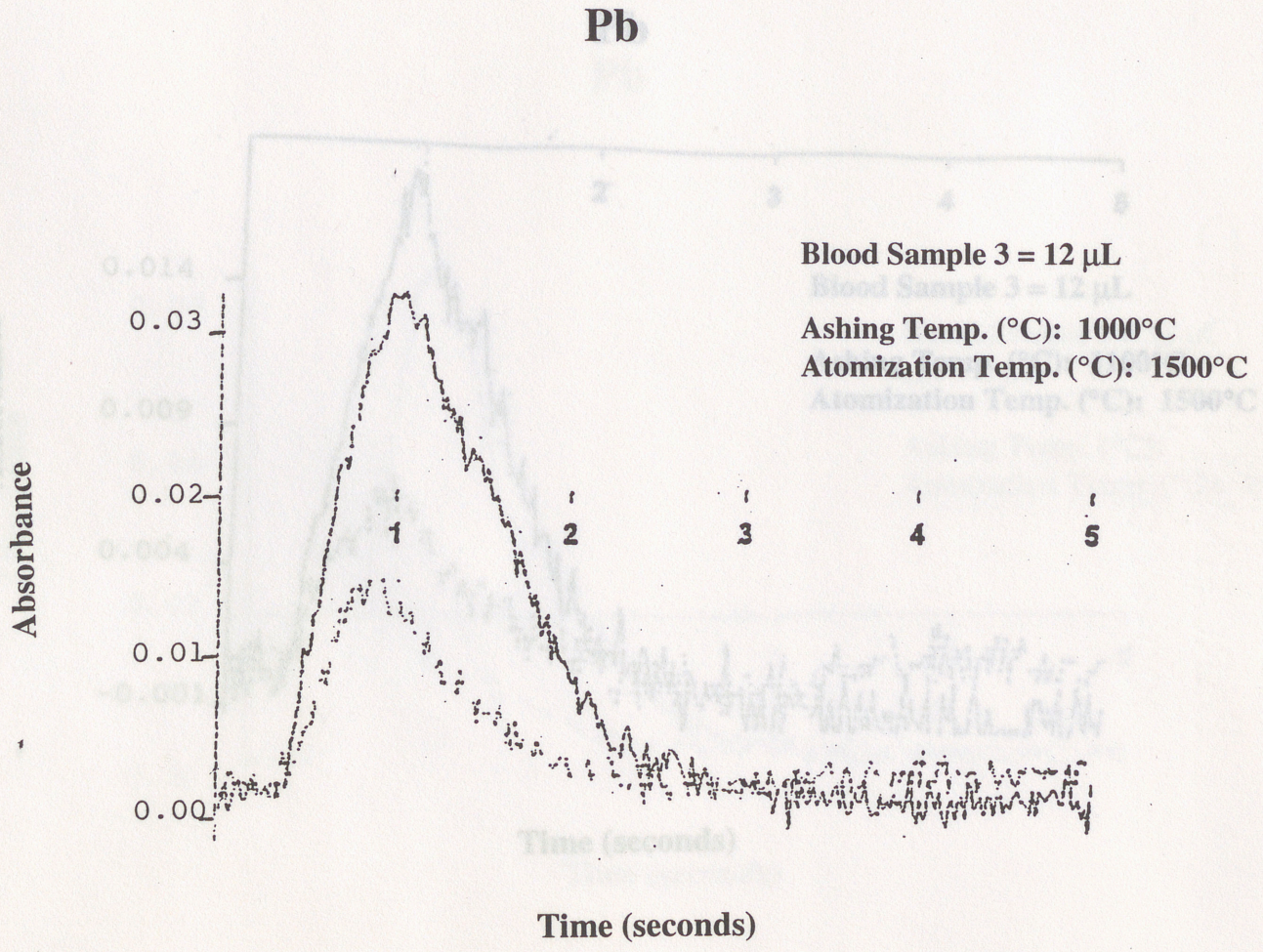


Figure 14. The Absorbance of 12 μL of the Blood Sample at an Ashing Temperature of 1100°C

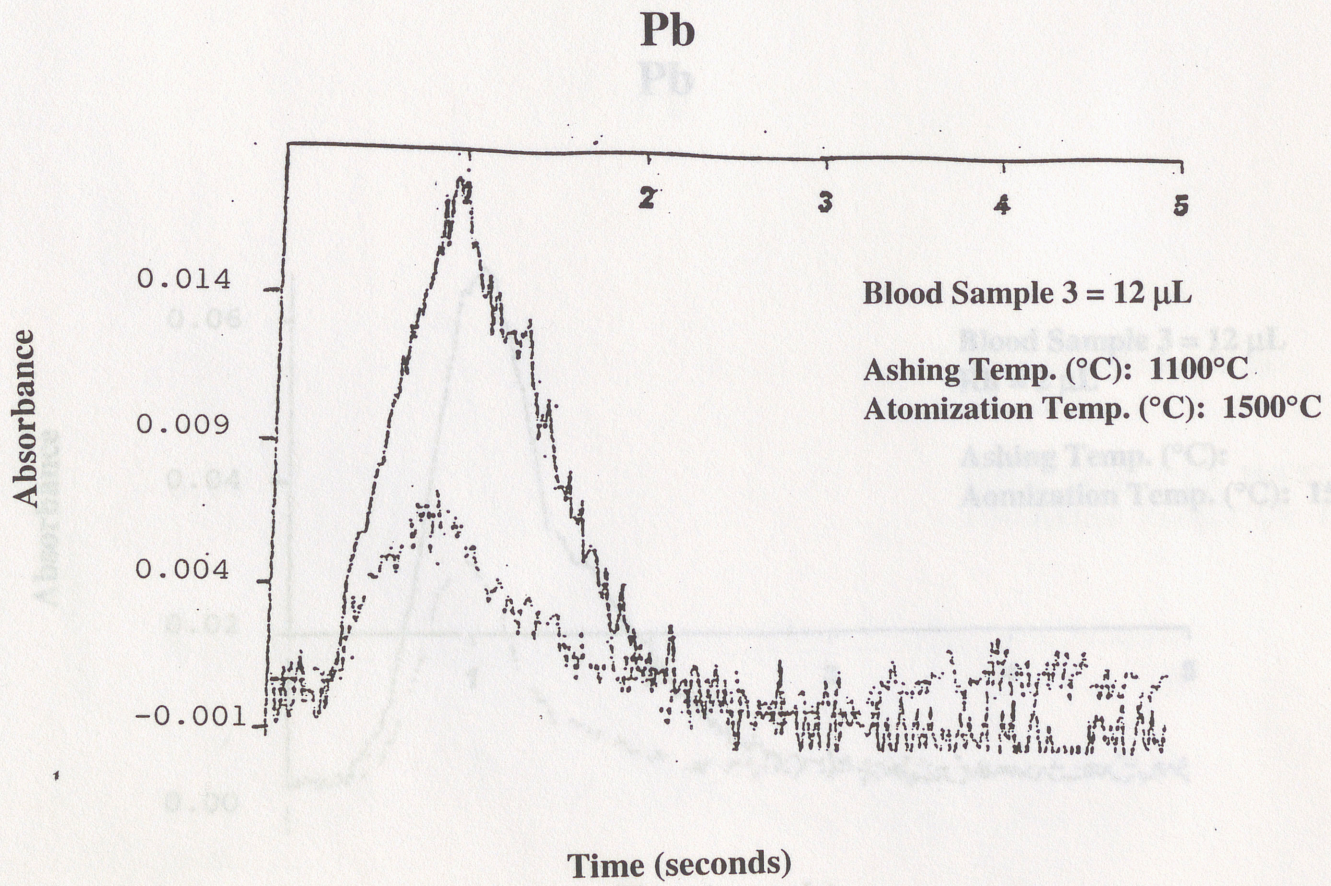


Figure 15. The Absorbance of 12 μL of the Blood Sample and 2 μL of Rh at an Ashing Temperature of 800°C

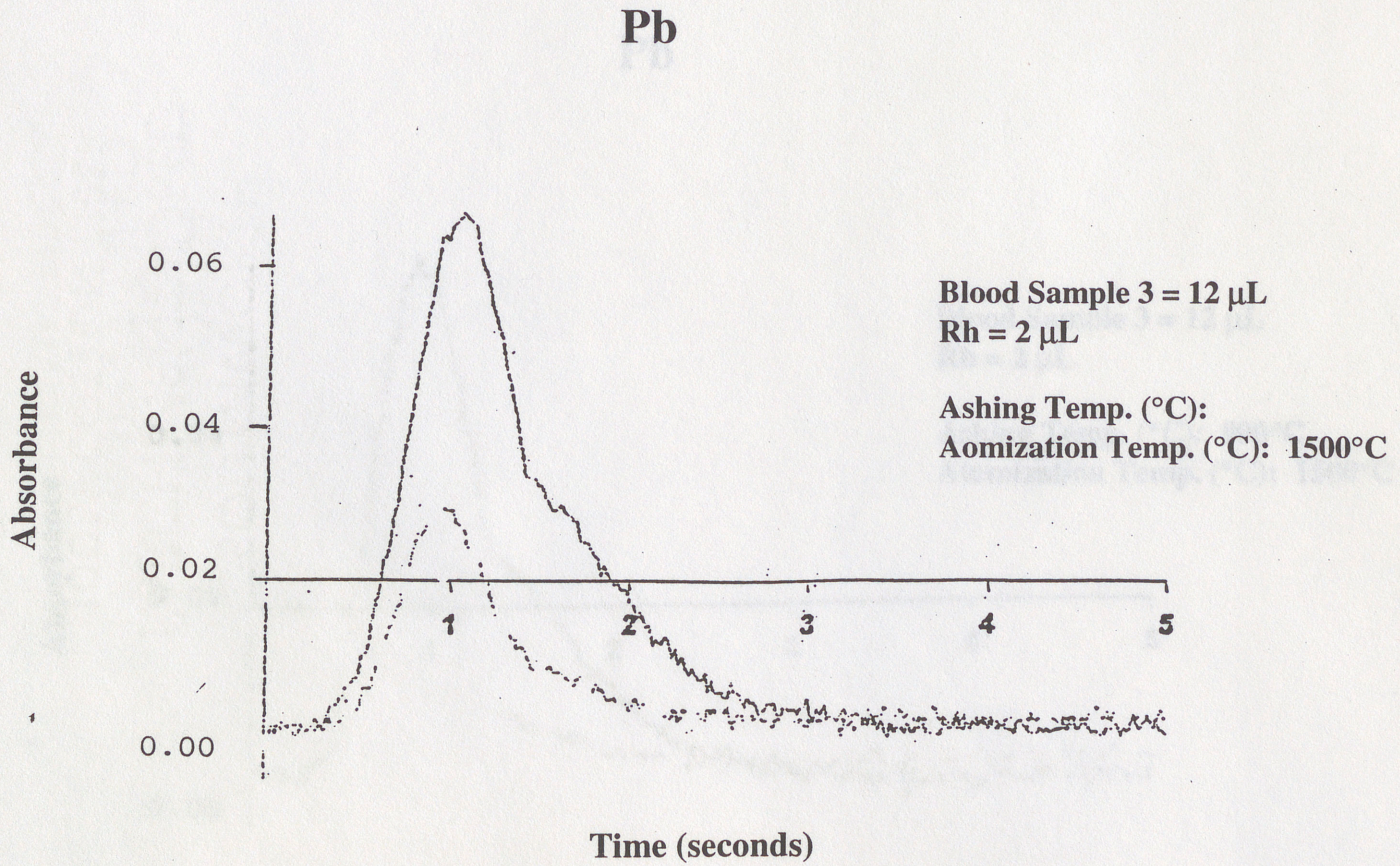


Figure 16. The Absorbance of 12 μL of the Blood Sample and 2 μL of Rh at an Ashing Temperature of 900°C

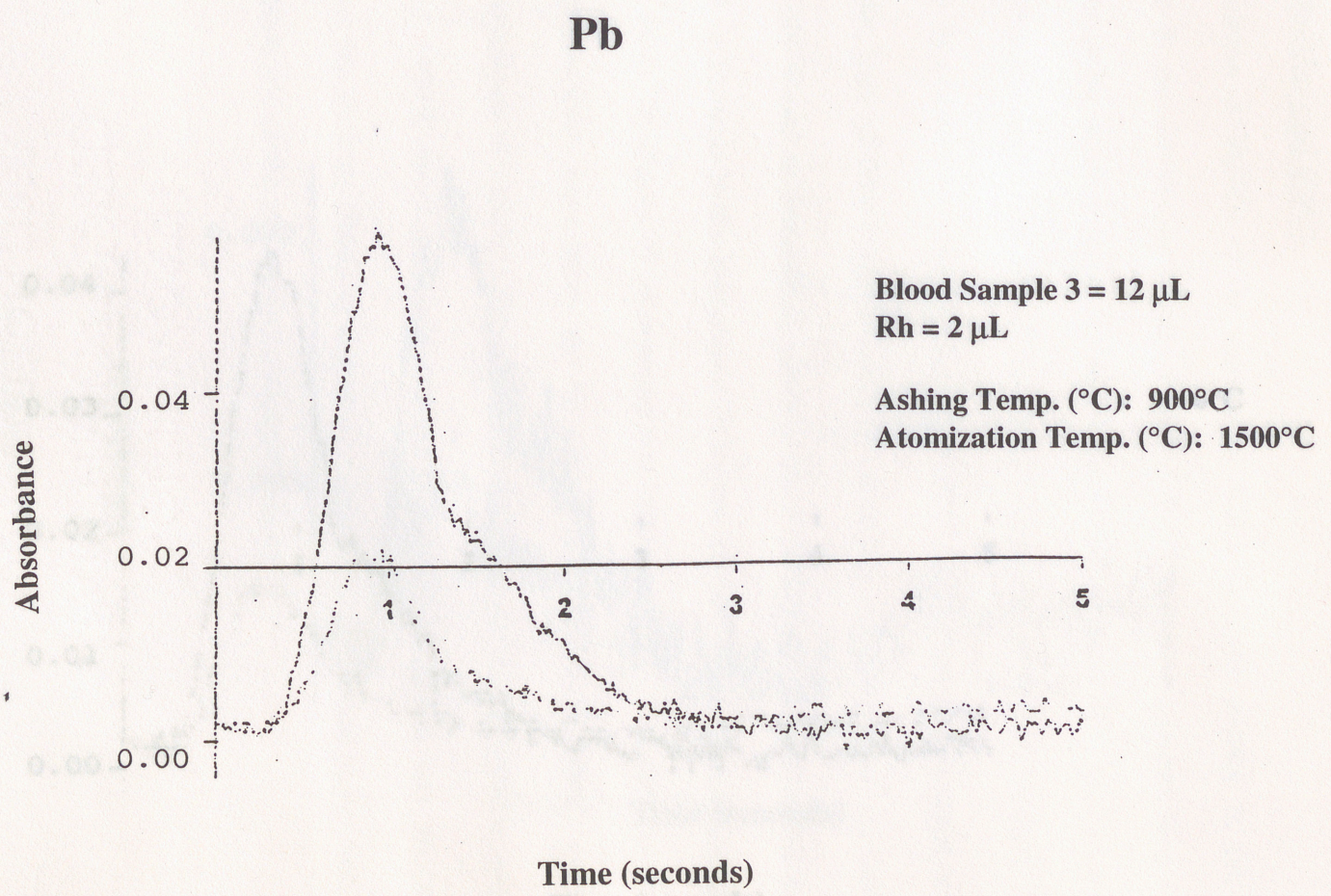


Figure 17. The Absorbance of 12 μL of the Blood Sample and 2 μL of Rh at an Ashing Temperature of 1000°C

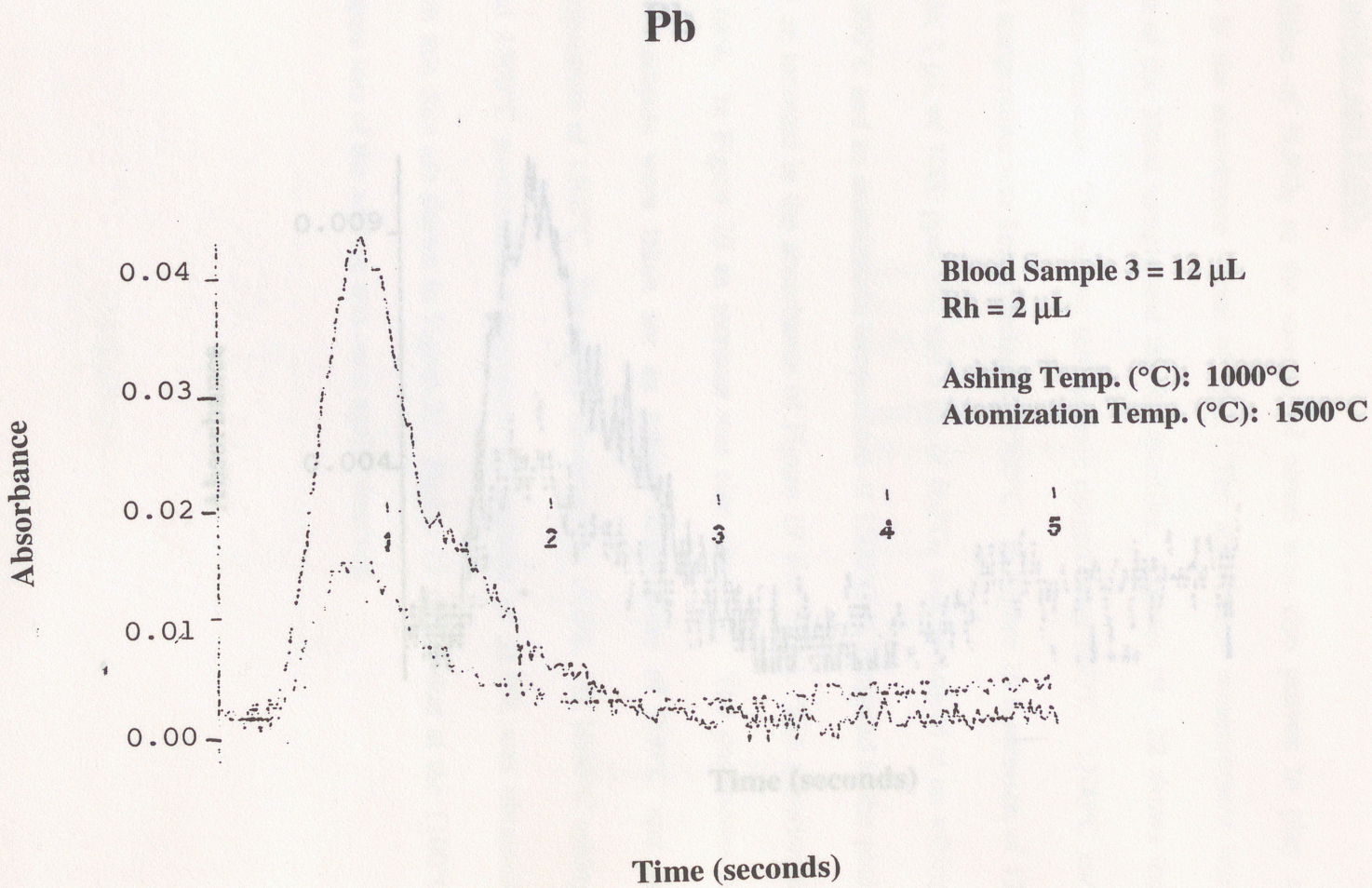
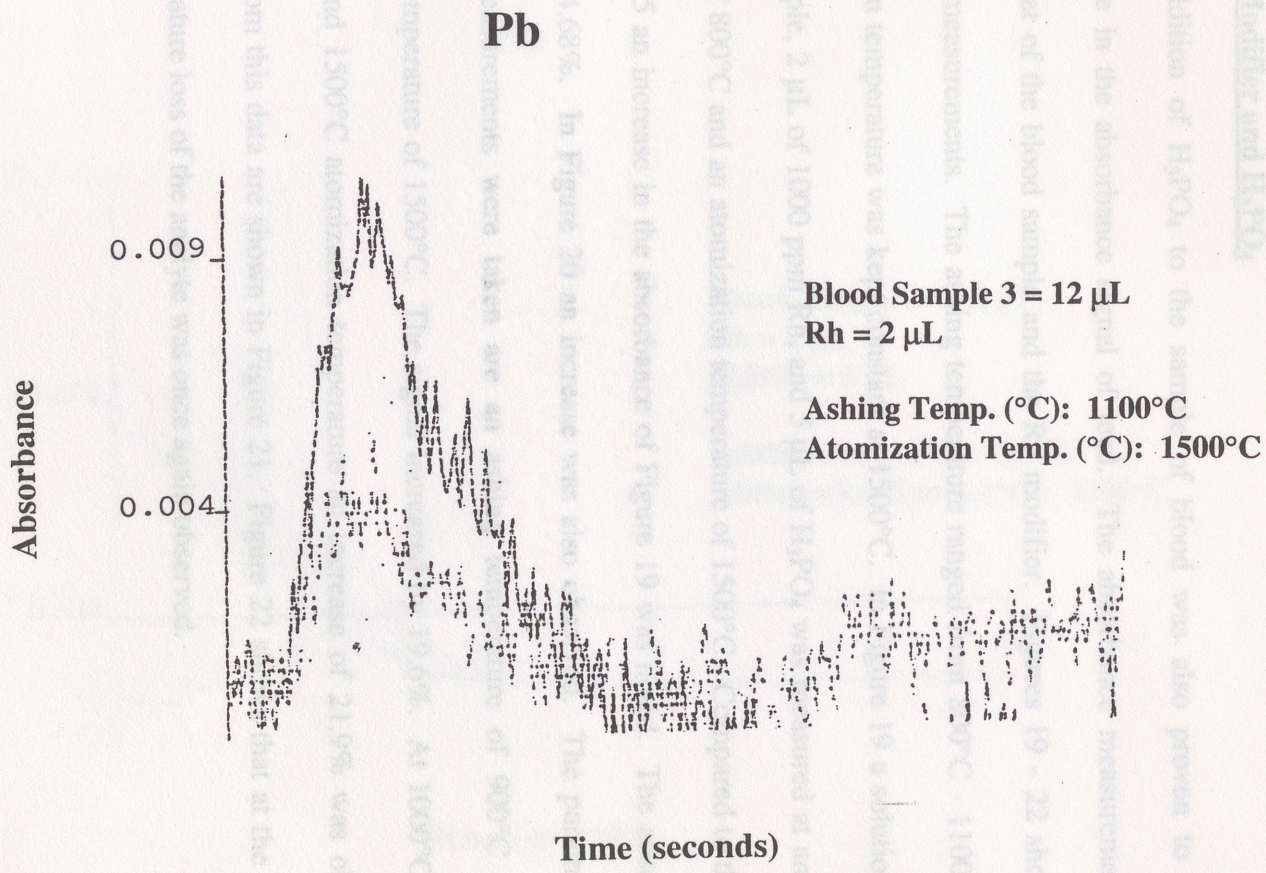


Figure 18. The Absorbance of 12 μL of the Blood Sample and 2 μL of Rh at an Ashing Temperature of 1100°C



Lead Analysis in a Biological System in the Presence of Rhodium Modifier and H_3PO_4

The addition of H_3PO_4 to the sample of blood was also proven to play a significant role in the absorbance signal of lead. The absorbance measurement was higher than that of the blood sample and the Rh modifier. Figures 19 - 22 shows the results of the measurements. The ashing temperature ranged from 800°C - 1100°C and the atomization temperature was kept constant at 1500°C. In Figure 19 a solution of 12 µL blood sample, 2 µL of 1000 ppm Rh, and 5 µL of H_3PO_4 was measured at an ashing temperature of 800°C and an atomization temperature of 1500°C. Compared to the peak from Figure 15 an increase in the absorbance of Figure 19 was noted. The absorbance increased by 4.68%. In Figure 20 an increase was also observed. The parameters at which the measurements were taken are an ashing temperature of 900°C and an atomization temperature of 1500°C. The signal increased by 19.6%. At 1000°C ashing temperature and 1500°C atomization temperature an increase of 21.9% was obtained. The results from this data are shown in Figure 21. Figure 22 shows that at the 1100°C ashing temperature loss of the analyte was once again observed.

Figure 19. The Absorbance of 12 μL of the Blood Sample, 2 μL of Rh and 5 μL of H_3PO_4 at an Ashing Temperature of 800°C

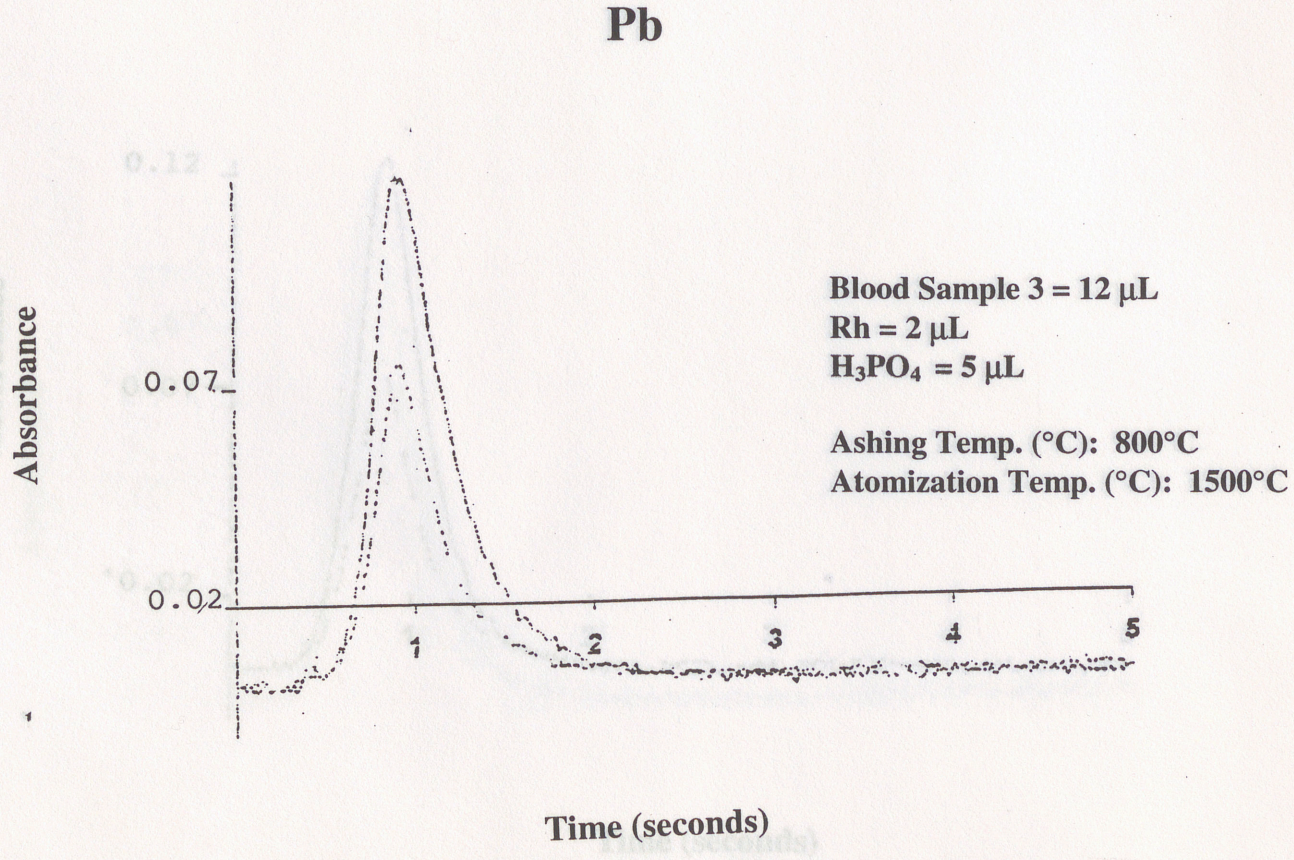


Figure 20. The Absorbance of 12 μL of the Blood Sample, 2 μL of Rh and 5 μL of H_3PO_4 at an Ashing Temperature of 900°C

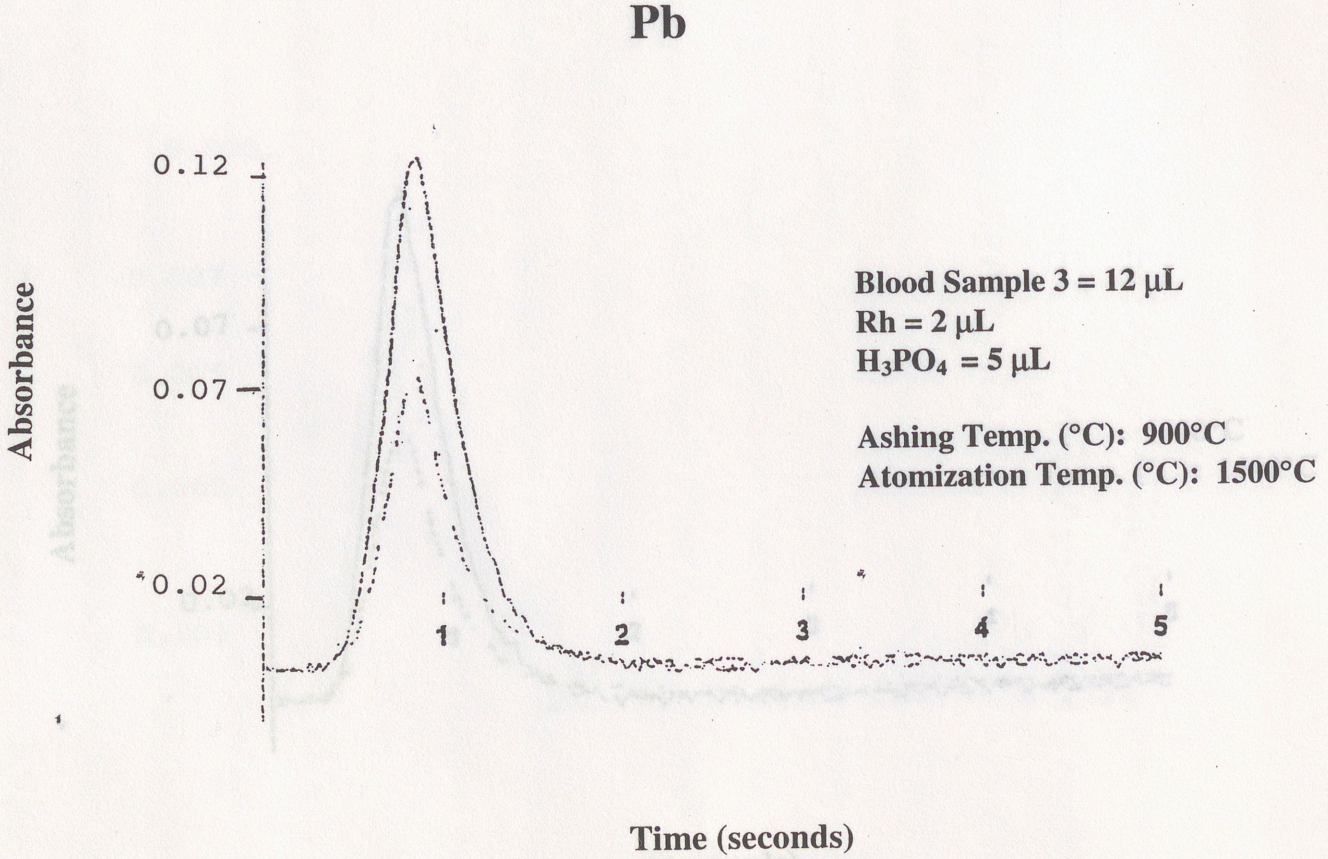


Figure 21. The Absorbance of 12 µL of the Blood Sample, 2 µL of Rh and 5 µL of H_3PO_4 at an Ashing Temperature of 1000°C

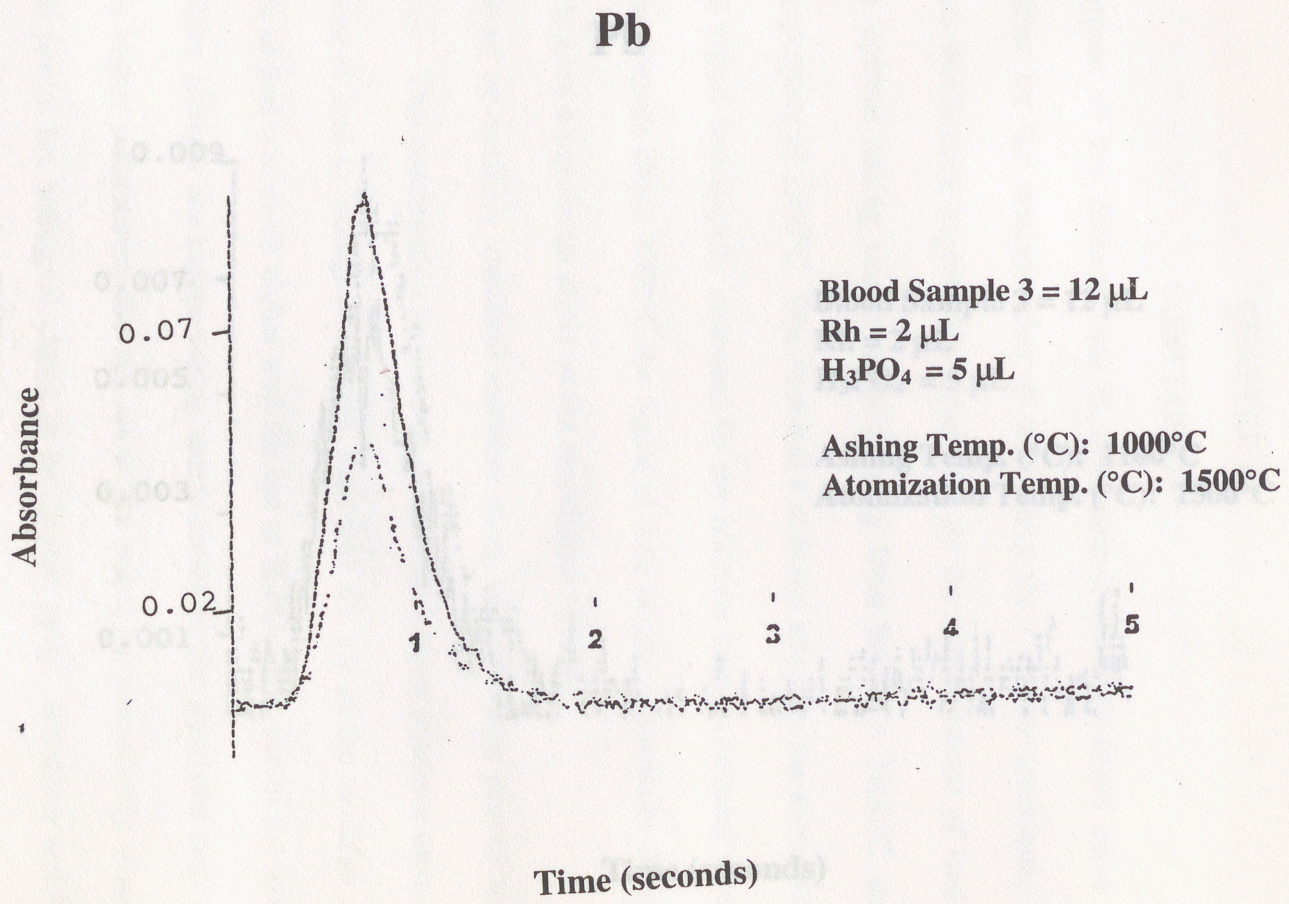
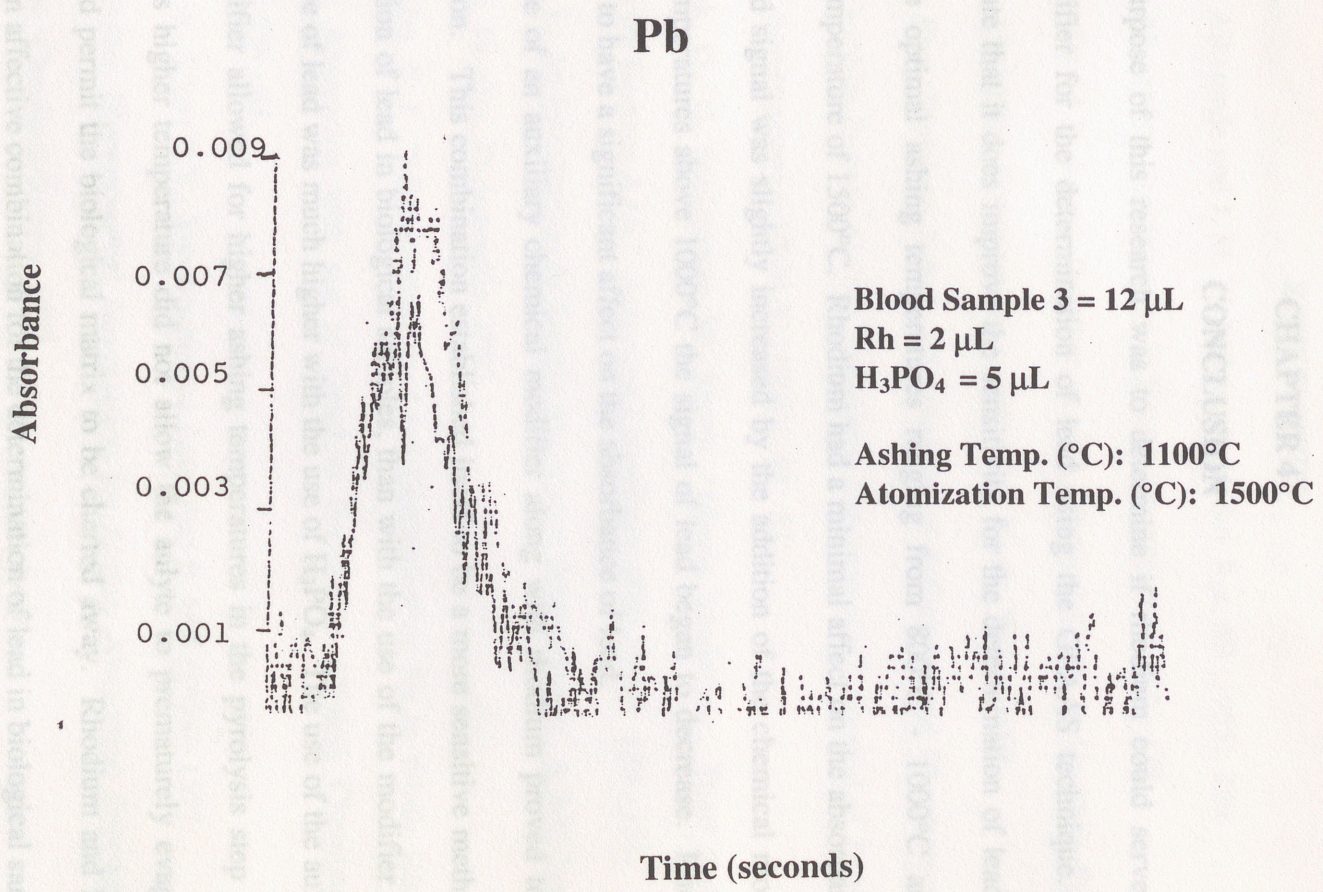


Figure 22. The Absorbance of 12 μL of the Blood Sample, 2 μL of Rh and 5 μL of H_3PO_4 at an Ashing Temperature of 1100°C



CHAPTER 4

CONCLUSION

The purpose of this research was to determine if rhodium could serve as a chemical modifier for the determination of lead using the GFAAS technique. The findings indicate that it does improve the sensitivity for the determination of lead very slightly at the optimal ashing temperatures ranging from 800°C - 1000°C and an atomization temperature of 1500°C. Rhodium had a minimal affect on the absorbance of lead. The lead signal was slightly increased by the addition of the chemical modifier, however at temperatures above 1000°C the signal of lead began to decrease. Rhodium does not seem to have a significant affect on the absorbance of lead.

The use of an auxiliary chemical modifier along with rhodium proved to be a positive addition. This combination established itself to be a more sensitive method for the determination of lead in biological samples, than with the use of the modifier alone. The absorbance of lead was much higher with the use of H_3PO_4. The use of the auxiliary chemical modifier allowed for higher ashing temperatures in the pyrolysis step of the analysis. This higher temperature did not allow the anlyte to prematurely evaporate. However it did permit the biological matrix to be charred away. Rhodium and H_3PO_4 proved to be an affective combination for the determination of lead in biological samples.

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