Stripping Voltammetry on a new Modified Glassy Carbon Electrode for Lead Content Determination in Soft Water

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This study develops a new electrochemical method for quantification of Pb in soft water using stripping voltammetry with a glassy carbon electrode modified with the functionalized azulene: (2E)-2-(azulen-1-ylmethylidene) hydrazine carbothioamide (L) as a complexing polymer film. The optimized steps of the proposed method consisted in experimental establishing of four parameters, namely: reduction time; reduction potential; complexation time; pH in acetate buffer and phosphate buffer. The modified electrodes were prepared in L solutions (1mM) in acetonitrile (CH_3CN) containing tetra n-butyl ammonium perchlorate (0.1 M TBAP) as supporting electrolyte. The electrochemical method includes four main operations: 1) polymeric film formation by controlled potential electrolysis (CPE) at 1.7V using a charge of 1 mC; 2) film conditioning in 0.1 M buffer acetate solution using cyclic voltammetry; 3) 25 min complexation time in a standard solution prepared from lead nitrate (II) using as matrix ultrapure water or a real sample; 4) stripping by differential pulse voltammetry method (DPV) in acetate buffer at pH 4.0, after 120 s reduction time at a reduction potential of -1.0 V. Determination time for a single standard solution or real sample was around 45 min. Evaluation of the method performance parameters (linearity, working range, detection limit, quantification limit, repeatability, and recovery) was done. It confirms that the proposed method is suitable to detect and quantify lead content over 1.2 µg/L in soft water samples.

Keywords: poly[(2E)-2-(azulen-1-ylmethylidene) hydrazine carbothioamide], lead, polymeric film, stripping voltammetry, soft water

The metals (arsenic, cadmium, chrome, copper, mercury, nickel, and lead) found in environmental samples as result of their toxicity, represent a major threat for living organisms, including humans. Due to their accumulation, the toxic metallic elements affect the normal functioning of vital organs and glands, such as: heart, brain, kidneys, bones, liver [1].

Lead is considered to be a carcinogenic metal. The intoxication with lead may come from different sources, such as: atmospheric emissions as result of the solid waste incinerators, drinking water distribution systems (at municipal and household level), ink paint, etc. [2-7]. Lead could affect the eyes and could induce disorders affecting gastrointestinal, cardiovascular, musculoskeletal, renal, reproductive, digestive systems, upper respiratory tract, chest and skin among men, etc. [5, 8].

Analytical methods applied for establishing metal content in water samples (drinking water, mineral, surface water, and wastewater) in relation to maximum permissible limits imposed by specific regulations must comply in terms of performance characteristics.

Laying down the environmental quality standards for water, the Directive 2013/39/EU [9] approaches the approval of measures against pollution, providing an updated list of priority polluting chemical substances. For each substance, the maximum allowable concentration is established in order to avoid irreversible consequences of acute short-term exposure for an ecosystem. Regarding lead content, maximum admissible value in drinking water was set to 10 µg/L. Therefore, the determination of lead in water samples required highly sensitive and selective methods. The most common methods for determination of lead are spectrometric methods, such as: ICP-MS, ET-AAS, HG-ICP-MS, HG-ICP-EOS, USN-ICP-EOS [10-14]. The main disadvantage of these techniques consists in the need of using expensive instruments and highly qualified specialists.

As an alternative, electrochemical methods using different types of electrodes were developed.

During the last two decades [15-17], new organic conducting polymers were synthesized and characterized, based on their electronic and electrochemical properties. Most of these new substances were obtained using various monomers, such as azulene, aniline, pyrrole and thiophene, as well as their derivatives [18-22]. Also, new methods for determination of lead using poly zincon film [23], 1H-pyrrole-1-hexanoic acid [24], bismuth-oxychloride particle-multiwall carbon nanotube composite [25], etc. were reported.

Therefore, designing new substances and materials necessary to prepare modified electrodes suitable for analytical applications in aqueous media became an area of major research interest.

In this regard, polyazulene derivatives, synthesized by oxidative polymerization of azulene derivative – a promising conducting polymer – have a great applicative potential. The electrochemical behavior of the functionalized azulene: (2E)-2-(azulen-1-ylmethylidene) hydrazine carbothioamide (**L**) and the film formation conditions have been previously established [15] in view of obtaining chelating modified electrodes for heavy metals.

The aim of this study was to validate an electrochemical method for Pb(II) determination in water samples using a

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glassy carbon electrode modified with **L** as a complexing polymer film.

Experimental part

Materials

The ligand **L** was synthesized according to the previously published procedure [15]. Acetonitrile (Sigma Aldrich, electronic grade 99.999% trace metals) and tetra-n-butyl ammonium perchlorate (TBAP, Fluka puriss, electrochemical grade >99%) were used as solvents and supporting electrolyte. Sodium acetate (Roth, 99.99%) and acetic acid (Fluka, >99.0%, trace select) were used for preparing acetate buffer solution; potassium phosphate monobasic (Sigma-Aldrich, 99.99% trace metals basis) and dipotassium phosphate dibasic (Sigma-Aldrich, 99.95% trace metals basis) were used for phosphate buffer solution. For Pb recognition experiments, lead (II) nitrate, ($Pb(NO_3)_2$, Sigma-Aldrich, ≥ 99.99% trace metal basis) was used as certified reference material. The buffer solutions and standard solutions were prepared with ultrapure water.

Equipment

PGSTAT 302N AUTOLAB potentiostat connected to three-electrode cell was used. *The working electrode was* a glassy carbon disk with 3 mm diameter (from Metrohm) bare and modified with polyL; *the auxiliary electrode* was a platinum wire; *the reference electrodes were*: either Ag/ 10 mM $AgNO_3$ in 0.1M TBAP/CH_3CN (in electrochemical experiments performed in acetonitrile solution), or Ag/AgCl, 3M KCl (in electrochemical experiments performed in water solution). The glassy carbon electrode was polished with diamond (2μm) paste before each experiment and cleaned with the solvent.

Millipore Direct - Q 3UV water purification system was used for obtaining ultrapure water.

Modified electrode preparation

The modified electrodes were prepared in CH_3CN containing 0.1 M TBAP as supporting electrolyte in 1mM **L** solution. **L** is [(2E)-2-(azulen-1-ylmethylidene) hydrazine carbothioamide. The structure of **L** is presented in figure 1. The electrochemical method includes three steps: *polymeric film formation* by controlled potential electrolysis (CPE); equilibration and over-oxidation *of the formed film* in 0.1 M aqueous buffer acetate solution using cyclic voltammetry (CV).

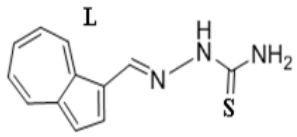

Fig. 1. Structure of azulene compound **L**

Lead analysis using modified electrode

The *complexation* has been performed in a standard solution prepared from lead nitrate (II) using as matrix ultrapure water or a real sample, followed by *stripping* by using differential pulse voltammetry method (DPV) in acetate buffer solution.

All calibration curves have been performed at 25°C, under argon atmosphere.

Validation of the method

Several experiments were performed in order to evaluate the performance of the electrochemical method based on modified electrodes (limit of detection LOD, limit of quantification LOQ, repeatability, intermediate precision, recovery, and uncertainty budget). The performed experiments are listed in table 1. The data from linearity, intermediate precision, and recovery, combined with the film formation precision have been used in uncertainty budget evaluation.

Results and discussions

In order to set the operational parameters for Pb(II) analysis based on modified electrodes, the following parameters have been optimized: reduction and complexation times, reduction potential, pH of the buffer solutions (acetate and phosphate).

The glassy carbon electrode was modified with **L** (1 mM in 0.1M TBAP/CH_3CN) by CPE at 1.7 V using a charge of 1mC according to the previously published work [15] (step1, *polymeric film formation).*

The poly**L** modified electrode was transferred than into 0.1 M acetate buffer solution and was equilibrated during 15 CV cycles (with a scan rate of 0.1 V/s, in the range -0.9 V to +0.6 V) and then overoxidized during 10 CV cycles (with a scan rate of 0.1 V/s in the range -0.2 V to +1.6 V) (steps 2 and 3 of *conditioning).*

In step 4 (*complexation*) the modified electrode (washed with ultrapure water) has been immersed in solution containing Pb $(NO_3)_2$ at different concentrations, under magnetic stirring for different time intervals.

During the *stripping* final step, the modified electrode has been polarized at -1.2 V, and the lead ions were reduced, then a DPV in the range -1.2 V to 0 V has been initiated, and the stripping currents were recorded.

Optimization of the reduction time

Experimental tests were carried out at 2.07 μg/L Pb ([Pb] = 10^{-8}M) by immersing the electrode for 10 min (*complexation*), and varying the reduction time, as follows: 60 s; 120 s; 180 s.; 300 s.

In accordance with the data presented in figure 2, the highest current was obtained at a reduction time of 120 s.

Optimization of the deposition potential

The experiments performed in order to establish the deposition potential were realized using a standard solution of 2.07μg/L Pb(II), a reduction time of 120 s, a complexation time of 10 min, and ranging the deposition potential from -0.8 V to -1.4 V. The highest current was obtained at a deposition potential of -1.0 V.

Table 1
IN-HOUSE VALIDATION EXPERIMENTS

Parameters	Experiments
Linearity test	- 5 solutions in the range 1.0 μg/L to 20.7 μg/L Pb(II)
LOD and LOQ	- 6 independent fortified blank solutions of 0.62 μg/L Pb(II)
Repeatability	- 10 independent standard solutions of 10.35 μg/L Pb(II)
Intermediate precision	- 4 experiments (3 standard solutions per experiment analyzed by 2 chemists in 4 different days), 12 independent standard solutions of 10.35 μg/L Pb(II)
Recovery	- 5 independent standard solutions of 5 μg/L Pb(II)

Optimization of the complexation time

Using the previously optimized parameters, the complexation time has been varied in the range 1 to 30 min, and the highest current value was obtained at 25 min (fig. 4).

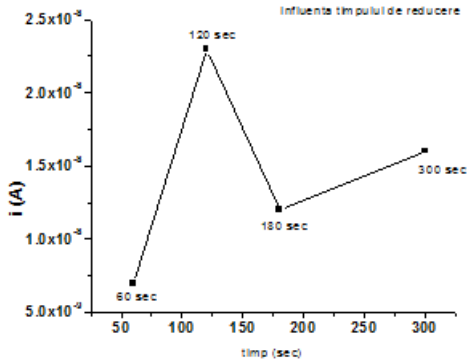

Fig. 2. Pb(II) stripping peak currents in buffer acetate 0.1 M (*p*H = 5.5) on poly**L** modified electrodes after 10 minutes of immersing in buffer acetate 0.1 M (*p*H = 5.5) containing [Pb] = 10^{-8}M, for different reduction times (reduction potential of -1 V)

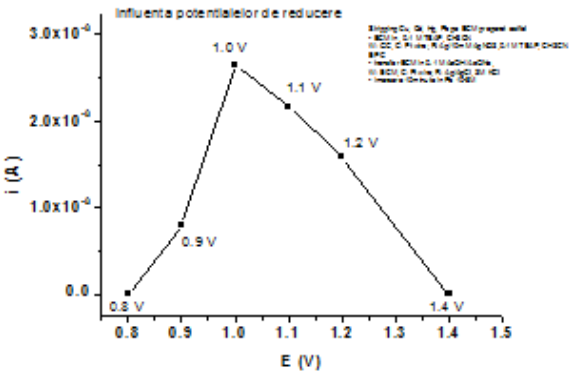

Fig. 3. Pb(II) stripping peak currents in buffer acetate 0.1 M (*p*H = 5.5) on poly**L** modified electrodes after 10 min of immersing in buffer acetate 0.1 M (*p*H = 5.5) containing [Pb] = 10^{-8}M, for a reduction time of 120 s at different reduction potentials

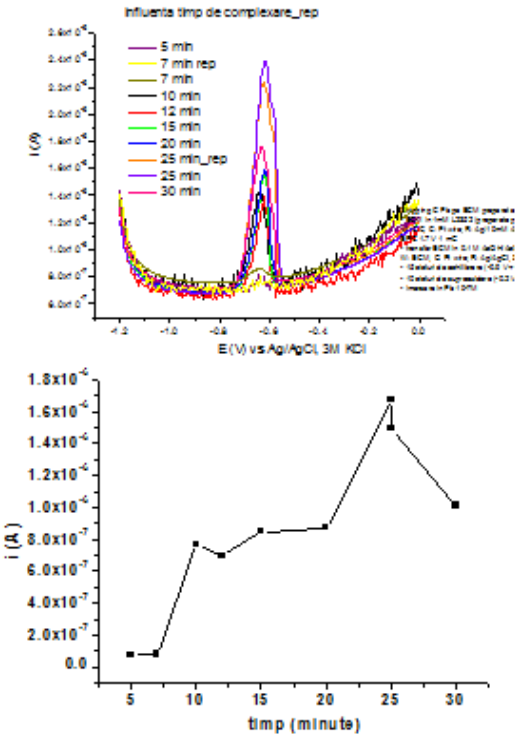

Fig. 4. Pb(II) stripping peak currents in buffer acetate 0.1 M (*p*H = 5.5) on poly**L** modified electrodes for different complexation times of immersion in buffer acetate 0.1 M (*p*H = 5.5) containing [Pb] = 10^{-8}M, a reduction time of 120 s at a reduction potential of -1 V

Selection of the matrix used in complexation step

In these experiments two different buffer solutions (acetate buffer and phosphate buffer) and also ultrapure water have been used for preparation of 20.7 µg/L Pb solution ([Pb] = 10^{-7}M). The experiment using phosphate buffer solution was performed at *p*H values of 5, 5.53, 6.01, 6.52, 7.02, and 8 (fig. 5a), while for the acetate buffer solution it was conducted at: 4.03, 4.5, 5.02, 5.51, 6.00, 6.50 (fig. 5b).

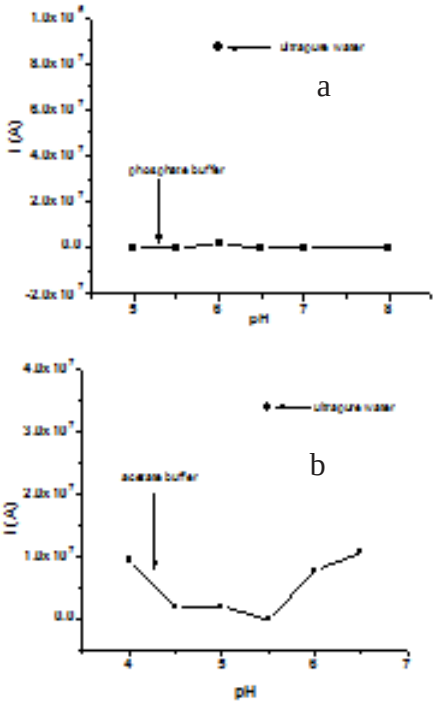

Fig. 5. Comparative results for Pb(II) stripping peak currents in different buffer solutions and ultrapure water on poly**L** modified electrodes for 25 min of complexation time of immersion in buffer acetate 0.1 M (a) and buffer phosphate 0.1 M (b), for reduction times of 120 s at a reduction potential of -1 V

All experiments were performed using the previously established optimized parameters, the only varied value being the *p*H of the complexation step, i.e. the solution used in the complexation step. In both experiments, the highest current was obtained when the Pb solutions were prepared with ultrapure water instead of any kind of buffered solution.

Optimization of acetate buffer pH

Pb(II) stripping peak currents form figures 5a obtained with the standards prepared in phosphate buffer solutions were lower than the corresponding currents shown by the standards prepared in acetate buffer solution. For this reason, the stripping was performed in acetate buffer solutions.

This experiment compared the currents obtained in different *p*H acetate buffer solutions (4.03, 4.5, 5.02, 5.51, 6.00, respectively 6.50). The best result was found at 4.03 *p*H (fig. 6).

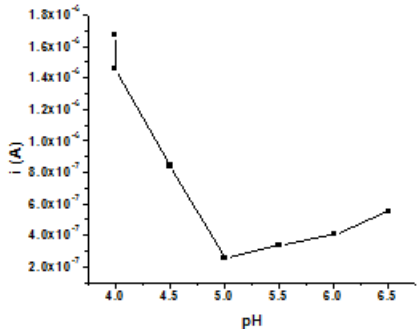

Fig. 6. Pb(II) stripping peak currents in different acetate buffer solutions on poly**L** modified electrodes for 25 min of complexation time of immersion in and ultrapure water, for reduction times of 120 s at a reduction potential of -1 V

Summary of the optimized electrochemical parameters of the Pb(II) analysis method based on polyL modified electrodes

1) Polymeric film formation by controlled potential electrolysis at 1.7 V using a charge of 1 mC under argon atmosphere. The cell contains 1mM **L** and 0.1 M TBAP in CH_3CN;

2) Film conditioning in 0.1M buffer acetate solution using cyclic voltammetry: equilibration (-0.9V ÷ +0.6V ÷-0.9V, 15 cycles) and over-oxidation (-0.2V ÷+1.6V ÷-0.2V, 10 cycles) under argon atmosphere;

3) Complexation in a standard solution prepared from lead nitrate (II) using ultrapure water as matrix or a real sample; the complexation time is 25 min;

4) Stripping by differential pulse voltammetry method in acetate buffer at 4.0 *p*H, after 120 s reduction time at -1.0 V reduction potential, under argon atmosphere.

The electrode preparation takes 18 min , and the determination time for a standard solution or real sample is around 27 min.

Validation experiments

Calibration curve was plotted in the range 1μg/L to 20 ìg/L Pb. The obtained data have been processed in two different ways. Table 2 summarizes the coefficients for unweighted linear regression (A) and lists the coefficients for weighted linear regression of the calibration curve (B), where x_i is Pb(II) concentration in μg/L, and y_i is Pb(II) stripping current in μA.

The experimental data for the limit of detection LOD and limit of quantification LOQ are presented in table 3. Six samples enriched with 0.62 μg/L Pb (II) were analyzed and the results were used for evaluation of LOD and LOQ.

In order to establish the precision of the method, ten samples of 10.35 μg/L Pb, prepared from $Pb(NO_3)_2$ were analyzed. The precision test was performed by one analyst, in the same day, using the same equipment and method. The experimental data are presented in table 4.

The intermediate precision test was performed by two analysts (six experiments each), using the same equipment and method. The experimental data are presented in table 5.

Table 2
LINEARITY TEST COEFFICIENTS

x_i (μg/L Pb(II))	1.04	2.07	6.21	10.35	20.7
y_i (μA)	0.053	0.134	0.440	0.736	1.500

y = -0.00755 + 0.0728 x		**(A)**
y-Intercept a = -0.00755 μA	Sensitivity = slope of the calibration curve b = 0.0728 (μAxL)μg^{-1}	Correlation coefficient R = 0,9999
Residual standard deviation S_{Y1} = 0.118 μg/L Pb(II)	Standard deviation of the method S_{x01} = 0.163 μg/L Pb(II)	Coefficient of variation of the method V_{x01} = 4.03 %
y = -0.0199+ 0.0734 x		**(B)**
y-Intercept a = -0.0199 μA	Sensitivity = slope of the calibration curve b = 0.0734 (μAxL)μg^{-1}	Correlation coefficient R = 0,9998
Residual standard deviation S_{Y1} = 0.004 μg/L Pb(II)	Standard deviation of the method S_{x01} = 0.052 μg/L Pb(II)	Coefficient of variation of the method V_{x01} = 0.65 %

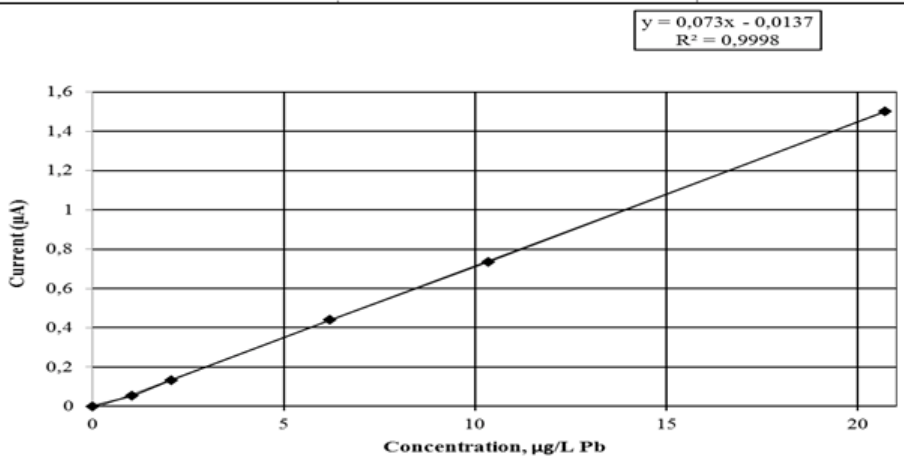

Fig. 7. Calibration curve for determination of Pb (II) in water using modified glassy carbon electrode with poly**L** in the optimized conditions

Table 3
PARAMETERS IN EXPERIMENTS FOR LOD AND LOQ

Measured values (μg/L)	0.61	0.79	0.50	0.53	0.72	0.75

Standard deviation of the results, s = 0.12 μg/L
Limit of detection, LOD = 3s = 0.36 μg/L
Limit of quantification, LOQ = 10s = 1.20 μg/L

Table 4
EXPERIMENTS FOR REPEATABILITY

Measured values (μg/L)	10.50	8.69	11.55	10.66	12.16
	9.72	10.31	8.10	8.93	10.4

Standard deviation of the results, s = 1.26 μg/L
Mean value, x_{mean} = 10.07 μg/L
Repeatability = 2.8*s= 3.54 μg/L
Relative standard deviation of the repeatability, RSD_{rv}= s/(x_{mean}*100)= 12.55%

Table 5
EXPERIMENTS FOR INTERMEDIATE PRECISION

Measured values (µg/L)	12.23	10.42	8.10	10.66	9.01	11.44
	12,04	9.83	9.64	13.89	10.88	9.52

Standard deviation of the results, s = 1.59 µg/L
Mean value, x_{mean} = 10.64 µg/L
Intermediate precision = 2.8*s= 4.45 µg/L
Relative standard deviation of the intermediate precision, $RSD_R = s/(x_{mean}*100)$ = 14.94%

Table 6
RECOVERY TEST

Measured values (µg/L)	3.83	3.89	4.01	4.42	4.35

Standard deviation of the results s = 0.27 µg/L
Mean value, x_{mean} = 4.10 µg/L
Recovery = 82.00 %
Accuracy = 5.00 – 4.10 = 0.90 µg/L

Table 7
QUANTIFICATION OF THE ELEMENT USED TO ESTIMATE THE UNCERTAINTY

	Value (µg/L)	Standard uncertainty (µg/L)	Rsu %
C_{vf}	9.98	2.4771	24.83
f_{rep}	1	0.0432	4.315
$CRM_{obtained}$	4.10	0.1204	2.937
CRM_{added}	5.00	0.0526	1.052
Value ± expanded uncertainty		12.07 ± 6.18 µg/L	50.77

The recovery test consists in measurement of five independent solutions, each containing 5µg/L Pb of certified reference material. The data are shown in table 6.

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

$$C_{Pb} = C_{vf} \times f_{rep} \times f_{rec} \text{ , µg/L} \quad (1)$$

where: C_{vf} = Pb(II) concentration in volumetric flask; f_{rep} = influence factor of the intermediate precision; f_{rec} = influence factor of the recovery (CRM_{added}/ $CRM_{obtained}$); CRM_{added} = 5 µg.

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

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

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 (table 7).

The uncertainties of the intermediate precision test and $CRM_{obtained}$ were estimated using data reported in table 5 and 6.

Pb(II) determination method using azulene modified electrodes based on poly**L** allows the determination of Pb(II) content in waters with lead content lower than 1.2 µg/L . The method can be used for determination of Pb(II) in surface water, wastewater, but for drinking water it does not provide the required performance characteristics (precision should be lower than 1 µg/L).

Conclusions

The study presents an electrochemical method for Pb(II) determination in water samples using a glassy carbon electrode modified with a functionalized azulene: (2E)-2-(azulen-1-ylmethylidene) hydrazine carbothioamide, (**L**) as a complexing polymeric film. The repeatability is 12.55%, while the intermediate precision test indicated a value of 14.94%. The detection limit of the method is 0.36 µg/L Pb(II), and the quantification limit is 1.2 µg/L Pb(II). Relative standard uncertainty of this new electrochemical method is 50.77% at 10 µg/L Pb(II). Low values of LOD/ LOQ and good precisions indicate that the method is suitable for monitoring and measurement of lead in surface and wastewater samples.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research - Program PN-II-PT-PCCA-2013-4-2151, financing contract no. 236/2014, SEMEMA.

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Manuscript received: 11.11.2017