Determination of heavy metals by a mercury-plated diamond-like carbon microelectrode array

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Abstract. Mercury-plated as well as bare nitrogenated diamond-like carbon (NDLC) microelectrode arrays have been investigated for application in in-situ determination of heavy metals (Cu, Pb and Cd) by differential pulse anodic stripping voltammetry (DPASV). A microelectrode array consisting of 50 625 microdiscs with 3 µm in diameter and interelectrode distances of 20 µm was fabricated on a highly conductive silicon substrate and characterized by CV measurements. Current responses of all metals were linear for metal concentrations in the range of 1.6×10⁻⁸ to 8.3×10⁻⁸ mol/L and preconcentration time 5 min. The stripping current responses of the bare microelectrode array reached under the same conditions were much lower in comparison with a mercury-plated array. A strong effect upon stripping current responses of metals was observed of adding a small amount of thiocyanate (2×10⁻³ mol/L) into the plating solution.

1. Introduction
Determination of heavy metals (Cu, Cd, Pb) by anodic stripping voltammetry (ASV) on a mercury film electrode in environmental analytes is very attractive due to its remarkable sensitivity, extremely low detection limits (< ppb) and ease of application [1]. High sensitivity is mainly given by the first step involving preconcentration of the analyte species in mercury, which is carried out under a fixed potential for a predetermined time. In the second, stripping step, the accumulated species are stripped from mercury into the solution by reoxidation. Current peaks are proportional to the concentration of the species in the solution.

The mercury film can be prepared either by ex-situ or in-situ mercury electroplating. The latter procedure is usually recommended because it gives better ASV performance in terms of sensitivity, selectivity and reproducibility. Another advantage of in-situ mercury film formation is the new surface generated at each analysis [2]. On the other hand, in-situ procedure can not be employed when additions of mercury into the analyte cause contamination, precipitation or changes in the speciation of the sample [3]. In the case of ex-situ procedure the stability of preplated mercury can be strongly influenced by experimental and storing conditions or during the transfer. Mercury microelectrodes have to be stored in a deoxygenated solution at a negative potential to prevent oxidation of mercury which causes a decrease of their performance in time [3, 4].

The choice of the electrode substrate that the mercury is deposited onto is crucial. Ag, Pt and Au are not suitable for mercury film formation because of their dissolution by mercury and formation of intermetallic compounds with the analyzed metals. Besides Ir, which was found to be a useful substrate for mercury electroplating, a thin layer of diamond-like carbon doped by nitrogen (NDLC) should be a candidate as a support in this field.
2. Experimental
The NDLC films (~300 nm thick) were prepared by vacuum pulse sputtering of graphite at nitrogen flow rate 100 sccm on highly conductive silicon substrates. The areas which act as working electrodes (array of 50 625 microdiscs with 3 µm in diameter and distance 20 µm between microdiscs) were defined photolithographically (figure 1).

Figure 1. Detail of the NDLC microelectrode array.

Figure 2. Raman spectrum for NDLC prepared at 100 sccm nitrogen flow rate.

The morphology of NDLCs was analyzed by scanning electron microscopy (SEM) and Raman spectroscopy. A typical Raman spectrum of the NDLC is shown in figure 2. Nitrogen atoms incorporated during sputter-deposition of the layer influence the bond formation in the diamond-like carbon (DLC) structure. In general, an excess of N atoms will lead to graphitization of DLC and, hence, the conductivity of DLC will be increased [5]. Electrochemical properties of the NDLC electrode array were investigated by cyclic voltammetry (CV).

Mercury-plated NDLC microelectrode arrays for in-situ determination of Cu, Pb and Cd were prepared by co-deposition of Hg(II) and Cu(II), Pb(II), Cd(II) at –0.8 V vs. the reference electrode in a solution of $1 \times 10^{-4}$ mol/L Hg(NO$_3$)$_2$ in a supporting electrolyte (0.1 mol/L KNO$_3$) at a constant stirring rate. All solutions including trace metals (Cu, Pb and Cd) and electrolyte were prepared from analytical grade chemicals in 18 MΩ cm deionized water. A three-electrode arrangement was used in all experiments. As a reference, a home-made Ag/AgCl/agar Cl$^-$(3 mol/L)/agar NO$_3^-$ (1 mol/L) electrode and, as a counter electrode, a platinum wire were used. Voltammetric experiments were performed with an electrochemical sensor interface (PalmSens, Palm Instruments BV) in combination with a personal computer. Differential pulse (30 mV/s scan rate, 25 ms pulse, 2 mV E step and 50 mV E pulse) anodic stripping voltammetry (DPASV) was used in the measurement.

The mercury coating had to be renewed after every in-situ measurement. Mercury was stripped from the NDLC surface using CV (20 cycles) from 0 to +0.5 V at a scan rate of 50 mV/s in 0.1 mol/L KNO$_3$.

3. Results and Discussions

3.1. NDLC microelectrode array characterization
The behaviour of the microelectrode array was characterized by cyclic voltammetry in 0.1 mol/L KNO$_3$ solution in a potential range from –1 to 0 V at a scan rate of 50 mV/s. For analyses of metals by ASV a low background current is very important in a broad potential range so as to achieve the highest signal to noise ratio and, thereby, the highest sensitivity. In figures 3 and 4, the current differences between bare and by mercury plated electrode arrays are shown.
In the case of bare NDLC the currents are much lower, most likely due to the higher resistance of NDLC. At approximately –0.5 V, a sharp increase of the reduction current was observed due to hydrogen overvoltage. On the other hand, for mercury plated electrodes characterized by very high hydrogen overvoltage the current dependences are linear in the whole range from 0 to –1V.

3.2. Heavy metals determination on bare NDLC microelectrode array

There are reports on the use of various types of bare carbon (glassy carbon, DLC, polycrystalline diamond) for determination of heavy metals by ASV [5-7]. Deposition of metals ions results in a film of atoms, which can occur as a monolayer or multilayer on the carbon surface [6]. Results of the determination of the Pb(II) ions in 0.1 mol/L KNO₃ by DP ASV confirmed our prediction that the sensitivity will be strongly reduced due to the absence of mercury with its accumulating capability. We obtained much lower current responses in comparison with results obtained on a mercury-plated microelectrode array (figure 5). Almost no current signal was recorded for concentration of Pb(II) 5×10⁻⁶ mol/L. Similar results, as regards sensitivity in Pb(II) determination on bare carbon, were referred [5-7].

**Figure 3.** Cyclic voltammogram of bare NDLC microelectrode array in 0.1 mol/L KNO₃.

**Figure 4.** Cyclic voltammogram of mercury-plated NDLC microelectrode array in 0.1 mol/L KNO₃.

**Figure 5.** Dependence of current response of bare NDLC microelectrode array on Pb(II) concentration in 0.1 mol/L KNO₃.
3.3. In-situ determination of heavy metals on a mercury-plated NDLC microelectrode array

The quality of the mercury-plated microelectrode greatly influences the sensitivity of ASV. A lot of parameters have an influence on the formation of the mercury deposit including plating solution, plating potential and time, etc. In our preliminary experiments, plating solutions consisting of 0.1 mol/L KNO₃ with different contents of mercuric ions were used. We obtained the highest response in the solution with concentration of Hg(II) 1×10⁻³ mol/L (figure 6).

In ASV it is very important to choose an optimum preconcentration time. In general, the longer the time, the lower the limit of detection. The dependence of the stripping current on the preconcentration time is given in figure 7.

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**Figure 6.** Dependence of current response of NDLC-Hg microelectrode array on mercuric ion content in plating solution; tₚ = 5 min, c Ме = 5×10⁻⁸ mol/L.

**Figure 7.** Dependence of current response of NDLC-Hg microelectrode array on preconcentration time in 0.1 mol/L KNO₃, c Ме = 5×10⁻⁸ mol/L.

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A mercury-plated DLC microelectrode array for in-situ simultaneous determination Cu, Pb and Cd was prepared by co-deposition of Hg(II), Cu(II), Pb(II) and Cd(II) at –0.8 V in a solution of 1×10⁻⁴ mol/L Hg(NO₃)₂ in 0.1 mol/L KNO₃ with different contents of heavy metals from 1.6×10⁻⁸ to 8.3×10⁻⁸ mol/L for 5 min preconcentration time under constant magnetic stirring. The dependences of current responses on heavy metals concentration, as well as calibration curves inside are shown in figure 8.

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**Figure 8.** Dependence of current response of NDLC-Hg array on concentration of metals with calibration curve inside; tₚ = 5 min.

**Figure 9.** Influence of thiocyanate addition on current response; tₚ = 2 min, c Ме = 5×10⁻⁸ mol/L.
Different sensitivity is observed of the mercury-plated microelectrode array to each metal. The highest sensitivity is to Pb. Different sensitivities are probably given by unique properties of electrodes. This is supported by the fact that all variations of sensitivity were referred for this group of metals [1, 8-10].

The influence of strongly complexing agents like thiocyanate (SCN⁻) on the stripping current of ASV has already been reported [11]. Addition of a small quantity of SCN⁻ into the mercury plating solution promoted the formation of the mercury film, improved apparently the sensitivity and repeatability at determination of metals. It was concluded that 5×10⁻⁵ mol/L SCN⁻ is the upper concentration limit [11,12] because for a higher concentration the mercury surface passivates. In figure 9, the dependence of the stripping current on the addition of thiocyanate into the solution is shown. The current peak at +0.1 V comes from oxidation of mercury to complex Hg(SCN)₂ [2]. Oxidation of mercury to a mercuric ion occurs at a more positive potential (+0.4 V) than that for the formation of the thiocyanate complex. Under our experimental conditions, the upper concentration limit of (SCN⁻) was found to be 2×10⁻³ mol/L. In our case, for higher concentrations the stripping currents decreased. Anyway, the stripping current for Pb was increased 10 times in comparison with that in the absence of thiocyanate.

4. Conclusions
A mercury-plated NDLC microelectrode array consisting of 50 625 microdiscs with 3 μm in diameter and interelectrode distances of 20 μm were fabricated on highly conductive silicon substrate and characterized by CV. It was proved that this array is sufficient to maintain the advantageous characteristics of microelectrodes. The mercury-plated as well as a bare array were investigated for application in heavy metals (Cu, Pb and Cd) in-situ determination by DPASV. The current responses of all metals were linear with concentration in the range from 1.6×10⁻⁸ to 8.3×10⁻⁸ mol/L for 5 min preconcentration time. The stripping current responses of the bare microelectrode array reached under the same conditions were much lower in comparison with the mercury-plated array. A strong effect was found of adding a small amount of thiocyanate (2×10⁻³ mol/L) into the plating solution on the stripping current responses of metals.

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