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GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY WITH MATRIX MODIFICATION FOR DETERMINATION OF LEAD IN DRINKING WATER

J.L. Manzoori* and A. Saleemi

Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Islamic Republic of Iran

Abstract

An ammonium vanadate plus sodium molybdate mixed modifier Graphite Furnace Atomic Absorption Spectrometric method has been developed for determination of traces of lead in drinking water. The concentration of lead in the sample is obtained by direct comparison to linear working graph prepared from aqueous standards in the modifier medium. The results indicate the better performance of the proposed modifier over Pd-Mg. Recovery of lead from spiked samples was 99.4%. The within-run and within-batch precisions, RSD, were less than 4%. The limit of detection based on three times the standard deviation of the blank was 0.07 $\mu g\ l^{-1}$. The sensitivity and simplicity of the method make it attractive for routine determination of lead in environmental samples.

Introduction

Lead is a major toxicant and interferes notably with the central nervous system, the hematopoietic system and the kidneys [1]. The determination of lead in environmental samples is, therefore, of great importance.

Trace amounts of lead have been determined in numerous sample materials using Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) [2], however, the routine determination of lead by this method suffers from spectral and chemical interferences. Several methods have been used to remove these interferences by adding chemical modifiers [3, 4]. Palladium and a mixture of palladium-magnesium have proved to be the most successful modifier in GF-AAS for many elements including lead [5,6]. However, it has been reported that in some cases the refractory behavior of lead can cause analytical errors in GF-AAS when palladium is used as matrix modifier [7].

Keywords: Electrothermal atomic absorption spectrometry; Lead determination; Vanadium modifier

Furthermore, better results have been obtained without the use of Mg-Pd modifier by a fast temperature programme for the determination of lead [8].

A number of workers [6,9] have reported that vanadium based modifiers are expected to be suitable chemical modifiers. In a recent paper [10], we reported the application of vanadium based modifiers for the determination of Cr in saline waters and serum samples. The aim of the present work was to evaluate the potential of vanadium as a chemical modifier in the determination of lead in water samples by GF-AAS.

Experimental Section

Apparatus

The experiments were performed using a Shimadzu Atomic Absorption Spectrometer Model AA 670 G with a Graphite Furnace Atomizer GFA-4A, an autosample changer 60G and a Graphtic Printer PR4. A lead Hollow Cathode Lamp, Hamamatsu Photonics, K, K, Japan, and pyrolytic graphite coated graphite tubes were used with

sample injection directly onto the tube wall. The sample injection volume was 10 µl in all experiments. The graphite tubes were conditioned by five injections of the modifier solutions and running the temperature programme before analysis. The instrumental parameters and temperature programme for the graphite furnace are listed in Table 1.

Reagents

Analytical-grade reagents (E. Merck) and doubly distilled deionized water were used throughout. All glassware was soaked in 5% V/V nitric acid for at least 24 h and washed with distilled deionized water. The lead stock solutions (1000 µg ml^{-1}) were prepared by dissolving lead nitrate in 1% V/V nitric acid. Working solutions were prepared daily from lead stock solution by serial dilution with distilled deionized water. Stock solution (10000 µg ml^{-1}) of V was prepared by dissolving NH_4VO_3 in 1% V/V H_2O_2. Stock solutions (10000 µg ml^{-1}) of W, Cr, Pd, Mo, Cu, and Mg were prepared by dissolving Na_2WO_4, $2H_2O$; $K_2Cr_2O_7$; Pd $(NO_3)_2$; Na_2MoO_4, $2H_2O$; Ca $(NO_3)_2$; $4H_2O$; and $Mg(NO_3)_2$ in 1% V/V nitric acid. None of these solutions contributed any measurable blank except ammonium vanadate which was purified by solvent extraction with oxine into chloroform.

Results and Discussion

Selection of Modifier

Initial experiments were conducted to investigate the effect of various chemical modifiers on the determination of lead by GF-AAS. The concentration of each modifier was optimized by plotting the absorbance versus concentration, under optimized conditions listed in Table 1. The concentrations giving the highest absorbance value were chosen as optimum. The effects of pretreatment and atomization temperatures on the absorbance peak height for lead using various chemical modifiers with optimized concentrations were studied.

In order to study the effects of pretreatment temperatures on the peak height, the atomization temperatures were fixed at 2000°C and pretreatment temperatures were varied from 400 to 1200°C. For the study of the effect of atomization temperatures on the peak height, the pretreatment temperatures were fixed at 600°C and atomization temperatures were varied from 1000 to 2400°C. The variations of peak heights versus pretreatment and atomization temperature were plotted. An example of these graphs is shown in Figure 1, for 10 µg l^{-1} of lead without and with V or Pd modifiers. The results of these experiments are summarized in Table 2. Consideration of

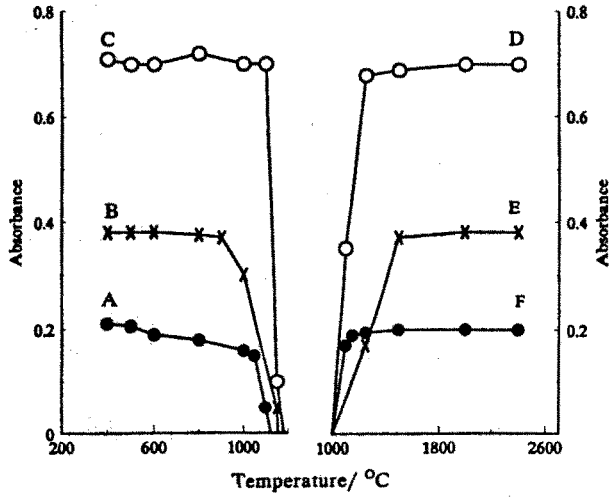

Figure 1. Pyrolysis (A, B and C) and atomization (D, E and F) curves for 10 µg l^{-1} of lead; A and F without; B and E with 10 µg of Pd; C and D with 10 µg of V modifier

Table 1. Instrumental parameters for lead analysis

Spectrometer				
Wavelength/nm	217			
Slit width/nm	0.3			
Lamp current /mA	7			
Integration time/s	3			
Absorbance measurement	peak height			
Graphite furnace				
Stage	Temperature/°C	Time/s		Argon gas
		Ramp	Hold	Flow/ml min^{-1}
Drying	120	10	20	500
Ashing	600	10	15	500
Atomization	2000	-	3	0
Cleaning	2500	-	2	500
Cooling	50	-	3	500

Table 2. Effect of various modifiers on the pyrolysis and absorption peak height of 10 μg l^{-1} of lead

Chemical modifier	Mass/μg	Maximum pyrolysis temperature/°C	Relative sensitivity
-	-	500	1
Ca	5	600	1.33
Mg	5	750	1.83
Ca +Mg	5+5	700	1.23
Pd	5	900	1.68
Pd +V	10+5	1050	2.64
Mo	10	700	1.78
Cr	5	550	1.42
V	10	1090	3
W	10	700	1

Table 2 reveals that the maximum pretreatment temperature and largest signal enhancement are obtained with V modifier.

As the efficiency of thermal stabilization is the prime requirement of chemical modifiers and on the basis of signal enhancement effect, V was thought to be the most suitable chemical modifier for lead.

The mechanism of thermal stabilization by chemical modifiers involves: formation of individual chemical analyte-modifier compounds with defined structure and properties [11], or formation of analyte-modifier solid solutions [12]. The experimental evidence that the lead thermal stabilization is attained with a large excess of ammonium vanadate, favours the formation of solid solutions rather than the formation of a stoichiometric chemical compound between analyte-modifier, though further work seems to be necessary to clarify the chemical modification mechanism of V.

Influence of the Modifier on the Performance of GF

The variation of the sensitivities and RSD (five replicate firings around each number indicated in figures) with respect to the graphite age with and without V modifier are shown in Figures 2 and 3, respectively. These figures show that without using V modifier a considerable decrease in sensitivity and increase in RSD are observed while with V modifier no discernible trend in sensitivity and RSD variation is observed throughout the analysis.

Determination of Lead in Water Samples

In order to validate the effectiveness of ammonium vanadate modifier in the determination of lead, analyses of water samples were attempted. The recoveries of lead spiked into drinking water using vanadium based modifiers are shown in Table 3. Values for lead in the sample were obtained by direct comparison to linear working curves prepared from aqueous standards in the modifier medium.

The results show that only with V + Mo mixed modifier

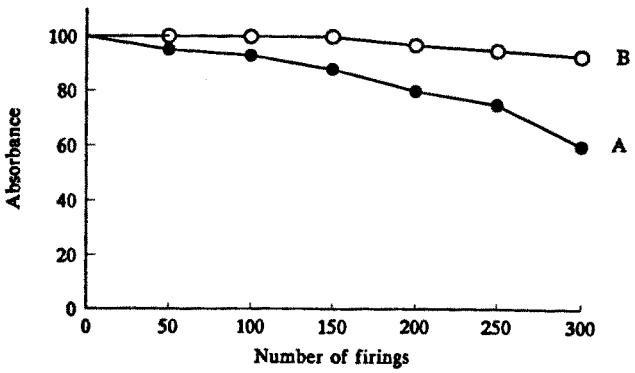

Figure 2. Variation of normalized absorbance with number of furnace firing for 10 μg l^{-1} of lead, A: without and B: with 10 μg of V modifier

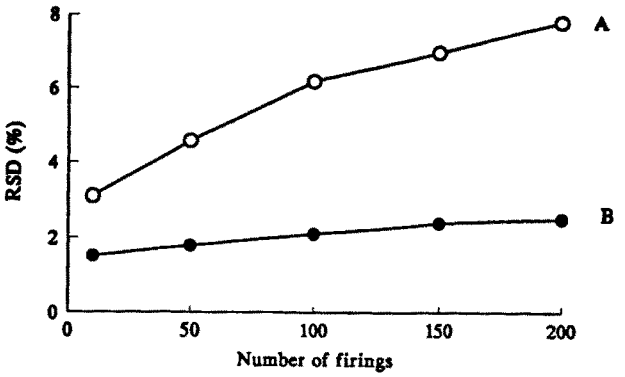

Figure 3. Variation of RSD with the number of furnace firing for 10 μg l^{-1} of lead; A: without and B: with 10 μg of V modifier

Table 3. Recoveries of lead from drinking water using various chemical modifiers

	Lead absorbance			
Chemical modifier 10 μg	Unspiked drinking water	10 μg l^{-1} in deionized water	10 μg l^{-1} in drinking water	Recovery (%)
-	-	0.120	0.034	28.3
V	0.065	0.201	0.243	91.3
V+Mo	0.078	0.280	0.356	99.4
V+T*	0.074	0.292	0.326	89.0
V+Ph**	0.096	0.205	0.271	91.3

* Thiourea

** Di ammonium hydrogen phosphate

the recoveries are good and there is no need to use the method of standard addition or matrix matched calibration graphs. The results of this work and our previous work [10] indicate that although V has a very good potential as a

chemical modifier, it should be mixed with another metallic modifier, e.g. Mo, in order to achieve good recoveries.

The concentration of lead in the drinking water of Tabriz using V + Mo modifier was calculated to be 2.7 $\mu g\ l^{-1}$. The proposed method was compared with oxine-chloroform-GF-AAS procedure, and a good agreement between the results was obtained.

Calibration, Detection Limit and Precision

Linear calibration graphs for direct determination of lead were obtained by standard solutions containing 0-20 $\mu g\ l^{-1}$ of lead with the optimum amount of the chemical modifier.

The limit of detection of the method was 0.07 $\mu g\ l^{-1}$ based on three times the standard deviation of the blank. The characteristic mass is defined as the mass of the analyte in picograms required to give a signal of 0.0044 for integrated absorbance. The characteristic mass was 1.1 pg.

The within-run precision, RSD, of the method obtained for six replicate analyses of a single sample during the same run was 1.4 (for 20 $\mu g\ l^{-1}$ of lead). The within-batch precision of the method, obtained for six replicates of three samples with different concentrations of lead added, was also investigated. To study within-batch precision, three samples with 2.5, 3.5 and 6.5 $\mu g\ l^{-1}$ of lead added were used and the results are 2, 4 and 3.4, respectively.

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