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DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY FOR MERCURY DETERMINATION

Paul C. Vereștiuc,[a*] Oana-Maria Tucaliuc,[a] Iuliana G. Breabăn,[a]
Igor Crețescu,[b] Gheorghe Nemțoi[c]

[a]*Faculty of Geography and Geology, "Al. I. Cuza" University Iasi, 11 Carol I Bd, Iasi 700506, Romania*

[b]*Faculty of Chemical Engineering and Environmental Protection, "Gh. Asachi" Technical University of Iasi, 73 Prof.Dr.docent D.Mangeron Blvd, 700050, Romania*

[c]*Faculty of Chemistry, "Al. I. Cuza" University Iasi, 11 Carol I Bd, Iasi 700506, Romania*

Abstract: In the present work voltammetric investigations have been performed on $HgCl_2$ aqueous solutions prepared from a Cz 9024 reagent. Carbon paste electrode (CPE), eriochrome black T modified carbon paste electrode (MCPE/EBT) and KCl 1M as background electrolyte, were involved within the experimental procedures. Cyclic voltammetry (CV) has been performed in order to compare the behaviour of the two electrodes in both $K_3[Fe(CN)_6]$ and mercury calibration aqueous solution. Differential pulse anodic stripping voltammetry (DPASV) was used to determine the most suitable parameters for mercury determination. All experiments were performed at 25 ± 1 °C, using an electrochemical cell with three-electrodes connected to an Autolab PG STAT 302N (Metrohm-Autolab) potentiostat that is equipped with Nova 1.11 software. The measured potential values were generated by using the silver chloride electrode (AgClE) as reference

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[*] Vereștiuc Paul, *email:* verestiuc_paul@yahoo.com

and a platinum wire electrode as auxiliary. A series of time depending equations for the pre-concentration and concentration steps were established, with the observation that a higher sensitivity can be obtained while increasing the pre-concentration time. DPASV were drawn using the CPE in 11.16 % coriander, as mercury complex, the voltamograms signals indicating mercury oxidation, with signal intensity increasing in time.

Keywords: stripping voltammetry, coal paste modified electrode, pre-concentration time

Introduction

Mercury is an environmental toxin which causes a wide range of adverse health effects in humans, posing a particular threat to the developing fetus and young children. It is known that apart from dental fillings, the main source of human organism intoxication with mercury is fish-rich diet (methylmercury) and polluted air (elemental mercury). Methyl mercury is readily bioavailable and biomagnifies the food chain so that fish at higher trophic levels regularly have mercury concentrations, a million times greater than the water in which they live.[1-3] Mercury has a variety of uses in chloralkali plants, electrical equipment, batteries, medicine, dentistry and paints. Natural emissions of mercury arises from the degassing of the earth's crust through volcanoes and by evaporation from the oceans.[4] Studies related to the above mentioned subject were previously published.[5-7]

A plant known for its efficiency in removing the heavy metals in human organism is coriander, a strong detoxifying of the body tissues. Mercurous chloride, a toxic compound, is used as depolarizing in electric batteries, as a reagent in organic synthesis and analytical chemistry.[8]

Mercury species from aqueous media may be involved in redox processes such as:

$$Hg^{2+} + 2e^- \rightleftharpoons Hg \qquad (1)$$

$$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+} \qquad (2)$$

$$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg \qquad (3)$$

which can be studied electrochemically using voltammetry methods.[9,10]

Classical electrochemical methods can detect organic and inorganic compounds from the analyzed samples up to 10^{-4} - 10^{-5} M. Among various electrochemical techniques, stripping voltammetry (SV) has been recognized as being a very sensitive method for trace and ultra-trace heavy metals analysis, due to the combination between pre-concentration capacity combined and different electrode materials.

A stripping method frequently used in voltammetry is anodic stripping voltammetry (ASV), method used in the present paper. Carbon paste electrodes belong to a special group of heterogeneous electrodes. These electrodes are made of a mixture of carbon powder and suitable liquid binder, introduced in a specific electrode frame.

Due to its physicochemical and electrochemical characteristics, carbon paste became one of the most popular electrodes material. Carbon paste electrodes are a convenient conductive matrix for designing chemical modified electrodes. These electrodes are inexpensive, with low residual currents and a wide interval of potential. They are easy to obtain and are rapidly regenerating with a simple mechanical polishing. Although there is an important availability of chemical modified carbon electrodes in order to analyze small quantities of toxic metals, there is a permanent demand for new electrodes with better accuracy, precision, time and reliability when analyzing different samples.[11] The aim of this study is to observe mercury behavior form standard aqueous solution of Hg and $HgCl_2$ using carbon paste electrode (CPE) and modified carbon electrode (MCPE) when applying cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV).

Materials and equipment

For the current study, a mercury etalon solution (Aqueous Calibration Solution Astasol-Hg Analytica Cehia, delivered by the supplier at 1g/L Hg in 5% HNO_3 aqueous solution (v/v)) and $HgCl_2$ aqueous solution in 1M KCl. An aqueous solution of $K_3[Fe(CN)_6]$ was used for comparing the sensitivity of carbon paste electrode (CPE) and modified carbon paste electrode (MCPE).

All experiments were performed at 25 ± 1 °C, using an electrochemical cell with three electrodes (Figure 1-b) connected to an Autolab PG STAT 302N (Metrohm-Autolab) potentiostat (Figure 1-a), equipped with Nova 1.11 software.

Silver chloride electrode (EAgCl) was used as reference electrode, to which the values of potential measured were expressed. A plan platinum electrode was used as auxiliary electrode.

a) b)

Figure 1. Autolab PG STAT 302N potentiostat (a) and the electrochemical cell (b)

Carbon paste electrode (Φ = 5 mm), was obtained from spectral coal powder (70%) and paraffin oil (30%).[12] The modified carbon paste electrode was obtained by applying polyeriochrome black T (MCPE/EBT) on the surface of the carbon paste electrode.[13]

Results and discussions

Cyclic voltamograms (Figure 2) were drawn in an etalon solution of 0.1 mM $K_3[Fe(CN)_6]$ with and electrolytic background of 1M KCl, at 50 mV/s a scan rate in order to compare CPE and MCPE.

The difference between the two voltamograms is relevant and presence of EBT on the coal paste electrodes leads to substantially higher values of the anodic and cathodic peak current. More than this, the quasi-reversible redox process are becoming reversible, thus, the electrode's accuracy had increased.[13-15]

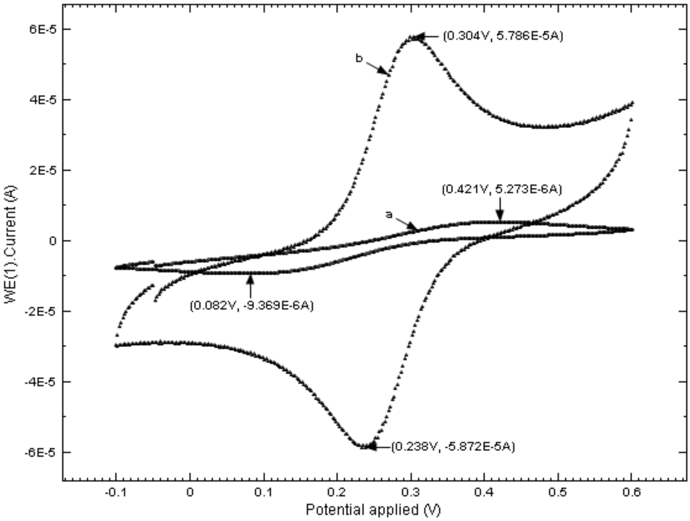

Figure 2. Cyclic voltamogram of 0.1 mM $K_3[Fe(CN)_6]$ in 1.0 M KCl on CPE (a) and MCPE (b) at 50mV/s.

The increase of MCPE's sensitivity (Figure 3b) takes place also for mercury from an 0.0233 mM Hg in 1M KCl aqueous standard solution, emphasized by the cyclic voltamogram outlined at 50 mV/s (Figure 3-b).

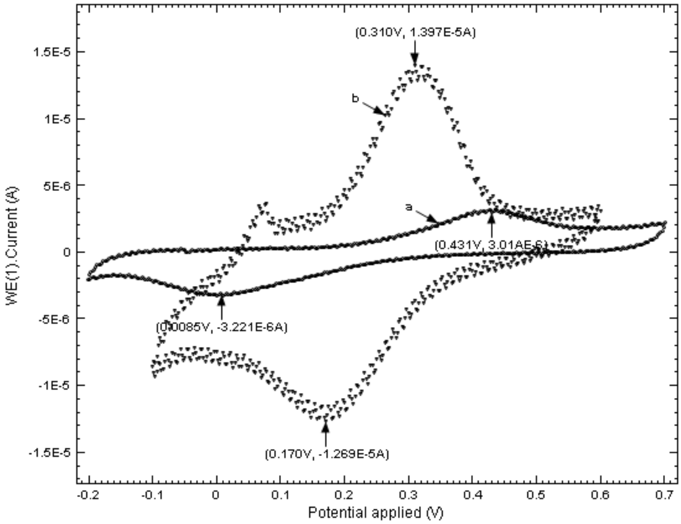

Figure 3. Cyclic voltamogram of 0.0233 mM Hg in 1M KCl, on EPC (a) and MEPC (b) at 50mV/s.

When applying the differential pulse anodic stripping voltammetry (DPASV) for the two standard solutions, the maximum signal was obtained at a deposition potential E_{dep} = -0.214V for both CPE and MCPE. Figure 4 shows the voltamograms obtained on MCPE in a 0.2584mM $HgCl_2$ aqueous solution at different deposition potentials, for 60 s, at 0.005 V, 0.05 s modulation time and time interval of 0.5 s.

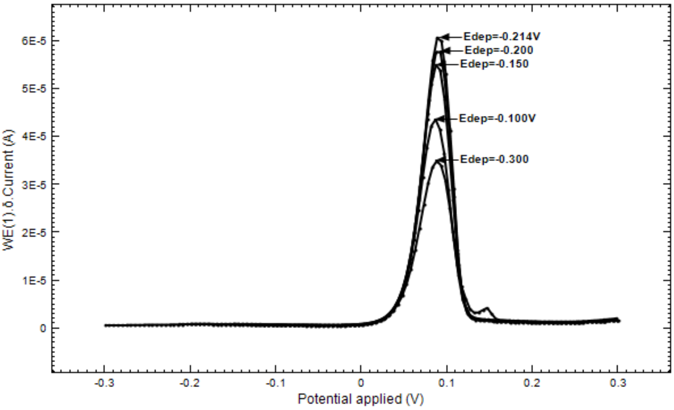

Figure 4. DPASV signal for 0.2584mM$HgCl_2$ on MCPE in 1M KCl.

DPASV sensitivity can be increased by extending the exposure time, as it can be observed in Figure 5, in 0.2584 mM $HgCl_2$ aqueous solution, on MCPE in 1M KCl, at different deposition time in the pre-concentration stage at E_{dep} = -0.214 V.

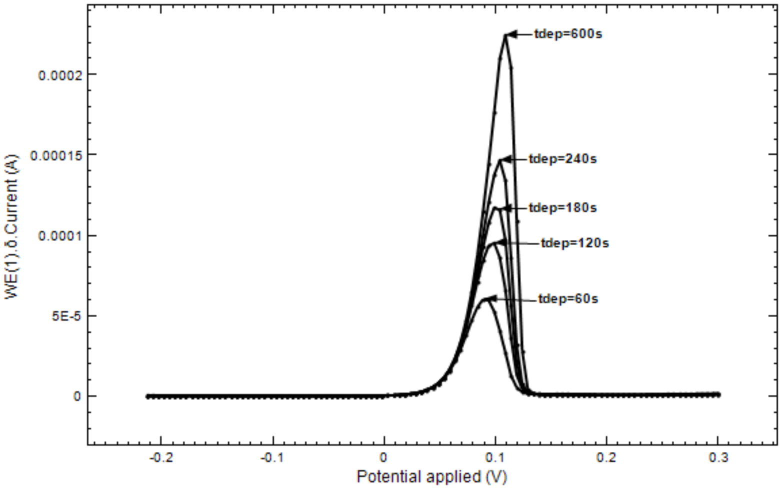

Figure 5. DPASV of mercury in 0.2584 mM $HgCl_2$) on MCPE in 1M KCl.

According to Figure 5, the signal in DPASV increases while extending the deposition time in the pre-concentration stage, so that at the optimal deposition potential previously set, the sensitivity can be increased by choosing a convenient time.

Within the 0 – 600 s time interval, the signal dependency in DPASV is a second order polynomial function type:

$\delta I(\mu A) = 16.032 + 0.681\ t - 5.548 \times 10^{-4}\ t^2$ (time expressed in seconds); R = 0.9969.

For diluted $HgCl_2$ aqueous solutions on MCPE in 1M KCl, with a concentration of 3.98 ÷ 51.7µM and a pre-concentration time of 480 s, E_{dep} = -0.214, the dependence of the stripping current is shown in Figure 6.

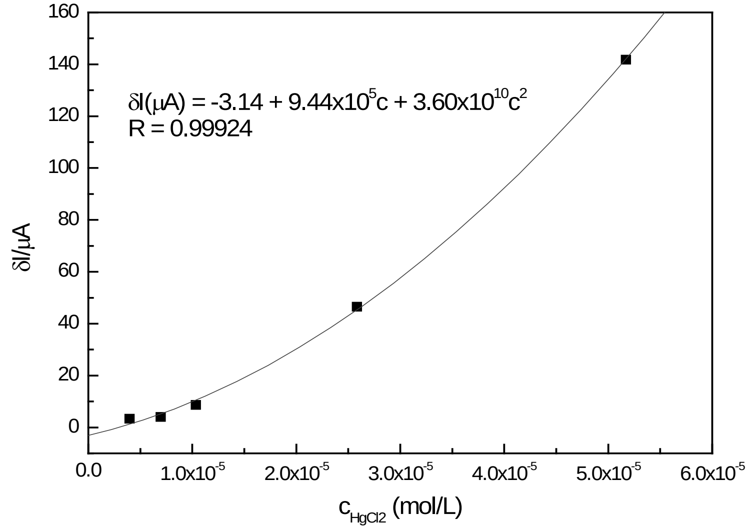

Figure 6. Stripping current's dependency of $HgCl_2$ concentration obtained using DPASV.

Using a diluted standard solution of 4.936 μM Hg in 1M KCl for longer time, Figure 7 shows the differential pulse anodic stripping voltamograms obtained when using MCPE.

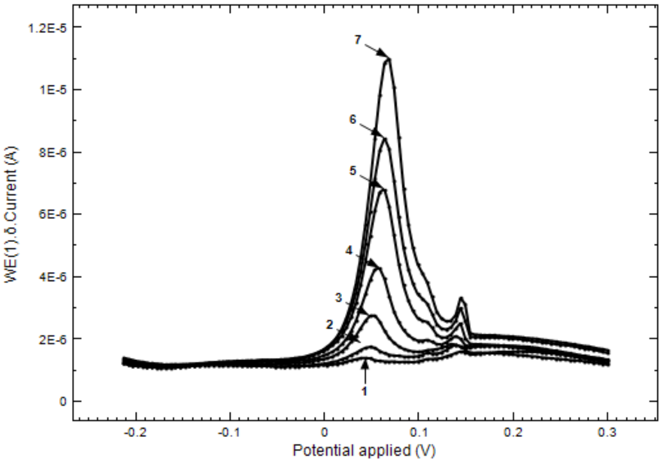

Figure 7. DPASV obtined in 1M KCl and etalon solution 4.936μM Hg on MCPE at different deposition times: 60s (1), 120s (2), 240s (3), 480s (4), 900s (5), 1200s (6), 1500s (7).

In this case it can be observed the fact that the voltamograms show a second signal that can be attributed to monovalent mercury oxidation. Time dependence of the peak signals was set for divalent mercury (first signal) and monovalent mercury (second signal):

$\delta I(\mu A) = 1.0699 + 6.46 \times 10^{-3}\, t\ (s)$; $R = 0.9985$ for the first signal on the voltamogram and $\delta I(\mu A) = 1.5508 + 1.16 \times 10^{-3} t\ (s)$; $R = 0.9911$ for the second signal.

Coal paste (62.19% spectral coal powder, 26.65% paraffin oil) and coriander powder (11.16%) were used to obtained a new electrode, plant recognized as being an efficiently complexant agent of mercury ions. The electrode containing coriander powder was introduced in 0.0895 mM $HgCl_2$ aqueous solution with 1M KCl, at $E_{dep} = -0.214V$, crossing DPASV at different time points of deposition (Figure 8).

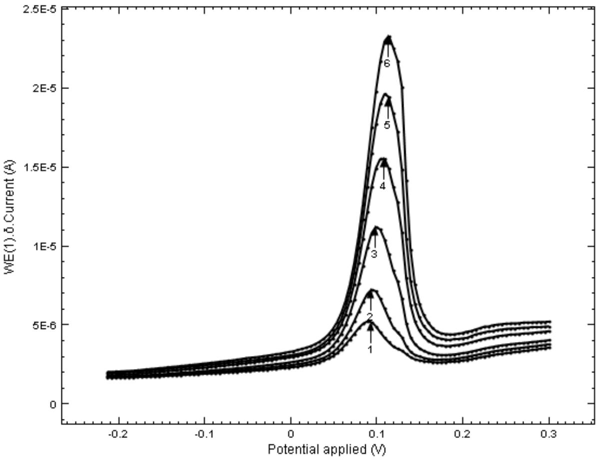

Figure 8. DPASV for 0.0895 mM $HgCl_2$ aqueous solution with 1M KCl, (1-120s, 2-240s, 3-480s ,4-960s ,5-1200s ,6-1500s).

Figure 8 shows an increase of the peak current in time and a shift of the peak potential from 88 mV (t = 120 s) to 113 mV (t = 1500s). The peak current dependence is a linear one, expressed by the equation:

$\delta I\ (\mu A) = 4.187 + 1.27 \times 10^{-2}\, t\ (s)$; $R = 0.9962$.

According to these results, the coriander is an efficiently complexant for mercury species in diluted solution and can be obviously correlated with DPASV data.

Conclusions

In this study, the cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV) were used in order to observe mercury behavior form standard aqueous solution of Hg and $HgCl_2$ using carbon paste electrode (CPE) and modified carbon electrode (MCPE). Electrodes efficiency regarding mercury determination in aqueous solutions was compared using cyclic voltammetry. The optimal parameters for mercury determination in aqueous solution were set using DPASV.

The pre-concentration and concentration time dependent equations were established, at a deposition potential (E_{dep} = -0.214V) using differential pulse anodic stripping voltammetry (DPASV).

This technique was used to obtain a voltamogram for the $HgCl_2$ solution with a modified electrode containing coriander, a complexant agent for mercury. Furthermore, the time dependency of the peak signal for a diluted solution of $HgCl_2$ was obtained.

Acknowledgements

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