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Graphite Furnace Atomic Absorption Spectrometric determination of Blood Lead with Palladium modification

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Summary. In this work we present a graphite furnace atomic absorption spectrometric method for blood lead using palladium as a chemical modifier. Whole blood was diluted 10- fold with a 0.1% v/v triton X-100 solution; 10 µL of this solution and 10 µL of the palladium-based modifier (2 mg Pd/L, 2% w/v citric acid and 0.01 M nitric acid) were injected onto the L'vov platform by using the alternate volume mode. The following furnace operating parameters were used: (a) **drying steps**, 120 °C for 10s and 250 °C for 30s; (b) **pyrolysis steps**, 800 °C for 45s (with oxygen) and 1100 °C for 25s; (c) **atomization**, 1600 °C for 3s; (d) **clean out**, 2700 °C for 4s. Accuracy was tested by using (i) a NIST standard (SRM-909) and the Behring Control Blood for Metal 1 (OSSD 21) with lead concentrations of 23.7 ± 2.1 µg/L (found: 21.2 ± 0.7 µg/L) and 413 ± 51 µg/L (found: 407 ±6 µg/L), respectively; (ii) recovery studies (ca. 100 ± 1 %), and (iii) a reported method (mean relative error: 5.1 %). Approximate standard deviations of 0.3 (within-run) and 0.7 (between-runs) µg Pb/L were found in the precision study. The detection limit (3σ) and the characteristic mass (for a 10- µL injection volume) were 0.1 µg Pb/L and 15 pg/0.0044 A•s, respectively. The proposed method was used to establish the lead levels of patients with renal insufficiency; a mean concentration (± SD) of 59 ± 39 µg Pb/L (range: 12 - 160 µg Pb/L) was found. The method was interference-free, reliable and reproducible.

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INTRODUCTION

In recent years, the anthropogenic activities have rapidly increased the accumulation of lead (Pb) in urban environments (2,5). High Pb levels are found in soil and dust located near busy roadways due to automobile combustion of leaded gasoline. Lead intoxication causes clinical disorders in the central nervous system, the hematopoietic sys-

tem and the kidneys (2,8). The deleterious effects are more notable in young children because they absorb Pb more efficiently than adults (2).

A wide variety of methods has been proposed for the determination of Pb in biological and clinical materials. Graphite furnace atomic absorption spectrometry (GFAAS) is the most selected technique for this purpose, in particular for the analysis of blood specimens. Modern GFAAS-based Pb methods must consider the *chemical modification* of the sample in order to prevent pre-atomization losses by volatilization of the analyte, as Pb halides or oxides. Recently, we reported (11) the use of a chemical modifier mixture, *e.g.*, $Mg(NO_3)_2$, $NH_4H_2PO_4$ and HNO_3, for the graphite furnace determination of Pb.

In 1981 palladium (Pd) was proposed as a chemical modifier for the GFAAS determination of tellurium (in organic and inorganic samples) and bismuth (in clinical samples) (17). Since then, Pd has been widely used for the GFAAS chemical modification of many unstable elements, such as arsenic, thallium, mercury, indium, etc. (1,3,17), probably because of its *"catalytic activity"* exercised inside the graphite tube. Some of the methods suppose the use of palladium alone (1) or a mixture of palladium and magnesium nitrate (17).

The aim of the present work was to develop a graphite furnace atomic absorption spectrometric method for the determination of lead in whole blood, employing palladium as the chemical modifier. The proposed method was applied to the evaluation of the Pb levels found in patients with chronic renal failure, undergoing periodical hemodialysis.

MATERIAL AND METHODS

Apparatus

A graphite furnace atomizer (Perkin-Elmer Model HGA-500) was mounted on an atomic absorption spectrometer (Perkin-Elmer Model 2380). Standards and samples were injected by using an autosampler (Perkin-Elmer Model AS-40). Data were recorded on a printer-sequencer (Perkin-Elmer Model PRS-10). Absorbance peaks were plotted on a recorder (Perkin-Elmer R-100A).

Table I gives the optimum furnace operating parameters used for the determination of lead. The light sources were an 8-mA lead hollow-cathode lamp and a deuterium arc for background correction; the wavelength used was 283.3 nm with a 0.2-nm spectral band width (11). All data presented below were obtained using pyrolytically-coated graphite tubes with L'vov platforms. Integrated absorbance (A•s) signals were used because they minimize errors in measurements associated with the different peak profiles exhibited by lead in unmatched standards and samples (13).

Reagents

All chemicals were of analytical-reagent grades. A Pb stock solution (*ca.* 1000 mg/L) was prepared by using Pb $(CH_3COO)_2 \cdot 3H_2O$ (BDH). The blanks of the $Pd(NO_3)_2$ (Aldrich), citric acid (Riedel-de-Haen), nitric acid (Fisher Scientific), sodium heparin (Lilly) and triton X-100 (Riedel-de-Haen) were below the GFAAS detection limit of lead. The chemical modifier contained 2 mg Pd/L, 2% w/v citric acid and 0.01 M nitric acid.

TABLE I

FURNACE TEMPERATURE PROGRAM FOR THE DETERMINATION OF BLOOD LEAD, USING PYROLYSIS UNDER AN OXYGEN ATMOSPHERE AND PALLADIUM AS THE CHEMICAL MODIFIER.

Step	Temperature,°C	Ramp,s	Hold,s	Gas
Drying 1	120	5	5	Ar
Drying 2	250	20	10	Ar
Pyrolysis 1	800	30	15	O_2 (Air)
Pyrolysis 2	1100	15	10	Ar
Atomization	1600	0	3	-
Clean out	2200	4	3	Ar

The accuracy of the proposed method was tested by using the Standard Reference Material Human Serum [SRM-909 supplied by the National Institute of Standards and Technology (NIST), Washington, DC, USA], as well as the Control Blood for Metal 1 (OSSD 21) standard from the Behring Institute (D-3550, Marburg 1, Federal Republic of Germany).

Procedure

Whole blood specimens were obtained from 31 chronic renal failure patients, undergoing periodical hemodialysis at Maracaibo University Hospital, and 69 healthy volunteers. Blood was collected by using 5-mL disposable polystyrene syringes and transferred into Pb-free polypropylene tubes (with polypropylene caps), which contained about 100 µL of sodium heparin. Samples were kept at -20 °C until required for analysis (within two days). Before GFAAS analyses, the blood test portions as well as the SRM-909 were diluted 10- fold in Pb-free microvials with a 0.1% v/v triton X-100 solution; the Behring standard was diluted 20-fold in the same fashion as described already. By using the alternate volume mode of the AS- 40 autosampler, 10-µL aliquots of blood (or aqueous lead standards) and 10 µL of the chemical modifier solution were injected sequentially into the graphite tube.

RESULTS

Fig 1 depicts the optimization procedure for the selection of the most adequate Pd concentration used for the preparation of the modifier solution; the effect of the citric acid on the atomic absorption signal of Pb is also shown. These two experimental parameters were worked out by monitoring sensitivity increments, up to reaching a maximum reading, and by matching the blood test portion concentrations reported in the analyses with those of the targeted values. A Pd concentration of 2 mg/L was found to be fully sufficient for the analysis of different types of samples; the addition of 2% (w/v) citric acid produced

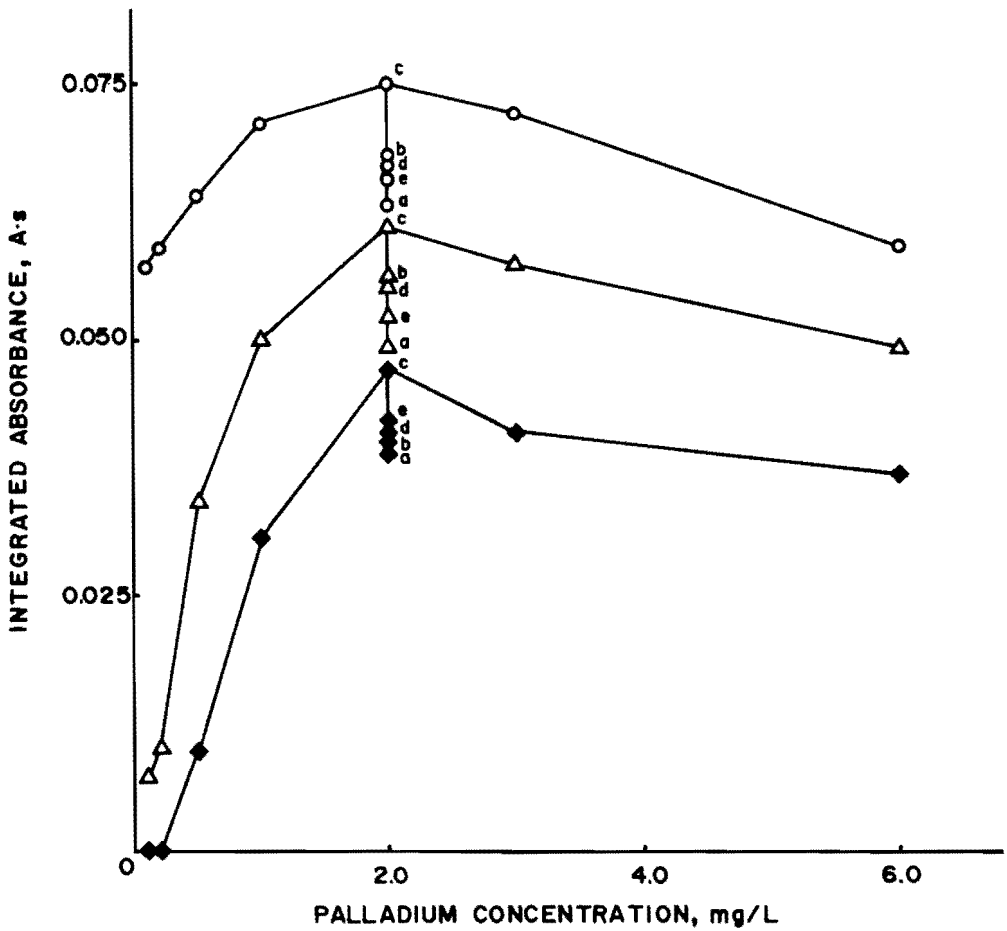


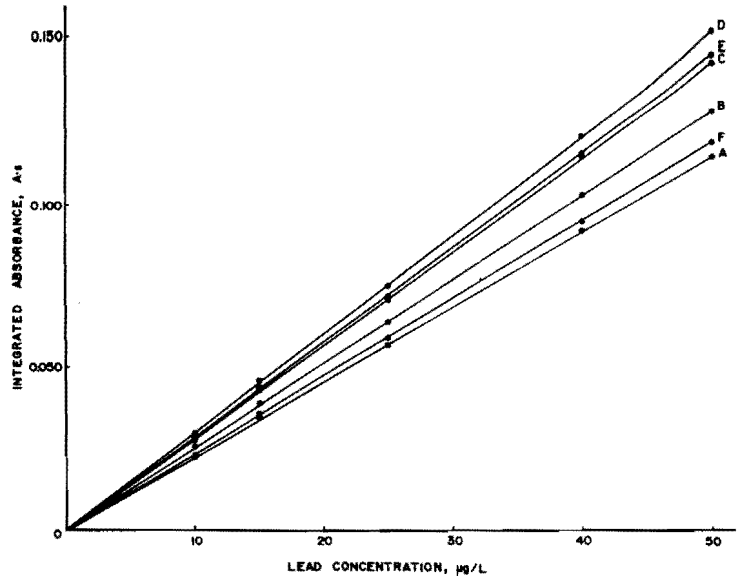
Fig. 1. Effect of the Pd concentration on the atomic absorption signal of Pb for (O) a 25-µg Pb/L aqueous standard, (Δ) the Behring Control Blood for Metal 1 (OSSD 21) standard with a 20-fold dilution (ca. 20.4 µg Pb/L) and (◆) a real whole blood test portion diluted 10-fold and containing 16 mg Pb/L. Citric acid concentration (%, w/v) as follows: a = 0, b = 1, c = 2, d = 3,e = 5. The effect of the citric acid on the Pb signal is only plotted for a Pd concentration of 2 mg/L, although a similar behavior was observed for the entire Pd range tested. Furnace conditions as shown in Table I.

the largest increase in the absorbance readings.

Graphite furnace sensitivities for aqueous Pb standards at different Pd concentrations are shown in Fig 2. The 2 mg Pd/L value was confirmed to be the most convenient modifier concentration for a wide range of Pb levels.

The absorbance-time profiles of aqueous and blood Pb were monitored for different Pd concentrations and results are in Fig 3. They further confirm the Pd concentration selected in this study.

Table II shows the influence exerted by the nitric acid on the integrated ab-



F ig. 2. Graphite furnace atomic absorption spectrometric sensitivities for aqueous Pb standards at different Pd concentrations (mg/L): A = 0.1, B = 0.5, C = 1.0, D = 2.0, E = 3.0, F = 6.0. Furnace conditions as shown in Table I. The citric acid concentration was 2% (w/v).

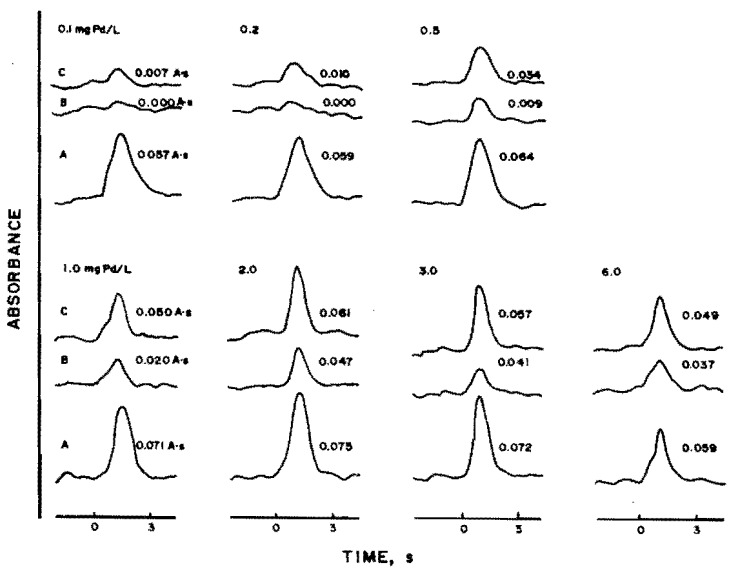


Fig. 3. Effect of the Pd concentration on the absorbance-time profiles (background-corrected) for lead in A, a 25- µg Pb/L aqueous standard, B, a real whole blood sample diluted 10-fold and containing 16 µg Pb/L and C, the Behring standard (20.4 µg Pb/L). Furnace conditions as shown in Table I. The citric acid concentration was 2% (w/v). Integrated absorbance (A·s) are presented for each profile.

sorbances of Pb. No significant differences ($p > 0.001$) were observed from 0.01 to 0.1 M nitric acid, on the Pb spectroscopic signal.

Optimization of the oxygen-ashing pyrolysis and atomization temperatures for Pb is seen in Fig 4; optimum temperatures were found to be 800 °C and 1600 °C, for the former and the latter, respectively. The proposed Pd modifier (2 mg/L) and citric acid (2% w/v) were used for aqueous standards, Behring material

TABLE II

BACKGROUND-CORRECTED INTEGRATED ABSORBANCE VALUES FOR Pb (± ONE STANDARD DEVIATION OF FIVE REPLICATES) OBTAINED FOR VARIOUS CONCENTRATIONS OF NITRIC ACID

Type of Sample	HNO_3 Concentration (mole/L) 0.01	0.05	0.1
Aqueous Standard (25 µg Pb/L)	0.075 ± 0.0013	0.074 ± 0.0042	0.074 ± 0.0068
Behring Material	0.064 ± 0.0009	0.062 ± 0.0032	0.062 ± 0.0057
Real Blood	0.048 ± 0.0004	0.047 ± .0023	0.047 ± 0.0032

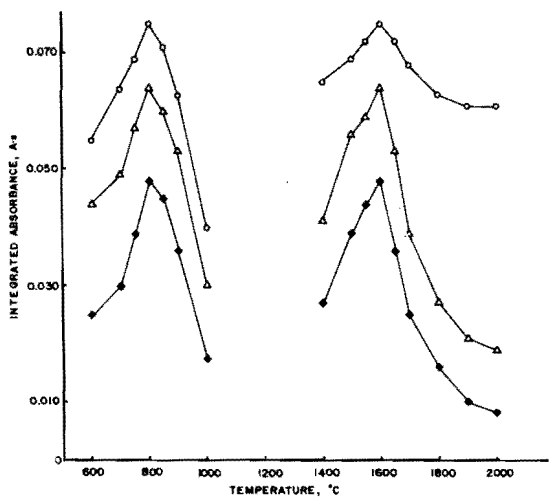


Fig. 4. Oxygen-ashing pyrolysis and atomization curves for Pb with the use of the proposed Pd modifier (2 mg/L) and citric acid (2%, w/v). (O) aqueous standard (25 µg Pb/L), (Δ) Behring material, (◆) real blood sample.

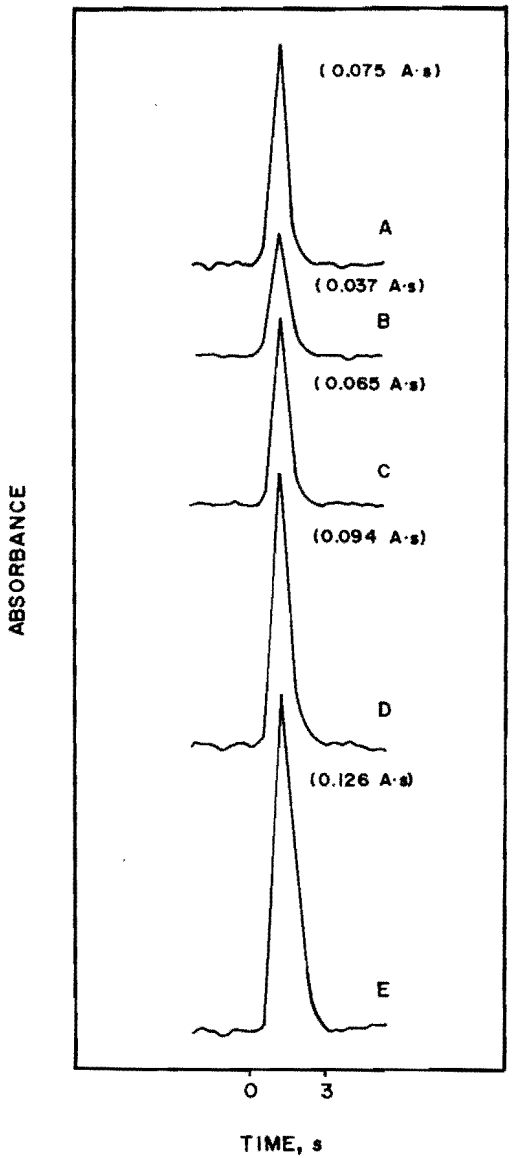


Fig. 5. Absorbance-time profiles for Pb using an atomization temperature of 1600 °C, a palladium concentration of 2 mg/L and 2% w/v citric acid. Integrated absorbances are shown in parenthesis. **A**, a 25-µg Pb/L aqueous standard, **B**, a real whole blood test portion diluted 10-fold (sample B), **C**, sample B + 10µg Pb/L, **D**, sample B + 20µg Pb/L, **E**, sample B + 30µg Pb/L.

and real blood samples.

The study of non-spectral interferences (multiplicative errors) was carried out by comparing the slopes of the calibration graphs with those obtained by the standard addition method (Figure 5). The whole blood (6 specimens) and the SRM blood standard, analyzed by the method of standard addition, yielded graphs with slopes (m = 0.0030, r = 0.9998) the same as those of the aqueous standard calibration curves.

Accuracy was tested by using the NIST standard (SRM-909) and the Behring material (0SSD 21). Samples were also analyzed with a methodology reported already (11) and comparisons were established against the proposed method. Results are presented in Table III. Recoveries studies were also performed by carrying out triplicate determinations of Pb in six whole blood test portions, as detailed in Table IV; the average recovery was 100 ± 1% (range 98 - 102%).

The within- and between-run precision values for the determination of Pb in three real samples are shown in Table V. Approximate standard deviations of 0.3 and 0.7 µg Pb/L were found for the former and the latter, respectively.

DISCUSSION

A palladium concentration of 2 mg/L was convenient to be used for a wide range of Pb concentrations and yielded to an excellent sensitivity (Figures 1 and 2). A citric acid concentration of 2% w/v was found to produce the highest absorbance signal for aqueous and blood Pb, leading to results that were in accordance with the target values of

TABLE III

ACCURACY OF THE DETERMINATION OF BLOOD LEAD (mean ± SD, µg Pb/L) BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

	Target	Found	Relative error,%
NIST standard (SRM-909)	23.7 ± 2.1 [a]	21.2 ± 0.7	11.8
Behring Control Blood for Metal 1 (0SSD 21)	413 ± 51 [b]	407 ± 6	1.5
Real Blood Test Portions			
1	95 ± 3 [c]	94 ± 4	1.1
2	64 ± 3 [c]	59 ± 8	7.8
3	48 ± 2 [c]	48 ± 7	-
4	51 ± 3 [c]	55 ± 5	7.8
5	47 ± 1 [c]	48 ± 10	2.1
6	89 ± 6 [c]	80 ± 10	10.1
7	71 ± 10 [c]	66 ± 9	7.0
8	158 ± 5 [c]	160 ± 8	1.3

[a] Value certified by NIST (USA)
[b] Value certified by Behring Institute (Germany)
[c] Value certified by using a reported methodology (11)

the certified blood lead materials supplied by NIST and Behring Institute. Citric acid originated a more favorable environment for the reduction of Pd, providing for a more consistent performance (18).

Decreased integrated-absorbance signals (Figs 1 and 2) were found when an excessive amount of Pd was used (*ca.* > 2 mg Pd/L). A comparable behavior was also observed by Puchades *et al.* (14) when studying the influence of the con-

TABLE IV

RECOVERY OF LEAD ADDED TO TEST PORTIONS OF REAL WHOLE BLOOD

Added (µg Pb/L)	Expected (µg Pb/L)	Found (µg Pb/L)	Recovery (%)
10	102	101	99
10	108	106	98
20	112	113	101
20	118	118	100
30	122	124	102
30	128	128	100
			$\overline{100 \pm 1}$ %

TABLE V

WITHIN- AND BETWEEN-RUN PRECISION VALUES FOR THE DETERMINATION OF BLOOD LEAD BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

Real Blood Specimens	Mean[1] Concentration (µg Pb/L)	Within-run[2] SD (µg Pb/L)	Within-run[2] RSD (%)	Between-runs[3] SD (µg Pb/L)	Between-runs[3] RSD (%)
1	12.0	0.3	2.5	0.9	7.5
2	10.2	0.5	4.9	0.8	7.8
3	8.5	0.2	2.4	0.3	3.5

[1] In blood test portions diluted ten-fold
[2] Triplicate samples; three runs each
[3] Triplicate samples per analysis; three runs each and analyzed over a five-day period.

centration of a phosphate modifier on the analytical atomic absorption signal of Pb in a graphite furnace. Two possible reasons could be argued: 1) an *"over-stabilization"* (11) of the analyte as a result of the coating of the graphite surface with Pd, making thus the carbon unavailable for the reduction of Pb to form elemental Pb in a quantitative fashion, and 2) an analytical sensitivity decrease caused by the gradual deterioration of the graphite platform induced by the corrosive effect of Pd (15). The mechanism(s) of stabilization of the Pd is not fully understood yet. However, it has been speculated that Pd may originate an *"alloy"* with the Pb (17). Our own idea on this matter is that Pd exercises a *"catalytic activity"* and forms an *"intermetallic cluster"* with the Pb. Whatever the reality is, the Pd concentration is crucial and should be carefully selected in order to be able to produce accurate analyses.

It can be observed from Fig 3 that the best Pb absorbance-time profiles, with respect to the shape of the atomization pulse (fairly symmetric with minimum tailing and returning to the base line within 1 to 2 s after its appearance) were obtained at a Pd concentration of 2 mg/L. Additionally, similar appearance times were obtained for both aqueous standards and blood samples, as reported by Hinds and Jackson (9) for soil lead. These findings contrast with the different peak shapes exhibited by lead in unmatched standards and samples when using phosphate modifiers (11,13) or without modifier (4).

Nitric acid did no exert any significant effect on the spectroscopic behavior of Pb, at concentrations ranging from 0.1 to 0.01 M. However, the higher the acid concentration the worse the reproducibility, probably due to the ability of HNO_3 to oxidize the surface of the graphite platform; the oxidized surface would then have fewer active reducing sites available for the reduction of Pb compounds to atomic Pb (6). Yet, the addition of a low concentration of HNO_3 prevents adsorption of the metal onto the container walls and the metal

hydrolysis; these are the reasons for us to advise its use.

The optimum conditions that we recommend for the preparation of the whole blood for the GFAAS determination of Pb are as follows: ten-fold dilution of the test portion with 0.1% v/v triton X-100, use of a modifier solution containing 2 mg Pd/L and 2% w/v citric acid in 0.01 M nitric acid, and sequential injection of 10 µL of blood and 10 µL of modifier solution onto the L'vov platform.

It should be emphasized that the new furnace parameters, used for the GFAAS determination of whole blood Pb, were achieved with (i) a pyrolysis step under an oxygen atmosphere and (ii) a modifier solution containing palladium and citric acid (as described above). The former circumstance favored the removal of concomitants (*e.g.*, by *combustion* of the organic matrix), preventing thus the build-up of carbonaceous residues, taking place inside the graphite tube, which may result in decreased sensitivities.

The optimum pyrolysis and atomization temperatures for Pb were determined by steadily increasing the temperatures for fixed concentrations of Pb in aqueous solution, blood standard and real samples, and noting the temperatures where the optimum signals for Pb were seen (Fig 4). Below the optimum pyrolysis temperature of 800 °C the effects of the matrix are seen and above that optimum a loss of Pb probably accounts for the decreasing signal. The successful use of O_2 (*e.g.*, air) during the pyrolysis cycle allowed for a more complete removal of the organic-based matrix by converting a pyrolysis process to a combustion process, eliminating the build-up of the carbonaceous residues, as cited already. These blocked the optical beam, increased the nonspecific absorbance signal during the atomization cycle and produced an erratic release of the analyte metal which affected the analytical accuracy. Similarities in the shape of the Pb pyrolysis optimization curves have been reported by others (6,7,10,14).

Besides the stabilization to higher pyrolysis temperatures, the application of a modifier usually permits the use of higher atomization temperatures. However, Schlemmer and Welz (17) reported that the effect of the Pd modifier on atomization temperature, in comparison with the traditionally recommended modifiers, is not uniformly in one direction. For instance, the optimum atomization temperatures for arsenic and antimony, which are fairly high if nickel is used as the modifier, can be lower with the application of Pd (ca. from 2400 °C down to 2100 °C). We found a comparable situation when switching from phosphate (ca. 2300 °C) (11) to Pd (ca. 1600 °C). It can be seen from Fig. 4 that the atomization curves exhibited a pronounced maximum. The drop to lower integrated absorbance values at higher temperatures was most likely caused by increasing diffusional losses of Pb atoms under these conditions. Thus, in accordance with these results Pb was quantitatively atomized from the L'vov platform at 1600 °C. This lower temperature contributed to extend the life of the pyrolytic graphite coated graphite tubes and of the platforms, allowing up to approximately 350 firings.

Results from the standard addition method served to demonstrated the absence of non-spectral interferences in

the GFAAS determination of whole blood Pb by the proposed method. For this reason, whole blood Pb levels were evaluated against aqueous Pb standard calibration graphs. Furthermore, no chemical interference from the diluent (triton X-100) was found; thus, it was unnecessary to add triton X-100 to the aqueous Pb standards.

The accuracy of the method (Tables III and IV) was tested in four different ways: (i) by analyzing the standard reference material from NIST (SRM-909) and (ii) the Behring Control Blood for Metal 1 (OSSD 21), (iii) by comparing the results with those obtained when using our method described previously (11), and (iv) by employing recovery studies. The precision was thoroughly evaluated (Table V) and results can be considered as adequate for this type of analysis. In general, the performance of these two analytical parameters attested to the excellence of the developed GFAAS-based methodology for blood Pb.

The detection limit (3σ) and the characteristic mass, m_o, (for 10-µL injection volume) were 0.1 µg Pb/L and 15 pg Pb/0.0044 A•s, respectively. The m_o values for Pb, reported by Pruszkowska *et al.* for river water (13), and Schlemmer and Welz for sea water (17), are 13 and 12 pg Pb/0.0044 A•s, respectively. As expected, these values are similar to ours, because m_o will be independent of the matrix under study if the GFAAS analysis is free from interference.

The proposed method has been used in our laboratory to establish the whole blood lead levels exhibited by 31 patients with chronic renal failure (CRF), undergoing hemodialysis treatment at Maracaibo University Hospital, Venezuela, and by control individuals. A mean Pb concentration of 59 ± 39 µg/L (range: 12 - 160 µg Pb/L) was found for the renal patients. This is somewhat lower that a value reported by us previously (*ca.* 135 ± 18 µg Pb/L), for a more homogeneous population of CRF patients (16). In any case, persons with a normal kidney function have a higher blood Pb (*ca.* 189 ± 33 µg Pb/L, n = 69 controls) (12,16), because Pb intoxication depends to a large extent on environmental and occupational exposure (2) and the restricted habits of patients with renal insufficiency protect them from overexposure (12).

It is concluded that the GFAAS method described above is sufficiently sensitive, accurate, and precise and can be applied to a wide range of Pb concentrations. It provides, therefore, an important alternative for the determination of lead in whole blood.

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RESUMEN

Determinación de Plomo Sanguíneo por Espectrometría de Absorción Atómica con Horno de Grafito y Modificación por Paladio. Granadillo V. A. (Laboratorio de Instrumentación Analítica. Facultad Experimental de Ciencias. Universidad del Zulia. Maracaibo 4011, Venezuela), Navarro J.A., Romero R.A. *Invest Clin 32(1): 27-39,1991*

En este trabajo se presenta un método para la determinación del plomo sanguíneo por espectrometría de absorción atómica con horno de grafito, empleando paladio como modificador químico. Las muestras de sangre se diluyeron 10 veces con una solución de triton X-100 al 0.1%; 10 µL de esta solución y 10 µL del modificador de paladio (2 mg Pd/L, ácido cítrico al 2% p/v y ácido nítrico 0.01M) se inyectaron sobre la plataforma de L'vov, empleando el modo de volumen alterno. Se usaron los siguientes parámetros de operación del horno: (a) **etapas de secado**, 120 °C por 10s y 250 °C por 30s; (b) **etapas de pirólisis**, 800 °C por 45s (con oxígeno) y 1100 °C por 25s; (c) **atomización**, 1600 °C por 3s; (d) **limpieza**, 2700 °C por 4s. La exactitud se evaluó mediante (i) standards de la NIST (SRM-909) y de la Behring (Control Blood for Metal 1, OSSD 21) con concentraciones de plomo de 23.7 ± 2.1 y 413 ± 51 µg/L, encontrándose 21.2 ± 0.7 y 407 ± 6 µg/L, respectivamente; (ii) estudios de recuperación (ca. 100 ± 1%), y (iii) contra un método reportado (error relativo promedio: 5.1%). En el estudio de precisión se encontraron desviaciones standards aproximadas de 0.3 (en la corrida) y 0.7 (entre muestras) µg Pb/L. El límite de detección (3σ) y la masa característica (para un volumen de inyección de 10 µL) fueron 0.1 µg Pb/L y 15 pg/0.0044 A•s, respectivamente. La aplicación de este método en el estudio de los niveles plúmbicos de una población renal reveló una concentración media (± SD) de 59 ± 39 µg Pb/L (rango: 12 - 160 µg Pb/L).

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