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DETERMINATION OF MERCURY BY ANODIC STRIPPING VOLTAMMETRY AT A GOLD NANOPARTICLE-MODIFIED GLASSY CARBON ELECTRODE

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Introduction

The utilization of mercury in the last century has substantially increased the content of this element in the environment. Anodic stripping voltammetry (ASV) is a suitable technique for mercury determination because it is highly sensitive and relatively inexpensive [1].
The aim of this work was to determine aqueous Hg (II) by ASV at a gold nanoparticle-modified glassy carbon electrode. The great surface area of the deposited nanoparticles permitted an improvement of the analytical performance (lower detection limit) in comparison to conventional gold electrodes [2].

Experimental

The glassy carbon electrode was polished with alumina, rinsed with ethanol and water and dried using a nitrogen stream. Modification with gold nanoparticles was performed by dipping the electrode into a 50 mg/l $HAuCl_4$ solution and applying a potential of -0.80 V for 6 min. The modified electrode was rinsed with Milli – Q water and kept in 0.1 mol/l NaOH for twenty minutes [3]. The actual formation of nanoparticles was confirmed by SEM analysis.
For ASV measurements, 10 ml test solutions of supporting electrolyte were delivered into the voltammetric cell. After 120 s of deposition at 0 V, a voltammetric scan from 0 to 0.80 V was performed. For the optimization of the experimental conditions (see below), the voltammogram of the blank was recorded, then aliquots of 20 µg/l of Hg were added and the corresponding signals were recorded.
After each measurement the working electrode was dipped into a mixture of $HClO_4$/NaCl/EDTA for 30 s applying a potential of 0.80 V, in order to remove the residues of mercury from the active surface of the electrode.

Results and discussion

We studied the effect of the following parameters on the electrode performance: composition of the supporting electrolyte (HCl, $HClO_4$/NaCl/EDTA mixture); potential scan mode (differential pulse, square wave); potential scan parameters (amplitude, frequency, step potential, interval time, modulation time, modulation amplitude); deposition potential; deposition time. Taking into account the mercury peak shape and intensity, the best response was obtained using HCl as supporting electrolyte and square wave potential scan. Optimal values for the scan parameters were: step potential 0.004 V, frequency 150 Hz, amplitude 0.03 V. The highest signal with the best baseline shape was obtained with a deposition potential of 0 V. As expected, the height of mercury peak increased with increasing deposition time; a value of 120 s was found to be suitable for concentrations up to 50 µg/l. No interference on the signal of mercury was observed after the addition of 200 µg/l of As, Bi^{3+}, Cd^{2+}, Cr^{3+}, Cu^{2+} Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Se^{4+}, whereas cobalt unexpectedly caused the disappearance of the mercury peak. The presence of a peak for copper in the investigated potential range did not interfere on the determination of mercury.

The analytical performance of the technique was investigated. As to the repeatability, the relative standard deviation for the determination of 10 µg/l of mercury in 10 independent analyses was 2.8 %.
The peak height linearly increased with concentrations up to higher 50 µg/l.
In the optimized experimental conditions, very low concentrations of mercury could be quantified with good accuracy: for instance the concentration measured for a 10 ng/l solution was 9.92 ± 0.05 ng/l. The detection limit was estimated as 0.15 ng/l. Therefore the sensitivity of the technique is comparable with that of cold vapour atomic absorption spectrometry (CVAAS).
The response of the gold nanoparticle glassy carbon electrode on real samples was tested. According to the national legislation, the maximum allowable Hg value in drinking water is 1 µg/l. A concentration of 450 ng/l of Hg in tap water could be determined with good accuracy (449 ng/l) without pretreatment.
Afterwards, a certified sample of estuarine sediment (BCR, CRM 277) was analyzed after dissolution in a microwave oven and dilution in the supporting electrolyte. The concentration found (1.72 ± 0.02 mg/kg) was in good agreement with the certified value (1.77 ± 0.06 mg/kg).
Therefore ASV at a gold nanoparticle-modified electrode can be applied for the determination of mercury in real samples, even in the presence of a complex matrix like that of dissolved sediments.

References

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