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Utilization of electrodeposition on a graphite probe modified with palladium in determination of lead by graphite furnace atomic absorption spectrometry in water and environmental samples

Reza Moradkhani, Ahmad Rouhollahi*, Hamid Shirkhanloo, Jahan B. Ghasemi

Department of Chemistry, Faculty of Science, K.N. Toosi University of Technology, P.O. Box 16315-1618, Tehran, Iran

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Abstract

In this work a rapid and selective procedure for separation and preconcentration of lead (Pb^{2+}) before determination by electrothermal atomic absorption spectrometry (ETAAS) was developed. The procedure is based on the electrodeposition on a graphite probe modified with palladium. The lead was deposited from acetate buffer solution at pH 5.5. Various parameters, such as pH of solutions, deposition potential, buffer concentration, stirrer speed, time of deposition and temperature program, were optimized. After optimization of the conditions, detection limit 17 ng L^{-1} by 3σ , and enrichment factor 61 were achieved for 2 min electrodeposition time and improved as deposition time was increased. Linearity of calibration was kept between $0.05\text{-}0.50 \text{ } \mu\text{g L}^{-1}$ with a correlation coefficient of 0.9979 and suitable precision, R.S.D. % = 5.1 ($n = 8$). Samples were digested completely in a closed microwave digestion system using only perchloric acid, and interference owing to various cations was also investigated. The procedure was successfully applied to determine the presence of lead in rice, radish, okra, onion and water samples.

Keywords: Lead; Palladium; Electrodeposition; Preconcentration; Microwave digestion.

1. Introduction

Lead is one of the most toxic elements which have strong negative effect on human and animal health. The excessively intake of Pb, even in low levels, can lead to serious problems and hazardous risks for humans, plants and animals. The important sources of lead are industrial processes such as smelting lead, recycling lead batteries, manufacturing lead paints, and automobile exhaust [1, 2]. Exposure to lead can occur through the drinking water and food contaminated with lead. The World Health Organization (WHO) establishes provisional tolerable weekly intakes of Pb of 0.025 mg kg^{-1} body weight for all human groups [3], and has released the guideline for drinking water quality containing the guideline value of $10 \text{ } \mu\text{g L}^{-1}$ for Pb [4]. Hence, the determinations of trace Pb in water and environmental samples is increasing importance in order to monitor the quality of samples resources and decrease the harm to humans, plants and animals.

* Corresponding author. Tel.: +98 21 23064222.

E-mail address: rouhollahi@kntu.ac.ir (A. Rouhollahi)

There are some convenient methods such as flame atomic absorption spectrometry (FAAS) [5], electrothermal atomic absorption spectrometry (ETAAS) [6], neutron activation analysis (NAA) [7] and inductively coupled plasma atomic emission spectrometry (ICP-AES) [8] that have been suggested for lead determination at trace and ultra-trace amounts in different samples. Using these techniques is limited, not only by insufficient sensitivity, but also by matrix interferences. The direct determination of ultra-trace elements such as lead in environmental samples may be difficult using these techniques, due to their low concentration and matrix complexity, which may cause serious interferences. Preconcentration and separation of ultra-trace analytes from the interfering concomitants could solve these problems and pave the way for a sensitive and accurate determination. Different methods, for example, liquid-liquid extraction (LLE) [9], cloud point extraction (CPE) [10, 11], and solid phase extraction (SPE) [12, 13], have been used for this purpose so far. Another preconcentration method is electrodeposition which has several advantages.

Electrodeposition coupled with different techniques such as electrothermal atomic absorption spectrometry, has demonstrated to be a powerful and reliable method to attain the sensitive determination of ultra-trace analysis in a complex matrix. The high sensitivity of these combined techniques is inherently associated with preconcentration and separation by the electrodeposition step. Furthermore, there is no contamination in the analytical matrix, no waste of samples and no waste of time [14]. One of the most important advantages of this technique is that it has the necessary potential to distinguish between labile and inert metal species. With accurate potential controlling, it is promising to preconcentrate only the portion of metal that is electrochemically active, which in turn allows the selective deposition of metals. This recent benefit is very important for determining the toxicity levels of different species of various elements. In this technique, electrolytic preconcentration is done by plating the metals on a pyrolytic graphite platform [15], with high melting-point metal wires such as W [16] and a tubular pyrolytic graphite coated furnace [17] used as an electrode. In some of these arrangements, flow systems have been designed [18]. After electrodeposition, analyte could be dissolved from the electrode in a small volume of acid and the whole volume of eluent was injected into the graphite tube atomizer [19].

Matousek et al. introduced the in-situ electrodeposition-ETAAS technique [20]. Another approach utilizes the electrodeposition of analyte from a larger volume of sample onto the graphite electrode in the form of a disc [21] and, recently, a probe [22]. These graphite parts were directly inserted into the graphite tube atomizer. The aim of the present work is to develop an electrodeposition system for preconcentration and separation of trace amounts of Pb^{2+} with a Pd-modified graphite probe as a working electrode for electrodeposition of lead and the introduction into the graphite furnace atomizer. The graphite probe surface was modified with electrochemically deposited Pd. The existence of palladium in the graphite surface was observed by the scanning electronic microscope (SEM). The procedure was successfully applied for the determination of lead in rice, radish, okra, onion and water samples.

2. Experimental

2.1. Apparatus

A GBC (GBC Scientific Equipment, Australia) double beam, Model 932 plus, atomic absorption spectrometer equipped with a GF-3000 graphite furnace atomizer and a PAL-3000 autosampler controlled by the AVANTA 1.33 software were used for the determination of lead. Deuterium lamp background correction was employed to correct for the non-specific absorbance. A lead hollow cathode lamp (GBC Scientific Equipment, Australia) was used as the radiation source. The operating conditions of a lead hollow cathode lamp were those recommended by the manufacturer. Pyrolytically coated graphite tubes were used throughout. Measurements were performed in the peak areas mode. The detailed graphite furnace conditions used for the

determination of lead is shown in Table 1. Controlled potential electrodeposition was made with a potentiostat / galvanostat AUTOLAB (EcoChemie, The Netherlands) model PGSTAT 30 controlled by the GPES 4.9 software (EcoChemie). A three-electrode cell containing a graphite probe as a working electrode, a Pt wire (Azar electrode Co., Iran) as a counter electrode and Ag/AgCl (Metrohm, Zurich, Switzerland) as a reference electrode was used. Dissolved oxygen was removed from the solutions by purging with nitrogen (99.999%) (Roham gas Co., Tehran, Iran) for at least 10 min prior to each electrodeposition.

Table 1

Instrumental parameters and temperature program for lead analysis.

Wavelength, nm	217			
Lamp current, mA	5			
Slit width, nm	1			
Measurement mode	Peak Area			
Background correction	Deuterium			
Graphite furnace temperature program				
Heating step	Temperature, °C	Time (s)		Ar gas flow rate, L min ⁻¹
		Ramp	Hold	
Drying	120	15	10	0.5
Pyrolysis	750	10	5	0.5
Atomization	2100	1	2	0
Cleaning	2200	1	5	0.5

All solutions were mixed by an adjustable magnetic stirrer during each deposition step. A scanning electron microscope (SEM) model S-4160 (Hitachi, Japan) was used for graphite surface image analysis. A Multiwave 3000 microwave sample preparation system (Anton Paar, Graz, Austria) was used in this study. The graphite probe was prepared from graphite rod (2 mm, Azar electrode Co., Iran) and the final rod was turned to a 0.9 mm thickness, ground by a fine emery paper and polished by a dense filter paper. The resulting thickness of the probe was 0.7 mm.

2.2. Reagents and solutions

All the reagents were prepared from the analytical reagent grade chemicals. De-ionized water obtained from a Milli Q-water purification system (Millipore, Bedford, MA, USA) was used for the preparation of all solutions. Analytical grade of acids, bases, salts and other chemicals used in this study was obtained from Merck (Darmstadt, Germany). Before use, laboratory glassware and pipettes for ultra-trace analysis were kept overnight in 10% (v/v) nitric acid aqueous solution, followed by ultra-sonication for 1 h and finally rinsed three times with deionized water. Lead work solutions were prepared daily by appropriate dilution of a 1,000 mg L⁻¹ lead solution (Darmstadt, Germany). In this study, all the real samples were obtained from Esfahan, Iran.

2.3. Sample preparation

2.3.1. Water samples

For water samples, little sample preparation is required. Samples were collected in acid-washed polyethylene bottles and brought to the laboratory. Upon arrival at the laboratory, an

aliquot of the water sample was filtered through a 0.45 μm membrane filter and stored in an acid-washed plastic bottle. At all stages during the sample collection procedure care was taken to avoid sample contamination. Prior to the analysis, sufficient 99% (v/v) acetic acid and sodium acetate were added to the samples until the buffer concentration reached 0.1 M at pH 5.5.

2.3.2. Rice, Radish, Okra, and Onion

1.00 g of powdered samples was accurately weighed by a microanalytical balance and transferred into a tetrafluoromethaxil (TFM) vessel, then processed with 5 mL of 70% HClO_4 in the microwave digestion system. Microwave digestion was done according the following program: step 1 (time: 2 min, power: 250 w), step 2 (time: 2 min, power: 0 w), step 3 (time: 6 min, power: 250 w), step 4 (time: 5 min, power: 400 w), and step 5 (time: 5 min, power: 600 w). After completing digestion, acquired solutions were heated to evaporate the perchloric acid, and then digested samples were transferred to volumetric flasks and diluted with 0.1 molL^{-1} buffer solution at pH 5.5.

2.4. Modification of the graphite probe surface

The graphite probe was firmly sealed with a Teflon band, except for the end part (2 mm) in which the metal was deposited. A 50 ml of solution contained 3 mgL^{-1} Pd in 1% HCl was put in a polyethylene vessel stirred with an electromagnetic stirrer and the galvanostatic electrolysis was performed. The electrodeposition of Pd on the graphite surface was carried out in two steps. In the first step, a current of 2 mA for 30 min and then immediately 10 mA for the next 30 min was applied. For removal of possible Pb contamination from the electrolyte, the unwrapped probe was inserted into a graphite tube and the heating program was applied as described in Table 1. A new Pd-modified probe was conditioned by processing 10 heating cycles according to the conditions in Table 1.

2.5. Electrodeposition of lead and AAS determination

The Pd-modified, purified and conditioned graphite probe was tightly sealed with Teflon and dipped into 25 ml of water samples, Rice, Radish, Okra, and Onion in a polyethylene vessel. The sample solution was stirred at 150 rounds per minute (rpm) by a magnetic stirrer, and -0.7 V potential (vs. Ag/AgCl) was applied. Based on the required sensitivity, Potentiostatic electrodeposition took between 0.5 to 5 min. After electrolysis, the Teflon strip was detached and the part with deposited analyte was rinsed with a small volume of double distilled water to diminish the amount of adhered matrix salt and dried at ambient temperature. Afterward, the probe was inserted into the graphite atomizer and the heating program was started according to the conditions in Table 1.

3. Results and discussion

3.1. Optimization of the effective parameters on the electrodeposition

A good effectiveness of electrodeposition influenced by several factors such as nature of substrates, supporting electrolyte, deposition potential, time of deposition and stirrer speed, was achieved. The optimum conditions for the efficient and rapid electrodeposition of lead were investigated by 25 mL of 0.3 $\mu\text{g L}^{-1}$ standard solution.

3.1.1. Deposition potential

One of the important parameters in the electrodeposition procedure is potential applied to the working electrode [23]. This parameter significantly influences the yield of deposition, thus it is essential to optimize the potential. A reasonable deposition yield can be achieved, when potential is suitable and adequate. On the other hand, by applying more negative potential, occurring hydrogen evolution is more possible. Hydrogen evolution on the electrode surface results in deposition yield reduction, in turn causing unstable metal precipitation on the electrode surface, which will probably waste by rinsing the electrode. In the presented work, electrodeposition was carried out under controlled cathode potential. With the aim of reaching optimum condition, potential was applied between (-0.3 to -1) V, and absorption of lead was measured for each potential. The results show that absorption raises with increasing in potential just about -0.7 V and then considerable absorption changes does not appear. The variation of the absorption signal versus deposition potential curve is shown in Fig. 1. In the first point of view, it seems that hydrogen evolution contributes to increased deposition yield because the solution is mixed by moving the hydrogen bubbles and thickness of diffusion layer decreases consequently the ions can transport to the electrode surface easily. Moreover, these bubbles cause the available surface area for ions resulting in reduction prevention.

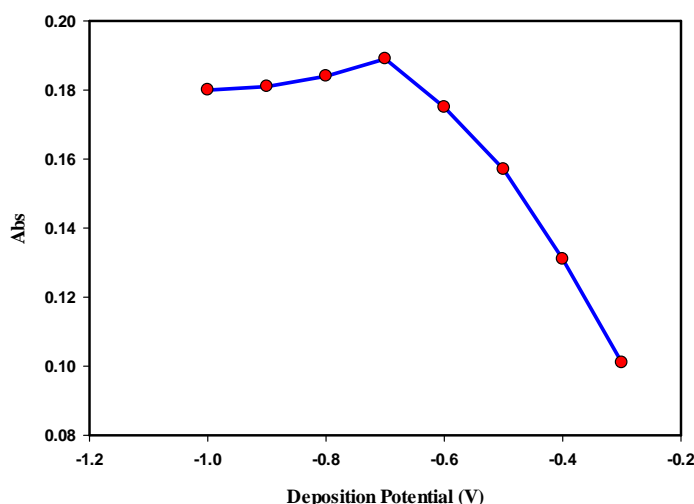


Fig. 1. Plot of lead absorbance signal versus deposition potential for 2 min electrodeposition from 25 mL solution containing $0.3 \mu\text{g L}^{-1} \text{Pb}^{2+}$ in 0.1 mol L^{-1} acetate buffer.

3.1.2. Supporting electrolyte

The yield of lead electrodeposition was affected by the type and concentration of supporting electrolytes. In this work, four electrolyte solutions, sodium nitrate, potassium chloride, acetate buffer, and HNO_3 were evaluated. Acetate buffer solution proved to be the best electrolyte with respect minimizing the interference and increasing deposition yield. The amount of deposited metals increased up to the concentration 0.1 mol L^{-1} of buffer solution. For concentrations higher than 0.1 mol L^{-1} the significant absorption changes did not appear.

3.1.3. Effect of the electrodeposition pH

The pH of an electrolyte plays an important role on the yield of deposition and subsequent signal of absorption. This parameter affects the chemical structure of lead complex or its dehydrated form. Precipitation, basic impurities and adsorption of extra components in the

solution have an effect on the electrode. Fig. 2 shows the effect of pH on absorption signal of lead. It can be seen, the optimum pH was obtained about 5.5 for Pb electrodeposition.

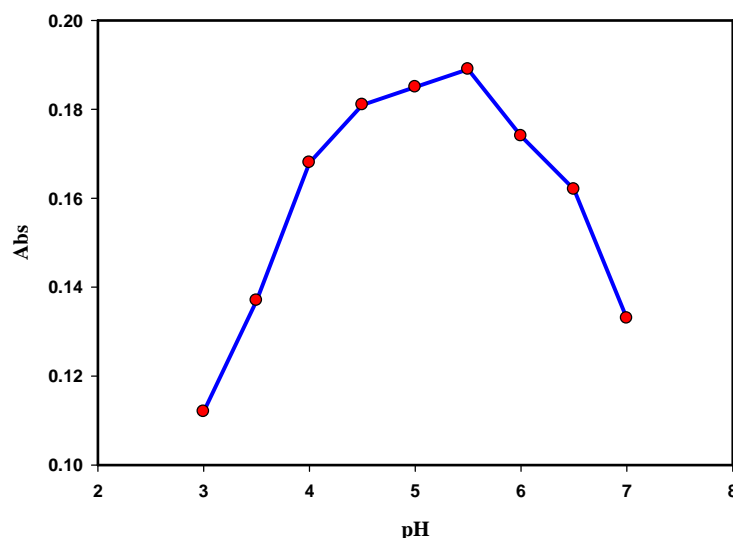


Fig. 2. The influence of pH on the deposition of Pb^{2+} at -0.7 V for 2 min electrodeposition from 25 mL solution containing $0.3 \mu\text{g L}^{-1}$ Pb^{2+} in 0.1 mol L^{-1} acetate buffer.

3.1.4. Time of deposition

A further significant factor that influences deposition of lead is time of deposition. The yield of the deposition depends strongly on electrodeposition time. In addition, the sensitivity of the method can be improved by increasing the electrodeposition time. The variation of the absorption signal against time shown is in Fig. 3. As can be seen, there is a more or less linear dependence between the absorption signal and deposition time. In order to keep the analysis time short, we chosen 2 min for electrodeposition time.

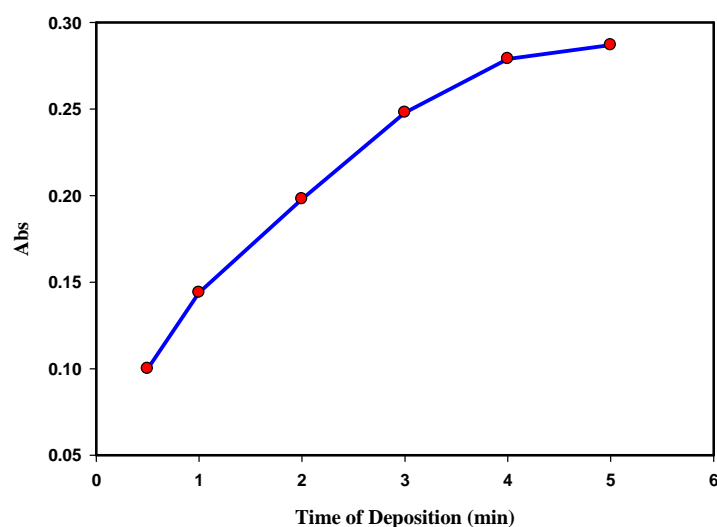


Fig. 3. Dependence of the lead absorbance signal on the time of electrodeposition at -0.7 V, from 25 mL solution containing $0.3 \mu\text{g L}^{-1}$ Pb^{2+} in 0.1 mol L^{-1} acetate buffer pH 5.5.

3.1.5. Stirrer speed

The yield of the deposition depends on the rate of mass transport to the surface electrode during the electrodeposition, and this rate is affected by the solution's stirring speed. To achieve the optimum mixing speed by a magnetic stirrer, the solution was stirred at different speeds and absorption of precipitated was measured. The maximum absorption was achieved at 200 rpm, and important absorption changes did not appear above 200 rpm. Hence, 200 rpm is selected as the speed for stirring.

3.2. Optimization of temperature program for ETAAS

Chosen of a suitable pyrolysis temperature is very significant to eliminate the matrix as much as possible and to prevent pyrolysis loss of the analytes prior to atomization. Fig. 4. shows the effect of pyrolysis temperature on the absorbance, in the range of 500–1000 °C. As could be seen, the utmost absorbance was achieved at 750 °C in the presence of chemical modifier. It is notable to mention that the chemical modifier increases the thermal stability of lead. However, when the pyrolysis temperature was over 800 °C, the signal of analyte decreased swiftly as the pyrolysis temperature increased. Consequently, 750 °C was selected as the optimized pyrolysis temperature for the lead determination. The effect of the atomization temperature, in the range of 1,700–2,400 °C, on the analytical signal of lead was also studied using a pyrolysis temperature of 750 °C. The results are shown in Fig. 4.

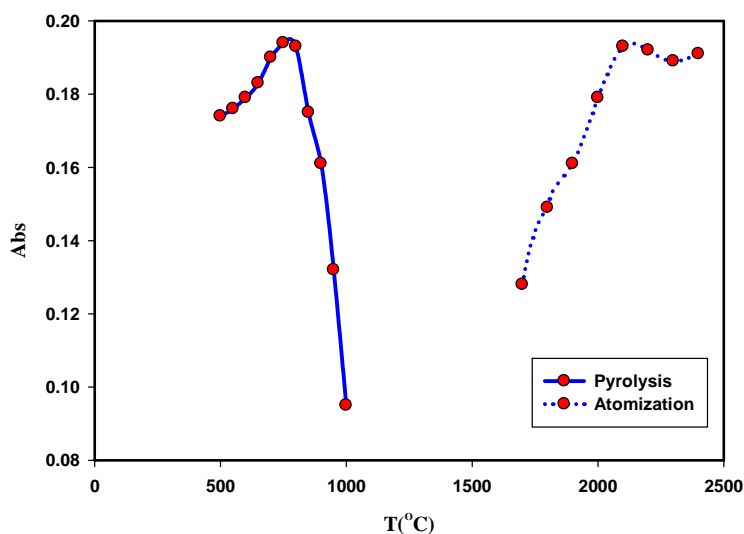


Fig. 4. Pyrolysis and atomization curve for 2 min electrodeposition at -0.7 V, from 25 mL solution containing $0.3 \mu\text{g L}^{-1}$ Pb^{2+} in 0.1 mol L^{-1} acetate buffer pH 5.5.

In the presence of chemical modifier, the maximum signal was obtained at about 2100 °C. Therefore the atomization temperature of 2100 °C was selected for the further experiments. The experimental outcome show that atomization time has little effect on the atomic signal of lead. Hence, an atomization time of 2 s was selected. The partly high pyrolysis and atomization temperatures for lead used in this work are owing to the fact that the lead atomized at solid form.

3.3. Palladium modification study

It has been observed that samples containing high concentration of acids and chloride ions results in corrosion of the graphite surface. To prevent such effect of acids, impregnation with a

solution of noble metal salts has been applied [24]. For this purpose, many researchers have used the electrochemical deposition of Pd method introduced by Matousek and Powell [25]. It is verified that the electrodeposited Pd used for modification purposes are distributed over the graphite surface in the form of globular islands. The palladium migration within the sub-surface part of the graphite and the formation of intercalation compounds with carbon play a considerable role in the permanent performance of the modification [26, 27].

This procedure has some advantages: for instance, the reservoir of noble metals in the sub-surface is available for several hundreds of heating cycles; also, this contributes to saving reagents and analysis time. Additionally, the thermal stabilization of volatile elements, a further aspect of Pd electrodeposition, could be related to impregnation of the graphite surface. Pd coating shielded the active sites to reduce the carbon-analyte interaction and prevented carbide formation. In the presented work, when the probe was immersed in a solution containing $0.05 \mu\text{gL}^{-1}$ Pb for 60 s, it was observed that a signal of 0.031 was obtained after rinsing the probe, even though no potential was applied and the probe was known to be free of Pb contamination. This was probably due to the diffusion of the lead into the graphite pores. By electrodeposition of Pd to modify the surface, the probe gave no measurable absorbance after immersing the probe in the Pb^{2+} solution.

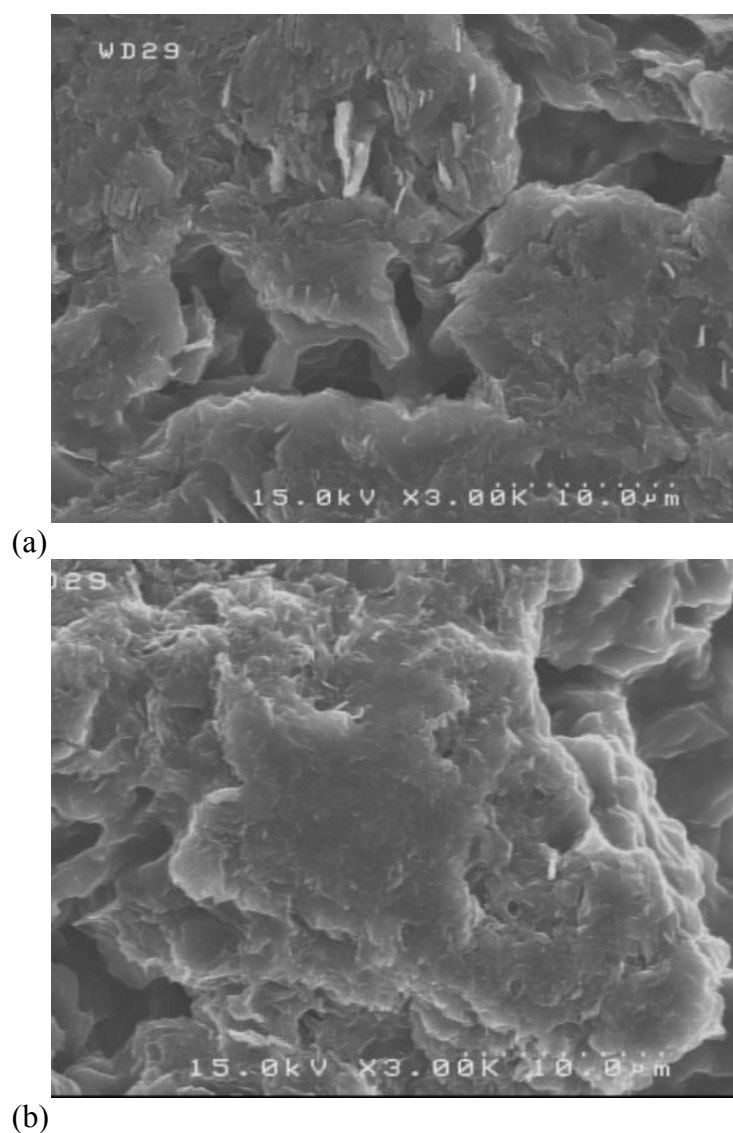


Fig. 5. The SEM images of the electrodeposited palladium on the surface of the graphite probe. (a) Probe surface without deposition, (b) with Pd.

It is necessary to mention that the long-term performance of the modifier was tested in detail for palladium. Based on the experiments, average 29 μg of Pd was deposited on the graphite probe during 30 min at 2 mA and the next 30 min at 10 mA. With an atomization temperature of 2,100 $^{\circ}\text{C}$, atomization cycles of 400 could be performed without significant losses of Pb during thermal stabilization, but after about 400 firings, Pd should be deposited again. With the intention of evaluate an estimated of Pd density on the surface, the amount of palladium in solution was calculated before and after electrodeposition. The concentration of Pd was determined by ETAAS with direct injection into a graphite tube. In this work, an average surface density of 6.2 $\mu\text{g mm}^{-2}$ was calculated for Pd. Similar Pd density (1.2 $\mu\text{g mm}^{-2}$) was reported by other investigation [28]. The SEM images of the surface of bare and modified graphite with palladium in the same magnitude were shown in Fig. 5a and 5b respectively. It can be seen that Pd electrodeposition can decrease the porosity of graphite surface.

3.4. Determination of lead in real samples

The proposed methodology was successfully applied to the determination of Pb^{2+} in several samples. In order to validate the proposed method, recovery experiments were also carried out by spiking the samples with different amounts of lead before any pretreatment. The solutions were analyzed using the standard additions calibration, and the percentage recoveries were calculated. Table 2 shows the obtained results. The slopes of the standard additions graphs for samples did not have any significant difference with that of the calibration graph. Also, the corresponding detection limits for each sample were found to be the same as those obtained from standard solutions. The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

Table 2
Determination of lead in real samples.

Samples	Pb^{2+} Added, μgL^{-1}	Pb^{2+} Found, μgL^{-1} (n = 3)	Recovery, %
^a Water	-----	0.228 ± 0.009	-----
	0.1	0.319 ± 0.012	97
^b Water	-----	0.043 ± 0.003	-----
	0.1	0.152 ± 0.010	106
Rice	-----	0.137 ± 0.007	-----
	0.1	0.233 ± 0.013	98
Radish	-----	0.036 ± 0.003	-----
	0.2	0.241 ± 0.017	102
Okra	-----	0.052 ± 0.005	-----
	0.1	0.148 ± 0.013	97
Onion	-----	0.028 ± 0.003	-----
	0.2	0.232 ± 0.017	101

^aWaste water, Esfahan, IRAN.

^b Drinking water, Esfahan, IRAN.

3.5. Interferences study

The selectivity of the technique was evaluated by addition different amounts of potentially interfering species. Different amounts of ions were added to the test solution containing 300 ngL⁻¹ of lead and followed by operated as described method under optimized parameters. An ion was considered to interfere when its presence produced a variation of more than 5% in the absorbance of the sample. For errors lesser than 5%, the permitted quantity of each coexisting ion is given in Table 3. Due to the electrodeposition step, there is no interference from ions when lead is determined by the present method. These results allow applying the recommended system for interference-free determination of trace lead in environmental samples.

3.6. Calibration and analytical performance

For the present procedure, the analytical characteristic data are shown in Table 4. Sensitivity was calculated from the mean of the slope of the calibration graph, as defined by IUPAC [29]. The results showed a noticeable improvement in LOD in comparison with ETAAS. This can be attributed to an improvement in the analyte signal due to the preconcentration step.

Table 3

Effect of interfering ions in the determination of Pb (0.3 µg L⁻¹) under the optimum experimental conditions.

Coexisting ion	Added as	Concentration of coexisting ion, µg mL ⁻¹	Recovery of lead ion, %
Ag ⁺	AgNO ₃	10	95
Cd ²⁺	Cd(NO ₃) ₂	10	97
Co ²⁺	CoSO ₄	20	100
Ni ²⁺	NiSO ₄	20	99
Mn ²⁺	MnSO ₄	25	95
Fe ²⁺	FeSO ₄	25	97
Bi ³⁺	Bi(NO ₃) ₃	25	101
Zn ²⁺	ZnSO ₄	10	96
Cu ²⁺	CuSO ₄	15	99
Mg ²⁺	MgCl ₂	800	100
K ⁺	KCl	800	101
Na ⁺	NaCl	800	102

This technique also showed an enhancement in the slope of the calibration curves in the measurement of Pb²⁺, due to the analyte being separated by deposition on the probe surface from the interfering matrix. With the aim of comparison, the analytical performance of the Pb²⁺ determination by simple injection into a graphite furnace was measured before using the probe as an electrodeposition. The enrichment factor was calculated as the ratio of the slope of preconcentrated samples to that obtained without preconcentration. Characteristics data of the present method at 2 and 5 min electrodeposition with direct injection for lead determination are compared in Table 4.

Table 4

Analytical characteristics of the proposed method.

Analytical characteristic	Direct Injection ^a	ED-ETAAS ^b	
		2 min	5 min
Linear Range, $\mu\text{g L}^{-1}$	3-35	0.05-0.5	0.05-0.5
Correlation coefficient	0.9989	0.9979	0.9974
Slope	0.007	0.427	0.506
R.S.D., % ($n = 8$)	3.6	5.1	5.4
Enhancement factor	-----	61	72
LOD, ng L^{-1}	350	17	14
LOQ, ng L^{-1}	1000	58	49

^a Direct injection of a 20 μL sample solution.^b Electrodeposition–Electrothermal Atomic Absorption Spectrometry

4. Conclusion

The results obtained in this work demonstrate an effective approach to improve the detection limit of ETAAS for lead determination. The method due to advantages such as high sensitivity, low detection limit and high tolerance limit of common ions is a powerful tool for rapid and sensitive determination of lead in complex matrixes. Also, the proposed method is easy, safe and inexpensive for preconcentration and separation of lead and determination by ETAAS in environmental samples.

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