

Study of Analytical Parameters of a Differential Pulse Voltammetric Method using Chemically Modified Electrodes for Lead Analysis in Water

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The development of a new voltammetric method for the determination of Pb²⁺ ions in water samples using glassy carbon electrodes modified with 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate is here presented. The analytical parameters for differential pulse voltammetry (DPV) were established and the method was applied for Pb²⁺ ions determination in acetate buffer solution at pH 5.5. For the developed DPV method the linearity of calibration curve was set up between 20.71 μg L⁻¹ - 103.6 μg L⁻¹ with a good correlation coefficient R²=0.9988, the intermediate precision was calculated for three lead concentrations: 20, 60, 100 μg L⁻¹. The obtained detection and quantification limits were 3.1 μg L⁻¹, respectively 10.4 μg L⁻¹. An uncertainty budget was developed and the value of expanded uncertainty was assessed. The optimized method was used to analyze Pb²⁺ ions from water samples and good correlation with standard method was obtained.

Keywords: stripping differential pulse voltammetry, lead, water quality, method development, 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate

Being the most important source to live, water needs permanent and systematic improvement of its quality. Access to a safe drinking-water is essential to health, a basic human right and a component of effective policy for health protection. The importance of water, sanitation and hygiene for health and development has been reflected in the outcomes of a series of international policy forums [1, 2]. In this context, the control of the presence of heavy metals, especially the presence of lead, in water sources is of crucial importance. Apart from its presence in natural rocks, lead is an element used in many productive fields such as lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes and plastic stabilizers. From a drinking-water perspective, the almost universal use of lead compounds in plumbing fittings and as solder in water distribution systems is important. Lead pipes may be used in older distribution systems and plumbing [3].

The presence of lead in the human body can generate serious health problems, damage to the brain, kidneys, nervous system, and red blood cells. Although only used in consumer products was incriminated causing health issues, lead is a toxic metal now known to be harmful to human health also if it is inhaled or ingested. Important sources of lead exposure include: ambient air, soil and dust (both inside and outside the home), food (which can be contaminated by lead in the air or in food containers), and water (from the corrosion of plumbing). On average, it is estimated that lead in drinking water contributes between 10 and 20 percent of total lead exposure in young children. In the last few years, federal controls on lead in gasoline have significantly reduced people's exposure to lead [4-6].

Given the importance of this subject, numerous studies have been conducted that have addressed lead poisoning in humans and animals in order to discover effective detox treatments, new and ingenious solutions being found [7,8]. Recently, Everardo Hernández-Plata *et al.* conducted a study of lead poisoning in rats using a treatment with melatonin, a hormone with antioxidant properties. It has been found that this hormone reduces lead concentrations in some rat organs, while increasing lead levels in excretion organs and fluids (liver, kidneys, urine and faeces), effects appearing to the highest tested lead dose. The metabolic mechanism of lead elimination is probably due to the formation of a lead - melatonin complex which is then easily excreted [9]. For the treatment of lead intoxication Manal H. Al Khabbas *et al.* [10] have synthesized and characterized new mono- and dihydroxypyridinethione ligands. The comparison with the classic treatment method with meso-2,3-dimercaptosuccinic acid (DMSA) or with calcium disodium ethylenediaminetetraacetic acid (CaNa₂EDTA) showed that the new compounds presented better results for lead excretion in comparison with DMSA.

Therefore, the presence of lead in water is a serious concern at the level of the whole society. That is why particular attention has been given to the methods of determination of this analyte. For the determination of lead in different types of water samples there are reported numerous studies in which different known advanced spectral methods are applied, such as GF-AAS, ICP-MS, HG- ICP-MS, etc. [11-13]. Recently the application of voltammetric methods using new glassy carbon modified electrodes based on azulene derivatives for lead analysis in water have been reported [14-17]. The present study is

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a follow up research of a previous reported work [18] in which the electrochemical characterization of **L**, 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate, denoted with **L**, by two voltammetric methods (CV and DPV) was described and the potential application of DPV method using glassy modified electrode with the mentioned **L** was revealed. Based on this conclusion, a stripping differential pulse voltammetry (DPV) method using a glassy carbon electrodes modified with the above mentioned **L** was developed for lead determination in water samples by setting the analytical performance parameters. The chemical structure of **L** compound is shown in the figure 1.

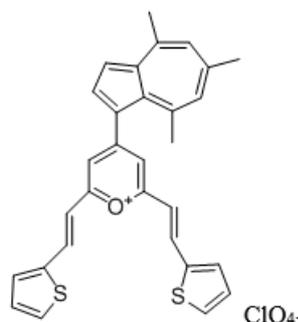


Fig. 1. Structure of 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate (**L**)

Experimental part

In the electrochemical experiments, for the supporting electrolyte was used acetonitrile (Sigma Aldrich, electronic grade 99.999% trace metals) and tetra-n-butyl ammonium perchlorate (TBAP, Fluka puriss, electrochemical grade >99%). 0.2 M Sodium acetate (Roth, 99.99%) and 0.2 M acetic acid (Fluka, >99.0%, trace select) were used for preparing acetate buffer solution $pH = 5.5$. For the preparation of lead standard solutions, $Pb(NO_3)_2$ (Sigma-Aldrich, 99.99% trace metal basis) was used. The buffer solutions and standard solutions were prepared with ultrapure water.

All the experiments were performed using a PGSTAT 12 AUTOLAB potentiostat connected to a three-electrode cell in which the working electrode was a glassy carbon disk

with 3 mm diameter (from Metrohm) modified with poly**L**, the auxiliary electrode was a platinum wire, and two reference electrodes were $Ag/10\text{ mM } AgNO_3$ in $0.1\text{ M TBAP}/CH_3CN$ (in electrochemical experiments performed in acetonitrile solution), or $Ag/AgCl, 3\text{ M } KCl$ (in electrochemical experiments performed in water solution). The glassy carbon electrode was polished with diamond (2im) paste before each experiment and then cleaned with the solvent (absolute ethanol) and distilled ultrapure water. Millipore Direct - Q 3UV water purification system was used for obtaining ultrapure water. All DPV determinations were performed with degassed solutions with a stream of argon for 20 minutes before each measurement and kept under argon atmosphere at $25^\circ C$.

Results and discussions

Glassy carbon modified electrodes were obtained by controlled potential electrolysis (CPE) at 1.5 V and 1.4 mC using a $0.1\text{ M TBAP}/CH_3CN$ as supporting electrolyte. The electrode was cleaned with solvent and transferred into a cell with acetate buffer $pH=5.5$ for the equilibration ($0.9\text{ V} \div +0.6\text{ V}$) and overoxidation ($-0.2\text{ V} \div +1.5\text{ V}$). The electrode was introduced into a Pb^{2+} solution at a certain concentration for 25 min. After that the electrode was cleaned with water and immersed into a cell with acetate buffer $pH 5.5$ for the anodic stripping differential pulse voltammetry (ASDPV) after a polarization at the potential of -1.2 V time for 300 s.

The calibration curve was obtained between $20.71\text{ }\mu\text{g L}^{-1}$ - $103.6\text{ }\mu\text{g L}^{-1}$. Table 1 and figure 2 present the results obtained for the calibration curve. It can be seen that was obtained a good correlation coefficient, $R^2 = 0.9988$ has been obtained.

Table 2 shows the results for the detection limit (LOD) and for the limit of quantification (LOQ). To calculate the LOD and LOQ five samples each of them containing $20.1\text{ }\mu\text{g L}^{-1} Pb^{2+}$ were analyzed.

Intermediate precision was calculated at 3 concentration levels ($20\text{ }\mu\text{g L}^{-1}$, $60\text{ }\mu\text{g L}^{-1}$, and $100\text{ }\mu\text{g L}^{-1}$) by 2 analysts using 2 different electrodes and the same

x_i ($\mu\text{g L}^{-1} Pb^{2+}$)	20.71	41.4	62.4	82.84	103.6
y_i (μA)	0.00061	0.00357	0.00590	0.00829	0.0107
$y = -0.00165 + 0.00012 x$					
y-Intercept $a = -0.00165\text{ }\mu\text{A}$	Slope of the calibration curve = sensitivity $b = 0.00012\text{ }(\mu\text{AxL})\mu\text{g}^{-1}$		Correlation coefficient $R^2 = 0.9988$		
Residual standard deviation $S_{y1} = 0.001\text{ }\mu\text{g L}^{-1} Pb^{2+}$	Standard deviation of the method $S_{x01} = 0.057\text{ }\mu\text{g L}^{-1} Pb^{2+}$		Coefficient of variation of the method $V_{x01} = 1.86\%$		

Table 1
STATISTICAL
PROCESSING OF
LINEARITY DATA

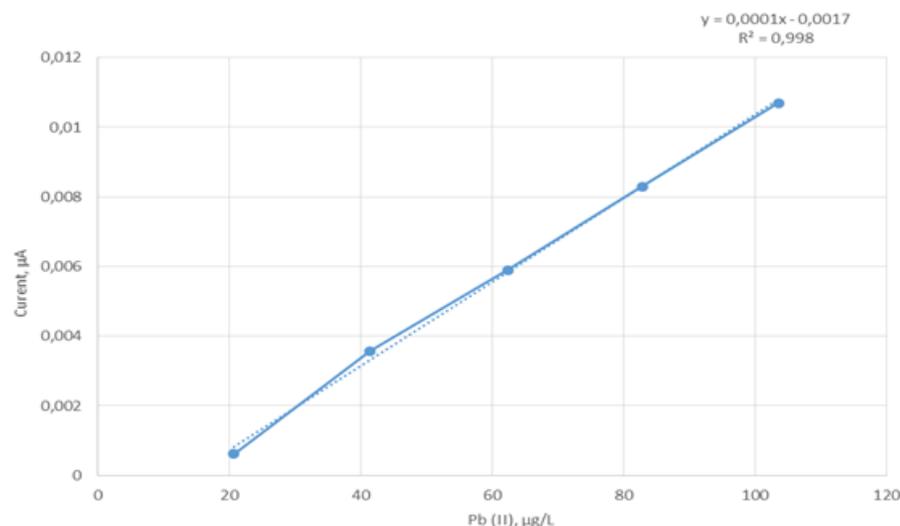


Fig. 2. Calibration curve for Pb^{2+} determination in water using poly**L** modified electrodes

Measured values $\mu\text{g L}^{-1} \text{Pb}^{2+}$	22.1	24.1	24.7	23.1	22.8
Standard deviation of results, $s = 1.04 \mu\text{g L}^{-1}$					
Limit of detection, $\text{LOD} = 3s = 3.1 \mu\text{g L}^{-1}$					
Limit of quantification, $\text{LOQ} = 10s = 10.4 \mu\text{g L}^{-1}$					

Table 2
EXPERIMENTAL DATA USED TO ESTABLISH THE DETECTION LIMIT AND THE QUANTIFICATION LIMIT

Measured values ($\mu\text{g L}^{-1} \text{Pb}^{2+}$)	22.1	24.7	23.1	22.8	24.1
Standard deviation of results, $s = 1.04 \mu\text{g L}^{-1}$					
Average value, $x_{\text{mean}} = 23.4 \mu\text{g L}^{-1}$					
Repeatability = $2.8*s = 2.91 \mu\text{g L}^{-1}$					
Intermediate precision = $1.6*2.8*s = 4.65 \mu\text{g L}^{-1}$					
Relative standard deviation of repeatability, $\text{RSDr} = s/(x_{\text{mean}}*100) = 4.44\%$					
Relative standard deviation of intermediate precision, $\text{RSDR} = 1.6*\text{RSDr} = 7.11\%$					

Table 3
INTERMEDIATE PRECISION FOR THE CONCENTRATION OF $20 \mu\text{g L}^{-1} \text{Pb}^{2+}$

Measured values ($\mu\text{g L}^{-1} \text{Pb}^{2+}$)	64.3	53.4	56.3	64.9	55.9
Standard deviation of results, $s = 5.04 \mu\text{g L}^{-1}$					
Average value, $x_{\text{mean}} = 59 \mu\text{g L}^{-1}$					
Repeatability = $2.8*s = 14.2 \mu\text{g L}^{-1}$					
Intermediate precision = $1.6*2.8*s = 22.8 \mu\text{g L}^{-1}$					
Relative standard deviation of repeatability, $\text{RSDr} = s/(x_{\text{mean}}*100) = 8.60\%$					
Relative standard deviation of intermediate precision, $\text{RSDR} = 1.6*\text{RSDr} = 13.8\%$					

Table 4
INTERMEDIATE PRECISION FOR THE CONCENTRATION OF $60 \mu\text{g L}^{-1} \text{Pb}^{2+}$

Measured values ($\mu\text{g L}^{-1} \text{Pb}^{2+}$)	124	119	113	122	109
Standard deviation of results, $s = 6.27 \mu\text{g L}^{-1}$					
Average value, $x_{\text{mean}} = 117.4 \mu\text{g L}^{-1}$					
Repeatability = $2.8*s = 17.55 \mu\text{g L}^{-1}$					
Intermediate precision = $1.6*2.8*s = 28.08 \mu\text{g L}^{-1}$					
Relative standard deviation of repeatability, $\text{RSDr} = s/(x_{\text{mean}}*100) = 5.34\%$					
Relative standard deviation of intermediate precision, $\text{RSDR} = 1.6*\text{RSDr} = 8.54\%$					

Table 5
INTERMEDIATE PRECISION FOR THE CONCENTRATION OF $100 \mu\text{g L}^{-1} \text{Pb}^{2+}$

equipment (PGSTAT 12). Tables 3-5 show the resulting of following statistical data: standard deviation of values, repeatability, intermediate precision, and repeatability, respectively the intermediate precision expressed as relative values.

To estimate recovery and accuracy, experimental data from intermediate precision tests were used. The results are summarized in table 6.

The method for the determination of Pb^{2+} using ASDPV allows the determination of lead content in waters with low concentrations. This method can be used for the determination of Pb^{2+} ions in surface water, but it cannot be used for the determination of Pb^{2+} in drinking water because the limit of quantification is equal to the maximum admissible value by law in drinking water ($10 \mu\text{g L}^{-1} \text{Pb}^{2+}$).

In the tests on real samples were used along with the optimized method two other methods of Pb^{2+} determination: inductively coupled plasma optical emission spectrometry using ultrasonic nebulizer (ICP-EOS-USN), inductively coupled plasma optical emission

spectrometry (ICP-EOS) with classic Meinhard glass nebulizer. The calibration curves were in the range $20 \div 100 \mu\text{g L}^{-1}$, the abscissa (y) representing in each case a different size. Table 7 shows the integrated peak height values (ICP-EOS-USN), integrated peak area (ICP-EOS) as well as the current intensities (electrochemical, DPV) values used for the calibration curves.

For the result comparison of the results, a sample of drinking water was collected, the samples was fortified; P1 sample is $20 \mu\text{g L}^{-1} \text{Pb}^{2+}$, P2 is $25 \mu\text{g L}^{-1} \text{Pb}^{2+}$, P3 sample $30 \mu\text{g L}^{-1} \text{Pb}^{2+}$, and sample P4 is $35 \mu\text{g L}^{-1} \text{Pb}^{2+}$. The samples were analysed and the results obtained are reported in table 8. It can be seen that the results obtained by different techniques are comparable, which indicate that the proposed and developed voltammetric method is suitable for the determination of lead in contaminated waters in the range between 20 and $100 \mu\text{g L}^{-1} \text{Pb}^{2+}$.

In order to assess the value of uncertainty, an uncertainty budget was developed. The equation used for estimation of the uncertainty was the following:

Added value, $\mu\text{g L}^{-1} \text{Pb}^{2+}$	20.7	62.1	103.6
Mean value, $\mu\text{g L}^{-1} \text{Pb}^{2+}$	23.4	59	117.4
Recovery, %	113	95	113
Accuracy, $\mu\text{g L}^{-1} \text{Pb}^{2+}$	2.7	3.1	13.8

Table 6
RESULTS CALCULATED FOR RECOVERY AND ACCURACY

Concentration $\mu\text{g L}^{-1}$	ICP-EOS-USN Integrated peak height	ICP-EOS Integrated peak area	Electrochemical DPV current (μA)	Abscissa $y_i, i=1 \div 5$
20	6761	135.2	0.00061	y_1
40	13982	279.6	0.00357	y_2
60	20612	412.2	0.00590	y_3
80	28312	566.3	0.00829	y_4
100	34800	696.0	0.01070	y_5

Table 7
ANALYTICAL DATA USED FOR CALIBRATION CURVES IN ICP-EOS-USN, ICP-EOS, AND ELECTROCHEMICAL (DPV) METHODS

Table 8
COMPARATIVE RESULTS FOR Pb²⁺ DETERMINATION IN A FORTIFIED TAP WATER SAMPLES (µg L⁻¹)
USING DIFFERENT ANALYTICAL TECHNIQUES

Analytical technique	Blank Tap water	Sample P1 Pb(II) µg/L	Sample P2 Pb(II) µg/L	Sample P3 Pb(II) µg/L	Sample P4 Pb(II) µg/L
ICP-EOS USN	1.52	22.8	23.9	30.8	35.5
ICP-EOS	1.75	20.6	25.7	29.3	34.4
Electrochemical	<10*	22.7	24.2	30.2	35.1

*Limit of quantification

	Value (µg/L)	Standard uncertainty (µg/L)	Rsu %
C _{vf}	57.9	4.597	7.95
f _{precision}	1	0.026	2.58
CRM _{obtained}	23.4	0.464	1.99
CRM _{added}	20.7	0.131	0.63
Value ± expanded uncertainty	51.3 ± 8.8 µg/L		17.2

Table 9
QUANTIFICATION OF THE ELEMENTS USED TO ESTIMATE THE UNCERTAINTY

$$C_{Pb} = C_{vf} \times f_{precision} \times f_{recovery} \cdot \mu\text{g/L} \quad (1)$$

where:

C_{vf} = Certified Reference Material (CRM) Pb(II) concentration in volumetric flask;

f_{precision} = influence factor of the precision;

f_{recovery} = influence factor of the recovery (CRM_{added}/CRM_{obtained}); CRM_{added} = 20 µg.

The uncertainty budget was estimated using data from linearity, precision and recovery tests. The uncertainty has been reported in percentage of the relative standard uncertainty (Rsu) and applied to each obtained value.

In the equation above, the value for precision is assumed to be 1, its contribution being important only for uncertainty budget measurement and not for determination of the concentration.

The standard uncertainty associated to the lead concentration was estimated using uncertainties of the certified reference material, volumetric flask and pipettes used. The uncertainty of the CRM_{added} was calculated from the quality certificate of the CRM_{added}, from mass balance certificate, volumetric flask and pipettes used, the final results being reported in table 9.

The uncertainties of the precision test and CRM_{obtained} were estimated using data reported in table 3 and 4. The expanded uncertainty is calculated as twice the combined uncertainty for a 95% confidence interval, as it was already presented in table 9.

Conclusions

The development of a voltammetric method for the determination of Pb²⁺ ions in drinking water samples using a modified glassy carbon based on 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate is presented, and the analytical performance parameters were established. It has been obtained a good correlation coefficient (R²=0.9988) and a good detection limit (3.1 µg L⁻¹). The quantification limit was (10.4 µg L⁻¹). The method can be used for the determination of Pb²⁺ ions in surface water, but it cannot be used for the determination of Pb²⁺ in drinking water because the limit of quantification is equal to the maximum admissible value by law in drinking water (10 µg L⁻¹ Pb²⁺). The proposed and developed voltammetric method is an appropriate method for the determination of lead in contaminated waters in the range of linearity of 20-100 µg L⁻¹ Pb²⁺.

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