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Electrochemical Sample Matrix Elimination for Trace Level Potentiometric Detection with Polymeric Membrane Ion-Selective Electrodes

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Abstract

Potentiometric sensors are today sufficiently well understood and optimized to reach ultra-trace level (sub-nanomolar) detection limits for numerous ions. In many cases of practical relevance, however, a high electrolyte background hampers the attainable detection limits. A particularly difficult sample matrix for potentiometric detection is seawater, where the high saline concentration forms a major interfering background and reduces the activity of most trace metals by complexation. This paper describes for the first time a hyphenated system for the online electrochemically modulated preconcentration and matrix elimination (EMPM) of trace metals, combined with a downstream potentiometric detection with solid contact polymeric membrane ion-selective microelectrodes. Following the preconcentration at the bismuth coated electrodes, the deposited metals are oxidized and released to a medium favorable to potentiometric detection, in this case calcium nitrate. Matrix interferences arising from the saline sample medium are thus circumvented. This concept is successfully evaluated with cadmium as a model trace element and offers potentiometric detection down to low parts per billion levels in samples containing 0.5 M NaCl background electrolyte.

Recent improvements in the detection limits of ISEs based on polymeric membranes containing selective receptors (ionophores) yielded potentiometric sensors for the direct measurement of ions down to the subnanomolar concentration range.¹ This was made possible by minimizing diffusional ion fluxes from the membrane into the sample solution.^{2, 3} Today potentiometry routinely achieves detection limits in the nanomolar or lower concentration range without any accumulation step and with essentially no sample perturbation.¹ Unfortunately, ISEs are normally incapable of reaching the same detection limits in undiluted seawater samples, primarily owing to the very high levels of electrolyte (salt) background and the complexation of the target metal ion. Additionally, seawater contains natural organic matter and surfactants that may interfere with the ISE response via adsorption and extraction processes.

To overcome related seawater matrix effects, detection techniques such as ICP-MS⁴ and electrospray MS,⁵ among others, make use of preconcentration methods that separate the target analyte from the complex matrix. The methods used for matrix separation include liquid-liquid extraction,^{6, 7} sorption on solid sorbents or exchangers,^{8, 9} coprecipitation¹⁰ and electrodeposition.⁵ It is the last one which is considered most suitable for preconcentration, because the procedures are relatively fast compared with chemical preconcentration and the technique can be automated to provide continuous accumulation. In addition, when used in an on-line format, these preconcentration methods minimize manual sample handling and offer

increased sample throughput, decreased cost, and minimal exposure to potentially hazardous samples.¹¹

Electrochemical preconcentration is an essential part of various electroanalytical methods of trace determination, such as anodic stripping voltammetry or potentiometry stripping analysis.¹² During the preconcentration process, the target metal ions are separated from the sample matrix and deposited on the electrode. The dissolution/stripping of the metal from the electrode provides the analytical signal.

Electrochemical preconcentration is very convenient; however, the electrodeposition of most heavy metals competes with the reduction of hydrogen ions. To avoid such competition an electrode material with high hydrogen overvoltage, such as mercury, is required.¹³ Despite the excellent performance of mercury, its widespread use is hampered by its high toxicity,¹⁴ which led to the investigation of alternate electrode materials. While a wide range of non-mercury electrodes, including gold, carbon, or iridium, has been examined,^{15, 16} bismuth film electrodes appear to offer the most attractive performance, comparable with that of mercury-coated electrodes.¹⁷ The “environmental-friendly” bismuth-coated electrode couples a favorable behavior, including simple (in situ) preparation and high sensitivity, with very low toxicity.¹⁸

This paper reports for the first time on the use of on-line electrochemically modulated preconcentration and matrix elimination (EMPM)¹⁰ to enhance the performance of ion-selective electrodes. Such matrix elimination is accomplished by replacing the original sample, containing high concentration of electrolyte background, with a medium favorable to ISE detection, hence facilitating potentiometric analyses of high-salt samples. Similar elimination of detrimental matrix effects has been reported for stripping analysis combined with ICP-AES and ICP-MS.¹⁹ The new electrolytic accumulation/ISE concept is evaluated and illustrated for the detection of trace cadmium as an example of high practical importance, since cadmium is known to be a hazardous environmental pollutant with toxic effects for the living organisms in aquatic ecosystems.²⁰ This initial work aims primarily at demonstrating the matrix elimination capabilities of the hyphenated system. Future work will focus on efficient preconcentration for potentiometric detection limits that may surpass that of state of the art electrochemical stripping methods.

Experimental

Reagents

The ionophores *N,N,N',N'*-tetradodecyl-3,6-dioxaoctane-dithioamide (ETH 5435), *N,N*-Dicyclohexyl-*N',N'*-dioctadecyl-diglycolic diamide (ETH 5234), lipophilic cation exchanger sodium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (Na-TFPB), lipophilic salt tetradodecyl ammonium tetrakis(4-chlorophenyl)borate (ETH 500), 2-nitrophenyloctylether (*o*-NPOE), poly(vinyl chloride) (PVC) and tetrahydrofuran (THF) were purchased in Selectophore[®] or puriss grade from Fluka (Milwaukee, WI). Methylene chloride was obtained from Fisher (Pittsburgh, PA). Poly(3-octylthiophene) (POT) was synthesized following the procedure of Jarvinen *et al.*²¹ and was purified according to the patent application.²² The synthesis of methyl methacrylate-decyl methacrylate (MMA-DMA) copolymer matrix was based on Qin *et al.*²³

The cadmium ion standard solution was purchased from Fluka while bismuth standard stock solution and acetate buffer were obtained from Sigma-Aldrich (St. Louis, USA). All stock solutions were prepared using double deionized water (18.2 MΩ cm).

Instrumentation

Potentiometric measurements were performed with a PCI MIO16XE data acquisition board (National Instruments, Austin, TX) connected to a four-channel high Z interface (WPI, Sarasota, FL). All potentiometric measurements in the cell were performed at room temperature (22 °C). An Electrochemical Analyzer (CH Instruments, Inc., TX, USA) connected to a personal computer was used for controlling the preconcentration and release processes of cadmium ions.

Electrochemical and potentiometric cells

A homemade electrochemical flow cell, which was made of transparent Plexiglass, was used for the electrodeposition of cadmium. The electrochemical accumulation cell consists of three electrodes system with a bismuth-coated glassy carbon (GC) working electrode and platinum disk as counter electrode. These electrodes were inserted into the cell body face to face, along with a Ag/AgCl reference electrode placed in line at the beginning of the flow cell (Figure 1).

The potentiometric cell, also shown in Figure 1 (right side) consisted of a four way polypropylene connector purchased from Scientific Commodities, Inc. (Lake Havasu, AZ, USA). The indicator electrode (cadmium ion-selective microelectrode) and pseudoreference (calcium ion-selective microelectrode) were installed face to face perpendicular to the solution stream (0.8 mm i.d. channel). Interconnections were made from Teflon tubing (0.5 mm i.d.). A model peri-star PRO (World Precision Instrument, Inc. Sarasota, FL, USA) peristaltic pump was used for guiding the solution through the cell. Measurements in conventional large 100-mL samples were performed against a commercial double junction reference electrode (type 6.0729.100, Metrohm AG, 9101 Herisau, Switzerland).

Ion-selective electrode preparation

The Cd²⁺-ISE membrane was prepared by dissolving 60 mg of the following components in CH₂Cl₂ (0.8 mL): ETH 5435 (1.27 wt%, 15 mmol kg⁻¹), NaTFPB (0.46 wt%, 5 mmol kg⁻¹), ETH 500 (1.15 wt%, 10 mmol kg⁻¹), and copolymer MMA-DMA (97.12 wt%). The membrane solution was degassed by purging it with N₂ before coating the microelectrodes.

The solid contact Cd²⁺-selective microelectrode was prepared by using a 2 cm long Au wire (200 μm diameter) as solid substrate soldered to a Ag wire for electric contact. Before use, the Au wires were thoroughly cleaned with 10% sulfuric acid and rinsed with water, then dried with acetone, and left in CHCl₃ for 5 min. The solution of POT (25 mM with respect to the monomer in CHCl₃) was applied along the Au wire at least three times or until the color of the wire became black, and then left to dry. The wires were inserted into a 10-μL polypropylene tip so that they were level with the end of the micropipette tip. Finally, the membrane solution was deposited on top of the wire three times at 15 min intervals and allowed to dry for 2–3 h until full evaporation of the CH₂Cl₂. The microelectrodes were conditioned first in 10⁻³ M Cd(NO₃)₂ and subsequently in 10⁻⁹ M Cd(NO₃)₂ with 10⁻³ M Ca(NO₃)₂ (1d each).

The membrane for the Ca-ISE used as a pseudoreference electrode was prepared by dissolving 140 mg of the following components in THF (1 mL): ETH 5234 (0.87 wt%, 10.9 mmol kg⁻¹), NaTFPB (0.47 wt%, 5.12 mmol kg⁻¹), PVC (32.2 wt%), and *o*-NPOE (66.3 wt%). The solution was allowed to evaporate for 1 h, after which it was filled into a 100-μL pipette tip and left to dry for at least 24 h. The final membrane was conditioned in 10⁻³ M Ca(NO₃)₂ for 1 day. Measurements were performed in a polypropylene cell with a sample volume of 20 μL.

Bismuth film preparation

The GC electrode was first mechanically polished with alumina slurry (0.5 μm), rinsed with deionized water, and further cleaned ultrasonically in 1M HNO₃, water and ethanol,

respectively. The bismuth film was then preplated in batch mode using a three electrode system, by immersing the polished glassy carbon electrode in a 5 mL cell containing 100 ppm of bismuth in 0.1 M acetate buffer (pH 4.6). A deposition potential (-0.6 V) was applied to the glassy carbon electrode for 10 minutes, while the solution was slowly stirred. The bismuth-coated electrode was then rinsed carefully with deionized water and became ready to use with a working life time of at least one day.

Electrochemical accumulation and release

The bismuth-coated electrode, along with a platinum and Ag/AgCl counter and reference electrodes, respectively, were inserted in the electrochemical cell. To start the accumulation process, the sample solution (usually in a 0.5 M NaCl medium) was pumped by peristaltic pump at a constant flow (typically 0.5 mL min^{-1}), while the potential was held at -1.2 V for 20 min to allow deposition of cadmium. In this step the remaining sample solution was directed to waste. After the deposition step the sample solution was exchanged by 10^{-2} M $\text{Ca}(\text{NO}_3)_2$ to wash the microcell during 1 min, while applying the accumulation potential. The electrodeposited cadmium was then stripped into the new detection solution of 10^{-2} M $\text{Ca}(\text{NO}_3)_2$ (20 μL volume), by scanning the potential linearly from -1.2 to -0.5 V at a rate of 50 mV s^{-1} . For the potentiometric sample detection, 20 μL of a 10^{-2} M $\text{Ca}(\text{NO}_3)_2$ solution containing the electrochemically released cadmium was directed to the potentiometric detection cell by changing the position of the valve (see Figure 1) and recording the cell potential after stabilization.

Results and Discussion

Electrochemical deposition coupled to a flow system has proven to be an effective tool for separating electroactive analytes from complex matrices.²⁴ In this work we used a flow cell, optimized to achieve good preconcentration efficiency and effective elution for the matrix elimination in connection with a downstream potentiometric detection. We use potentiometric detection since modern ion-selective electrodes offer detection limits down to the subnanomolar range.²⁵⁻²⁷ It was also shown that these electrodes can reach extremely low detection limits in small sample volumes, corresponding to hundreds of attomoles at the 10^{-10} M level.^{28, 29} Despite the extremely attractive detection limits of these electrodes, their practical use is limited when high salt concentrations are present, as in seawater samples. For this reason we explore the potentiometric detection of cadmium following an electrodeposition step for replacing the original (salt-rich) sample matrix by a medium that is optimally amenable to potentiometric detection. Sample components that are commonly detrimental to potentiometric measurements are thus no longer affecting the ISE response.

We employ here a solid contact cadmium ion selective electrode developed recently³⁰ and characterized for low detection limits. Such electrode offers a potentiometric response for cadmium ion in the range of 3×10^{-10} to 10^{-6} M with a Nernstian response slope (29.5 mV) and a subnanomolar detection limit (2×10^{-10} M) in 100 mL samples in a 10^{-2} M $\text{Ca}(\text{NO}_3)_2$ electrolyte background. This detection limit could be maintained for at least one month. The cadmium ion-selective microelectrode in the flow cell needed to be paired with a reference electrode of similar size. For this reason, a calcium ion-selective electrode was used as a pseudoreference electrode, allowing convenient measurements in ultrasmall sample volumes, with the background electrolyte ensuring that the calcium activity remained constant.

The cadmium ion-selective electrode was subsequently evaluated with this calcium selective reference in the microvolume cell (20 μL) following the electrolytic deposition, as shown in Figure 1. The system was characterized between 10^{-10} to 10^{-6} M cadmium ions, with the same calcium nitrate background. The electrode exhibited a Nernstian behaviour (28.9 mV) and a detection limit of 10^{-9} M. The slightly inferior detection limit is attributed to the much larger

surface to volume ratio, making the setup more susceptible to adsorption and impurity issues. The observed detection limit corresponds to about 20 femtomoles, keeping in mind that the definition of potentiometric detection limits is orders of magnitude more conservative compared to that of other analytical methods³¹ and that much lower levels are still reliably detectable with careful experimentation.²⁹

The potentiometric detection cell was explored for the measurement of cadmium ions at trace levels in a saline background typical for seawater, specifically 0.5 M NaCl. The behaviour of the cadmium electrode in 100 mL samples in a batch mode was evaluated first with a commercial reference electrode. As shown in Figure 2A the potential observed for the 0.5 M NaCl solution, in the presence and absence of 5 ppb Cd²⁺, is high compared to that for 10⁻² M calcium nitrate. Subsequent additions of cadmium ions up to 50 ppb give no discernable signal change. Analogous performance was observed for direct measurements in the potentiometric cell without electrodeposition, see Figure 2B. The sample matrix forms two major obstacles to the potentiometric detection step. The high sodium ion background dramatically increases the detection limit of the membrane on the basis of an equilibrium ion-exchange process, thereby increasing the counterdiffusion cadmium ion flux from the membrane in direction of the sample. Analogous processes have been observed and characterized earlier with copper and hydrogen ions interfering with lead ion-selective electrodes near the detection limit.³² The second obstacle is the complexation of cadmium by chloride ions of the matrix, thereby decreasing the activity of the uncomplexed ion (to which the membrane is responsive to) in relation to the total concentration. This imposes substantial demands on the selectivity of the membrane that can normally not be achieved in practice. Note, however, that literature examples exist where solid state ion-selective electrodes were successfully used in such complex media for the assessment of extremely low free ion activities.³³ In these cases, however, the total concentration was kept at elevated levels so that these experiments did not strictly fall into the category of ultratrace level measurements.

Potentiometric detection of cadmium at the ppb level in the saline medium became possible by preceding the measurement by an on-line electrochemical matrix replacement step. This was accomplished with a bismuth coated glassy carbon electrode. Indeed, Figure 2C demonstrates that the detection of 5, 10 and 50 ppb Cd²⁺ becomes possible if the original 0.5 M NaCl sample background is replaced via electrochemical deposition by a 10⁻² M Ca (NO₃)₂ medium that is amenable to potentiometric detection of trace cadmium.

The parameters of electrodeposition were optimized using the on-line coupling of the flow-through electrolytic cell with the potentiometric detection cell. For cadmium measurements, the solution was transported by a peristaltic pump into the cell and a negative potential was applied at the working electrode. The applied potential influences in the efficiency of the electrodeposition process since the deposition of cadmium competes with the reduction of hydrogen ions. A bismuth-coated electrode was used to overcome this limitation because such bismuth film extends the available cathodic potential range.³⁴ In the optimization of the applied potential a high response was obtained when -1.2 V was used for deposition while the signal decreased considerably at less negative potentials (data not shown).

The influence of the deposition time was examined over the 5 to 30 min range in connection with a 10 ppb cadmium concentration level. The potentiometric signal strongly increased with deposition time up to 15 minutes, and then more slowly (see Figure 3). Further experiments employed a 20 min deposition time to strike a balance between signal and time. The influence of the flow rate was examined over a 200 to 1000 $\mu\text{L}/\text{min}$ range. A flow rate of 500 $\mu\text{L}/\text{min}$ offered the highest efficiency of the cadmium deposition (data not shown), reflecting the competing effects of convective transport and residence time in the preconcentration cell.

After the key parameters were optimized, a calibration curve was obtained in the concentration range of 1 to 100 ppb, see Figure 4. A residual signal for a 0.5 M NaCl sample without cadmium was observed relative to a sample containing only 10 mM calcium nitrate, corresponding to ca. 0.5 ppb Cd²⁺. This is likely attributable to cationic impurities in the NaCl salt that accumulate during the 20 min deposition step and are potentiometrically detectable.³⁵ Despite the signal from background alone, the sample corresponding to 1 ppb cadmium is easily differentiated from the background. In contrast, ASV detection alone (without hyphenation with the potentiometric microelectrode) did not give a significant signal difference between the 1 ppb sample and the background.

The reproducibility of the system was evaluated with six different samples of 10 ppb cadmium in 0.5 M NaCl. Such series yielded a relative standard deviation of 5%, indicating the reproducibility is not compromised by the high salt content of the sample.

Conclusions

We demonstrate here for the first time that ion-selective microelectrodes can be used for monitoring cadmium ions at ultra-trace levels in the presence of a high concentration of background electrolyte. This was possible by coupling the microliter potentiometric detection to an efficient on-line electrochemical matrix elimination step. This work opens new opportunities for applications of ion-selective electrodes with a low detection limit, particularly in marine environments. The concept can be extended to a wide range of environmentally important analytes. Electrochemical matrix elimination of metals that cannot be electroplated, such as uranium or chromium, can be achieved via nonelectrolytic adsorption processes as in adsorptive stripping voltammetry. Coupling to cathodic stripping voltammetry may be suitable for the potentiometric trace level detection of anions such as halides (especially iodide) and sulfide. The goal of this work was to demonstrate that an on-line electrochemical cell can be used very effectively for matrix elimination purposes so that potentiometric detection at trace levels becomes possible even for complex electrolyte-rich samples. In this early work, the system was not yet optimized for optimal preconcentration, and there is significant scope to further develop such hyphenated systems to reach ultra-trace detection limits down to the low parts per trillion levels. These efforts are part of ongoing research in our laboratories.

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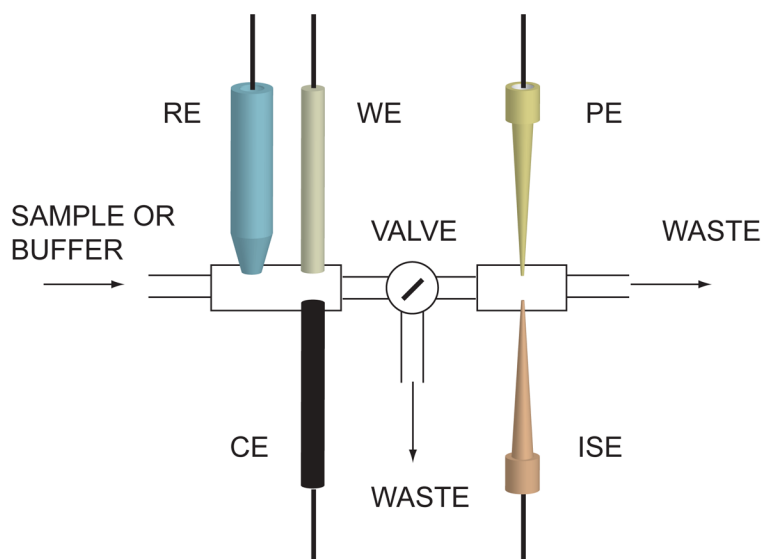
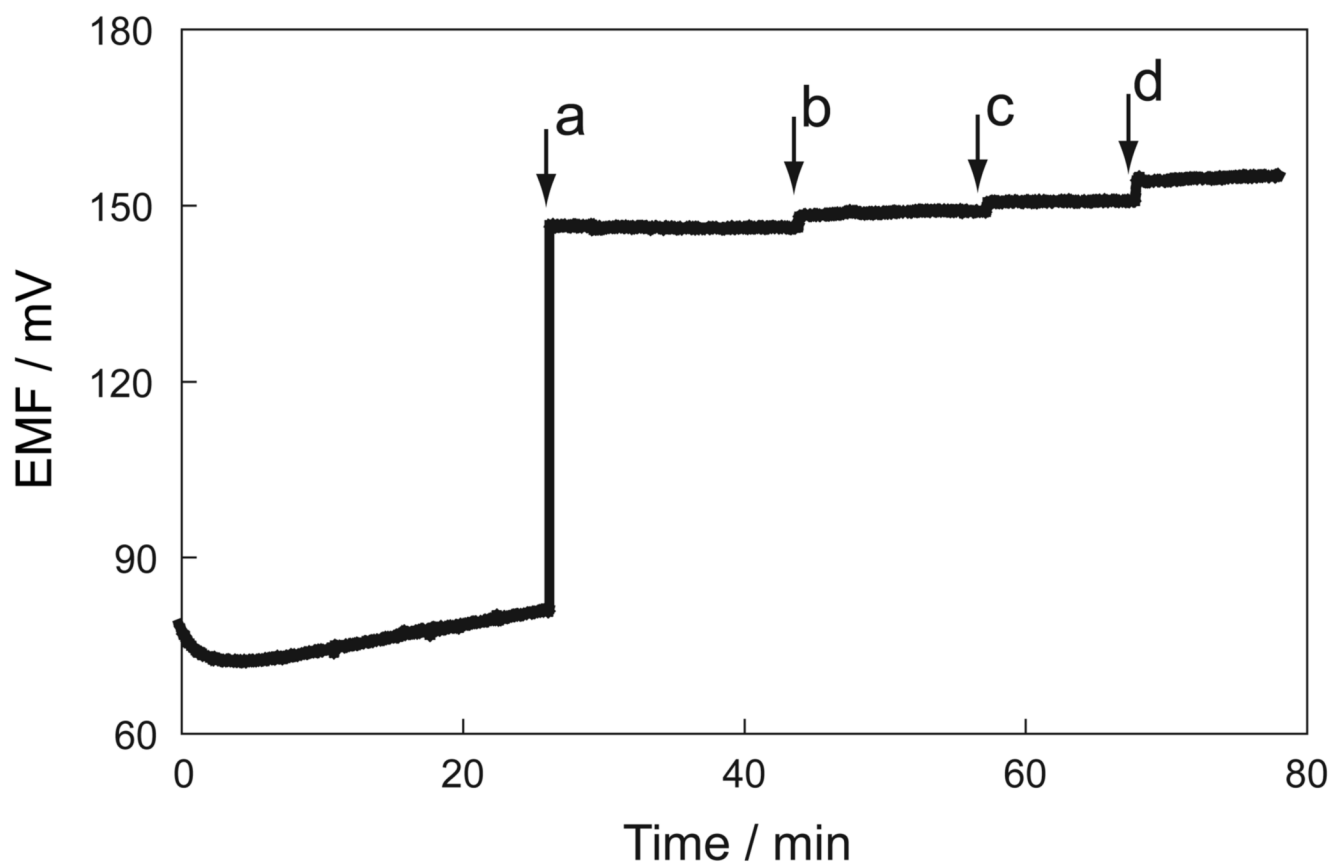
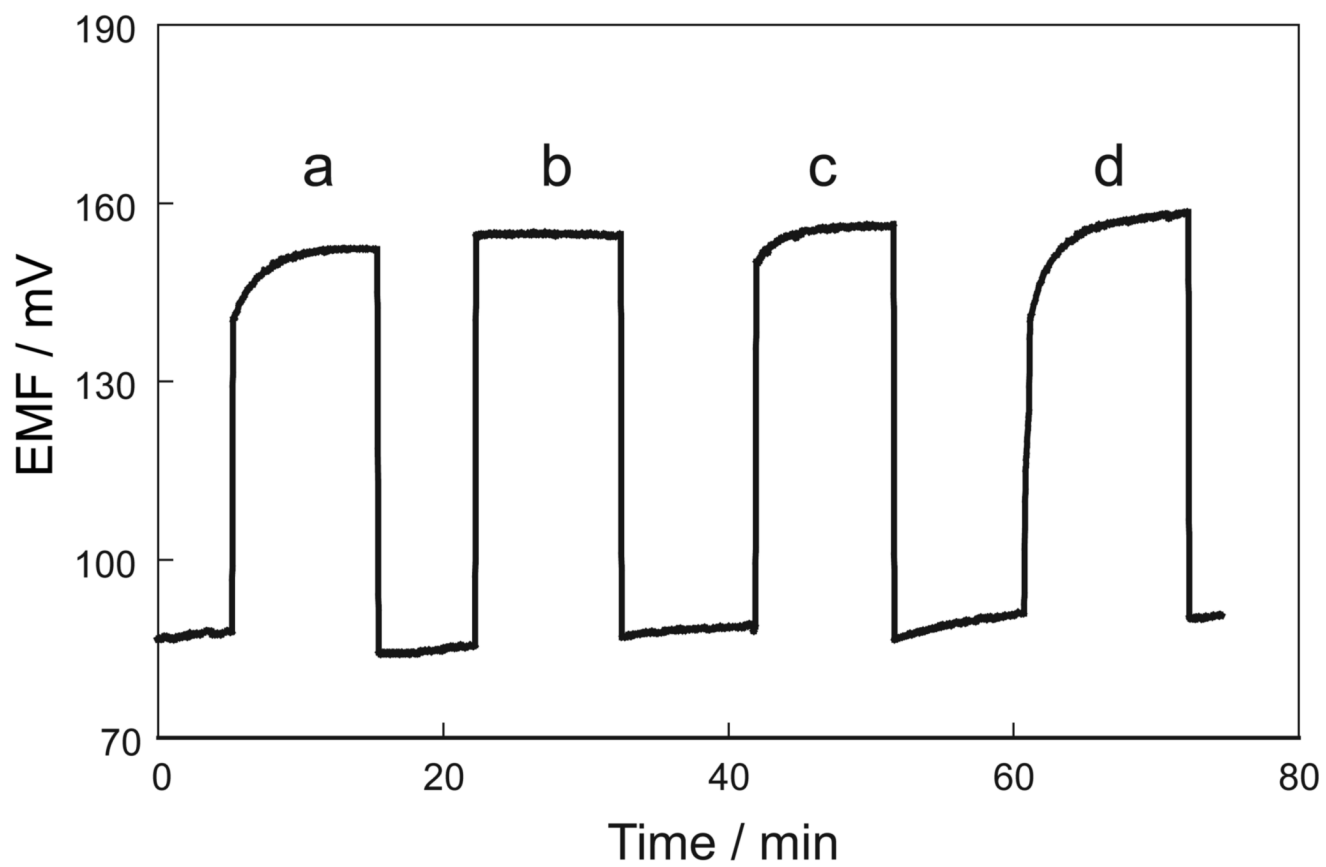


Figure 1. Schematic of the on-line electrochemically modulated preconcentration and matrix elimination (EMPM) cell (WE, working electrode, RE, reference electrode, CE, counter electrode) hyphenated to the potentiometric detection cell (ISE, ion-selective electrode, PE, pseudoreference electrode).





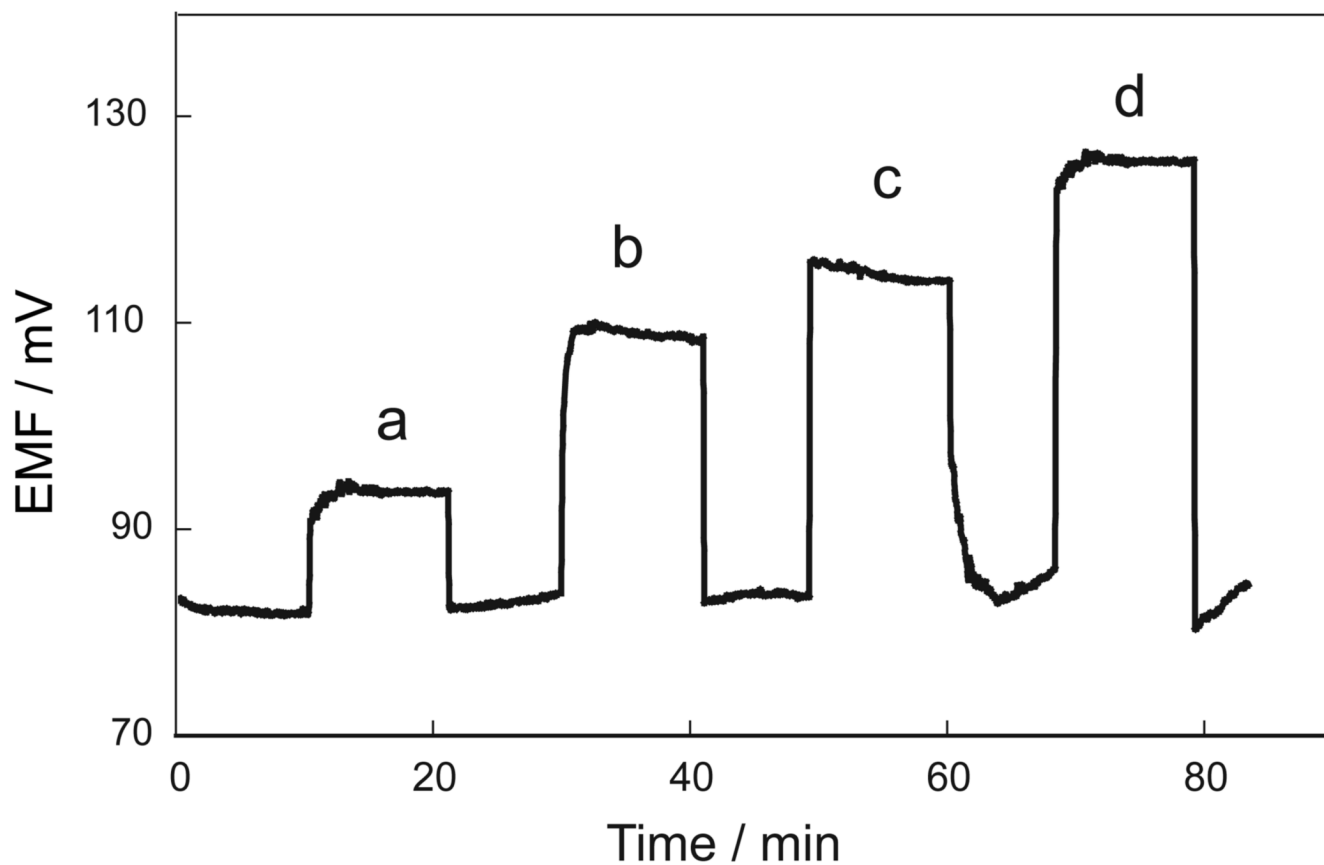


Figure 2. ISE response for direct measurements A) in a batch mode in 100 mL sample volumes and B) in a 20 μL flow cell of 0.5 M NaCl and the following added cadmium ion levels: a) no cadmium, b) 5 ppb, c) 10 ppb and d) 50 ppb. C) Corresponding measurements in the 20 μL cell following electrochemical matrix elimination. In all cases, baseline traces are for the 10^{-2} M $\text{Ca}(\text{NO}_3)_2$ background.

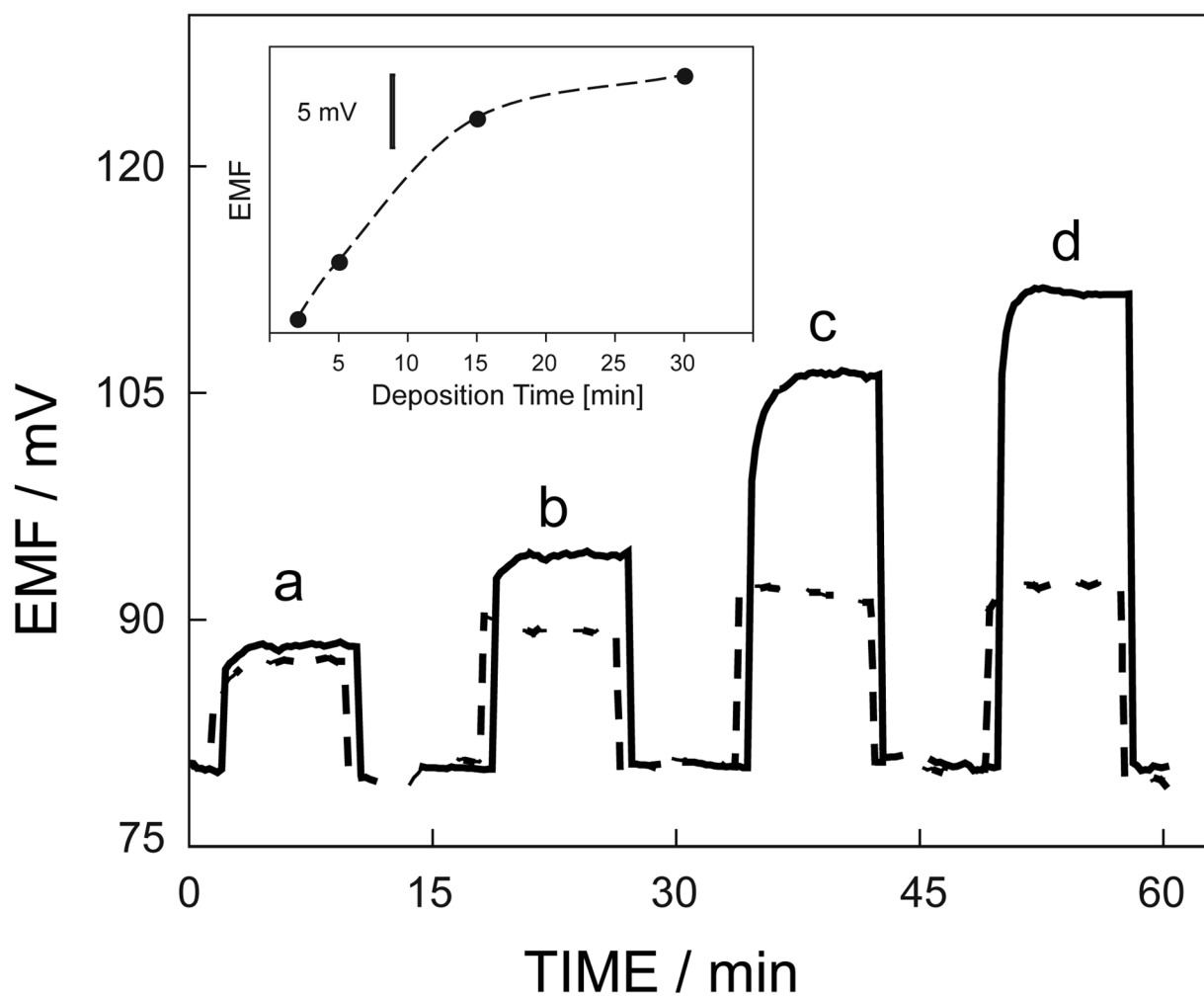


Figure 3. Potentiometric time response towards 10 ppb cadmium in 0.5 M NaCl sample for a) 2 , b) 5, c) 15 and d) 30 min deposition time at a flow rate of 500 μ L/min. Inset: Corresponding potentiometric response curve.

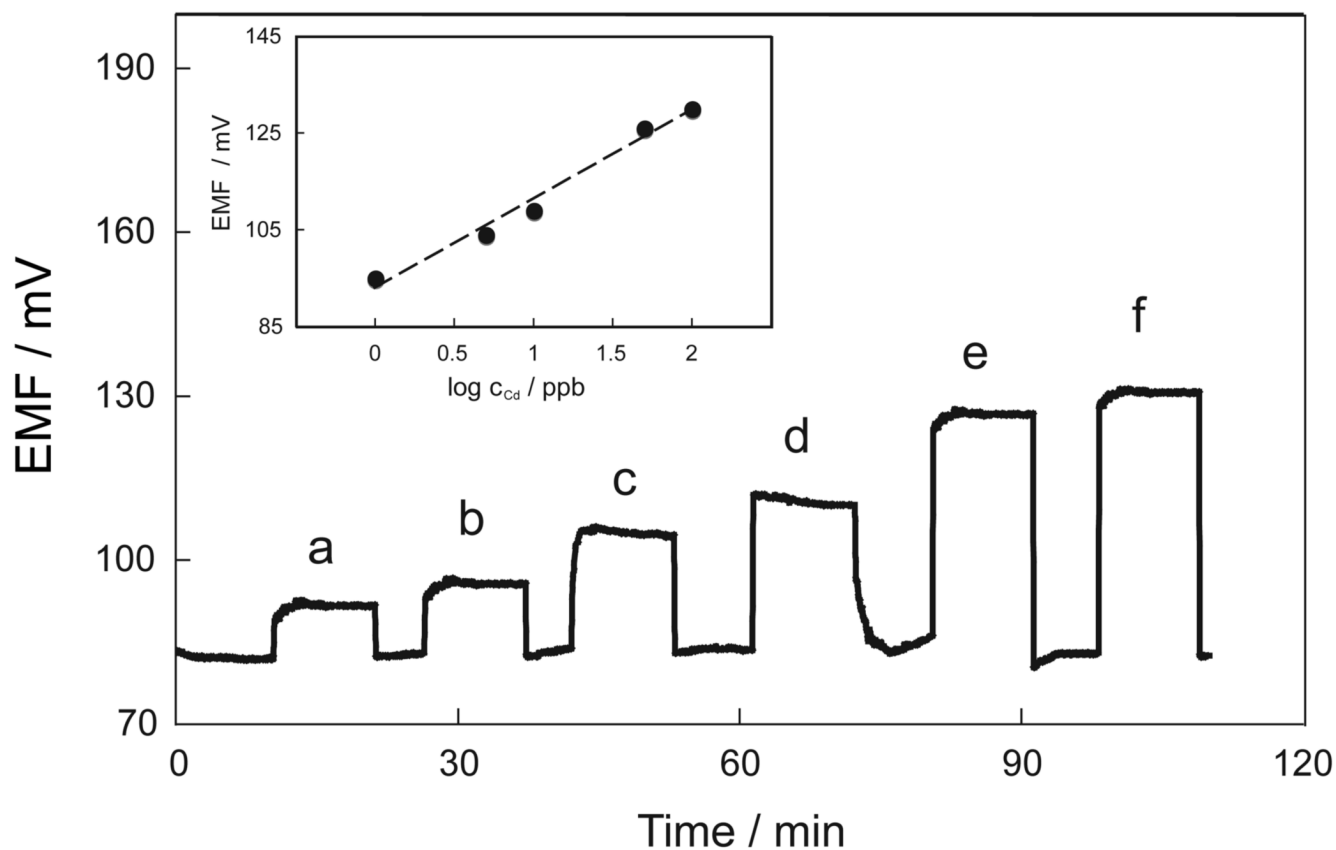


Figure 4. Trace line of potentiometric response for additions of cadmium at increasing levels of a) 0, b) 1, c) 5, d) 10, e) 50 and f) 100 ppb following 20 min electrodeposition at -1.2 V at $500 \mu\text{L}/\text{min}$. Inset: Corresponding calibration curve.