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Electrochemical assay for metal traces in marine environment by the Peaks Shift Analysis during catalysis

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Summary:

An innovative electrochemical methodology is proposed for the quantitative *in situ* detection of trace metals in marine environment. This new method uses electrocatalysis to detect the catalyst instead of the substrate of the catalyst. As an example, we demonstrate that peak potential of proton reduction on copper during cyclic voltammetry is an effective method for the accurate detection of copper traces in aqueous media, with a detection limit (LOD) significantly lower than that of conventional electrochemical stripping methods (LOD = 1 nMol/L compared with 40 nMol/L, respectively).

Keywords: Copper sensor, Modified graphite electrode, Electrolyte engineering, Hydrogen evolution reaction, Peak shift analysis.

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Background, Motivation an Objective

The detection of copper (Cu) at nanomolar concentrations represents a major challenge for marine water monitoring. Due to their relatively high sensitivity, selectivity and adaptability to *in-situ* measurements, electrochemical Cu(II) sensors appear to be ideally suited [1].

Description of the New Method

This innovative approach is based on a two-step procedure: (i) metal preconcentration at the surface of a specially modified electrode and (ii) the use of a reaction that can be electrocatalyzed by the metal, such as the HER (Hydrogen Evolution Reaction). Here, the originality lies in the use electrocatalysis to assay the catalyst (Cu) rather than the substrate. This approach uses the concentration-dependence of the peak potential in cyclic voltammetry to precisely determine metal surface concentration. Indeed, as stated by equation (1) for a case of Nernstian charge transfer (i.e. fast and reversible), the catalytic peak potential increases logarithmically with catalyst surface concentration :

$$E_{cat}^{0,ap} = E_{P/Q}^{0} + \frac{RT}{nF}\ln\left(\frac{k\Gamma_{P/Q}^{0}}{\sqrt{\frac{D_A nF\nu}{RT}}}\right) \qquad (1)$$

With $E_{cat}^{0,ap}$ being the apparent standard catalytic potential, $E_{P/Q}^{0}$ the standard potential of the P/Q couple, $\Gamma_{P/Q}^{0}$ the surface concentration of the catalyst, D_s the diffusion coefficient of the substrate, k the rate constant of the catalytic reaction and υ the scan rate.

The so-called Peak Shift Analysis (PSA) method is based on collecting experimental data (peak potentials, metal stripping) to construct a calibration curve.

We illustrate this new procedure with copper detection. For this purpose, we fonctionalized pencil graphite electrodes (PGE) surfaces with different chelating molecules through a diazonium approach. The copper accumulated on the modified electrode was then used as catalyst for proton reduction in acidic media for further peak potential analysis.

Results

We first used *p*-aminobenzyl-*C*-functionalized Cyclam for electrode modification for its selectivity towards Cu(II) and its powerful chelating capability. However, this selectivity limits its application to other ions. To broaden the scope of our detection method, we sought a non-selective grafting molecule. Our choice fell on 4-Aminobenzoic acid (ABA), which promotes metal accumulation on the electrode through electrostatic interaction.

Electrodes modified with Cyclam (data not shown) and ABA shows an obvious concentration-dependence of the HER peak potential in cyclic voltammetry, as illustrated in Fig.1: increasing the concentration of copper in solution shifts the potential towards positive values. For the Cyclam and ABA-modified electrode, a copper concentration of less than 40 nmol/L can be detected with the PSA, while this is not possible with the conventional stripping analysis.

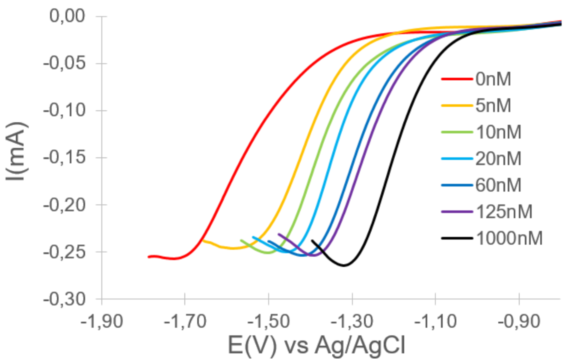

Fig. 1. Forward scan of the catalytic peaks measured after incubation of PGE/ABA in solution containing increasing Cu^{2+} *concentrations (v=50mV/s, 0.1 mol/L* Na_2So_4*, pH=2.5)*

Finally, 4-Bromobenzenediazonium tetrafluoroborate (BDT) was used as an ideal negative control due to its lack of electrostatic inte action with copper(II). No peak shift was recorded using this modified electrode.

The next step of this work is to demonstrate the versatility of this procedure in testing iron and manganese detection with PSA.

References

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