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The Study of Ruthenium as a Matrix Modifier for Determination of Lead in Graphite Furnace Atomic Absorption Spectrometry

Serkadis Tefera

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THESIS

BY

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By

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Texas Southern University

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Texas Southern University, 1997

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The problems of lead as an environmental toxicant are well established. These problems are complicated by the need for better analytical methods to determine trace quantities of lead in various biological samples, particularly biological fluids. The most widely used method which clinical laboratories use is the Graphite Furnace Atomic Absorption Spectroscopic (GFAAS) technique. The problems of determining lead in biological fluids such as blood are due to the low melting point of lead and the large amount of biological materials such as blood cell fragments. These cell fragment must be destroyed in the graphite furnace during the analysis. The addition of matrix modifiers have been suggested as a technique to improve the determination of lead in various biological materials using GFAAS. This study indicates that ruthenium can be used as a matrix modifier to stabilize lead several hundred degrees higher than is possible without the use of a modifier. It shows lead can only be pyrolyzed up to 600°C in the absence of a

modifier, but with the addition of ruthenium, it can be pyrolyzed up at temperature of 1000°C. Consequently, separation of the analyte from the concomitants can be achieved.

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This work is dedicated to my father,

Mr. Tefera Hailemeskel

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CHAPTER 1

INTRODUCTION

Lead, the most ubiquitous toxic metal, is detectable everywhere, including both inert and biological systems. The use of lead may have begun prior to 2000 B.C., when abundant supplies were obtained from ores as a by-product of smelting silver. Hippocrates is credited in 370 B.C., with the first description of abdominal colic in a man who extracted metals. It comes as no surprise therefore that in 1817, Orfila declared "if we were to judge the interest excited by any medical subject by the number of writings to which it has given birth, we could not but regard the poisoning by lead as the most important to be known of all those that have been treated of, up to the present time" (12).

Lead is used for a variety of applications because it is stable, readily available, easy to handle and process. Recently, there has been renewed concern about the adverse health effects of lead exposure at levels previously thought to be safe. The Center for Disease Control and Prevention (CDCP) lowered the concentration of blood lead, (BPb) considered harmful to young children, from 25 to 10 μg/dL (22). The major effect of this change in U.S. public health policy has been to render a previously widely used biochemical test for lead exposure [the erythrocyte protoporphyrin (ZPP) test] virtually useless for screening purposes (25). For many years, ZPP had been used throughout the U.S. to screen children at high risk for lead poisoning. The diagnostic sensitivity of the ZPP test is very poor at BPb levels as low as 10 μg/dL. Consequently, BPb is now

generally agreed that blood lead concentration is the best indicator of recent lead exposure (22).

There has been some debate over the capability of clinical laboratories to determine blood lead accurately and precisely at the lower detection level (25). There is an increasing need for more accurate and precise measurements of low blood lead concentrations (10 μg/dL) in clinical medicine. This is due to both the projected increase in the number of individuals with BPb levels below 15 μg/dL and the recent identification by the EPA's Science Advisory Board and the CDCP of 10 μg/dL as the BPb level of concern for early toxic effects (21,22). While those relatively low BPb levels are within the range of sensitivity of current instrumentation, the accuracy and precision of many routine BPb measurements below 10 μg/dL are still inadequate.

The importance of accurate and precise measurements of relatively low blood lead concentrations has become more apparent as the magnitude of lead contamination in humans is quantified. It is now recognized that baseline lead concentrations in contemporary adults are 500 to 1000 times greater than natural lead concentrations in pre-industrial individuals. This estimate is based on the measured levels of lead in ancient human skeletal remains (10). This increase of contaminant lead levels in human blood has not been documented because no suitable samples of blood from pre-industrial humans are known to exist. The magnitude of lead contamination in the environment is high relative to that of any other trace element (22). On a global scale most trace element cycles have not been substantially affected by anthropogenic processes, but those processes have

not been substantially affected by anthropogenic processes, but those processes have greatly affected the natural lead cycle. This is due to the extensive processing of lead ores, which has released 300 million metric tons of contaminant lead into the environment over the past five millennia (10).

The most severe lead contamination has occurred in urban and industrial regions, where resulting lead levels are often 10 times greater than they are in remote areas. The magnitude of lead contamination among individuals within an area may also vary by several orders of magnitude because of different levels of exposure. The most susceptible populations are children, particularly toddlers and infants in the neonatal period and the unborn fetuses (39).

Various human activities involve the use of lead in one form or the other. According to the National Lead Information Center, these are some examples of occupations, activities, products and environmental effects which involve the use of lead.

Occupational

Plumbers/pipe fitters
Auto repairs
Glass manufacturers
Shipbuilders
Printers
Plastic manufacturers
Lead smelters
-and refiners
Police officers
Steel welders/cutters
Construction workers
Rubber product
-manufacturers
Gas station employees
Battery manufacturers
-and recyclers
Bridge, tunnel and
-elevated highway
-workers
Firing range instructors
Lead miners

Hobbies & Related Activities

Glazed pottery making
Target shooting at
firing ranges
Lead soldering (e.g.,
electronics)
Painting
Preparing lead shot
fishing sinkers
Stained-glass making
Car or boat repair
Furniture refinishing
Home remodeling

Environmental

Lead -containing paint
Soil/dust near lead
-industries, roadways,
-lead paint homes
Plumbing leachate
Ceramicware
Leaded gasoline

Substance Use

Bridges
Fork remedies
"Health foods"
(such as some
calcium supplements)
Cosmetics
Moonshine whiskey
Gasoline "huffing"-
(sniffing gasoline
from a container)

The variability between individuals has made it especially difficult to assess procedural bias resulting from contamination in BPb measurements.

Lead poisoning can affect people of any age, race, geographic region or socioeconomic level; but young children are under greater risk of intoxication because they absorb lead more efficiently than adults. Children and adults can get lead into their bodies mainly by ingesting or breathing it. Lead enters children's bodies primarily through hand to mouth activities. Fetuses, pre-natal and young children can experience a range of illnesses due to lead exposure. Symptoms of lead poisoning depend on the concentration of lead in the blood. In many cases, there are no visible symptoms of elevated blood-lead levels or lead poisoning. Symptoms of lead poisoning generally do not appear until blood-lead levels exceed 50 μg/dL.

- Low levels in children are 10-35 μg/dL and 10-40 μg/dL in adults. Most often, there are no symptoms at such levels.
- Moderate levels are 35-50 μg/dL in children and 40-60 μg/dL in adults. In this case there may be no symptoms; but if symptoms do occur, they may include general fatigue, irritability, difficulty concentrating, headaches, abdominal pain, vomiting, weight loss or constipation. These symptoms may be mistaken for other disorders.
- High levels for children are over 50 μg/dL and over 60 μg/dL for adults. There may be no symptoms or the symptoms may be those mentioned under "moderate levels" above.

- High levels for children are over 50 µg/dL and over 60 µg/dL for adults. There may be no symptoms or the symptoms may be those mentioned under "moderate levels" above.

- At very high levels, symptoms can include convulsions, paralysis, coma or death. Children with blood-lead levels of over 70 µg/dL are considered a medical emergency. Toxic effects include nervous and reproductive system disorders, delay in neurological and physical developments, cognitive and behavioral changes and hypertension.

The human body has no need for nor benefits from even the smallest amounts of lead. In fact, there has been an accumulation of research showing that lead significantly affects animals and humans in a negative manner. Lymphocytes were studied in 31 men working in a plant producing plastic material (2). This study was done by the Center of Occupational Medicine and Eryophtalmology, University, G.D'Annunzio, Chuti, Italy. Combined exposure to toxic agents produces specific modifications in the lymphocyte. The data have conformed that exposure to lead or chromate induces reduction of lymphocytes in the peripheral blood. Environmental lead measurements around a Los Angeles county battery recycling facility and its effects on children living nearby were studied (40). Lead levels in the surface soil near the stationary lead source were elevated compared to the rest of the community. Other studies show similar results for children living within 500 meters of a primary lead smelter in Brazil (31). Lead ratios in blood

The identification of elevated BPb in older children, particularly females, is a concern because there is a potential for release of endogenous lead during pregnancy and lactation. In response to concerns raised by the Kuwait Ministry of Public Health, the levels of lead in some commercial water coolers were studied (6). Samples of drinking water and fingernails from 129 healthy donors (77 males and 52 females) were collected. The study showed that high levels of lead in their drinking water were deposited in their fingernails (36). It was proven from this study that the drinking water from the cooler company, A1-Hassawi, contributed significantly to a Kuwait's lead exposure.

Analytical Methods for Determining Lead

Several methods have been identified in recent years for the determination of BPb. In Anodic Stripping Voltammetry, a minute volume of blood, about 100 µl, is mixed with a special reagent and placed in a cell. The cell is stripped by the instrument producing a current which reads out in concentration units. This method of lead determination is still in use today in source chemical laboratories because of its simplicity.

People with chronic lead poisoning or who suffer from iron deficiency anemia have the tendency to accumulate zinc protoporphyrin (ZPP) in their blood. So, a determination of the amount of ZPP in people's blood can tell the level of lead poisoning or iron deficiency anemia. As would be expected, this is not a very reliable test.

Atomic Absorption Techniques

In flame atomization, a solution of the sample is sprayed into a flame by means of a nebulizer, which converts the sample solution into a mist made up of tiny liquid droplets. A complex set of interconnected processes lead to a mixture of analyte atoms, analyte ions, sample molecules, oxide molecules of the analyte and other species being formed. The sample analysis by flame atomic absorption is fast. This method has proved to be very good for determining lead in the parts per million (ppm) range.

With the introduction of the use of graphite furnace in place of flame atomic absorption method, analytes in parts per billion (ppb) were able to be determined. Delves method involved placing blood samples in nickel boats and inserting them in carbon tubes for atomization (1) Atomization evolved into aspirating the sample directly to the carbon cup, using a tantalum ribbon or using laser excited flame atomic fluorescence spectrometry (18,33).

L'vov and Woodriff independently developed the field of Graphite Furnace Atomic Absorption Spectroscopy during the 1960s. Both used rather large furnace cells held at constant temperature in conjunction with small sample size introduction for AAS measurements. These researchers saw the advantage of the furnace approach in order to avoid large dilution factors which are inseparable in the use of flames as atom cells. Instrument manufacturers likewise, who realized the tremendous advantage of increased sensitivity developed and commercialized smaller versions of these devices during the

1970's under the name of carbon or graphite furnaces. The commercial devices consisted of graphite that is resistively heated by means of an electrical current after the introduction of a very small sample. The graphite furnace increased the sensitivity to the parts per billion (ppb) range. With the emergence of GFAAS, analytes in parts per billion (ppb) are readily determined in a very short period of time. The only setback so far with the GFAAS is its price and the need for highly trained personnel.

GFAAS is based on a linear relationship between the concentration of the lead in blood and the absorbance of the gaseous lead atoms in a graphite furnace. It involves the following steps - drying, charring, atomization and clean out.

Drying is a removal of the solvent from the sample by applying a furnace temperature of 125 °C for 20's.

Charring is performed to free the blood from materials associated with lead. These would include cell fragments, anti coagulants etc. which would otherwise cause interference in the determination of lead (20).

Atomization is the process in which atomization a compound is decomposed into its atoms at high temperature.

Clean out is the process of heating the furnace up to 2400°C - 2500°C for 3 seconds in order to clean out any remaining residue.

The atomization surface is known to play a key role in the detection of metals by graphite furnace AAS. An improved precision and extended lifetime are features of

coated graphite tubes. The use of the platform, instead of atomization off the tube wall, has been shown to reduce interferences. Interference in graphite furnace AAS is attributed to particulate (scatter) molecular and atomic background. Background correction is affected in graphite furnace by Zeeman or Smith-Hieftje background correction device (32).

GFAAS has seen wide applications. In Germany, GFAAS has been used in the past for various studies. It was used to study the trace metallic ions in the digestive gland-gonad complex of helisoma trivolvis snails infected with the daughter rediae of echinostoma trivolvis and in unaffected snails (DGG) (2). In a study done in the United States the toxic effects of chromium, nickel and cobalt extracts on invitro cultured lymphocytes were evaluated. Graphite Furnace Atomic Absorption Spectrometry was used to measure the various ion concentration (6).

Human tissue samples (liver, kidney cortex, 5 brain regions: gray matter of cerebrum, white matter of cerebrum, nucleus lentiformis, cerebellum, brain stem) from 173 deceased persons were analyzed for silver (Ag) by GFAAS. The results were compared with the number of teeth containing amalgam fillings and the concentration of inorganic mercury (Hg), which has been determined in the same tissue samples in a previous study (6).

GFAAS was also used for determining selenium in human brain samples. The matrix interferences were avoided by using high temperature, a prolonged pyrolysis step

and palladium matrix modifier. The technique of standard addition was used to evaluate the sample concentrations.

Matrix modifier

Despite its tremendous successes the GFAAS was besieged by one problem, which is matrix effects. The solution to this problem was the introduction of matrix modifiers into GFAAS. The concept of the addition of matrix modifiers is to convert the element of interest into a phase of higher thermostability and/or increase the volatility of concomitants.

The development of the concept and application of matrix modifiers to the graphite furnace has been an important part of the evolution of the technique as a sensitive, reliable method for the measurement of trace metals in a large variety of samples. The concept of matrix modification was developed not long after the introduction of commercial graphite furnaces in an effort to overcome limitations in early instrumentation and techniques. Looking back at the early papersdealing with matrix modification, one must remember that the equipment and techniques available in the early 1970's were different from those that are available today. In addition to the need to separate analyte and matrix volatilization, since peak integration was not used at that time, analyte peak symmetry and the magnitude of the peak height absorbance were important criteria. It was not until about 1975 that peak integration became commercially available. Hence, much of the early matrix modification work was concerned with increasing analyte peak absorbance for a given

concentration. In theory, an increase in the peak height to absorbance ratio would provide lower detection limits.

Matrix modification has enjoyed widespread use in the analytical community involved with GFAAS in the routine analysis of aqueous as well as slurry and solid samples (27). The analytical benefits derived from the presence of a chemical component, i.e. matrix or chemical modifier, in relatively large excess over the analyte concentration include enhancements in the efficiency of the ashing step to remove interference, shifts in the atomization peak to higher temperatures more favorable to the generation of free atomic analyte species and improvements in the consistency of absorbance signals for samples of different compositions (27).

The effect of matrix modifiers is to alter and, thus, be able to tolerate certain unfavorable features of:

- the analyte (extremely high or low volatility; the presence of various analyte species in real samples and calibration standards)
- the matrix (the presence of interfering contaminants; unmanageable background absorbance)
- the atomizer (temporal and spatial non-isothermality; porosity and reactivity of graphite)
- the gas phase (e.g. the partial pressure of certain active components)(32).

Modification of the analyte to achieve a temporal separation can be accomplished by making the analyte more or less volatile (32). The sample matrix may be modified in a

similar way. Matrix modifiers most frequently proposed for single metal AAS include ammonium phosphate, magnesium nitrate, palladium, and nickel.

The first publications in which matrix modifiers were used appeared 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 by more than tenfold. One of the most promising matrix modifiers is Palladium (Pd). Pd has been introduced into the furnace as an aqueous chloride and/or nitrate solution together with the sample to be analyzed (27). An early application was its introduction as PdC_{l2} for the determination of Pb in urine. In 1979, Shan and Ni introduced this element, either alone or combined with ascorbic acid or $Mg(NO_3)_2$. Palladium matrix modification has been used for the determination of bismuth, arsenic, selenium, mercury, lead and other elements in a variety of environmental and biological samples (29).

In 1975 Ediger improved the determination of selenium with the addition of nickel. He postulated that in the graphite furnace, nickel will react with selenium to form nickel selenide, which has a much higher melting point of selenium 217°C.

It was not long thereafter that the use of matrix modifiers gained popularity in blood lead determinations. Subramarian and Meranger used ammonium hydrogen phosphate $[(NH_4)_2HPO_4)]$ while Fernandez and Hilligoss used magnesium ammonium phosphate $[(Mg\ (NH_4)\ (PO_4)]$. Both groups of investigators postulated the formation of

lead phosphate, with a mp of 1014°C, resulted a lot higher than that of lead, with a mp of 327°C.

This thesis investigation is to determine if ruthenium can be used as a matrix modifier for the determination of lead in various media including blood. It will also determine the role which ruthenium plays in the graphite furnace during the analysis of lead in blood.

CHAPTER 2

DESIGN OF STUDY

Apparatus

All absorbance measurements were made on a Perkin- Elmer Model 4110ZL atomic absorption spectrometer equipped with a transverse heated graphite atomizer (THGA) graphite furnace and an As-72 autosampler. A typical temperature program for the determination of lead is given under Graphite Furnace Conditions. The 283.3 nm wavelength was used for all of the absorbance measurements. Tables 1 and 2 list all relevant parameters for this instrument.

Graphite Tubes

A new THGA graphite tube was used for each series of measurements. The tube was conditioned prior to analytical use by using a high temperature. The conditioning process removes impurities on both the tube surface and the tube material. Table 3. shows the nine step program used to condition the tube.

TABLE 1

GRAPHITE FURNACE PARAMETERS

Model 4110 ZL AAS parameters	
Slit width	0.7 nm
Calibration mode	peak area
Current	10 mA
Integration time	5 sec
Purge gas	argon

Reagents

All reagents used were of the highest purity available and at least of analytical reagent grade. The ruthenium chemical modifier was prepared from atomic absorption standard solutions obtained from Sigma Chemical Company, St Louis, Mo. The lead solutions were prepared from atomic absorption standard lead nitrate in 2% nitric acid from the Fisher Scientific Company Pittsburgh, PA., Dilute working solutions of lead and the modifiers were prepared by dilution with .5% nitric acid. The .5% nitric acid solution was prepared by dilution of analytical grade nitric acid with high purity water obtained using a milli-R06 system (Millipore). The water contained no detectable amounts of Pb.

Cleaning of Equipment

All glassware was kept in HNO3 (1% V/V) prior to use. Polystyrene plastic-ware was soaked overnight with HNO3 (1% V/V), rinsed repeatedly with de-ionized water and dried at a low temperature.

Procedures

The study involved measuring the absorbance of a number of lead-matrix modifier systems by varying the amount of the modifier, the charring temperature and the atomization temperature. The sample sizes, which includes the lead and the modifier, were either 20 µL or 25 µL. The computer on the atomic absorption spectrometer was programmed to instruct the instrument to obtain and mix the appropriate quantities of lead and matrix modifiers and deposit them into the graphite furnace. Under normal operating conditions, each sample, standard and blank is atomized twice (n = 2). All the statistics for the interference studies were based on two determinations (n = 2). The operating conditions are shown in table 1.

TABLE 2

GRAPHITE FURNACE CONDITIONS

Model 4110ZL Graphite Furnace Paramete					
Step	Function	Temp. C	Ramp Time (sec)	Hold Time (sec)	Flow Rate (ml/min)
1	dry	110	1	20	250
2	dry	140	5	30	250
3	ash	variable	10	20	250
4	atomization	variable	0	5	0
5	Clean out	2600	1	3	250

TABLE 3

GRAPHITE FURNACE PROGRAMS

Furnace Program to Condition a Graphite Tube			
Step	Temperature	Ramp Time	Hold Time
1	2000	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

CHAPTER 3

RESULTS AND DISCUSION

Figure 1 shows the maximum ash and atomization temperature of lead without a modifier. Ashing of the lead sample without a modifier began around 600°C, and completely pyrolyzed at about 800°C. Many analytes are subjected to losses during the pyrolysis step. As mentioned earlier in the introduction, matrix modification techniques are recommended to decrease the volatility of the analyte and extend the pyrolysis temperature.

The Effect of Atomization Temperature

Flameless atomic absorption with an electrothermally heated graphite atomizer gives a much higher sensitivity of Pb but often suffers from the appearance of double peaks and time-shifted signals (see Figure 2[a-f]). In addition to identity of the analyte and the composition of the matrix, the absorbance signal for GFAAS is dependent on many factors, such as ash and atomization temperatures, mass of the modifier, etc.

The focus of this particular research was to determine if the atomization signal for lead would change by changing the atomization temperature and keeping the other furnace parameters constant. The results are shown in Figure 2(a-f). Figure 2(a) represents an atomization temperature of 1400°C. It shows a shoulder at about 0.8 seconds and the major peak at 1.3 seconds. At an atomization temperature of 1500°C, the shoulder at 8

seconds became more pronounced (Figure 2[b]). At an atomization temperature of 1600°C two distinct peaks are observed (Figure 2[c]). Increasing the atomization temperatures up to 1,700°C and 1800°C resulted in an increase of the first peak while the second peak decreased (Figure 2[d]) and (Figure 2[f]). At 1900°C, the first peak became the major peak while the second peak was reduced. The data, thus, indicates that an increase in the atomization temperature improved both the curve resolution and the peak separation.

The Effect of Ruthenium Concentration

The main purpose of using chemical modification in Graphite Furnace Atomic Absorption Spectrometry is to stabilize the analytes while increasing the charring temperature as much as possible. A high charring temperature efficiently removes the sample matrix in the thermal pre-treatment stage, thus reducing the effect of interference in the final atomization process. Of course, the control of the chemical environment is also an equally important factor in chemical modification. A comparison was made between the maximum charring temperatures for thermal pretreatment without loss of analytes in the absence of chemical modifier and in the presence of ruthenium modifier. The char and atomization plots for lead with and without ruthenium areillustrated in Figure 3. It shows that lead can be pyrolyzed up to 600°C in the absence of a modifier without significant volatilization loss. At 800°C the lead sample completely pyrolyzes. The

addition of ruthenium increases the char temperature to 1100°C. The optimum atomization temperature for this method is 1400°C with a slight decrease in absorbance at increased temperatures. The effect of ruthenium concentration is shown by the data in Table 4.

As temperature affects the shape and time of the peak, the quantity of the modifier also changes the peak's shape. The results for this study are shown in figures 4(a - f). These experiments were carried out at an ash temperature of 800°C and an atomization temperature of 1,700°C. The amount of lead was kept constant at 4ng and the amount of ruthenium varied from 0 ng to 18 ng. The results indicated that in the presence of ruthenium lead, the plot exhibits two sharp peaks and the test time was about 1 second. Increasing the concentration of ruthenium while keeping the lead constant increased both the absorbance level of the second peak and raised the test time to 2 seconds. The peak also became broader. When larger quantities of ruthenium were used, peak number one almost disappeared and become a shoulder. As a result, the second peak became the main peak and the formation of a third peak was observed.

Mechanism of Ruthenium Matrix Modification

In order to determine whether ruthenium formed any intermetallic compound with lead in a graphite tube, two known series of lead-ruthenium (Pb-Ru) solutions were prepared. The amount of lead in the first series of solutions was kept constant at 4ng, while the amount of ruthenium was varied from 2 ng to 20 ng. The char and atomization

temperatures were 800°C and 1,400°C respectively. In the second series of solutions, the amount of lead was kept constant at 6 ng while the amount of ruthenium was varied from 3 ng to 30 ng. For this series, a char temperature of 800°C and an atomization temperature of 1700°C were used. Figures 5 and 6 show the results of absorbance vs mole ratio of ruthenium for series 1 and 2, respectively. The two graphs are similar to each other. Both graphs show a Ru-Pb absorbance maximum at a mole ratio of 2, and an absorbance minimum at a mole ratio of 8. However, these results were obtained only when the ruthenium-lead mole ratios were small. Very high ruthenium-lead ratios do not show similar curves of maximum and minimum absorbance and resulting graph is shown in Figure 7. The peak at a ruthenium-lead mole ratio of 2 indicates the formation of an intermetallic compound of $PbRu_2$ and supports other theories of Palladium-lead intermetallic compounds (37-39). However, there is no logical explanation for the result of a minimum absorbance at mole ration of 8.

Figure 8 compares the sensitivity of ruthenium, palladium and rhodium. Ruthenium shows higher sensitivity with respect to palladium and rhodium. Increasing mole ratio from 100 to 700 does not change the absorbance of these three elements significantly. Figure 9 shows that an increase in the concentration of ruthenium leads to an increase in absorbance. In deed, one can observe a consistent increase in absorbance as the concentration of ruthenium increases from .1ppm to 50ppm. The data in Figure 9 suggests that ruthenium can be used as a chemical modifier to detect lead.

TABLE 4

THE EFFECT OF RUTHENIUM

Tempt.	Char/Pb 2ng	Char/Pb2ng+R	Atom./Pb2ng	Atom./Pb 2ng+R
300	0.2304			
400	0.2324	0.2165		
500	0.2295	0.2162		
600	0.2272	0.2167		
700	0.1780	0.2156		
800	0.0250	0.2167		
900	0.0027	0.2132		
1000		0.2100		
1100		0.1458		
1200		0.0085	0.2805	
1300			0.2835	0.2590
1400			0.2878	0.2765
1500			0.2818	0.2596
1600			0.2750	0.2479
1700			0.2637	0.2385
1800			0.2556	0.2286
1900			0.2465	0.2191
2000				
2100				
2200				

TABLE 5

MOLE RATIO Ru/Pb (1 TO 10)

ONE

Ru (ng)	Ratio (Ru:Pb)	Abs.
0.000	0.000	0.065
2.000	1.000	0.233
4.000	2.000	0.252
6.000	3.000	0.248
8.000	4.000	0.216
10.000	5.000	0.214
12.000	6.000	0.223
14.000	7.000	0.176
16.000	8.000	0.141
18.000	9.000	0.139
20.000	10.000	0.169

TABLE 6

MOLE RATIO Ru/Pb (1 to 10)

TWO

Ru (ng)	Ratio (Ru:Pb)	Abs.
0.0000	0.0000	0.0615
2.0000	1.0000	0.1617
4.0000	2.0000	0.2150
6.0000	3.0000	0.1862
8.0000	4.0000	0.1503
10.0000	5.0000	0.1416
12.0000	6.0000	0.1415
14.0000	7.0000	0.1195
16.0000	8.0000	0.0896
18.0000	9.0000	0.1132
20.0000	10.0000	0.0923

TABLE 7

THE CONCENTRATION OF RUTHENIUM

FROM 1PPM TO 50PPM

Ru (ng)	Ratio (Ru:Pb)	Abs. Ru 1ppm	Abs. Ru 5ppm	Abs. Ru 10ppm	Abs. Ru 50ppm
0.00					
1.00	0.50				
2.00	1.00	0.0923			
3.00	1.50				
5.00	2.50	0.0974			
8.00	4.00	0.0767			
10.00	5.00	0.0316			
15.00	7.50	0.0231			
20.00	10.00		0.0874		
40.00	20.00		0.1186	0.1318	
50.00	25.00		0.1149		
60.00	30.00		0.1449		
75.00	37.50		0.1554		
80.00	40.00			0.2610	
120.00	60.00			0.3303	
150.00	75.00			0.3638	
200.00	100.00				0.3701
400.00	200.00				0.3917
600.00	300.00				0.3913
750.00	375.00				0.3788

TABLE 8

MOLE RATIO OF Ru/Pb

(100 to 750)

Ru /ng	Ratio (Ru/Pb)	Abs.
1.00	0.50	0.0715
2.00	1.00	0.1638
5.00	2.50	0.1689
8.00	4.00	0.1482
10.00	5.00	0.1031
15.00	7.50	0.0981
20.00	10.00	0.1478
40.00	20.00	0.1790
50.00	25.00	0.1753
60.00	30.00	0.2053
75.00	37.50	0.2158
80.00	40.00	0.3095
120.00	60.00	0.3788
150.00	75.00	0.4123
200.00	100.00	0.4246
400.00	200.00	0.4463
600.00	300.00	0.4450
750.00	375.00	0.4334
800.00	400.00	0.4238
1200.00	600.00	0.4049
1500.00	750.00	0.4017

TABLE 9

THE EFFECT OF ASH AND ATOMIZATION

TEMPERATURE WITHOUT MODIFIER

Temperature	Ash/Abs.	Atom/Abs.
300	0.1396	
400	0.1419	
500	0.1378	
600	0.1371	
700	0.1155	
800	0.0328	
900	0.0018	
1000		0.0054
1100		0.1097
1200		0.1498
1300		0.1527
1400		0.1577
1500		0.1554
1600		0.1497
1700		0.1461
1800		0.1408
1900		0.1345
2000		0.1283
2100		
2200		

FIGURE 1

THE GRAPH OF ASH AND ATOMIZATION TEMPERATURE

WITHOUT MODIFIER

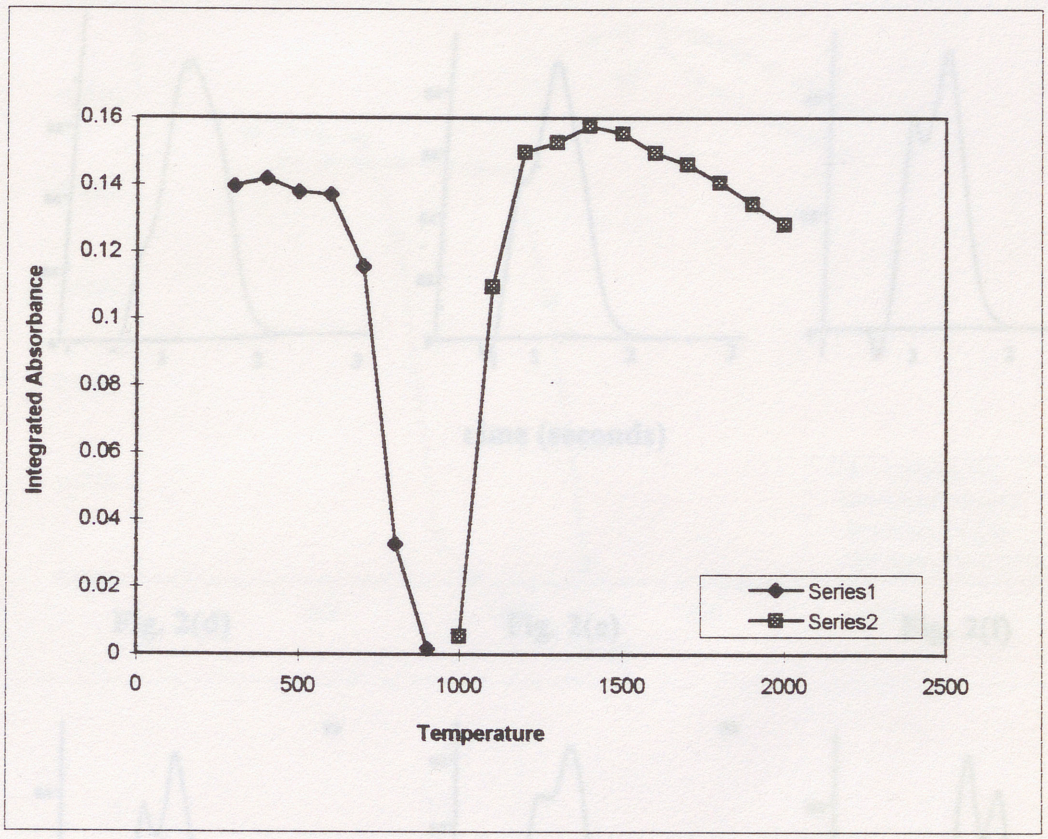
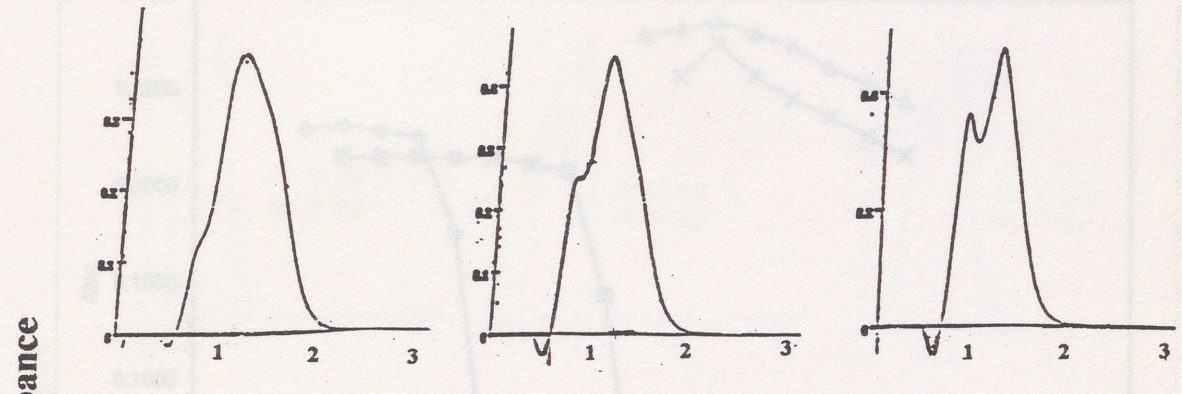


FIGURE 2

THE EFFECT OF TEMPERATURE

ON Pb

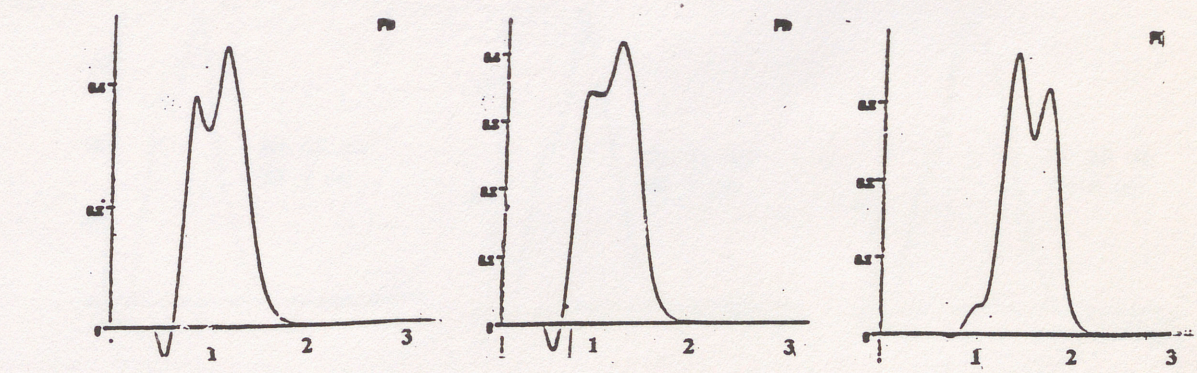
Fig. 2(a) Fig. 2(b) Fig. 2(c)



Integrated Absorbance

Time (seconds)

Fig. 2(d) Fig. 2(e) Fig. 2(f)



Time (seconds)

FIGURE 3

THE EFFECT OF RUTHENIUM

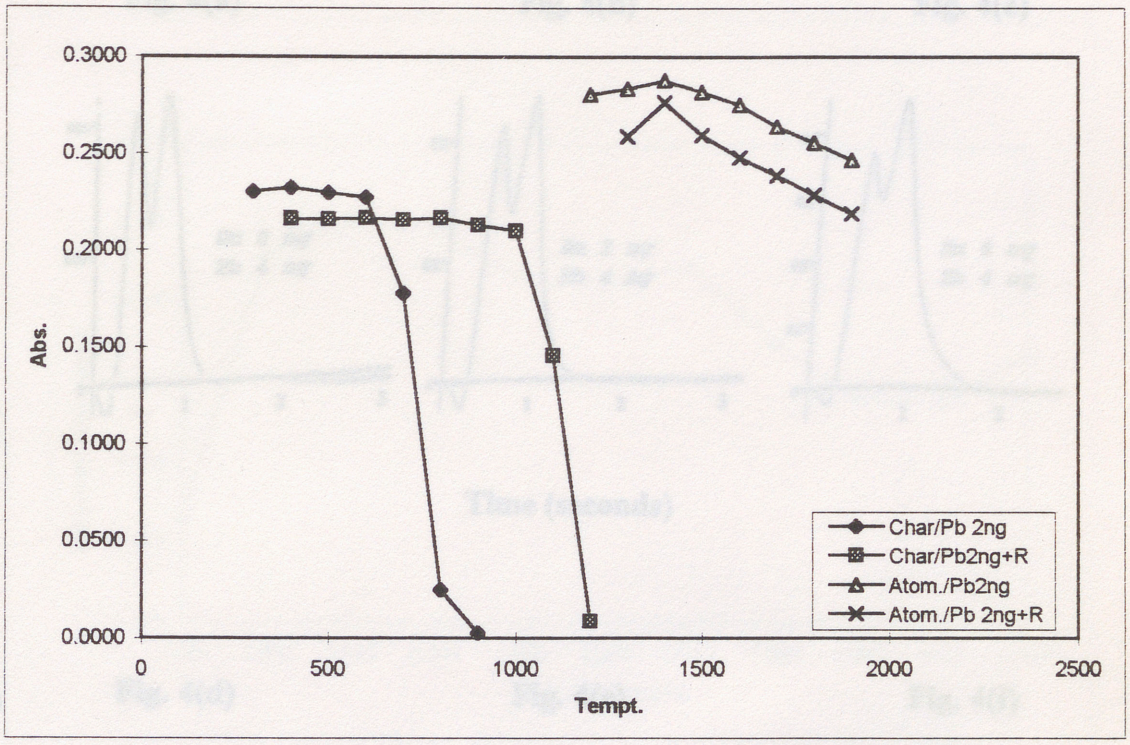


FIGURE 4

THE EFFECT OF RUTHENIUM ON Pb

ONE

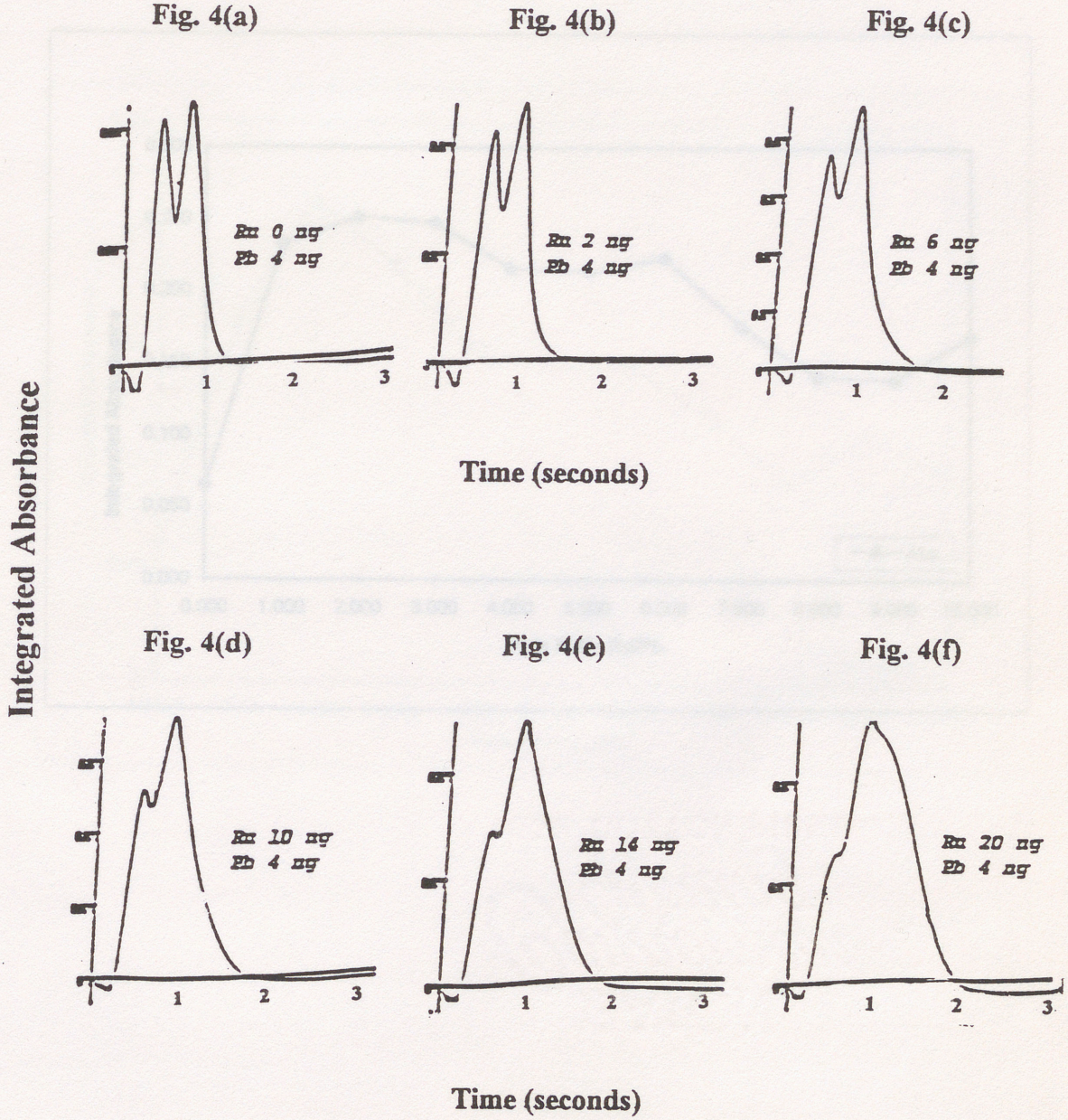


FIGURE 5

MOLE RATIO Ru/Pb (1 TO 10)

ONE

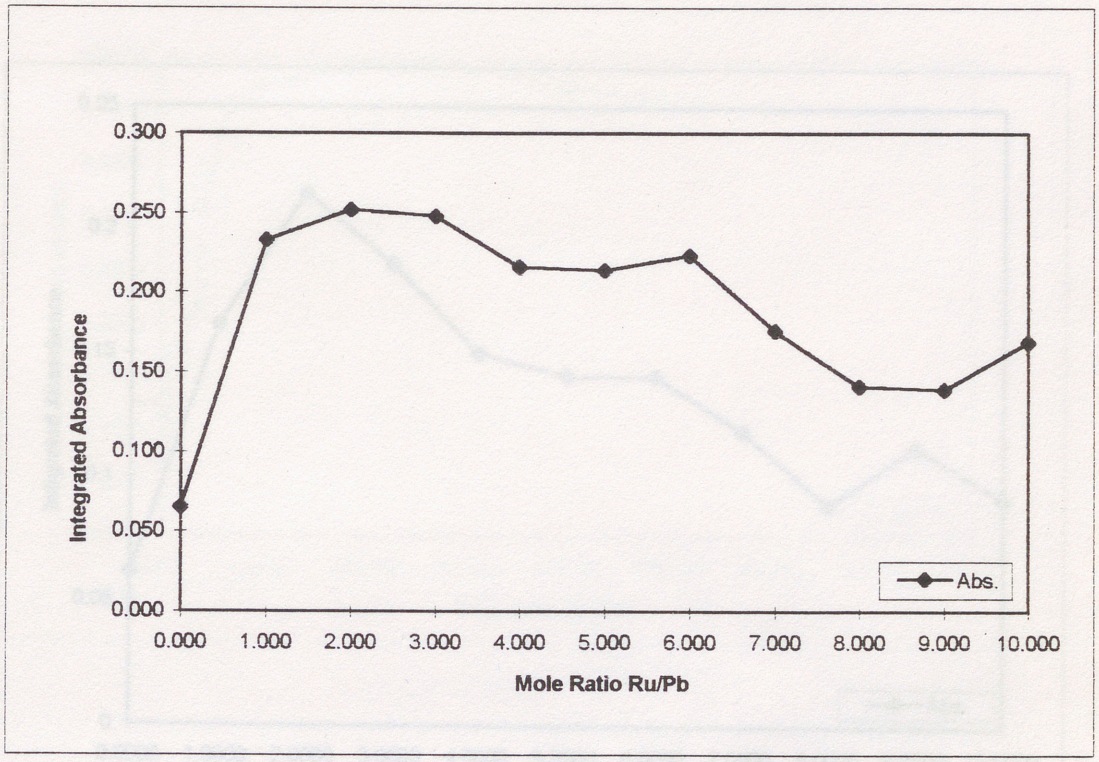


FIGURE 6

MOLE RATIO Ru/Pb (1 to 10)

TWO

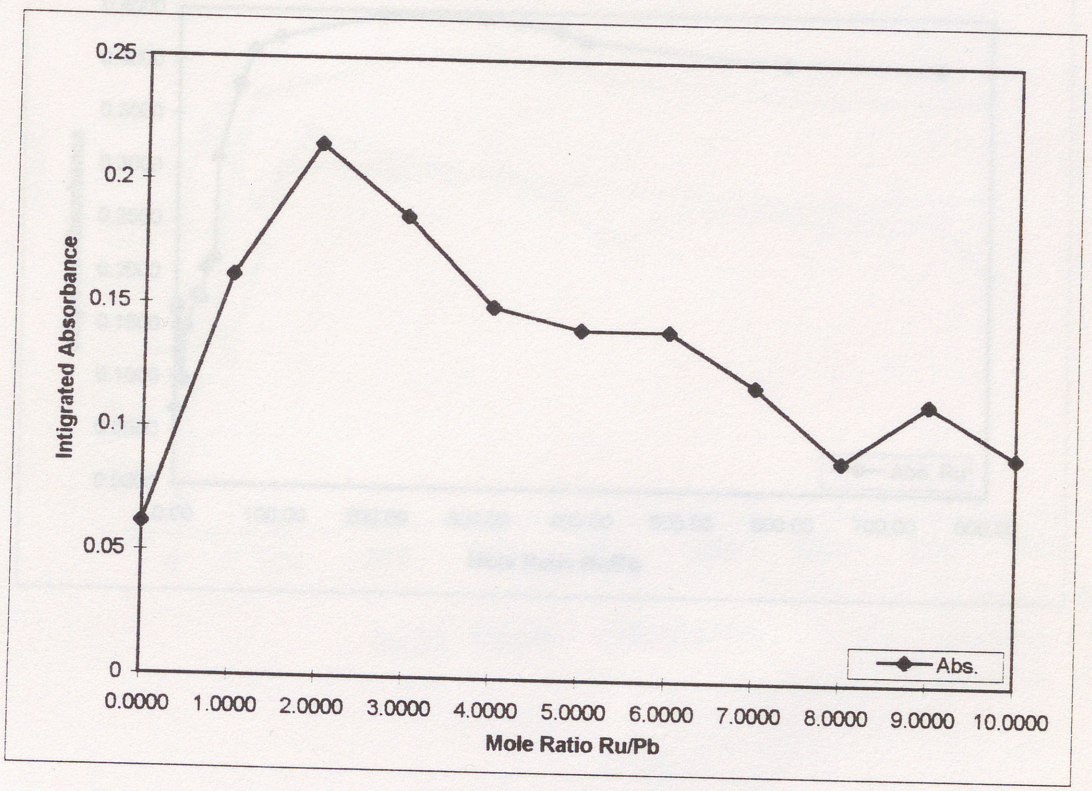


FIGURE 7

MOLE RATIO OF Ru/Pb

(100 to 750)

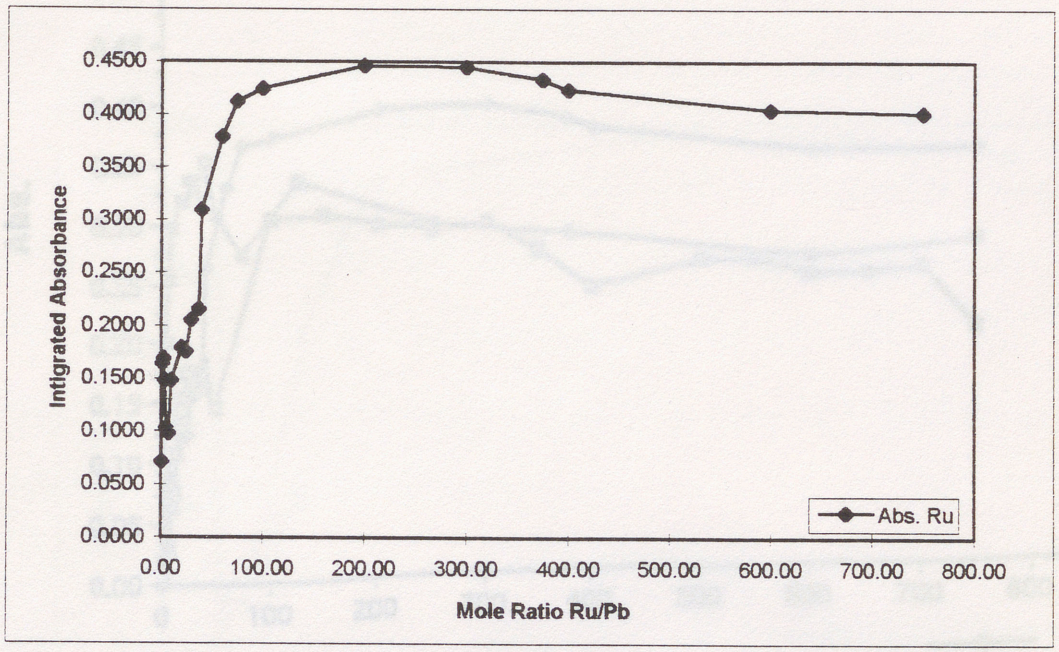
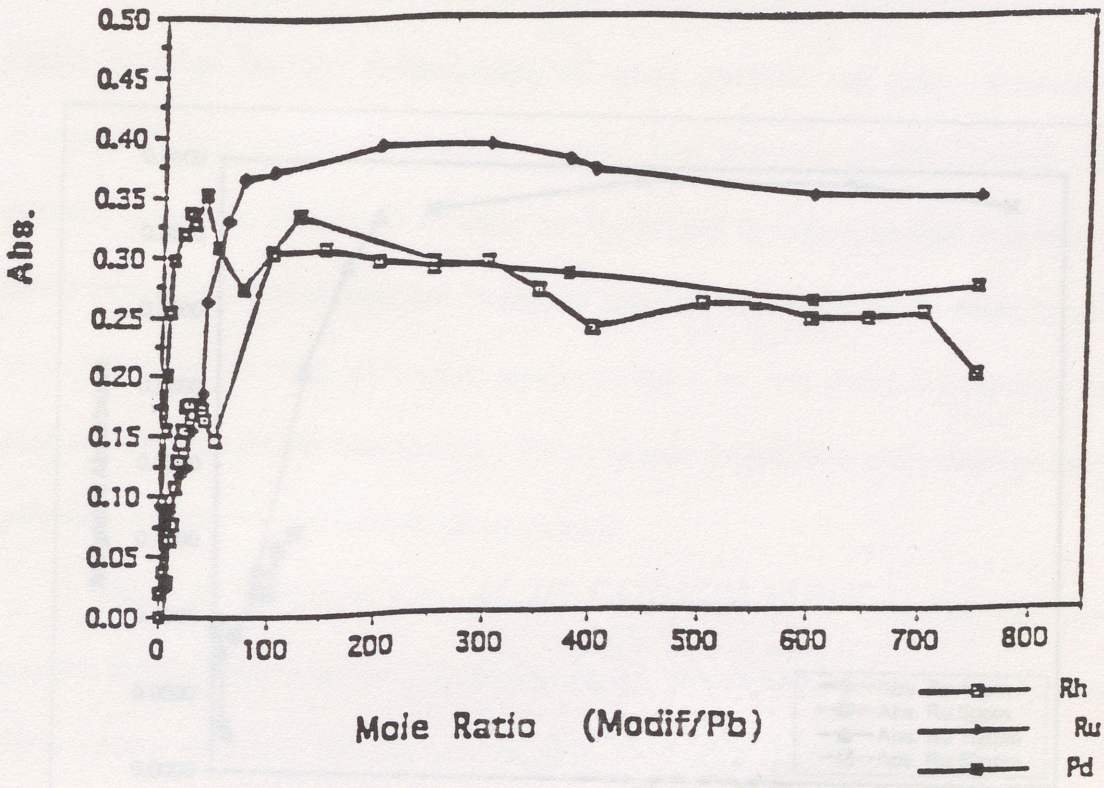


FIGURE 8

Abs. vs The Mole Ratio of Ru, Pd, and Rh to Pb

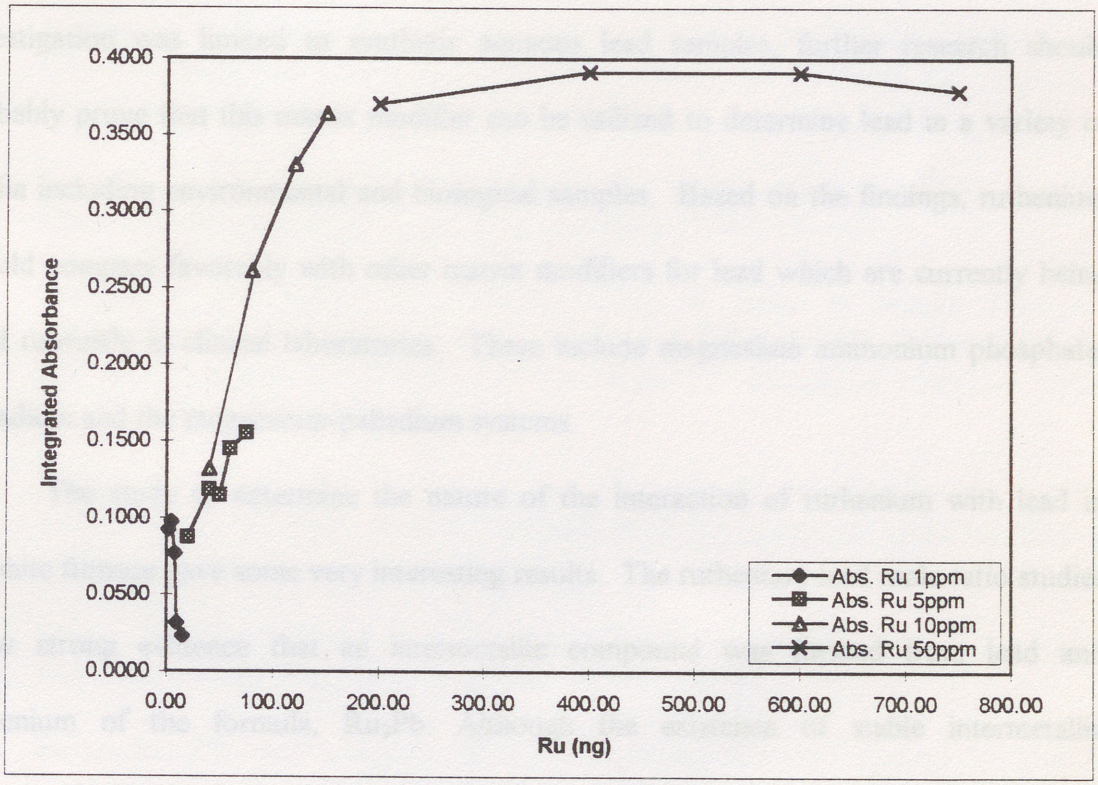


4ng Pb
Ash Temp 800°C
Atomization Temp 1900°C

FIGURE 9

THE CONCENTRATION OF RUTHENIUM

FROM 1PPM TO 50PPM



CHAPTER 4

CONCLUSION AND RECOMMENDATIONS

This investigation shows that ruthenium has the potential of serving as an excellent matrix modifier for the determination of trace quantities of lead. Although this investigation was limited to synthetic aqueous lead samples, further research should probably prove that this matrix modifier can be utilized to determine lead in a variety of media including environmental and biological samples. Based on the findings, ruthenium should compare favorably with other matrix modifiers for lead which are currently being used routinely in clinical laboratories. These include magnesium ammonium phosphate, palladium and the magnesium-palladium systems.

The study to determine the nature of the interaction of ruthenium with lead in graphite furnace gave some very interesting results. The ruthenium-lead mole ratio studies show strong evidence that an intermetallic compound was formed from lead and ruthenium of the formula, Ru_2Pb. Although the existence of stable intermetallic compounds remains somewhat uncertain, the results give evidence that these compounds may exist at least in the graphite furnace at high temperatures.

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