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The use of carbon and gold electrodes in anodic stripping voltammetric heavy metal sensors

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Abstract. The use of anodic stripping voltammetry (ASV) has been proven in the past to be a precise and sensitive analytical method with an excellent limit of detection. Electrochemical sensors could help to avoid expensive and time consuming procedures as sample taking and storage and provide a both sensitive and reliable method for the direct monitoring of heavy metals in the aquatic environment. Solid electrodes which have been used in this work, were produced using previously developed methods.

Commercially available and newly designed, screen printed carbon and gold plated working electrodes (WE) were compared. Good results were achieved with the screen printed and plated electrodes under conditions optimized for each electrode material. The electrode stability, reproducibility of single measurements and the limit of detection obtained for Pb were satisfactory (3×10^{-6} mol/l on screen printed carbon WEs after 60 s of deposition and 6×10^{-6} mol/l on gold plated WEs after 5 min of deposition).

Complete 3-electrode-sets (counter, reference and working electrode) were screen printed on different substrates (glass, polycarbonate and alumina). Also here, both carbon and gold were used as WE. Using 3-electrode-sets with a gold plated WE on glass was a limit of detection of 7×10^{-7} mol/l was achieved after only 60 s of deposition.

1 Introduction

Pollution from various sources must be identified quickly to prevent damage to aquatic flora and fauna and to avoid a negative effect on human health. Pb may cause anaemia (low intoxication) and damage of central nervous system and kidneys (acute intoxication) [1]. In drinking water up to 50 µg/l of Pb are permitted according to EU guidelines as well as recommended by the WHO [2]. In natural waters in the USA Pb was found in 19.3 % of all samples in a trial with an average concentration of 23 µg/l and a maximum concentration of 140 µg/l. Concentrations in sea water are around 0.03 µg/l in the open ocean or 0.05 µg/l in the north sea [3]. Here, Pb is found mainly as PbCO_3 and Pb^{2+} -ions [3]. Enrichment factors for living matter can be very high, between 3300 - 5300 e.g. in Sørjord, Norway up to 3000 mg/kg

were found in mussels [4]. Sediments usually contain about 50 - 200 mg/kg Pb (2175 mg/kg were found in the estuary of the river Gannel north of Cornwall) [3, 4]. The sea takes up between 2600 - 7400 tonnes per year from the atmosphere, 920 - 980 tonnes from rivers and 640 tonnes from other sources (1987, north sea) [3]. Emissions amount to about 470 tonnes/a (~ 450 tonnes/a from anthropogenic sources such as industry (steel and coal) and vehicles (TEL) [1]. Heavy metals as Pb may be released from sediments by dissolution in the presence of complexing agents (e.g. EDTA), as aquo complexes, chloro complexes or by methylation [5]. The high level of Pb in the environment indicates the necessity for a reliable and quick method of determination for toxic heavy metals.

To avoid expensive and time consuming procedures as sample taking and storage, sensitive and reliable electrochemical sensors for the direct monitoring of heavy metals in the aquatic environment would be ideal. In addition a possible contamination of the samples or analyte loss due to sorption effects in containers could be avoided [6].

The use of anodic stripping voltammetry (ASV) for heavy metal determination has been proven to be suitable regarding precision, sensitivity and limit of detection [7]. The method has been improved in the past ten to twenty years for many applications by chemical and instrumental developments, especially by improvements in the field of appropriate working electrodes [8]. Solid working electrodes have overcome difficulties that used to limit the application of the method outside the laboratory compared to polarography, and miniaturization of the electrodes as well as the development of voltammetry flow cells enable on-site, on-line or even in-situ measurements [9-14]. The use of screen printed electrodes could be a possibility to provide cheap and reliable electrochemical sensors for monitoring purposes in the environment [15-17].

In this work validated methods [18] have been used for the production of screen printed and gold plated WEs which do not involve the use of toxic mercury. The performance of screen printed carbon and gold plated electrodes as WEs has been compared with commercially available gold and carbon electrodes. Commercially available Ag/AgCl-reference and Pt-counter electrodes have been replaced by screen printed carbon reference and counter electrodes.

2 Experimental

2.1 Reagents

Pb standard solutions were diluted from a commercially available AAS standard solution (Fisher Scientific International Company). The natural water matrix was created using analytical grade NaCl (Fisher Scientific International Company) dissolved in distilled water or milli-Q water.

2.2 Apparatus

The electroanalytical apparatus consisted of a potentiostat with computer interface (Electrochemical Trace Analyzer, Model 394, EG&G Princeton Applied Research), a polarography and electrode stand (SMDE, Model 303A, EG&G Princeton Applied Research), and alternatively a microcell kit with fitting counter and reference electrode (K0264 and C0175, EG&G Princeton Applied Research).

Commercially available working electrodes such as a glassy carbon electrode (G0197, EG&G Princeton Applied Research) and a gold electrode (G0227, EG&G Princeton Applied

Research) were used in comparison to newly designed, screen printed and gold plated electrodes (developed by CRL).

3 Results and discussion

The objective of the research was the development of a sensor which could be used in-situ in natural waters. Consequently, all results were obtained without a deoxygenation of the electrolyte/sample solutions. No further electrolytes were added to the solutions where the NaCl-content mimicked sea water. Calibrations were obtained by stocking the blank solution step-by-step with sufficiently small amounts of highly concentrated standard solutions.

3.1 Commercially available electrodes

The analytical method was optimized for the use of both a glassy carbon (GC) and a gold electrode in a natural water matrix. By use of a commercial GC electrode a limit of detection of 1×10^{-6} mol/l was achieved after a pre-enrichment time of 60 s. The pre-conditioning time applied was 30 s and the scan rate 20 mV/s. In the case of the gold electrode using a deposition time of 5 min the limit of detection was found to be 3×10^{-6} mol/l. Due to the longer deposition times required the peaks observed using the gold electrode were less sharp than those obtained using the GC (see Fig. 1 a and b).

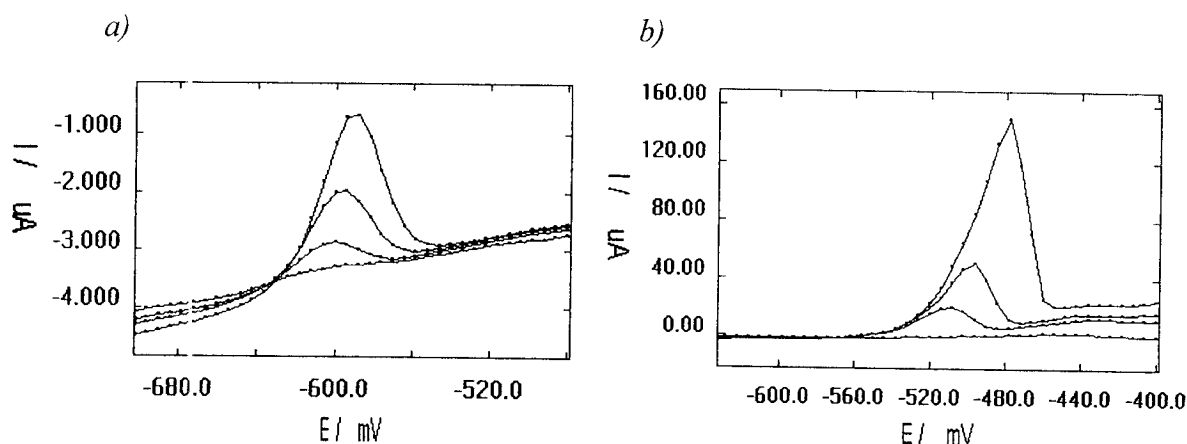


Fig. 1: overlaid voltammograms showing a calibration for the GC electrode (3×10^{-6} - 10^{-5} mol/l) (a) and the gold electrode (10^{-5} - 10^{-4} mol/l) (b).

3.2 Screen printed and gold plated electrodes

Screen printed carbon and gold plated working electrodes (WE) provided good results under conditions optimized. The electrode stability, reproducibility of single measurements and the limit of detection obtained for Pb were satisfactory (3×10^{-6} mol/l on screen printed carbon WEs after 60 s of deposition and 6×10^{-6} mol/l on gold plated WEs after 5 min of deposition). Calibration graphs for screen printed and gold plated electrodes are shown in Fig. 2 a and b.

3.3 Three-electrode-sets with carbon reference and counter electrodes

The influence of both carbon and gold screen printed reference electrodes (RE) and counter electrodes (CE) on the analytical signal was investigated. Their performance was compared to commercially available Ag/AgCl REs and platinum CEs. Both gold and carbon electrodes

were found to be suitable as CE materials, while as RE only carbon provided to sharp stripping peaks. It has been previously reported that with GC-REs the peak potentials [19] shifted negatively by about 0.68 V compared with conventional REs. In this investigation a shift of only 0.03 V was observed when screen printed electrodes were compared with Ag/AgCl REs. The use of gold as RE resulted in peak broadening. For screen printed 3-electrode-sets therefore carbon was found to be the suitable RE and CE material.

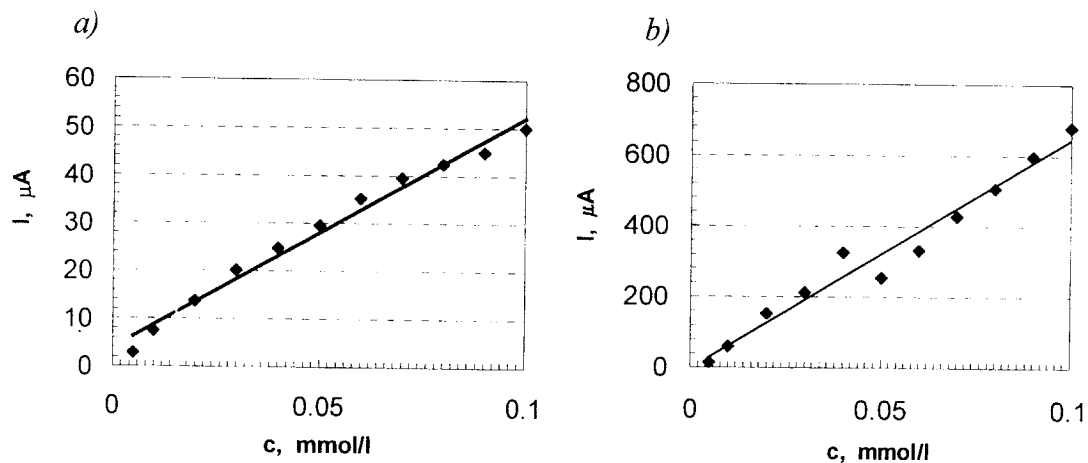


Fig. 2: calibration graphs for a screen printed WE (a) and a screen printed, gold plated WE (b).

The use of both carbon and gold plated WEs was investigated to show the better stability of the latter. Different substrates were used for the 3-electrode-sets. Glass was found to be the more suitable substrate in terms of the reproducibility of the peak current observed in comparison with polycarbonate. By means of a 3-electrode-set printed on glass, containing a gold plated WE, a limit of detection of $7 \cdot 10^{-7}$ mol/l was achieved after only 60 s of deposition. Fig. 3 shows a calibration graph for a 3-electrode-set with a gold WE on a glass substrate.

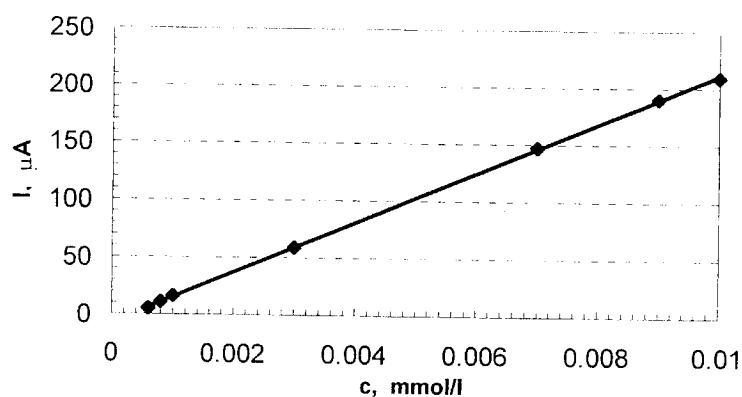


Fig. 3: calibration graph for 3-electrode-set gold electrode

The fact that the sensor is planned to be used for monitoring purposes had to be taken into account in terms of stability and repeatability of long-term analyses. The life time of the electrodes could be increased by narrowing the potential range used for deposition, conditioning and scan. The number of analyses the 3-electrode-sets with an Au-WE gave reproducible results, could be increased to more than 120. In comparison, using all-carbon 3-electrode-sets the number of measurements that could be carried out without much change in electrode performance was about 10 under optimized conditions.

Using a different electrode geometry, the stability of the screen printed carbon electrodes could be further improved. With these electrodes a limit of detection as low as 2.4×10^{-6} mol/l was obtained. Fig. 4 shows a calibration graph for one of the electrodes which was printed on a polycarbonate sheet. Using this type of electrode more than 60 measurements could be carried out.

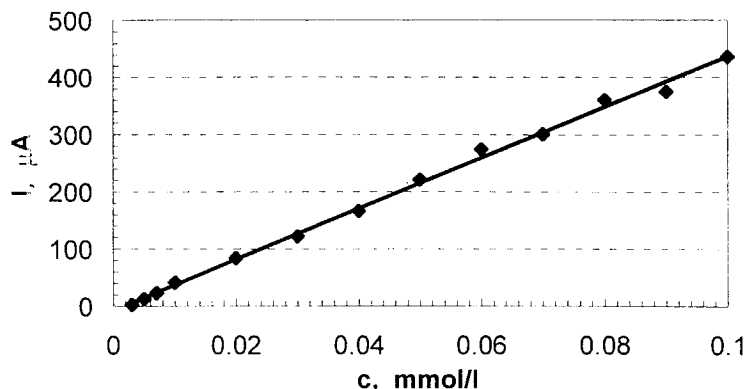


Fig. 4: calibration graph for screen printed all-carbon 3-electrode-set with different geometry

4 Comparison and conclusions

Table 1: Comparison of different working electrodes for ASV

<i>Electrode</i>	<i>Optimum deposition time</i>	<i>Optimum deposition potential</i>	<i>Sensitivity</i>	<i>Detection limit</i>
Au (EG&G)	5 min	-0.7 V	1500 $\mu\text{A}/(\text{mmol/l})$	3×10^{-6} mol/l
Glassy C (EG&G)	60 s	-0.75 V	596 $\mu\text{A}/(\text{mmol/l})$	1×10^{-6} mol/l
Plated Au	as Au (EG&G)	as Au (EG&G)	6872 $\mu\text{A}/(\text{mmol/l})$	6×10^{-6} mol/l
Printed C	60 s	-0.75 V	483 $\mu\text{A}/(\text{mmol/l})$	3×10^{-6} mol/l
printed 3-electrode-set on glass, Au WE	60 s	-0.63 V	21743 $\mu\text{A}/(\text{mmol/l})$	7×10^{-7} mol/l
printed all-C-3-electrode-set on polycarbonate	60 s	-0.45 V	4439 $\mu\text{A}/(\text{mmol/l})$	3×10^{-6} mol/l

Gold WEs generally offer a higher sensitivity than carbon ones. In comparison to the commercially available electrodes screen printed and gold plated ones can achieve similar detection limits, only the long-term stability is still a problem aiming at in-situ applications. Although gold is the more stable electrode material, plated on screen printed carbon electrodes it is still affected by the slow erosion of the quite porous carbon layer. A limited scan range

and very continuous and homogeneous gold surface should help to overcome these problems in order to enable the reliable use of screen printed electrodes sets with an Au-WE.

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