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Letters

A NEW ELECTRODE SYSTEM WITH EFFICIENT MIXING OF ELECTROLYTE

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In the last decade, many authors have emphasized the exceptional possibilities of polarography and the related advanced techniques for the determination and physico-chemical characterization of dissolved trace metals in natural aquatic systems. In addition to the quantitative aspects, it is also possible to characterize the physicochemical state of ionic species in natural and polluted waters. This is of particular importance for the investigation of basic biogeochemical processes. These methods could be used for the elucidation of mechanisms and pathways in the biogeochemical cycles of a particular metal in natural and polluted aquatic systems (1-5).

Many heavy metals and other microconstituents in natural waters appear at a concentration level below the determination limit by direct polarographic techniques. Consequently, for direct determination, highly sensitive techniques (with reasonable precision and selectivity) are required. Only more advanced electroanalytical techniques offer sufficient sensitivity for direct measurements and determination. For this purpose even the most advanced methods must be utilized frequently to the limits of their sensitivities, which means, of course some sacrifice in precision.

The sensitivity and selectivity of electroanalytical procedures have been developed in two directions: (1) improvement of instrumentation (applying excitation potential of different forms and increasing the sensitivity and selectivity of current response) and (2) construction of new electrodes (after DME, HMDE, CMGE, RMGCE, etc.).

In order to increase the sensitivity and/or decrease the deposition time, a differential stripping voltammetry with a split-disc rotating glassy carbon electrode was developed (6). Recently, a new method consisting of differential pulse anodic stripping voltammetry (in the subtractive mode) at a rotating twin disc gold electrode was used to study mercury traces in sea water and inland waters (7).

In order to overcome certain difficulties concerning mechanical problems and the electrical connections of the rotating electrode (especially in the case of multi-electrodes, such as ring-disc, twin electrode, etc.), we propose a new electrode system with efficient mixing of the electrolyte which streams toward a stationary solid working electrode. The reproducible transport of the electroactive species from the bulk of the solution towards the electrode during preelectrolysis is achieved by a conically perforated vibrating disc. The applied vibration frequency was 50 cycles per second, and the amplitude was less than 1 mm. A schematic representation of the electrode system is shown in Fig. 1.

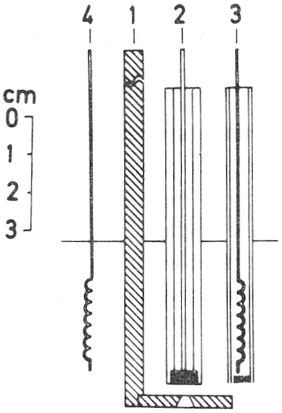

Fig. 1. A new electrode system with efficient mixing of electrolyte:
(1) perforated vibrating perspex disc;
(2) stationary glassy-carbon electrode.
(3) Ag/AgCl reference electrode, and
(4) Pt counter electrode.

A universal voltammetric cell (8) in connection with the electrode system was used. Measurements were performed with PAR 174A using differential pulse anodic stripping polarography. This mercury-film-plated glassy carbon electrode with an active surface of about 0.3 cm^2 was used. Mercury film was obtained 'in situ' by the addition of 4×10^{-5} M $HgCl^2$ to the samples (9). Anodic stripping voltammograms were recorded after preelectrolysis with efficient mixing of the electrolyte for 4-40 minutes.

In Fig. 2, typical anodic stripping voltammograms of unpolluted sea-water samples, and samples after the addition of a known quantity of Zn, Cd, Pb and Cu, demonstrate the efficiency of the new system for the analysis of natural-water samples.

To estimate the detection limits of the proposed method, a sufficiently pure supporting electrolyte is needed. The sea-water samples used contain fewer metal ions (approximately 500 ng Zn/l, 20 ng Cd/l, 100 ng Pb/l and 80 ng Cu/l) than the

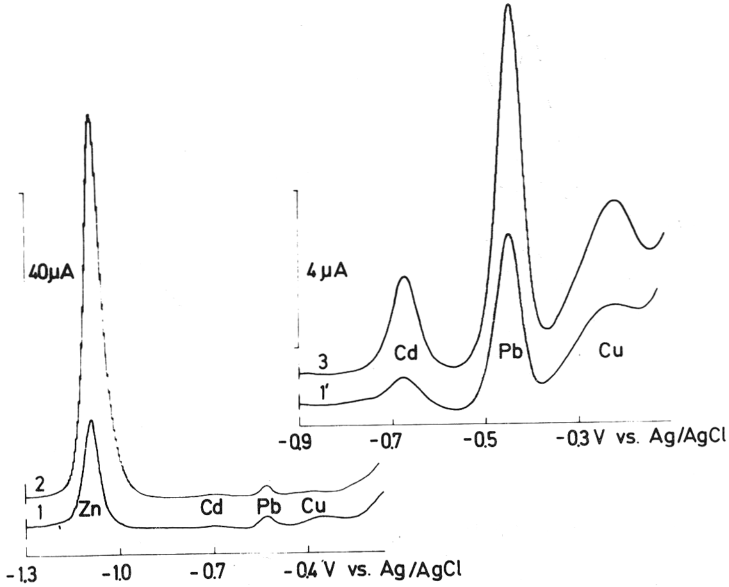

Fig. 2. Typical anodic stripping voltammograms:
(1) Sea water plus 4×10^{-5} M $HgCl_2$, 4 min preelectrolysis at - 1.3 V vs. Ag/AgCl, and 25 mV DPP-amplitude,
(2) Same as (1) plus 1.2 µg Zn^{2+}/l,
(1') Sea water plus 4×10^{-5} M $HgCl_2$, 5 min preelectrolysis at - 0.9 V vs. Ag/AgCl, and 50 mV DPP-amplitude,
(3) Same as (1') plus 40 ng Cd^{2+}, 120 ng Pb^{2+}, and 120 ng Cu^{2+} per liter

corresponding solution of 0.6 M NaCl prepared from p.a. Merck salts. After purification of the sea-water sample (through a Chelex-100 column, and 3 hrs. preelectrolysis at a constant potential of -1.5 V vs. Ag/AgCl electrode), a very low blank level was obtained (Curve (1) at Fig. 3A). After addition of only 1 ng Cd/l, (after 20 min. preelectrolysis with mixing at -0.9 V vs. Ag/AgCl, and addition of 4×10^{-5} M $HgCl_2$) a remarkable anodic peak current was noticed. Taking into account that the linearity between the preelectrolysis time and the peak current is valid (for the applied electrode system and the volume of electrolyte of 50 ml up to 40 minutes), one can conclude that the detection limit for cadmium in sea water is about 0.1 ng Cd/l (about 10^{-12} M), i.e., a quantity of about 0.005 ng cadmium.

Similar sensitivities have been recently published for the rotating thin film electrode in connection with computerized electrochemical instrumentation (10). Interconnection of such sophisticated instrumentation with the proposed electrode system would most probably result in higher sensitivity and precision.

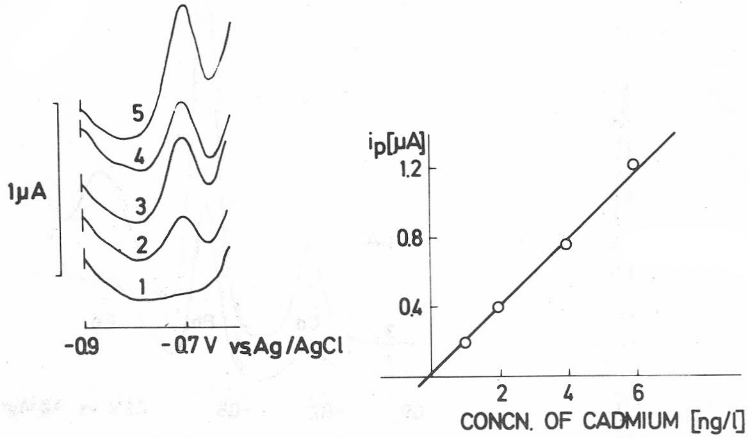

Fig. 3. (A) Anodic stripping voltammograms, with 50 mV DPP-amplitude, of:
(1) sea water purified with Chelex-100, plus 4×10^{-5} M $HgCl_2$,
(2) and (1) plus 1 ng Cd^{2+}/l
(3) as (1) plus 2 ng Cd^{2+}/l,
(4) as (1) plus 4 ng Cd^{2+}/l,
(5) as (1) plus 6 ng Cd^{2+}/l.
Preelectrolysis time: (1), (2), (3) - 20 min; (4), (5) - 10 min at -0.9 V vs. Ag/AgCl on glassy carbon electrode (0.3 cm^2 surface) and 4×10^{-5} M $HgCl_2$.
(B) Calibration curve for cadmium evaluated from A with anodic peak current normalised to 20 min. preelectrolysis time.

The new electrode system has all the electrochemical characteristics of the previously described thin film electrodes but its mechanical properties are improved and the mass transfer between bulk and electrode surface is more efficient.

Conclusively, the new electrode system offers interesting possibilities in electrochemical characterization at nanogram per liter concentration level of microconstituents in concentrated inert electrolytes.

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