



Fully electrochemical hyphenated flow system for preconcentration, cleanup, stripping, capillary electrophoresis with stacking and contactless conductivity detection of trace heavy metals

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ABSTRACT

Successful coupling of electrochemical preconcentration (EPC) to capillary electrophoresis (CE) with contactless conductivity detection (C^4D) is reported for the first time. The EPC–CE interface comprises a dual glassy carbon electrode (GCE) block, a spacer and an upper block with flow inlet and outlet, pseudo-reference electrode and a fitting for the CE silica column, consisting of an orifice perpendicular to the surface of a glassy carbon electrode with a bushing inside to ensure a tight press fit. The end of the capillary in contact with the GCE is slant polished, thus defining a reproducible distance from the electrode surface to the column bore. First results with EPC–CE– C^4D are very promising, as revealed by enrichment factors of two orders of magnitude for Tl, Cu, Pb and Cd ion peak area signals. Detection limits for 10 min deposition time fall around 20 nmol L^{-1} with linear calibration curves over a wide range. Besides preconcentration, easy matrix exchange between accumulation and stripping/injection favors procedures like sample cleanup and optimization of pH, ionic strength and complexing power. This was demonstrated for highly saline samples by using a low conductivity buffer for stripping/injection to improve separation and promote field-enhanced sample stacking during electromigration along the capillary.

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1. Introduction

The scope and application range of capillary electrophoresis (CE) and related electrokinetic separation techniques is expanding steadily although detection limits, as a rule, fall behind chromatography due to the reduced capillary dimension and small amount of sample injected. Demands of higher sensitivity for trace analysis stimulate research aiming for improvements in detection as well as preconcentration techniques for CE, preferably on-line [1,2]. Electrochemical preconcentration (EPC) is used in stripping voltammetry (ASV and CSV) and has been frequently coupled with atomic spectrometry (AAS and ICP) [3,4], followed by mass spectrometry [5,6], and rarely with potentiometry [7]. A single attempt to combine EPC with ion chromatography was found in the literature [8], while this is a pioneering work on the use with CE. Nevertheless, detection of radical species formed during an electrode process by on-line electrophoretic analysis was reported by Esaka et al. [9], while Matysik introduced CE with pre-column

electrochemical conversion, termed electrochemically assisted injection [10]. These authors used batch cells, while a flow cell is proposed here to achieve high sample throughput and better repeatability.

Due to the reduced internal diameter of the capillary column (20–100 μm), high voltage applied and small volume of injected sample, effective and reproducible coupling with the working electrode of an amperometric or voltammetric detector is challenging, and various strategies have been proposed [11,12]. Similar challenges were faced in the design of an EPC–CE interface, and a novel and simple solution has been devised, which will be described in detail below.

Sample matrices can severely interfere with the determination of trace constituents in various techniques so that cleanup procedures are required. The saline background of seawater, for example, is unfavorable for techniques like atomic spectrometry, CE or potentiometry and wherever applicable to the analytes, EPC is an effective matrix exchange technique [7]. In CE, substitution of a high conductivity matrix by a medium of conductivity lower than the background electrolyte (BGE) promotes increased separation efficiency, achieved by the effect of field-enhanced sample stacking [1,2]. The lower conductivity inside the sample plug against the BGE results in higher electrical field in the injected zone. Consequently, the ions

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inside this zone move rapidly towards the interface with the BGE, where stacking occurs, followed by electrophoretic separation in the BGE, governed by differences in the ionic mobility of the analytes.

2. Experimental section

2.1. Materials and reagents

Histidine (HIS), 2-morpholinoethanesulfonic acid (MES) and α -hydroxyisobutyric acid (HIBA) were purchased from Sigma (St. Louis, MO). Standard solutions of metals in acidic medium were purchased from Merck (Darmstadt, Germany) and diluted daily with a solution containing 30 mmol L⁻¹ of MES + 30 mmol L⁻¹ of HIS and 10 mmol L⁻¹ of suprapure HCl. This matrix was replaced by 6 mmol L⁻¹ of MES + 6 mmol L⁻¹ of HIS before stripping, to lower the conductivity. For direct CE-C⁴D (as reference for enrichment factor calculation), less acidic metal standards were prepared by dissolving solid reagents of analytical grade or better in 6 mmol L⁻¹ MES + 6 mmol L⁻¹ HIS buffer. Deionized water (18 M Ω cm) was obtained from a Nanopure UV system (Barnstead, Dubuque, IA).

2.2. Capillary electrophoresis

A self-made equipment, described elsewhere [13], was adapted for the implementation of EPC-CE-C⁴D. The separations were performed using a fused-silica capillary with 75 μ m I.D. and 360 μ m O.D. The negative high voltage (HV) end of the power supply was connected to the electrode at the detector end of the capillary, immersed in a reservoir coupled with a pressurization air pump (for back flushing) and an aspiration pump, for hydrodynamic sample injection (5.0 kPa for 20 s). The C⁴D [14,15] was excited at 550 kHz, 3.4 V_{p/p}. The total capillary length was 45 cm (34 cm of effective length to the C⁴D), operated at 20 kV for Pb²⁺, Cd²⁺ and Cu²⁺ and 80 cm (69 cm) at 30 kV for Tl⁺, Pb²⁺, Cd²⁺, Zn²⁺ and Cu²⁺. The column was preconditioned by washing with 0.1 mol L⁻¹ NaOH solution (10 min), deionized water (10 min), and BGE (10 min). Before the first injection, high voltage was applied for approximately 10 min.

2.3. Design and construction of the interface for EPC-CE-C⁴D

The EPC-CE interface is depicted in Fig. 1. The CE column is inserted through the upper block, designed and built in the laboratory and comprising two orifices for flow inlet and outlet and two extra

orifices to introduce the capillary and the silver pseudo-reference electrode, placed closely together. The silver wire was pressure fitted, while a bushing, made from a short section of Tygon capillary tube, was used to hold the silica column tightly in place. The lower part of the cell was an MF-1000 block (Bioanalytical Systems, West Lafayette, IN) with dual 3 mm circular glassy carbon electrodes: one connected to the self-made potentiostat as a working electrode and the other one, used as auxiliary electrode of the flow cell (h in Fig. 1) during deposition/stripping and as grounded anode during CE separation. Between the blocks that are screwed together a 200 μ m thick spacer gasket defines a 3-mm wide flow channel carrying circa 4.5 μ L of liquid. No finishing other than wet sanding with 600 grit abrasive paper is required for the working GCE.

To establish a fixed distance from the capillary orifice to the GCE surface (50 μ m), the capillary was first polished to a slant angle of $\sim 15^\circ$ with 1000 grit abrasive paper with the help of a template consisting of an acrylic block with a slanted hole and a bushing similar to (b) in Fig. 1. While being abraded, the column is flushed with water under pressure.

A four channel peristaltic pump Reglo (Ismatec, Switzerland) was used for flow propulsion throughout the work. Software to control the potentiostat timing and potentials (GCE cleaning, analytes deposition and stripping) as well of CE high voltage, injection and data acquisition was developed in LabVIEW (National Instruments, Texas, USA). Peak areas of the electropherograms were evaluated with the Origin software (OriginLab, Northampton, MA).

2.4. EPC-CE-C⁴D procedure

Firstly, a potential of +0.4 V vs. Ag pseudo-reference (corresponding to 0.15–0.20 V vs. Ag/AgCl_{KCl(sat)}) was applied to the GCE under BGE flow to remove impurities from the electrode surface. Next, under sample flow of 0.5 or 0.75 mL min⁻¹, a potential of -1.2 V was applied for the cathodic deposition of metals from samples without Zn²⁺ or -1.5 V for samples containing this ion. Before stripping, the flow was switched to BGE (or another stripping electrolyte) while the capillary was washed by back-fluxing BGE from the reservoir at the detector end semi-cell (positive pressure) for 30 s. Then, hydrodynamic injection into the column was activated for 20 s simultaneously with stripping at 0.2 V. Finally, the residues were displaced from the flow cell with BGE, all electrodes were disconnected from the potentiostat and the high voltage was applied to promote electrophoretic separation.

3. Results and discussion

The fully electrochemical EPC-CE-C⁴D prototype was found entirely operational, although not yet optimized as required for electrochemical flow systems [16], with regard to material, treatment and size of the working electrode, cell geometry, capillary tip slantness and orientation in relation to the flow lines at the GCE. The procedure combines a perhaps unsurpassed number of electrochemical phenomena to promote the preconcentration, cleanup, dissolution, stacking, electroosmotic flow migration, electrophoretic separation and conductance detection of traces of metal ions.

No modification other than disconnecting the working electrode is required to operate the system without preconcentration, e.g., for the evaluation of major cations (and anions) in a sample matrix.

3.1. Electrochemical cleanup and stacking

Besides controlled multi-analyte enrichment and release, EPC in a flow system was found particularly attractive and effective to overcome interferences from complex matrices otherwise observable in trace metal analysis by CE-C⁴D (e.g., system peaks, peak broadening and superposition and undetectable peaks in saline or acidic samples). The selection of the stripping electrolyte is very

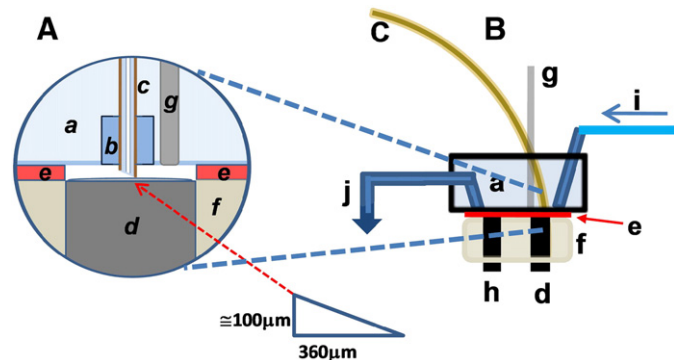


Fig. 1. EPC-CE interface. (A) Cross section cut through the capillary and the working electrode, with flow channel perpendicular to the plane; (B) lateral schematic view of the upper and lower blocks of the interface, tightly screwed together (screws not shown). Relevant parts: a – acrylic body; b – bushing (Tygon capillary tube); c – polyimide-coated fused-silica capillary; d – GCE; e – spacing gasket; f – Kel-F block; g – Ag wire (pseudo-reference electrode); h – auxiliary electrode and CE ground electrode (switchable between the potentiostat and the HV supply); i – flow inlet; j – flow outlet.

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