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Functionalised resin-modified carbon paste sensor for the voltammetric determination of Pb(II) within a wide concentration range

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Abstract

A carbon paste electrode bulk-modified with a functionalised macroporous resin is described as a voltammetric sensor for Pb(II) ions. The commercially available product, QuadraPure™TU, admixed into the paste at a ratio of 30% (v/v), contains thiourea residues that act as a highly effective functional group for chelating Pb(II). By combining with square-wave anodic voltammetry and "open-circuit" accumulation, the stripping peak of lead in 0.1 M acetate buffer could be calibrated over a wide concentration range of 0.005–5 mg l^{-1} Pb, with possible extension up to 25 mg l^{-1}, when the signal of interest was not seriously affected by the presence of other common metals. Applicability of the sensor in practical analysis has been tested on selected water samples or a certified reference material and the respective results agreed well to those obtained by ICP-MS and to the content declared.

Keywords: QuadraPure™TU resin; Modifier; Carbon paste; Stripping voltammetry; Pb(II); Calibration range; Determination

1. Introduction

In electroanalysis, lead as a common toxic metal is of continuing interest [1] and within a myriad of electrodes or detection systems recommended for its determination, one can choose those made of carbon paste (see e.g. tabled surveys in [2,3]). This substrate represents one of the most flexible electrode materials used for chemical modifications, allowing the utilisation of highly sophisticated measuring principles. The respective methods are characterised by the use of cheap and easy-to-prepare electrodes that offer high selectivity towards the Pb(II) and are usually able of operating down to the trace or even ultratrace level, thus being applicable to various environmental samples, including natural waters [1–3].

It is believed that these features are also the case of an electrode introduced in this article based on carbon paste bulk-modified with a thiourea-functionalised resin, QuadraPure™TU. It should be mentioned that such macroporous resins are now used in industry as purification agents preventing metal contamination during production of pharmaceuticals and fine chemicals [4]. The substance of choice is active *via* the thiourea functional groups which, during our studies, have been found highly effective for chelating Pb(II) ions. To the authors' knowledge, this material has not hitherto been used as modifier for carbon pastes or related carbonaceous matrices [2,3] and hence, the QuadraPure™TU residue functionalised resin-modified carbon paste electrode ("TUR-CPE"), is worth to be presented herein – due to its extraordinary calibration characteristics and a very promising analytical performance.

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of analytical grade (Merck or Sigma Aldrich). A stock solution of acetate buffer (mixture 1 M CH_3COOH + 1 M CH_3COONa) was used as the

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main supporting electrolyte and appropriately diluted before use. Standard solutions of Pb(II) and other metal ions were made as 0.01 mol l^{-1}. All the solutions used were purged with nitrogen (AGA AS; Oslo, Norway) when deionised water was used prepared in a Millipore system (18 MΩ cm).

2.2. Apparatus

All the measurements were performed with an AUTOLAB electrochemical analyser (model PGSTAT 30; Ecochemie, Utrecht, The Netherlands) operated *via* the GPES 4.9 software (ibid). A three-electrode cell used comprised the working electrode, Ag|AgCl|3 M KCl as the reference, and a Pt-plate (3 × 5 mm) as the counter electrode. Where applicable, stirring was performed using a magnetic bar rotated at *ca.* 300 rpm.

2.3. Working electrode

Originally granulated resin ("QuadraPure™TU"; *Sigma Aldrich*, cat. No: 655 422); was finely pulverised and its 0.2 g portion mixed with the same amount of graphite (Ringsdorff-Werke, Germany). Subsequently, carbon powder modified in this way was soaked with 0.2 ml silicone oil (Lučební závody Kolín, Czech Republic) and the mixture obtained thoroughly homogenised. The resultant carbon paste was packed into piston-driven electrode holder [3].

2.4. Procedure

A typical experiment by square-wave anodic stripping voltammetry (SWASV) consisted of three consecutive steps: time-controlled "open-circuit" accumulation, potentiostatic reduction to Pb(0) for a constant period, and anodic stripping within the potential range chosen where the response of interest was recorded, evaluated as the peak height with base-line correction.

2.5. Samples

Two water samples were analysed: (i) a specimen of natural water collected in a small pond and (ii) tap water; the latter being spiked with 30 μg l^{-1} Pb(II).

The third sample was a certified reference material of sewage sludge ("WT-H 12-3-14"; Pb-anal, Košice, Slovakia), representing a heavily polluted waste material.

3. Results and discussion

3.1. Mechanism of accumulation via the QuadraPure™TU resin

According to the reported chelating capabilities of the resin [4] and based on some analogy with similar compounds [5], thiourea residue is protonated and undergoes the following tautomeric transformation

$$\text{®–NH} - C(-NH_2) = S + H^+ \rightarrow \text{®–NH}^+ = C(-NH_2) - SH \qquad (1a)$$

Consecutively, highly reactive immino-thiolic groups [5] chelate the target ions

$$2\text{®–NH}^+ = C(-NH_2) - SH + Pb^{2+} \rightarrow [\text{®–NH}^+ = C(-NH_2) - S -]_2Pb + 2H^+ \qquad (1b)$$

In an alternate scheme, corresponding to our previous hypothesis [6], the thiourea fragment converts the Pb(II) ions to the respective sulphide

$$\text{®–NH} - C(-NH_2) = S + Pb^{2+} \rightarrow PbS + 2e^- + (\text{products}) \qquad (2)$$

The precipitate formed is then expected to be adsorbed onto the electrode surface and subsequently reduced to the elemental lead prior to anodic re-oxidation. Both mechanisms admit that, besides Pb(II) itself, the thiourea-active sites may interact with some other metal ions with affinity towards thiol groups. This is the case of Zn(II), Cd(II), Cu(I), Bi(III), Ag(I), Co(II), and Ni(II) [5–7]; all of which being considered as potentially interfering species.

3.2. The function of the QuadraPure™TU Resin as modifier in carbon paste

For modification, the QuadraPure™TU resin was initially tested in the original granular form. Its morphology, however, had been shown unsuitable due to difficult homogenisation with the native carbon paste and a very poor electroanalytical performance of the resultant electrode. Hence, it was necessary to grind the resin into a fine powder which had already been found fully applicable. Regarding the content of resin in carbon paste, ratios from 5% up to 50% (v/v) were examined; the amount of *ca.* 30% being optimal.

3.3. Method development

A method elaborated is based on the open-circuit accumulation with subsequent reduction of the deposited analyte(s) and its immediate re-oxidation in the SWASV mode. This procedure allowed us to avoid the cathodic scanning where a parasitic reduction of oxygen (present in the carbon paste mixture) could affect the signal of interest. In accordance with preliminary measurements (some of them made also in the differential pulse voltammetric mode [7]), the following experimental conditions and parameters have been selected:

- 0.1 M acetate buffer (pH 4.5) as the optimal supporting electrolyte for accumulation, deposition, as well as stripping step (when other supporting media tested were 0.01–0.5 M acetate buffers, 0.1 M CH_3COONH_4, 0.1 M HCl, 0.1 M KCl, and 0.1 M $HClO_4$);
- accumulation up to 15 min (with no marked enhancement of the signal beyond this value);