

DETERMINATION OF MERCURY IN REAL SAMPLES BY ATOMIC SPECTROMETRY AND STRIPPING VOLTAMMETRY

Luisa-Roxana POPESCU¹, Eleonora-Mihaela UNGUREANU², G.-O. BUICĂ³,
Cristina DINU⁴, Mihaela IORDACHE⁵

The mercury detection from real samples of soil using chemically modified electrodes with films based on pyrrole-EDTA monomer was performed and the results were compared to those obtained by Atomic Absorption Spectroscopy, currently used in environmental laboratory analysis. The ligand used for electrode modification is ethylenediaminetetra-N-(3-pyrrole-1-yl)propylacetamide (L). The electrochemical method used for mercury detection was the anodic stripping voltammetry on polyL modified electrodes. The experiments have shown that mercury levels obtained by both methods are comparable.

Keywords: atomic absorption spectrometry, mercury, modified electrodes, anodic stripping voltammetry

1. Introduction

Mercury is one of the most harmful pollutants and it has become widespread into the environment mainly because of anthropogenic activities. Mercury has no beneficial biological function, and its presence in living organisms is associated with cancer, birth defects, and other undesirable outcomes. The toxic effects of divalent mercury can be prevented to some extent either by chelating or enhancing antioxidant defence mechanisms. Mercury and its compounds are still used in many areas and it is also generated in significant amounts from processes in which it is contained in raw materials (energy industry, extractive industry - oil and gas, metals, cement industry, chemical industry etc.).

¹ PhD student, Department of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: mandoc_lui@yahoo.com

² Prof., Department of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: em_ungureanu2000@yahoo.com

³ PosPhD, Department of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: buica_george@yahoo.com

⁴ Eng., National Research and Development Institute for Industrial Ecology – Ramnicu Valcea Subsidiary, Romania

⁵ PhD student, eng., Department of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, National Research and Development Institute for Industrial Ecology – Ramnicu Valcea Subsidiary, Romania

Consequently, the approach of new methods for the determination of mercury in real samples of soil is a challenging issue.

Among these metals, mercury is one of the most poisonous elements for humans and animals [1, 2]. Determination of tracing amounts of this element in the environment is an urgent necessity, yet posing analytical problems because he can be found in several chemical forms. For accurate determination of mercury at trace and ultra-trace levels analytical methods are needed with high sensitivity and selectivity. Spectroscopic techniques have been successfully used for mercury detection. Having good sensitivity and reproducibility these methods generally can meet practical needs. However, their use requires expensive instruments, well-controlled experimental conditions, sample making and relatively large samples volumes. Thus, there are currently great demands for simple methods allowing rapid measurements of trace mercury in contaminated samples.

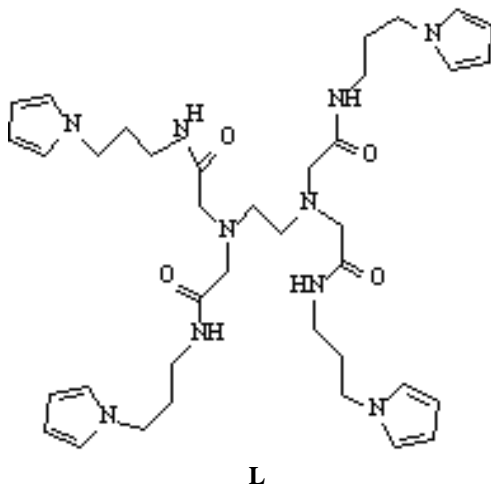
Electrochemical detection of trace metals offers important advantages, such as remarkable sensitivity, inherent miniaturization and portability, remote monitoring and decentralized measurements, low cost and compatibility with turbid samples and with advanced micromachining technologies [3-5].

Stripping voltammetry using mercury electrodes based on amalgam formations and stripping of electroprecipitated metals has proved to be one of the most sensitive electrochemical methods to analyze trace metals [6, 7]. Because of the toxicity of mercury, alternative solid electrode materials have been used as possible alternative to mercury [8-10]. Moreover, stripping analysis using chemically modified electrodes (CME) exhibit however higher selectivity due to specific interactions between metal ions and complexing matrix [11]. Uses of CMEs furthermore greatly limit chemical interferences and allow sensing of metals as mercury or silver, which can not be analyzed with conventional mercury, based anodic stripping voltammetry.

Modification of electrodes surface with complexing polymer films is an interesting approach because it leads to immobilization large amounts of ligand on the electrode surface and thus allows the accumulation of metal ions.

Electropolymerization of functionalized heteroaromatics monomers provided a direct and effective way to attach polymer films on electrode surface. Conductive polymer films have been tested to generate useful analytical modified electrodes for trace metal detection. Two pyrrole – EDTA derivatives, having two and four polymerizable pyrrole units, N,N-ethylenebis[N-[(3-(pyrrole-1-yl) propyl) carbamoyl) methyl]-glycine and ethylenediamine tetra-N-(3-pyrrole-1-yl) propylacetamide, have been investigated in our group in order to build modified electrodes for mercury recognition [12, 13]. The best detection limit for mercury has been obtained using the modified electrodes obtained by electropolymerization of the ligand with four pyrrole units, ethylenediamine tetra-

N-(3-pyrrole-1-yl) propylacetamide (**L**). This ligand has been used in the current investigation.



2. Materials and methods

Samples collection

The real samples of soil were taken and prepared according to the standard procedure. For the soil samples the dry matter was determined. Then they were mineralized after the normal procedure, SR ISO 11466:1999 [14]. The soil solutions so prepared were analyzed by AAS and ASV and the results were expressed in respect to the dry weight (D.W.).

Reagents and apparatus

For Atomic Absorption Spectroscopy (AAS) measurements 10% SnCl₂ solution and concentrated nitric acid, from Merck, have been used. The samples were analyzed by AAS according to the procedure described in SR ISO 11466:1999 and SR EN 1483: 2007 [14, 15]. The measurements have been done using an AAS Unicam atomic spectrometer.

For electrochemical investigation acetonitrile (Rathburn, HPLC grade), tetra-n-butylammonium perchlorate (TBAP) from Fluka were used as received for solvent and supporting electrolytes in the preparation of modified electrodes. The analysis was performed in aqueous acetate buffer (0.1 mol L⁻¹) solutions.

The modified electrodes were prepared by controlled potential electrolysis in a classical three compartments cell using a three-electrode system following the procedure described in [13]. The working electrodes were glassy carbon disks (3 mm diameter from CH Instruments) from Metrohm, the counter electrode was a platinum wire and the reference electrode was Ag/10⁻² mol L⁻¹ Ag⁺ in CH₃CN + 0.1 mol L⁻¹ TBAP.

Metal cation sensing experiments were conducted in, using a conventional three electrodes system. The working electrodes were the glassy carbon disks modified with polyL, the counter electrode was a platinum wire and the reference electrode was Ag/AgCl/KCl (3 M) with double junction (Methrom). All potentials in this paper were referred to the saturated calomel electrode, unless otherwise noted.

Denver Instrument Model 220 pH-conductivity meter was used to measure the pH.

Electrochemical experiments were conducted under argon atmosphere at 25°C using a PGSTAT 12 AUTOLAB potentiostat. CV experiments were usually performed at 0.1V/s, and DPV curves were recorded at 10mV/s with a pulse height of 25mV and a step time of 0.2s.

3. Results and discussion

After identification of contaminated areas with mercury by analysis of all available data from INCD ECOIND data banks, public data (MEC, MMGA, APM, and economic units sites, INS publications), the sampling of soils was performed using standard procedures. Soil samples from industrial area were taken from two different locations (P1 and P2) at varying depth: 0-10cm (I), 40-50cm (II), 70-80cm (III). Their collection was conducted over several periods of the year.

The soil solutions were analysed according to a traditional method: Atomic Absorption Spectroscopy (AAS) and using a new method proposed in literature [13] anodic stripping voltammetry on chemically modified electrodes (ASV). The last method is based on covering the electrode surface with a complexing layer of a polymer film. Both methods were used to detect the mercury from soil samples. Its content was expressed in mg per kilogram of dry matter (mg/kg DW)

3.1. Atomic Absorption Spectroscopy measurements (AAS)

The determination of mercury in the soil solutions was first achieved by the AAS standard method (SR ISO 11466:1999 and SR EN 1483:2007) [14, 15], and the results are shown in Table 1.

Table 1 shows that the values are very spread, between 0,66 and 311 mg/kg DW. The mercury content is generally higher on the second level then the first level of sampling. For instance: P2(II), > P2(I); P2(II) > P2(I) in June and September. The evolution of mercury content in samples with less 25 mg/kg DW, during the time of sampling was shown in detail in Fig. 1. No clear tendency can be put in evidence. However, the results show that the pollution is persistent, but

no systematic variation can be observed. The horizontal red line marks the allowable limit according to regulations.

Table 1

Concentration of mercury from soil samples in mg / kg D.W.						
Soil samples	P1-I	P1-II	P1-III	P 2-I	P 2-II	P 2-III
March	1.05	3	0.66	11.18	4.6	0.85
June	2.99	2.25	1.07	0.86	18.49	1.17
September	3.79	4.93	12.35	8.94	311	91

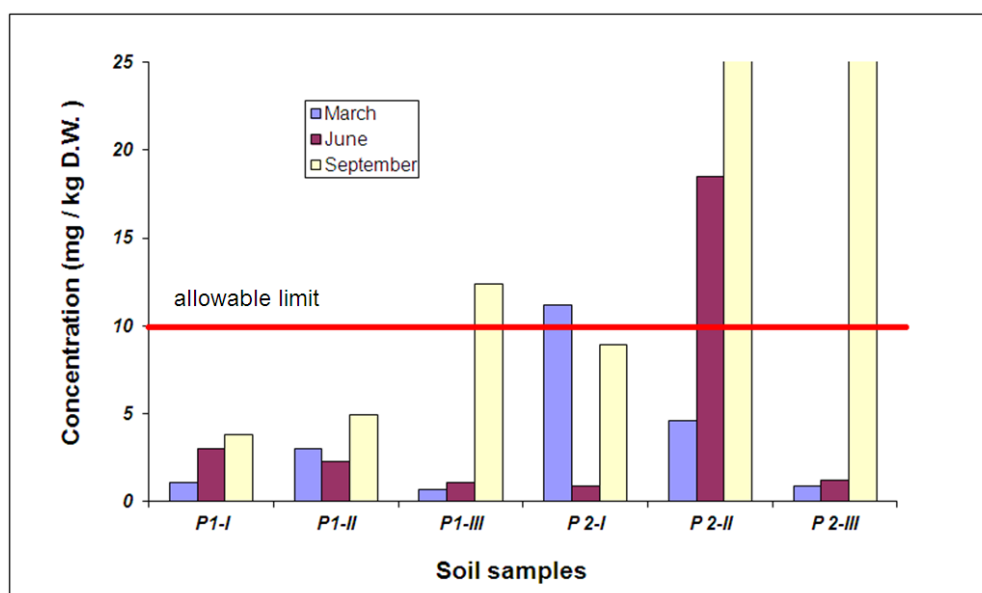


Fig. 1. Results obtained by Atomic Absorption Spectroscopy for soil samples taken in March, June and September

3.2. Anodic Stripping Voltammetry measurements (ASV)

The results for determination of mercury from the soil solutions obtained using AAS method were compared with those obtained using the new proposed method: anodic stripping voltammetry on chemically modified electrodes.

The modified electrodes were prepared according to the procedure described in [13] by oxidation at controlled potential (CPE). The electropolymerization was carried out at +0.85 V vs. Ag/Ag⁺, up to 1.5 mC polymerization charge (which corresponds to a surface concentration of the monomer $\Gamma = 10^{-8}$ mol cm⁻²). The characteristic signal of polyL film was

evidenced by cyclic voltammetry in transfer solution ($\text{CH}_3\text{CN} + 0.1 \text{ mol L}^{-1}$ TBAP) as shown in Fig. 2. Then the electroactivity of the polypyrrole matrix was destroyed during 15 cycles between -0.2 V and $+1.2 \text{ V}$ in a acetate buffer (pH 5.5), in order to obtain clean voltammograms in the positive potential region. The corresponding glassy carbon electrodes modified with polyL films were further called C|polyL.

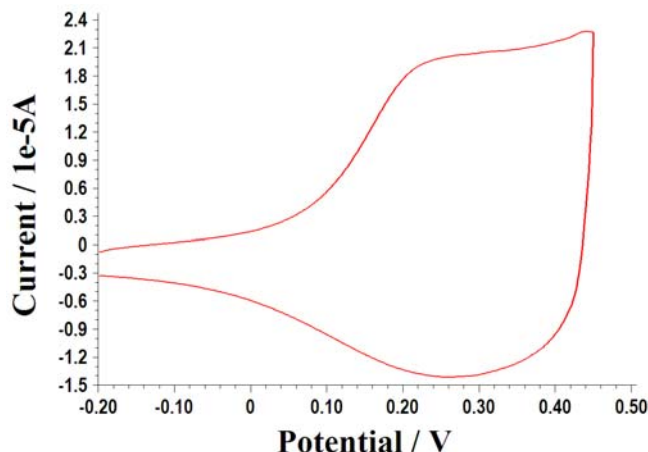


Fig. 2. Cyclic voltammetry curve of the C|polyL modified electrode in transfer solution ($\text{CH}_3\text{CN} + 0.1 \text{ mol L}^{-1}$ TBAP).

The analysis of mercury on polyL modified electrodes has been done using anodic stripping voltammetry. The calibration curve has been obtained using solutions of in buffer acetate at pH 4.5. The C|polyL modified electrode was dipped in for 20 min into the stirred solution containing Hg(II) ions of 10^{-7} M . Then the electrode was thoroughly washed with purified water to remove unbounded ions from the surface and was transferred into the electrochemical cell containing 0.1 mol L^{-1} acetate buffer solutions, and polarized at -1.8 V for 3 min to ensure full reduction of the entrapped metal ions. The characterization was performed under quiescent conditions by differential pulse voltammetry (DPV).

DPV anodic experiments were recorded for various concentrations of mercury ions using freshly prepared electrodes in order to get the calibrations curves (Fig. 3).

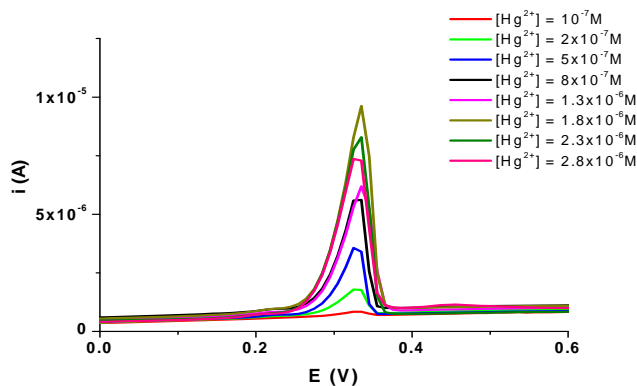


Fig. 3. DPV curves recorded using C|polyL modified electrodes ($\Gamma = 10^{-8} \text{ mol cm}^{-2}$) in acetate buffer (pH 4.5) after a preconcentration time of 20 minutes in acetate buffer containing different concentrations of Hg (II) ions; metal ions reduction was achieved at -1.8 V vs. Ag, AgCl/Cl⁻ for 3 minutes.

The graphical representation of the calibration curve is shown in Fig. 4. Linear calibration plots were obtained in the concentration range from 10^{-7} to $8 \times 10^{-7} \text{ mol L}^{-1}$ with correlation coefficient of 0.997 (Fig. 4). This domain can be used for Hg(II) detection. In parallel some interference effects were studied (and the calibration curves for copper, lead, and cadmium were obtained).

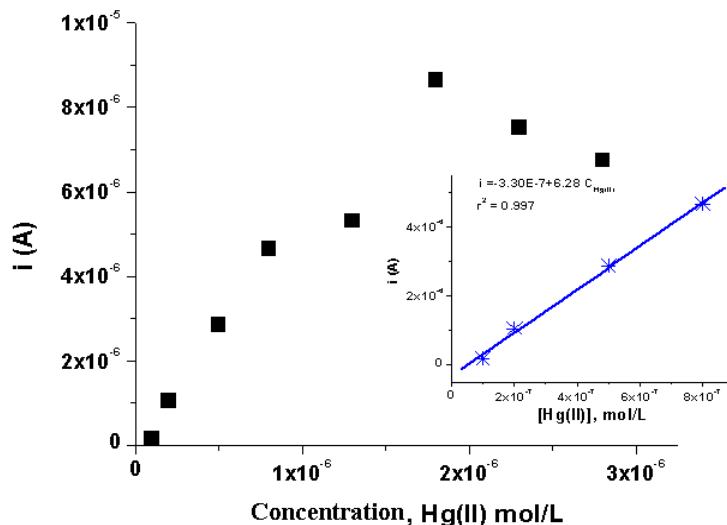


Fig. 4. Calibration curve from DPV measurements recorded at different C|polyL electrodes ($\Gamma = 10^{-8} \text{ mol cm}^{-2}$) as a function of Hg(II) concentration in the accumulation solution (acetate buffer, pH 4.5, accumulation time 20 min, reduction for 3 min at -1.8 V). Inset: Linear parts of the calibration plots.

Soil samples were prepared and analyzed similarly to solutions used in the calibration procedure. The soil solutions were diluted with buffer acetate and adjusted at pH 4.1. The C|polyL modified electrode was dipped in for 20 min into the stirred solution containing the soil sample. Then the electrode was thoroughly washed with purified water, transferred into the electrochemical cell containing 0.1 mol L⁻¹ acetate buffer solutions, and polarized at -1.8V for 3 min. The characterization was performed under quiescent conditions by differential pulse voltammetry (DPV) in the same conditions as for the calibration curve. An example of DPV curve for a soil solution (P2-II september) is shown in Fig. 5. Hg, Pb, and Cu metals were put in evidence at their specific potentials established in previous experiments performed for each of these ions. Using the calibration curve the concentrations of Hg (II) in the samples were estimated. They were compared to the values obtained by AAS standard method.

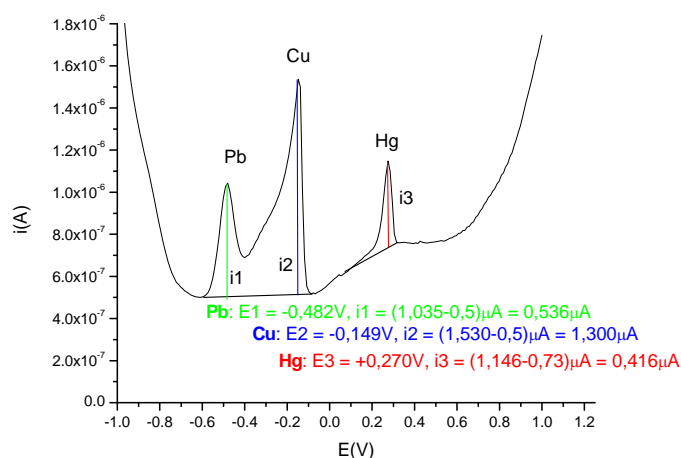


Fig. 5. DPV curve recorded at C|polyL modified electrode for the soil solution from sample P2 II September (acetate buffer, pH 4.5; 20 minutes accumulation, 3 minutes reduction at -1.8 V).

DPV peak current leads to a concentration of 7.15×10^{-7} mol L⁻¹, corresponding to a content of 143 mg/L or 230 mg Hg (II) / kg dry matter (DW). This value represents 74% of the value obtained by atomic absorption spectroscopy analysis. Results of the proposed method have an error of 26% compared to the standard method.

The results obtained by the two methods used (AAS and modified electrodes with polyL) were similar. The observed differences could be attributed to different speciation of mercury in these samples.

4. Conclusions

The result obtained using the traditional method (Atomic Absorption Spectroscopy) and the new proposed method based on modified electrodes with polyL was quite similar. However, the differences should be diminished by a carefully investigation of the interferences, and study of mercury speciation. The work is in progress.

This method of stripping voltammetry applied on modified electrode with complexing polymer films is an interesting approach for Hg(II) analysis, as it allows a low cost evaluation, with potential portability for decentralized measurements.

Acknowledgements

The authors acknowledge the financial support from the European Social Fund through POSDRU/107/1.5/S/76909 "Valorification of human potential in research by PhD scholarships (ValueDoc)" and POSDRU/107/1.5/S/76813 "Doctoral Scholarships: investment in research and development and innovation for the future (DocInvest)" projects.

REFERENCES

- [1] A., Bhan, N.N., Sarkar, Mercury in the environment: effect on health and reproduction. Rev. Environ. Health 20, (2005), 39-56.
- [2] D.W. Boening, Ecological effects, transport, and fate of mercury: a general review, Chemosphere 40 (2000) 1335–1351.
- [3] J. Wang, B. Tian, J. Wang, J. Lu, C. Olsen, C. Yarnitzky, K. Olsen, D. Hammerstrom, W. Bennett, Stripping analysis into the 21st century: faster, smaller, cheaper, simpler and better. Anal. Chim. Acta, 385 (1999), 429-435.
- [4] R. De Marco, G. Clarke, B. Pejic, Ion-Selective Electrode Potentiometry in Environmental Analysis. Electroanalysis, 19-20, (2007), 1987-2001.
- [5] J. Wang, B. Tian, J. Lu, J. Wang, D. Luo, D. MacDonald, Remote Electrochemical Sensor for Monitoring Trace Mercury Electroanalysis 1998, 10, 399-402.
- [6] J., Wang. Stripping Analysis: Principles, Instrumentation and Applications, VCH, Weinheim (1985).
- [7]: G.-O. Buica, E.-M. Ungureanu, L. Birzan, A.C. Razus, M.-R. Bujduveanu, Films of poly(4-azulen-1-yl-2,6-bis(2-thienyl)pyridine) for heavy metal ions complexation, Electrochim. Acta 56, (2011), 5028-5036.
- [8] Jingming Gong, Ting Zhou, Dandan Song, Lizhi Zhang, Monodispersed Au nanoparticles decorated graphene as an enhanced sensing platform for ultrasensitive stripping voltammetric detection of mercury(II), Sensors and Actuators B 150 (2010) 491–497
- [9] Claudia Gilsanz, Rui Gusmao, Elena Chekmeneva, Nuria Serrano, Jose Manuel Diaz-Cruz, Cristina Ariño, Miquel Esteban, Electroanalysis of the binding and adsorption of Hg²⁺ with

- seleno aminoacids by differential pulse and elimination voltammetry at the Au-disk electrode, *Electrochimica Acta* 56 (2011) 5988– 5992
- [10] *Kamal Alizadeha, Razieh Parooia, Payman Hashemia, Behrooz Rezaeia, Mohammad Reza Ganjali*, A new Schiff's base ligand immobilized agarose membrane optical sensor for selective monitoring of mercury ion, *Journal of Hazardous Materials* 186 (2011) 1794–1800
- [11] *J.-M. Zen, A. S. Kumar, D.-M. Tsai*, Recent Updates of Chemically Modified Electrodes in Analytical Chemistry *Electroanalysis* 15, (2003), 1073-1087.
- [12] *G.-O., Buica, E.M., Ungureanu, C., Bucher, J.C., Moutet, E., Saint-Aman*. Poly(pyrrole-EDTA like) Modified Electrodes for Mercury Ions *Electroanalysis. Journal of optoelectronics and advanced materials.* 11(8), (2009), 1152-1159.
- [13] *G.-O., Buica, C., Bucher, J.C., Moutet, G., Royal, E., Saint-Aman, E.M., Ungureanu.* Voltammetric Sensing of Mercury and Copper Cations at Poly(EDTA-like) Film Modified Electrode. *Electroanalysis*, 21(1), (2009), 77-86. [14] SR ISO 11466:1999, Soil quality – Extraction of trace elements soluble in aqua regia
- [15] *SR EN 1483/2007*, Water quality. Determination of mercury. Method using atomic absorption spectrometry.