Parameters affecting the determination of mercury by anodic stripping voltammetry using a gold electrode

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Abstract

The electrochemical determination of aqueous Hg(II) by anodic stripping voltammetry (ASV) at a solid gold electrode is described. The aim of this work is to optimise all factors that can influence this determination. Potential wave forms (linear sweep, differential pulse, square wave), potential scan parameters, deposition time, deposition potential and surface cleaning procedures were examined for their effect on the mercury peak shape and intensity. Five supporting electrolytes were tested. The best responses were obtained with square wave potential wave form and diluted HCl as supporting electrolyte. Electrochemical and mechanical surface cleaning, aimed at removing the amount of mercury deposited onto the gold surface, were necessary for obtaining a good performance of the electrode. Response linearity, repeatability, accuracy and detection limit were also evaluated.
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1. Introduction

The determination of metals at trace and ultratrace levels is an important issue in environmental and clinical sciences, owing to their potential toxicity at concentrations above certain threshold limits. Much attention is devoted to mercury, which is particularly harmful even at low concentrations: strict legislation limits are imposed in many countries for its concentration in all environmental compartments, e.g. waters, soils and organisms [1].

The analytical techniques preferred for mercury quantification are cold vapour atomic absorption spectrometry (CV-AAS) [2], cold vapour atomic fluorescence spectrometry (CV-AFS) [3], inductively coupled plasma mass spectrometry (ICP-MS) [4] and, for relatively high concentrations, inductively coupled plasma atomic emission spectrometry (ICP-AES) [5]. Several chromatographic techniques coupled with spectrometric methods have also been used for mercury speciation [6,7]. Among these, CV-AFS procedure is the preferred detection method due to its sensitivity. All these techniques require expensive and

sophisticated instrumentation and/or the use of specific instruments (which cannot be applied to the determination of other analytes), in combination with complicated sample preparation processes [8]. Stripping electrochemical methods represent an interesting alternative for mercury determination owing to their sensitivity, versatility and low costs. The recommendation of the US Environmental Protection Agency (EPA) for the adoption of stripping analysis for the quantification of heavy metals as mercury [9] is a very representative example of this application. Electroanalytical techniques for the detection of aqueous mercury, either alone or in conjunction with such emerging technologies as piezoelectric sensors, were utilized for the development of sensors capable of remote quantification of mercury in the environment [10]. A number of papers were devoted to the determination of mercury by anodic stripping voltammetry (ASV) at different solid electrodes [e.g. 11,12]. Gold was found to be the best electrode material for the determination of mercury by ASV, with conventional [13], film- [14,15] and micro-[16,17] electrodes. Also stripping chronopotentiometry at a gold wire microelectrode was adopted for trace measurements of mercury [18]. One reason for the use of gold is its high affinity for mercury, which enhances the preconcentration effect.

The main disadvantage of gold electrodes is the well known phenomenon of structural changes of their surface, caused by

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amalgam formation, and the time-consuming cleaning treatments that are needed to achieve reproducibility [19].

Many parameters influence the analytical signal of mercury and we did not find in literature a paper reporting a complete study of their effect on the determination of mercury with gold electrodes. Moreover, the information about the optimal working conditions and the electrode performance is heterogeneous and sometimes discordant. For these reasons, in the present study, the use of a solid Au electrode for Hg(II) determination by ASV was investigated in terms of the parameters that normally can influence the analytical response. The shapes and intensities of the mercury peak in five supporting electrolytes were compared. The effects of different potential wave forms, namely linear scan (LS), differential pulse (DP) and square wave (SW), scan parameters (amplitude, frequency, step potential, interval time, modulation time, modulation amplitude) and of deposition time and potential were examined. The linearity, repeatability, detection limit and accuracy of the method were determined. The possible interference of As(V), Bi(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Mn(II), Ni(II), Pb(II) and Se(IV) was evaluated and compared with some data in literature [1,14,19].

The findings of this study can be useful for analysts in order to evaluate the real potentialities of the gold electrode and to choose the best conditions for the determination of mercury by ASV.

2. Experimental

2.1. Apparatus and reagents

Voltammetric analyses were performed with a PGSTAT 10 potentiostat (Eco Chemie, Utrecht, The Netherlands) coupled to a 663 VA Metrohm (Herisau, Switzerland) stand, equipped with a rotating solid gold electrode as working electrode, a Ag/AgCl reference electrode and a glassy carbon counter electrode. The analyzer was interfaced to a personal computer. High purity water (HPW) obtained from a Milli-Q (Millipore, Bedford, MA, USA) apparatus was used throughout. Analytical grade reagents were used. In particular a 1000 mg/l standard solution of mercury was prepared from $HgCl_2$ in 0.012 M HCl. More diluted Hg(II) standard solutions were prepared from the concentrated standard in the desired supporting electrolytes. HNO_3 and HCl were obtained by sub-boiling distillation in a quartz still.

2.2. Procedures

Ten-millilitre test solutions of supporting electrolyte were delivered into the voltammetric cell.

After 120 s of deposition a voltammetric scan was performed. Initially, the scan parameters were: (i) for SWV: frequency 100 Hz, step potential 0.002 V, amplitude 0.02 V; (ii) for DPV: modulation amplitude 0.05 V, modulation time 0.05 ms, interval time 0.3 ms, step potential 0.002 V; (iii) for LSV: step potential 0.002 V, interval time 0.30 s. Initial and final potentials were 0 V and 0.80 V, respectively.

For the values of the scan parameters after optimization, refer to Section 3.3.

After recording the voltammogram of the blank, aliquots of Hg(II) were added and the corresponding signals were recorded.

A cell containing 50 µg/l of Hg(II) was utilized to investigate the effects of the different parameters on the signal of mercury.

The detection limit was estimated as three times the standard deviation of the blank signal.

All experiments were performed in triplicate.

3. Results and discussion

The voltammetric behaviour of Hg(II) was investigated in different supporting electrolytes and in different conditions of analysis.

3.1. Preliminary considerations

A brand-new gold electrode displays an ill-defined anodic stripping voltammogram for mercury. In order to overcome this drawback the electrode was dipped into a solution composed by 10 mM HNO_3 and 10 mM NaCl and activated by applying a potential of 0.90 V for 60 s between the working electrode and the reference electrode. The activation procedure applied is identical to that used by Bonfil et al. [19]. This simple 1-min electrochemical pre-treatment was found to be of utmost importance [20], as can be seen by comparing the anodic stripping voltammograms of 50 µg/l of mercury in HCl before and after activation (Fig. 1).

The measurement of an analytical signal for Hg(II) on a gold surface is somewhat hindered by the baseline (background current) behaviour. This problem results from the nature of the deposit on the electrode, i.e. the amount of mercury deposited and/or the type of interaction between gold and mercury [16]. A possible origin of the high background, when working with HCl as supporting electrolyte, is the formation of calomel onto the electrode surface [16,21]. The definition of a proper baseline is difficult. Good results in terms of accuracy and repeatability were obtained considering a horizontal baseline from the right base of the peak.
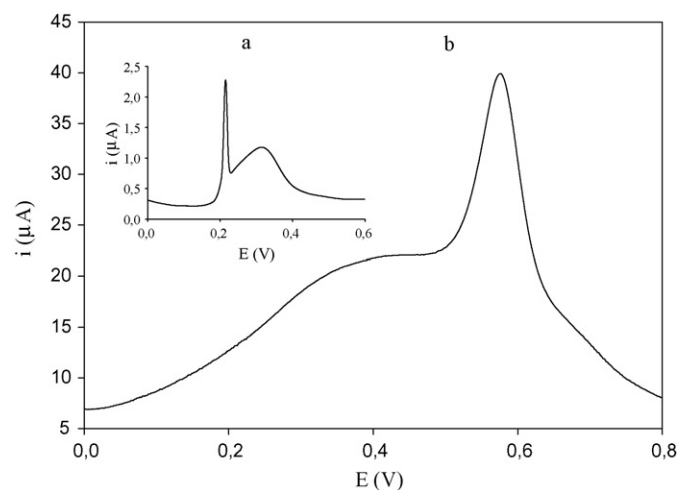

Fig. 1. Anodic stripping voltammograms of 50 µg/l of Hg(II) in HCl using SW (a) before and (b) after activation of the electrode.