PALLADIUM-INDUCED ANALYTE ISOFORMATION EFFECTS ON LEAD AND VANADIUM IN THE GRAPHITE FURNACE

VICTOR A. GRANADILLO, ROMER A. ROMERO and JANETH A. NAVARRO

Laboratorio de Instrumentación Analítica, Facultad Experimental de Ciencias, Universidad del Zulia. Maracaibo, Zulia 4011. Venezuela

Abstract The graphite furnace atomic absorption spectrometric (GFAAS) determination of lead and vanadium in medical and environmental materials was accomplished by using palladium as the analyte isoformer. Citric acid promoted the formation of active deposits of carbon in the graphite tube. Pd demonstrated to be equally useful for the GFAAS evaluation of volatile as well as refractory metals.

Key words analyte isoformation, graphite furnace, lead, palladium, vanadium

The determination of metals in medical, biological and environmental materials is commonly achieved by using graphite furnace atomic absorption spectrometry (GFAAS), because of the high sensitivity exhibited by this technique, its excellent selectivity and decreased sample handling requirements. However, GFAAS is prone to spectral and non-spectral interferences, many of which may induce severe analytical errors [1,2].

The use of chemical and physical modifiers is a valid analytical approach to overcome the non-spectral interferences found in the GFAAS [3,4]. We propose the "**analyte isoformer**" expression in substitution of the traditional terms, because it suggests the process that is actually accomplished by the modifier: the analyte isoformation. Thus, it summarizes the chemical or physical actions that the modifier performs on the analyte and/or matrix under study. Analyte isoformation contributes to the elimination by volatilization of the concomitants during the pyrolysis steps and promotes the thermal stabilization of volatile analytes and the lessening of the atomization temperature for refractory elements. In general, the analyte isoformer must guarantee that the analyte element, independently of the form(s) in which it was originally present, is transformed into the same form in samples and standards [5].

In the last 15 years a great variety of analytical isoformers have been reported, generating some sort of "environmental pollution" in GFAAS. 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) [3]. Since then, Pd has been widely used for the GFAAS chemical modification of many unstable metals, such as arsenic, thallium, mercury, indium, etc. [3,6,7], probably due to the catalytic activity exercised inside the graphite tube to form some kind of metal clusters. Recently, palladium has gained more attention and has even been considered as a universal isoformer.

The aim of this work was to study the palladium-induced analyte isoformation present during the determination of lead (Pb) and vanadium (V) in several types of research materials (e.g., whole blood, urine, pond sediment, etc.). The absorbance-time profiles, obtained from the atomization of Pb and V in the graphite furnace, were used to investigate the spectroscopic behavior of these two analytes in the real matrixes.

EXPERIMENTAL

Apparatus A graphite furnace atomizer (Perkin-Elmer Model HGA-500) was

mounted on an atomic absorption spectrophotometer (Perkin-Elmer Model 2380). Standards and samples were injected via 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 1 gives the optimum furnace operating parameters used for the determinations of Pb and V. The light sources were the hollow cathode lamps for Pb and V, and a deuterium arc for background correction. The wavelengths (nm) and spectral band widths (nm) were 283.3 and 0.2 (for Pb) [2], and 318.4 and 0.7 (for V) [8]. All data presented below were obtained using pyrolytic graphite coated graphite tubes with L'vov platforms.

TABLE 1. Furnace temperature programs for lead and vanadium

Step	Temperature/°C		Ramp/s		Hold/s	
	Pb	V	Pb	V	Pb	V
Dry	120	100	5	20	5	15
	150	130	20	5	10	5
Pyrolyze	600*	800*	30	20	15	15
	600	800	0	0	10	10
		1100		10		10
		1700		5		5
Atomize**	2000	2700	0	0	5	5
Clean out	2700	2500	1	1	3	3
		2700		1		2

*Internal alternate gas: air

**Internal flow of Ar: 0 ml/min

Reagents All chemicals were of analytical-reagent grades. Stock solutions (ca. 1.000 g/l) were prepared by using $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (BDH) and NH_4VO_3 (Riedel-de-Haen). Blanks of the $\text{Pd}(\text{NO}_3)_2$ (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 limits of Pb and V. The analyte isoformer solutions contained 500 μg Pd/l and 2% w/v citric acid (for Pb), and 100 μg Pd/l, 2% w/v citric acid and 0.1% v/v triton X-100 (for V); both in 0.01 M nitric acid.

The accuracy of the GFAAS methods for lead and vanadium was tested by analyzing different Standard Reference Materials supplied by the National Institute of Standards and Technology, NIST, USA (Human Serum SRM-909 and Toxic Metals in Freeze-Dried Urine SRM-2670), Behring Institute, Federal Republic of Germany (Control Blood for Metal OSSD 21), Kaulson Laboratories, Inc., USA (Blood Lead Control # 0100 MED and Urine Lead Control # 0110 MED), and the National Institute for Environmental Studies, NIES, Japan (Pond Sediment NIES No. 2, Chlorella NIES No. 3, Tea Leaves NIES No. 7, Vehicle Exhaust Particulates NIES No. 8 and Sargasso NIES No. 9).

Procedure Metal determinations were carried out with the L'vov platform arrangement and an oxygen pyrolysis step just before atomization. Samples mixed up with the analyte isoformer either before injection into the graphite tube (for V) or on the platform by using the alternate volume mode of the autosampler (for Pb). The optimum amounts of Pd were: 5 μg / 10- μl injection and 2 μg / 20- μl injection, for Pb and V, respectively. Before GFAAS analysis, the test portions were diluted with triton X-100 (0.1, 0.5 or 1.0% v/v, for whole blood, plasma and serum), with nitric acid (0.01 or 0.1 M, for mineralization samples, e.g., biological samples and environmental specimens), or with triton X-100 and nitric acid (0.01% v/v + 0.01 M, for urine). Whole blood, blood components and urine were analyzed directly by GFAAS (after dilution as described already); other materials were mineralized before the GFAAS analysis, by using microwave irradiation and following procedures reported previously [9].

RESULTS AND DISCUSSION

The use of palladium permitted the application of higher pyrolysis temperatures without significant losses of the analytes under study.

Additionally, Pd contributed to decrease the atomization temperatures; for instance, Pb atomized at 2300 °C when using the phosphate/magnesium oxide analyte isoformer [2]. The refractory V atomized at 2700 °C probably due to the formation of a Pd-V cluster with a higher vapour pressure than V itself. Fig. 1 shows the absorbance-time profiles for Pb and V with and without Pd-induced analyte isoformation. In the case of the Pb, the isoformation led to similar appearance times in both aqueous standards and real samples; contrarily, Pb appeared having different spectroscopic behaviors in samples and references when the phosphate/magnesium oxide isoformer was used (Fig. 2). Preliminary results from our research group have showed that the appearance time for the atomic peak of Pb is related to the amount of active carbon capable of reducing the atomic precursor to the free analyte atom.

Fig. 1. Absorbance-time profiles of (A) Pb and (B) V, without (i) and with (ii) Pd. For Pb, 25 µg/l aqueous standard (—) and 21 µg/l whole blood (---). For V, 5.0 µg/l aqueous standard (—) and 3.1 µg/l blood plasma (---).

Fig. 2. The analytical profiles of Pb with: (a) palladium and (b) phosphate/magnesium. (—) 25 µg Pb/l aqueous standard and (---) 21 µg Pb/l whole blood.

Fig. 3 depicts the oxygen effect on the appearance time of lead due to the reaction:

where the presence of oxygen causes the equilibrium position of the reaction to shift to the left. Thus, the oxygen step allowed to eliminate the carbonaceous residues left in the graphite tube and favored the formation of lead oxide which seems to chemisorbe nondissociatively on the Pd substrate. Lead and vanadium absorbance profiles indicated absence of the background attenuation-type spectral interferences (Fig. 1). Moreover, sensitivity increments of 23% and 77% were achieved for Pb and V, respectively.

Tables 2 and 3 present the results for the accuracy evaluation of Pb and V. Mean relative errors of 3.3% and 2.6% were obtained for Pb and V, respectively, attesting to the excellence of the Pd-induced isoformation.

Fig. 3. Oxygen effect on the analytical atomic signal of lead in an aqueous standard (ca. 25 µg/l), (---) with and (—) without oxygen.

TABLE 2. Accuracy for the GFAAS determination of lead

Reference material	Target	Found	Relative error, %
SRM - 2670 ($\mu\text{g/l}$)	109 $\pm$ 4	106 $\pm$ 5	2.8
OSSD 21 ($\mu\text{g/l}$)	413 $\pm$ 51	424 $\pm$ 28	2.7
0100 MED ($\mu\text{g/l}$)	480 $\pm$ 80	494 $\pm$ 60	2.9
0110 MED ($\mu\text{g/l}$)	500 $\pm$ 100	489 $\pm$ 42	2.2
NIES No. 2 ($\mu\text{g/g}$)	105 $\pm$ 6	102 $\pm$ 4	2.9
NIES No. 3 ($\mu\text{g/g}$)	0.60	0.65 $\pm$ 0.03	8.3
NIES No. 7 ($\mu\text{g/g}$)	0.80 $\pm$ 0.03	0.78 $\pm$ 0.01	2.5
NIES No. 8 ($\mu\text{g/g}$)	219 $\pm$ 9	214 $\pm$ 4	2.3
NIES No. 9 ($\mu\text{g/g}$)	1.35 $\pm$ 0.05	1.31 $\pm$ 0.02	3.0

TABLE 3. Accuracy for the GFAAS determination of vanadium

Reference material	Target	Found	Relative error, %
SRM - 909 ($\mu\text{g/l}$)	2.70 $\pm$ 0.56	2.80 $\pm$ 0.62	3.7
SRM 2670 ($\mu\text{g/l}$)	120	125 $\pm$ 26	4.2
NIES No. 2 ($\mu\text{g/g}$)	250	250 $\pm$ 28	
NIES No. 8 ($\mu\text{g/g}$)	17 $\pm$ 2	17.5 $\pm$ 1.0	2.9
NIES No. 9 ($\mu\text{g/g}$)	1.0 $\pm$ 0.1	0.98 $\pm$ 0.05	2.0

The detection limits (3σ) were 0.1 and 0.6 $\mu\text{g/l}$, for Pb and V, respectively. Characteristic masses (m_0) were 12 pg Pb/0.0044 A.s and 44 pg V/0.0044 A.s, for 10 and 20 μl injection volumes, respectively. The m_0 values for Pb, reported by Pruszkowska et al. for river water [10] and Schlemmer and Welz for sea water [3], are 13 and 12 pg Pb/0.0044 A.s, respectively. For V, Slavin and Carnrick [11] reported an m_0 of 40 pg V/0.0044 A.s. As expected, these values are similar to ours because m_0 will be independent of the matrix under study if the GFAAS analysis is free from interferences.

It is concluded that Pd was useful for the GFAAS determination of volatile and refractory analytes, the analytical sensitivity was improved and the accuracy and precision were excellent, as certified by the analyses performed in complex reference materials.

ACKNOWLEDGEMENT

This research was partially supported by grant S1-1994 from Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT). Authors wish to acknowledge the certified materials endowed by the National Institute for Environmental Studies (NIES), Japan.

REFERENCES

1. D.A. Bass and J.A. Holcombe, *Anal. Chem.*, **59**, 974 (1987).
2. J.A. Navarro, V.A. Granadillo, O.E. Parra and R.A. Romero, *J. Anal. At. Spectrom.*, **4**, 401 (1989).
3. G. Schlemmer and B. Welz, *Spectrochim. Acta*, **41B**, 1175 (1986).
4. R.D. Ediger, *At. Absorpt. Newsl.*, **14**, 127 (1975).
5. B. Welz, *Fresenius Z. Anal. Chem.*, **325**, 95 (1986).
6. L. Beach and T. Rettberg, Paper No. 601, XVI FACSS Meeting, Chicago, USA (1989).
7. G.R. Carnrick, G. Schlemmer and S. McIntosh, Paper No. 602, XVI FACSS Meeting, Chicago, USA (1989).
8. J.A. Navarro, V.A. Granadillo and R.A. Romero, Paper No. 361, XVII FACSS Meeting, Cleveland, USA (1990).
9. O.E. Parra and R.A. Romero, *Acta Cient. Ven.*, **39**, 145 (1988).
10. E. Pruszkowska, G.R. Carnrick and W. Slavin, *At. Spectrosc.*, **4**, 59 (1983).
11. W. Slavin and G.R. Carnrick, *At. Spectrosc.*, **6**, 157 (1985).