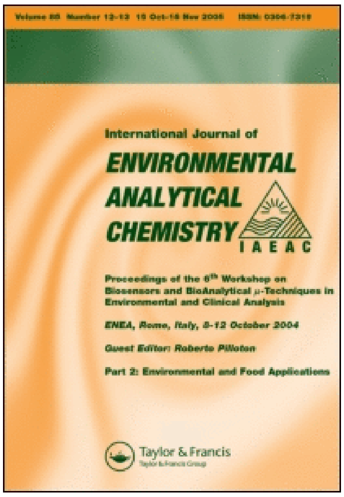

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Stripping Analysis of Trace Metals at a Flow-Through Reticulated Vitreous Carbon Electrode after the Preconcentration by Supported Liquid Membrane Technique

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STRIPPING ANALYSIS OF TRACE METALS AT A FLOW-THROUGH RETICULATED VITREOUS CARBON ELECTRODE AFTER THE PRECONCENTRATION BY SUPPORTED LIQUID MEMBRANE TECHNIQUE

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The performance of a flow-through mercury coated reticulated vitreous carbon (RVC) electrode in the potentiometric stripping analysis (PSA) of trace metals has been examined. A wall-jet glassy carbon cell was used for the comparative experiments. Experimental parameters influencing the stripping signals have been optimised in order to use the stripping analysis after the preconcentration and matrix isolation by supported liquid membrane (SLM) technique. The SLM with di-2-ethylhexylphosphoric acid (DEHPA) as the extractant in the membrane liquid for proton driven transport of trace metals across the membrane has been chosen. Results presented for lead determination in river water demonstrate the analytical advantages of coupled technique SLM-PSA.

Keywords: Supported liquid membrane; potentiometric stripping analysis; reticulated vitreous carbon; mercury film electrode; trace metals; natural waters

INTRODUCTION

The supported liquid membrane (SLM) enrichment coupled on-line to a detection technique is one of the most efficient ways of minimising matrix effects and lowering the detection limit of trace metals in natural waters [1,2]. The principle of the SLM enrichment is a liquid extraction and back-extraction of the analyte from an aqueous donor phase, through a hydrophobic liquid membrane, into an

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aqueous acceptor phase. A proton concentration gradient across the membrane may be used as the driving force for the transport of metal ions when a complexing agent like di-2-ethylhexylphosphoric acid (DEHPA) is used as the extractant in the membrane liquid [3]. By using an acceptor solution volume much smaller than the volume of the sample pumped through the donor side of the membrane the enrichment and separation of the analyte can be achieved at the same time.

Among the trace analysis techniques which can be coupled on-line with SLM enrichment, stripping analysis has several important advantages. These advantages are high sensitivity, good selectivity, relatively low price of instrumentation and compatibility with various flow systems [4]. One of the promising approaches in flow stripping analysis is the use of a porous flow-through electrodes, e.g., reticulated vitreous carbon (RVC). RVC is an open pore material with a foam structure which combines the electrochemical characteristics of glassy carbon with a high surface area and good hydrodynamic properties [5]. However, only a few papers have been published on the use of RVC for trace metal analysis by anodic stripping voltammetry [6–8].

The objective of this study was to evaluate the performance of a flow-through mercury coated reticulated vitreous carbon electrode in the stripping analysis of trace metals after SLM enrichment.

EXPERIMENTAL

Apparatus

Electroanalytical instrumentation, cells and electrodes

A computer controlled potentiostat for electroanalysis μAUTOLAB with GPES 4.3 software (Eco Chemie B.V., Utrecht, The Netherlands) was used for potentiometric stripping analysis (PSA) in all experiments.

A three electrode flow-through RVC cell with a total volume of 0.3 ml was made of Plexiglas material (Figure 1). Working electrode was cut from a RVC block (porosity grade 100-S, Energy Research & Generation Inc., Oakland, USA) with a cork borer. The RVC cylinders were 5 mm in diameter and 5 mm long (volume about 0.1 cm^3). The electrical contact to working electrode was made through Rh-Pt wire. For comparison, a wall-jet glassy carbon (GC) cell based on the design described in [9] was used. The distance between the jet nozzle and GC electrode was 1.5 mm and their diameters were 0. 5 mm and 3 mm, respectively. For both types of cells a silver wire was used as reference electrode and Rh-Pt wire as auxiliary electrode.

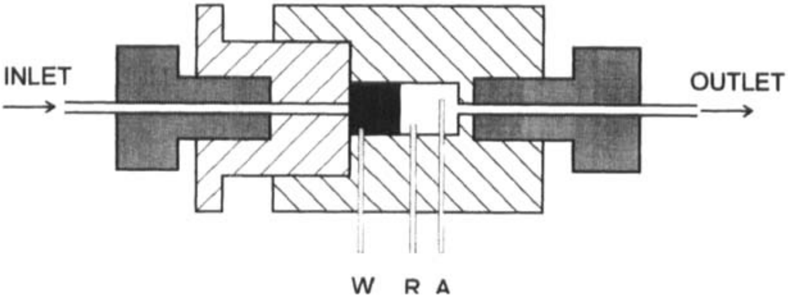

FIGURE 1 Flow-through RVC cell. W – RVC working electrode with contact from PtRh wire, R – reference electrode (Ag wire), A – auxiliary electrode (PtRh wire)

The SLM equipment and flow system

The SLM device used was similar to one described previously [10]. It consists of two identical circular Teflon blocks (diameter 90 mm, thickness 10 mm) with grooves cut in an Archimedes spiral (depth 0.25 mm, width 1.5 mm and length 125 cm), giving channels with a total volume of 0.5 ml. A porous PTFE membrane (Type FG, Millipore, Bedford, MA, USA; pore size 0.2 µm, porosity 0.70, total thickness of 175 µm of which 115 µm is the polyethylene backing) was impregnated by soaking it for at least 15 min in kerosene containing 40 % w/w of DEHPA as the selective extractant. The membrane was then placed between the Teflon blocks and clamped using two aluminium disks and stainless steel screws.

The flow system used is described in details elsewhere [11].

Reagents

All solutions were prepared in high purity water from a MilliQ-RO4 unit (Millipore, Bedford, MA). Nitric acid (65 %, *pro analysi)* was obtained from Merck (Darmstadt, Germany), DEHPA (95%) from Sigma Chemical Co. (St.Louis, MO, USA), mercury (II) nitrate *(pro analysi)* and kerosene from KEBO lab AB (Malmö, Sweden). Stock standard solutions (1000 mg l^{-1}) of lead (II) and cadmium (II) were from BDH Chemicals Ltd. (Poole, England). Stock solution (5000 mg l^{-1}) of mercury (II) was prepared from mercury nitrate dissolved in 1 mol l^{-1} nitric acid.

Procedures

Deposition of mercury film

The RVC cylinders were placed into the electrochemical cell without special pre-treatment except washing by water to remove small particles of crushed RVC. Before deposition of mercury small air bubbles were removed by pumping water or plating solution rapidly through the cell. Filling of the cell by ethanol before the water solutions can help to completely avoid air bubbles inside RVC. The mercury film was deposited by electrolysis from non-deaerated 100 mg l^{-1} mercury (II) solution (pH about 2) for 10 min at −1.10 V *versus* Ag/AgCl and at a flow rate of 0.5 ml min^{-1}. After mercury plating the cell was immediately filled with water. Mercury plated RVC electrode when not in use was held in water without any external potential. Mercury film renewal was repeated daily by additional deposition for 5 min at the conditions described. Normally, after about two weeks of using, the RVC electrode was replaced because of a rather complicated procedure of complete removal of the mercury film.

The mercury film on a glassy carbon electrode in a wall-jet cell was deposited daily from 50 mg l^{-1} mercury (II) solution for 5 min. All other conditions were the same as for the RVC electrode. The utilised mercury film was wiped off with a wet tissue.

Potentiometric stripping analysis

For the PSA measurements, using both GC and RVC cells, the required deposition potential was applied for deposition times from 15 s to 15 min. After the deposition, the flow was stopped and the same deposition potential was held for the rest time (up to 15 s). Chemical (currentless) stripping of the deposited lead and/or cadmium was performed in quiescent conditions by naturally dissolved oxygen. The stripping curve dt/dE *versus* E with characteristic peaks $(dt/dE)_p$ was recorded over the potential interval of interest. Peak heights were recorded using the GPES software.

Determination of lead in river water

River water samples were collected into polyethylene bottles and the pH was adjusted immediately to 3.0 with a few drops of 65 % Suprapur nitric acid. The acidified river water samples were analysed without any further pretreatment.

The acceptor side of the supported liquid membrane, a peristaltic pump tubing and a cell with mercury coated RVC electrode were filled by pumping 0.1 M nitric acid through the open line prior the SLM enrichment. Then the open line was connected into a closed loop (total volume 0.8 ml) recycling acceptor solution and the second peristaltic pump was switched on to pump the sample through the donor side of SLM. The flow rates were kept 0.5 ml min^{-1} for both sample and recycling flows. After 5 min of SLM enrichment a deposition potential of -1.1 V vs. Ag/AgCl was applied to the RVC working electrode during the next 10 min of enrichment. After the enrichment, both pumps were stopped and after a rest time of 15 s, the analytical curve *dt/dE versus E* was recorded. The analytical system including switching of valves, pumps, potentiostat control and, also, data accumulation were all computer controlled using GPES software.

RESULTS AND DISCUSSION

In order to evaluate the performance of the flow-through RVC electrode in stripping analysis, a comparative study of the electrochemical properties of RVC and wall-jet GC cells was undertaken. The study was focused on the influence of the main parameters affecting the stripping signals of trace metals in both cases, i.e., deposition potential and time, hydrodynamic conditions in flow-through cells, and medium composition.

Figure 2 illustrates the dependencies of lead and cadmium stripping signals on normalised deposition potential in GC and RVC cells. The deposition potentials were normalised by subtracting the stripping peak potential (E_p) from the corresponding deposition potential (E_d). This simple operation allows the elimination of ohmic potential drop effects when comparing results obtained using flow cells of different configuration and clearly shows the differences between the dependencies. It is seen from Figure 2 that the optimum normalised deposition potentials for lead and cadmium on GC are more negative than on RVC in spite of a poorer quality of the RVC mercury film, which is clearly visible microscopically. This effect is most likely caused by differences in shape of the surfaces of RVC and GC working electrodes. The surface area of three-dimensional RVC electrode of 0.1 cm^3 volume can be as high as 6.6 cm^2 [5] when the flat surface of GC electrode used was only 0.07 cm^2. The experimental ratio of total deposition currents through RVC and GC electrodes was about 15–20, i.e., much lower than one between geometric surface areas. Of course, the difference in currents is greatly influenced by different hydrodynamic properties of electrochemical cells, however, different condition of surfaces and uneven distribution of current may effect the process of the electrochemical reduction of the analyte. The much higher deposition current densities for the frontal edges of RVC compared to the flat surface of GC may result in metal deposition at "more positive" potential.

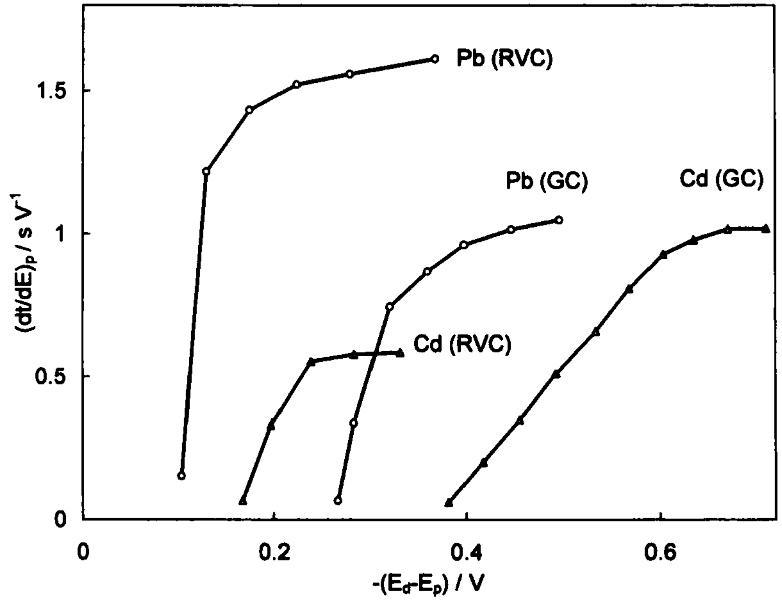

FIGURE 2 Comparison of the dependencies of lead and cadmium stripping signals on normalised deposition potential using GC and RVC cells. Conditions: 100 μg l^{-1} Pb and Cd in 0. 1 M HNO_3; deposition time 30 s; flow rate 0.5 ml min^{-1}

The influence of deposition time on stripping signals in flow-through RVC was tested using solutions with lead concentrations up to 50 μg l^{-1} and deposition times from 0. 5 min to 20 min. Under conditions tested no saturation of mercury film was observed and the dependence of stripping signals on deposition time was strictly linear ($r^2 > 0.997$).

Convective transport of metal ions to the surface of working electrode in flow-through cells is a function of a flow rate of the solution through the cell [12]. It was found that for the flow rates in the range 0.04–0.77 ml min^{-1} the stripping signals in RVC and wall-jet GC cells were proportional to the flow rate raised to the power 0.38 and 0.24, respectively. Moreover, the coefficient of proportionality in the case of RVC cell was about 2.7 times higher than for GC cell. Thus, in conclusion, the stripping signals in the flow-through RVC cell are more sensitive to the flow rate what can be used to enhance the sensitivity of the technique.

It should be noted that in the case of the PSA, an increased transport of oxidants to the electrode during the stripping step decreases the stripping signals considerably. For this reason, in the end of the deposition step the rest period is highly recommended to ensure the stripping in quiescent solution. The duration of the rest period should be optimised for every specific configuration of the cell [13]. It has been found during the present study that in the case of the RVC electrode the rest period of 15 s increases the stripping signals about 5 – 7 times whereas the signals are increased only about twice under the same conditions in GC cell. Preliminary experiments showed that possible explanation of this difference can be an efficient electrolytic deoxygenation of the solution during the rest period in the case of the RVC electrode. This effect is negligible for glassy carbon cell because the total deposition current is about 15 times lower than in the case of RVC when volumes of the solutions in the cells are of the same range.

The deposition and stripping medium was predetermined by SLM system using proton-driven transport across the membrane. Usually, 1 M nitric acid is used as acceptor solution in order to keep the pH gradient between the donor and acceptor sides constant during all SLM preconcentration period [1,10]. However, such sensitive technique as stripping analysis does not need a long SLM preconcentration and less acidic acceptor solutions can be used. Figure 3 shows the dependencies of lead stripping signals on the pH of nitric acid solutions in the case of RVC and GC cells. It can be seen that the shape of curves for RVC electrode depends on the deposition potential (curves a and a′). However, this dependence is only apparent because the real reason of the effect is the decrease of conductivity with dilution of solution. As a result, the increasing ohmic potential drop decreases the slope of the dependence "stripping signal – deposition potential" and, finally, more negative deposition potential is needed to keep the deposition efficiency constant. These effects are negligible using the glassy carbon electrodes because the total deposition current is substantially lower in the latter case (Figure 3, curves c,d). It should be noted that the conductivity effects using RVC electrodes sometimes can appear in quite unexpected ways, e.g., stripping signals can decrease with increasing of the flow rate when total deposition current increases but deposition potential is not negative enough.

Relatively high total deposition currents using the RVC electrode at the potentials more negative than -1.1--1.2 V (vs. Ag/AgCl) may cause intensive formation of hydrogen bubbles on the working electrode and oxygen bubbles (or chlorine if chloride medium is used) on the auxiliary electrode. These effects make the determination of cadmium using the RVC electrode less advantageous in comparison with lead. It should be noted that, on the other hand, the mercury film on RVC is much less sensitive to accidental small air bubbles in the flow system than film on GC substrate.

It should be noted that during the SLM enrichment small losses of DEHPA and kerosene from the membrane are unavoidable. However, these traces of organic compounds had no effect on PSA stripping signals in the range of potentials used

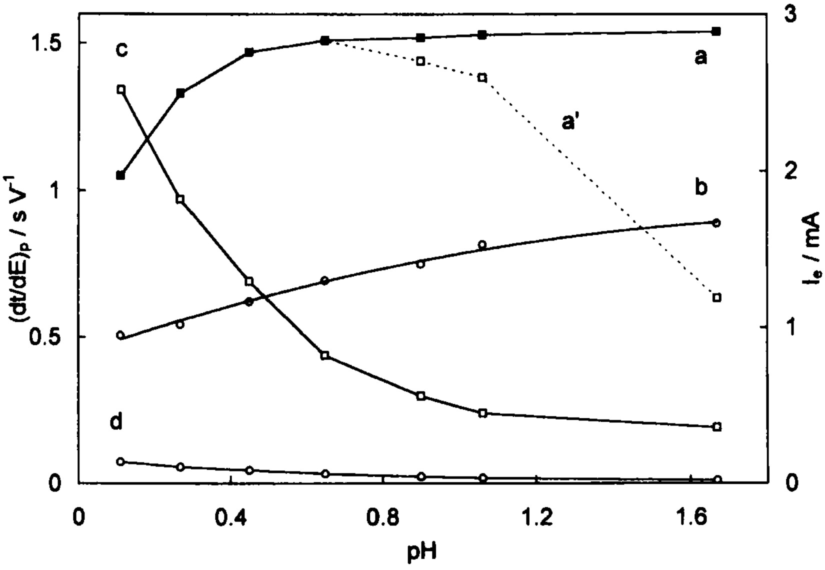

FIGURE 3 The influence of pH on lead stripping signals (curves a,a′,b) and deposition currents (curves c,d) using GC and RVC working electrodes. a, a′ – stripping signals on RVC at the deposition potential – 1. 1 V and -1.0 V, respectively; b – stripping signals on GC electrode; c,d – deposition currents on RVC and GC electrodes, respectively. Conditions: 100 μg l^{-1} Pb in HNO_3 solutions; deposition potential -1.1 V vs. Ag/AgCl (except curve a′); deposition time 30 s; flow rate 0.5 ml min^{-1}

and on the stability of the mercury film. The long-term stability of the SLM itself was evaluated as about 30 h at least in the case of river water samples [1]. Thus, it can be concluded that the long-term stability of the overall SLM-PSA system is about one week provided that the mercury film renewal is repeated daily.

The examination of a flow-through RVC cell properties and optimisation of the analysis conditions directed towards coupling SLM and PSA techniques enabled to develop the flow system and the procedure for determination of trace metals in natural waters. An example of lead determination in river water by direct PSA and coupled SLM-PSA technique is presented in Figure 4. The labile form of lead was measured in both cases because the same non-filtrated and acidified to pH=3 water sample was used. Since the volume of sample used was 7.5 ml (15 min enrichment at a flow rate 0.5 ml min^{-1}), the acceptor volume 0.8 ml and the extraction efficiency about 60 % [1], the preconcentration factor is about 5.6. However, it is clearly seen from the potentiograms that for the same total duration of analysis the stripping peaks using SLM-PSA technique are only about twice higher than for the direct PSA. This experimental fact is understandable taking into account that in the case of SLM-PSA the deposition time was shorter and, also, the deposition was performed simultaneously with enrichment, i.e., in the conditions of increasing preconcentration factor. The concentrations of lead in the sample calculated from standard additions plots were 0.47 and 0.48 µg l^{-1} for direct PSA and SLM-PSA, respectively. Relative standard deviation using SLM-PSA technique usually does not exceed 5 % for concentration range 0.5 – 25 µg l^{-1}.

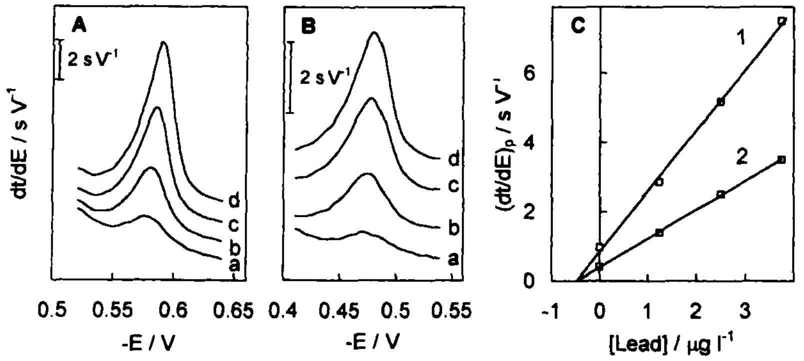

FIGURE 4 Stripping potentiograms of lead in river water sample in the RVC cell obtained by SLM-PSA technique (A) and by direct PSA (B) and corresponding standard addition plots (C). Potentiograms: a – unspiked water sample, b – d - additions of 1.25, 2.5 and 3.75 µg l^{-1} of lead, respectively. Standard addition plots: 1 - SLM-PSA technique, 2 – direct PSA. Conditions of the direct PSA: sample acidified to pH=3; flow rate 0.5 ml min^{-1}; deposition and rest times 15 min and 15 s, respectively; deposition potential – 1.2 V vs. Ag/AgCl. For procedure of SLM-PSA technique see text

It should be noted that the sample flow rates of 0.5 ml min^{-1} are optimal for this type of membrane design, hence, further increasing of sensitivity of the overall SLM-PSA system can be achieved by miniaturisation of the flow-through cell.

CONCLUSIONS

The electrochemical properties of the mercury coated reticulated vitreous carbon allows to use it successfully for the trace metal determination by potentiometric stripping analysis. The main advantages are the simple configuration of a flow-through cell, long-term stability of mercury film, and increased sensitivity compared to glassy carbon cells. The disadvantage of RVC cells is high total deposition current resulting in considerable ohmic potential drop and bubble formation on the working and auxiliary electrodes. The combination of potentiometric stripping analysis on RVC with the supported liquid membrane technique allows to achieve higher sensitivity together with minimising the matrix effects. In principle, due to the latter properties the SLM-PSA technique may be applied for in *situ* measurements of trace metals in natural waters. The overall sensitivity of SLM-PSA system depends greatly on the volume of acceptor solution and may be enhanced further by improved cell and membrane design.

Acknowledgements

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