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# **Complexing porous polymer monoliths for online solid-phase extraction of metals in sequential injection analysis with electrochemical detection**

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## **ABSTRACT**

A monolithic column affording complexing groups was synthesized for automated solid-phase extraction of potentially toxic metal ions in a low-pressure sequential injection analyzer. Poly(glycidyl methacrylate-co-ethylene dimethacrylate) monoliths were synthesized by free-radical polymerization in the coffins of fused silica-lined stainless-steel tubes (2.10 mm i.d.  $\times$  5–6 cm length). High permeability ( $4.33 \times 10^{-13} \text{ m}^2$ ) was achieved for monoliths polymerized for 24 h at 60 °C from a mixture of 30 wt % glycidyl methacrylate, 10 wt % ethylene glycol dimethacrylate, 35 wt % n-propanol, 20 wt % 1,4 butanediol and 5 wt % water. Azobisisobutyronitrile (1 wt % with respect to the monomers) initiated the free-radical polymerization. These generic columns were modified with iminodiacetate to create complexing functionalities on the polymer surface, being further used for online solid-phase extraction of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  from natural, tap and drinking waters prior to their determination by stripping chronopotentiometry. The high permeability of the column allowed the loading,

washing, eluting and reconditioning steps to be made at flow rate of  $10 \mu\text{L s}^{-1}$ . The limits of detection and quantification achieved by processing  $1500 \mu\text{L}$  of sample were  $0.51$  and  $1.7 \mu\text{g L}^{-1}$  for  $\text{Cu}^{2+}$ ,  $1.4$  and  $4.7 \mu\text{g L}^{-1}$  for  $\text{Pb}^{2+}$ , and  $1.2$  and  $3.8 \mu\text{g L}^{-1}$  for  $\text{Cd}^{2+}$ , respectively. Recoveries were between  $75.5$  and  $117\%$ , obtained by quantification via external calibration curves, thus eliminating the need for the laborious standard addition strategies.

*Keywords:* Metal complexing monoliths; Potentially toxic metals; Solid-phase extraction; Matrix exchange; Sequential injection automation; Water samples

## 1. Introduction

Quantification of trace metals in environmental waters is an important issue because whereas some metals, such as Cu, Zn and Mn, are essential micronutrients at low concentrations, they become toxic at concentrations not much higher than those required for healthy metabolism. Other elements, such as Pb, Cd and Hg, are toxic at any concentration [1]. The determination of these elements is usually carried out by atomic spectrometry [2], relying on high-cost instrumentation, especially in the cases of inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Electroanalytical methods are well-known for the use of low-cost and portable instrumentation, especially if using battery-powered potentiostats and screen-printed sensors [3,4]. Quantification of trace metals in natural water is difficult because of their low concentrations. Additionally, the results may be affected by severe matrix effects caused by natural organic matter (humic substances) and major inorganic constituents, such as Ca, Mg, Fe, Al, etc. In some

cases, standard addition circumvents the matrix effects, but for trace analyses, extraction is often necessary to enrich the target analytes and separate them from the complex matrix.

Sample preparation for determination of trace metals was conventionally based on liquid-liquid extraction (LLE) using toxic organic solvents and complexing reagents such as dithizone, ammonium 1-pyrrolidinedithiocarbamate (APDC), 8-hydroxyquinoline, etc [5–7]. Currently, modern strategies of dispersive liquid–liquid extraction of metal complexes and solid-phase extraction (SPE) [7,8] have been implemented to overcome the drawbacks of conventional LLE.

SPE can easily be coupled online to analyzers, thus eliminating the handling of samples between the enrichment and analysis [6,8,9]. This hyphenation minimizes errors caused by losses of analyte and sample contamination that arise from extensive sample handling. Additionally, the online approach injects all the extracted analyte into the analyzer, substantially reducing the sample volume required for analysis [10,11].

Monolithic columns are formed by single pieces of porous material having large flow-through pores (1–2  $\mu\text{m}$ ) responsible for their high permeability. These pores enable separations at high flow rates and moderate backpressures [12,13]. Monoliths can be prepared from organic, inorganic (mainly silica) and hybrid organic-inorganic materials [14,15]. Organic porous polymer monoliths are easily prepared in a variety of chemistries and shapes by in-situ thermal- or photo-polymerization of a mixture of monomers (functional and crosslinker), porogenic solvents and a free radical initiator [16]. The reaction of the epoxy group of glycidyl methacrylate (GMA) with complexing agents such as ethylene diamine (EDA), iminodiacetate (IDA) and thiols has long been exploited to construct columns suitable for the SPE of metals [17].

Porous monoliths are currently attracting much attention for offline and online SPE, as denoted by several reviews [15,18–20]. The high permeability of monolithic columns is largely exploited to speed up extractions and separations in high-pressure liquid chromatographs. Conversely, this high permeability is yet underexplored in low-to-moderate-pressure systems used in flow injection or sequential injection analysis (SIA) [21]. Sequential injection analyzers are flexible instruments to perform chemical derivatization, in-line dilution, pre-concentration, matrix exchange, chromatographic separations, etc. [22–25]. SPE of metals in SIA has exploited both fixed solid reactors and bead injection (BI) strategy in a lab-on-valve (LOV) system [26–29]. Backpressure has not been reported to be an impediment, but the swelling of polymer particles upon changes in pH may cause significant variations of the bed volume of the short columns used [30].

In the present work, we demonstrate for the first time that the generic monolithic columns formed by copolymerization of GMA with ethylene glycol dimethacrylate (EDMA) can be tuned to work in SI analyzers. A commercial SI system coupled to a chelating column performed automated online extraction of potentially toxic metals from water samples using stripping chronopotentiometric detection. This is an original approach exploiting two steps of analyte enrichment/matrix exchange, based on a first step of selective on-column complexation, followed by elution and electrodeposition of the analytes on a working electrode.

## 2. Experimental

### 2.1. Chemicals and reagents

Glycidyl methacrylate (GMA) and ethylene dimethacrylate (EDMA) were purchased from Sigma-Aldrich (St. Louis, MO, USA), and purified on an aluminum oxide column to remove polymerization inhibitors. Azobisisobutyronitrile (AIBN), 3-(trimethoxysilyl)

propyl methacrylate, 1-propanol, 1,4-butanediol, iminodiacetic acid (IDA), 2-(*N*-morpholino) ethanesulfonic acid (MES) were obtained from Sigma-Aldrich and used as received. Standard solutions of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  were prepared at different concentrations by appropriate dilution of the respective 1000 mg L<sup>-1</sup> atomic absorption standards purchased from Merck (Rio de Janeiro, Brazil). Working solutions were prepared in 0.050 mol L<sup>-1</sup> MES buffer (pH = 6.0) and 0.010 mol L<sup>-1</sup> NaCl. Nitric acid at a concentration of 0.50 mol L<sup>-1</sup> was prepared by dilution of the concentrated analytical grade HNO<sub>3</sub> (65 vol %) in 0.10 mol L<sup>-1</sup> NaCl, both from Merck, and used as eluent solution. Reconditioning solution was composed of 0.010 mol L<sup>-1</sup> NH<sub>4</sub>OH/NH<sub>4</sub>Cl (pH = 10) from Merck. All the solutions were prepared in deionized water with resistivity >18.2 MΩ cm from a Simplicity 185 system from Millipore (Billerica, MA, USA).

## 2.2. Apparatus

Sequential injection experiments were made in a FIALab 3200 instrument (FIALab Instruments, Seattle, WA, USA) equipped with two syringe pumps (SP<sub>1</sub> and SP<sub>2</sub>) and their respective 3-way solenoid valves (SV<sub>1</sub> and SV<sub>2</sub>, Figure 1). Syringe pump 1 (capacity of 2.50 mL) was connected to the 8-port rotary selection valve (RV) through a 780 μL holding coil (HC). Syringe pump 2 (1.0 mL) was connected directly to the six-port 2-way injection valve (IV) where the SPE monolithic column was installed. The maximum pressure handled by the selection and injection valves was 250 psi, but the limiting pressure components were the syringe pumps, which could usually support pressures of up to 50 psi. Connections between the solutions and flow cell and the RV were made of 0.5 mm i.d. PTFE tubing and PTFE nuts and ferrules (Upchurch, Oak Harbor, WA). Fused silica-lined stainless-steel tubing of 3.18 mm o.d. and 2.1 mm i.d. were purchased from Sigma-Aldrich and used as support for the monolithic polymers.

Connections between the column tube and the flow system were made with P-702 PEEK unions, XP-335 PEEK nuts, and P-300 ETFE ferrules from IDEX Health and Science (Oak Harbor, WA, USA). A syringe infusion pump (KD Scientific, New Hope, PA, USA) was used to pump IDA solution through the poly(GMA-*co*-EDMA) monolith.

Electrochemical measurements were made with a PalmSens potentiostat (Palm Instrument BV, Houten, The Netherlands) using PSTrace 2.4 software for instrument control and data acquisition. The electrochemical flow cell was assembled with “University of Florence” Screen-Printed Sensors, consisting of a Hg-film working electrode (area 7.06 mm<sup>2</sup>), a Ag pseudo-reference and a graphite counter electrode [31]. Spectrophotometric measurements were carried out with a USB 4000 spectrophotometer (Ocean Optics, Dunedin, FL, USA) fitted out to a 1-cm optical-path SMA-Z-10  $\mu$ vol PEEK flow-through cell (6  $\mu$ L internal volume) from FIALab (FIALab Instruments) and an LS-1-LL tungsten halogen lamp from Ocean Optics. Two 600- $\mu$ m diameter UV/vis optical fibers (20 inches long) were used to transmit radiation from the source to the flow cell and to the spectrometer. Scanning electron microscopy (SEM) was performed with a Fesem Jeol JSM-7401F instrument (Jeol Ltd, Tokyo, Japan).

### 2.3. Procedures

#### 2.3.1. Synthesis of poly(GMA-*co*-EDMA)-IDA

Preparation of the surface-vinylized fused silica-lined tubes used to support the monoliths is described elsewhere [32–34]. The porous monolith was prepared from a mixture of 300 mg GMA, 100 mg EDMA, 350 mg 1-propanol, 200 mg 1,4-butanediol, 50 mg water and 4.0 mg AIBN (1 wt % in relation to the monomers) weighed in an

amber vial [35]. The vial was closed, and the solution was vortex mixed for 1 min, sonicated for 10 min and bubbled with N<sub>2</sub> for another 10 min. Then, the septum was perforated by one end of the column tube, which was then immersed in the reaction mixture. The opposite end was fitted to a 1.0 mL polypropylene syringe using a piece of Pharmed® tubing. Part of the reaction mixture was carefully aspirated inside the syringe after filling the column tube. The vial was closed, keeping one end of the column tube immersed in the remaining reaction mixture [34]. The system was heated at 60 °C for 24 h inside the oven of a gas chromatograph for the free-radical thermally initiated polymerization. After that, the column was washed with acetonitrile for 1 h at 500  $\mu\text{L min}^{-1}$  to remove the porogenic solvents and unreacted monomers, using an HPLC pump. Finally, the column was washed with deionized water for a further 1 h to remove the excess acetonitrile. The functionalization solution was prepared from 5 g iminodiacetic acid, 1 g NaCl, and 10.6 g Na<sub>2</sub>CO<sub>3</sub> dissolved in about 30 mL deionized water, adjusting the pH to 10.5 with NaOH. Then, the mixture was diluted to 50.0 mL with deionized water. Using an infusion pump, 9.50 mL of the IDA solution was pumped at 6.6  $\mu\text{L min}^{-1}$  for 24 h through the poly(GMA-co-EDMA) column immersed in a water bath at 80 °C [34,36,37]. Finally, the column was washed with deionized water to remove the excess IDA.

### 2.3.2. Sequential injection procedure for solid-phase extraction

The procedure is based on the instrumental scheme shown in Fig 1. While the SIA performed sample loading and column washing, the potentiostat applied a conditioning potential of  $-0.2\text{ V}$  vs. Ag/AgCl pseudo-reference. First, 1000  $\mu\text{L}$  of B1 was aspirated inside SP1 (SV1 In). Meanwhile, SP2 aspirated 300  $\mu\text{L}$  of eluent solution (E). When SP1 had finished aspiration, RV commuted to port 5 and SP1 (SV1 out) aspirated

750  $\mu\text{L}$  of sample into the HC at  $100 \mu\text{L s}^{-1}$ . After this, the RV commuted to port 2 and the sample was injected through the column at  $10 \mu\text{L s}^{-1}$  via ports 6–1 of the IV (position shown in Fig 1). This step was repeated, totaling 1500  $\mu\text{L}$  of sample. After the end of the second cycle of sample loading, the contents of B1 inside SP1 was emptied through the monolithic column (MC), thus removing the non-retained sample components, clearing the column of matrix substances. Then, the potentiostat applied the deposition potential of  $-1.0 \text{ V}$  (45 s) and the IV commuted to the injection position, placing SP<sub>2</sub> in line with the MC through ports 3–4. The eluent solution was delivered through the MC ( $10 \mu\text{L s}^{-1}$ ) to the electrochemical flow cell (EFC), eluting the adsorbed analytes and carrying them to be electrochemically deposited on the working electrode. At the end of this step, the deposited metals were re-oxidized by a current of  $2 \mu\text{A}$  until the potential on the working electrode changed from  $-1.0$  to  $-0.1 \text{ V}$ . While the re-oxidation was running, SP1 aspirated sequentially 500  $\mu\text{L}$  of B1 (SV1 In) and 500  $\mu\text{L}$  of B2 (SV1 Out) into the HC through port 4 of the RV ( $100 \mu\text{L s}^{-1}$ ). After re-oxidation had finished, the IV switched back to the loading position, and SP1 was emptied at  $10 \mu\text{L s}^{-1}$  through port 2 of the RV, reconditioning the MC. Finally, the species that had just been oxidized were washed from the EFC. This was performed by keeping the potential of working electrode at  $-0.1 \text{ V}$  while SP2 injected 300  $\mu\text{L}$  of E, at  $100 \mu\text{L s}^{-1}$ , through ports 3–2 of the IV (Fig 1).

#### 2.4. Samples

Tap-water samples were collected at the campus of the University of São Paulo (USP), supplied by the Guarapiranga dam, and at Guarulhos city (São Paulo, Brazil), supplied by the Cantareira dam system. The water sample collected at the USP campus was analyzed before and after purification in a domestic filtration system. Another sample

was collected directly from a dam located in a forest reserve in Sumaré city (São Paulo, Brazil). This sample was filtered through a 0.45  $\mu\text{m}$  cellulose filter prior to analysis, whereas the other samples were analyzed directly.

### 3. Results and discussion

#### 3.1. Composition of the poly(GMA-co-EDMA) monolith

For use in non-chromatographic SI analyzers, the porous structure of monoliths has to enable flow rates compatible with pressures handled by the glass syringe pumps typically used in automatic burettes (50–80 psi). The monolith should have high permeability and high extraction capacity. However, these two features conflict with each other because high extraction capacity implies large surface areas, with small microglobules and mesopores, whereas high permeability requires mainly large flow-through pores [38,39]. In the present work, the permeability was investigated by varying the percentages of crosslinker (EDMA), functional monomer (GMA) and the percentages and type of porogenic solvents in the reaction mixture (Table 1). The permeability of each column (Table 1) was computed according to the Darcy Law:

$$K_0 = \frac{L\eta\mu_s}{\Delta_p} \quad (1)$$

where  $K_0$  is the permeability in  $\text{m}^2$ ,  $L$  is the length of the column in m,  $\eta$  is the viscosity of the mobile phase (acetonitrile) in cp ( $1 \times 10^{-3} \text{ N m}^{-2} \text{ s}^{-1}$ ),  $\mu_s$  is the linear flow velocity ( $\text{m s}^{-1}$ ) and  $\Delta_p$  is the backpressure ( $\text{N m}^{-2}$ ) (measured at flow rate of  $500 \mu\text{L min}^{-1}$ ).

Monoliths 1 and 4 (Table 1) were not permeable and were no longer considered for the use in SIA. The permeability of monolith 2 was compatible with HPLC pumps

(500  $\mu\text{L min}^{-1}$ ), but not with the syringe pump of the SI analyzer. Monolith 3 exhibited a pressure that could be handled at a very low flow rate, making the analysis time too long, and so implying reduced sampling throughput. Aiming to increase the permeability of monolith 3, we tried to increase the size of the flow-through pores by increasing the percentage of porogenic solvents from 70 to 80 wt %, keeping the same GMA to EDMA ratio. However, this high proportion of porogens produced a monolith with poor mechanical stability, which collapsed under the flow of acetonitrile, thus blocking the flow-through pores.

Pore size distribution is affected by the solubility of the polymer in the porogenic solvents. If the porogens are bad solvents for the polymer, the phase separation of the formed polymer nuclei from dissolved monomers occurs in the early stages of polymerization. The nuclei become better solvents for the monomers than are the porogenic solvents. Consequently, the monomers dissolve preferably in these nuclei and not in the original solvent. As the polymerization and crosslinking proceeds in these swollen nuclei, larger clusters of globules and flow-through pores are formed, increasing the permeability [40]. The porogenic solvents used to synthesize monolith 5 differed from the others because they form a tertiary system containing water. As water is a very poor solvent for the polymer and monomers, early phase separation occurs, thus producing large flow-through pores, which explain the low backpressure of monolith 5 [41]. Thus, monolith 5 was chosen for development of the method.

### 3.2. Scanning electron microscopy (SEM) characterization

Figures 2a and 2b reveal that the monolith was firmly attached to the fused silica surface, with no voids between the polymer and the tube wall. The globules of poly(GMA-co-EDMA) were estimated at around 0.35–0.80  $\mu\text{m}$ , with regular spherical shape, arranged in clusters sized between 1 and 2  $\mu\text{m}$  (Fig 2d), and separated by large

flow-through pores with dimensions of about 2 to 5  $\mu\text{m}$  (Fig 2c), which were responsible for the low flow resistance of the columns.

### 3.3. Adsorption capacity

After conditioning the column with 0.010 mol L<sup>-1</sup> NH<sub>4</sub>OH/NH<sub>4</sub>Cl (pH = 10) and removing the excess of buffer with deionized water, a 20 mmol L<sup>-1</sup> Cu<sup>2+</sup> solution was pumped at 150  $\mu\text{L min}^{-1}$  using an infusion pump, while the spectrophotometer monitored the absorbance at 790 nm at the column end. The breakthrough volume was assumed at an absorbance corresponding to 1% of the signal measured at the stationary state (Figure 3) [42]. The adsorption capacity of the columns was  $4.4 \pm 0.3$  mg Cu(II) m<sup>-1</sup> (mean for three columns, implying an RSD of 6.8%), computed as:

$$q_e = \frac{(t_{BIDA} - t_0) \times Q \times c_{Cu(II)} \times 63.54}{L \times (1 \times 10^6)} \quad (2)$$

where  $q_e$  is the adsorption capacity (g m<sup>-1</sup>), and  $t_{B-IDA}$  and  $t_0$  are the times corresponding to breakthrough and dead volumes, respectively.  $Q$  is the flow rate ( $\mu\text{L s}^{-1}$ ),  $c_{Cu(II)}$  is the analytical concentration of Cu<sup>2+</sup> (mol L<sup>-1</sup>), 63.54 is the atomic mass of copper and  $L$  is the length of the column (m).

The adsorption capacity for Cu<sup>2+</sup> is significantly higher than that described for some other monolithic columns coupled online to analyzers [18]. For instance, adsorption capacities of 43.2 and 82.5  $\mu\text{g m}^{-1}$  were reported for EDA-modified poly(GMA-co-EDMA) [43] and hybrid APTES-silica columns [44], respectively. In these works, the monoliths were prepared inside 530  $\mu\text{m}$  i.d. fused silica capillaries from mixtures containing 25 wt % of monomers [43] or 52 vol % silica precursors [44]. Assuming that the conversion of monomers/precursors into monoliths was 100%, and

that the monolith density is  $1 \text{ g cm}^{-3}$ , adsorption capacities of  $0.78$  and  $0.72 \text{ mg g}^{-1}$  were estimated for the poly(GMA-co-EDMA)-EDA [43] and APTES-silica [44] columns, respectively. Making similar assumptions, the adsorption capacity of our column was  $3.5 \text{ mg g}^{-1}$ . This adsorption capacity is comparable to that of poly(GMA-co-EDMA)-IDA prepared in syringe filter tips ( $5 \text{ mg g}^{-1}$ ) [37]. However, the capacity of our column was significantly lower than that described by Wang et al. [17] for poly(GMA-co-EDMA) columns obtained by photo-polymerization and modified with EDA in polypropylene syringes for offline SPE ( $70 \text{ mg g}^{-1}$ ).

The low adsorption capacity of the column is related to the low degree of incorporation of IDA. Elemental analysis revealed incorporation of only  $0.095 \pm 0.005 \text{ wt \%}$  of N. In an ongoing work in our laboratory, a similar generic poly(GMA-co-EDMA) column was modified with EDA following the procedure described by Wang et al. [17], resulting in an incorporation of  $5.72 \text{ wt \%}$  of N. The breakthrough curve of this poly(GMA-co-EDMA)-EDA (Fig 1S) column resulted in an adsorption capacity of  $41 \text{ mg g}^{-1}$  ( $52.5 \text{ mg m}^{-1}$ ), which is about 10-fold higher than that of the IDA column. Despite the high adsorption capacity of the EDA-modified column, we developed the method with the poly(GMA-co-EDMA)-IDA column because of the widespread use of this chelating functionality in SPE materials for determination of metals. To the best of our knowledge, neither IDA- nor EDA-modified poly(GMA-co-EDMA) monoliths have previously been used in SI analyzers for online extraction of metals.

After saturating the column with  $\text{Cu}^{2+}$ , the excess metal was flushed through with deionized water, followed by elution with  $0.50 \text{ mol L}^{-1} \text{ HNO}_3$  (Fig 3). The retention and elution of  $\text{Cu}^{2+}$  from the poly(GMA-co-EDMA)-IDA column can be clearly observed in comparison with the non-modified column (Fig 3). Acidification of the non-modified poly(GMA-co-EDMA) column does not show the transient peak

corresponding to the elution of  $\text{Cu}^{2+}$ , confirming that  $\text{Cu}^{2+}$  was not retained. For the poly(GMA-co-EDMA)-IDA column, a high transient absorbance peak was observed upon acidification, indicating that  $\text{Cu}^{2+}$  was retained from the neutral solution, and released after acidification with  $0.50 \text{ mol L}^{-1} \text{HNO}_3$ .

### *3.4. Method development*

First, the influence of the sample volume, as well as the composition and volume of the eluent solution, on the analytical signal of a  $100 \text{ } \mu\text{g L}^{-1} \text{Cd}^{2+}$  solution were systematically investigated. The flow rate was fixed at  $10 \text{ } \mu\text{L s}^{-1}$  due to the pressure limitations of the SI analyzer.

#### *3.4.1. Sample volume*

The sample volume affects the amount of metal retained in the column and deposited downstream on the working electrode. Large sample volumes increase the analytical signal, as observed in Figure 4. The sample volume of  $2000 \text{ } \mu\text{L}$  produced a shoulder in the chronopotentiogram at more negative potentials, suggesting saturation of the thin mercury film electrode. Thus,  $1500 \text{ } \mu\text{L}$  was the sample volume chosen because the sampling throughput was at the reasonable value of 6.8 analyses per hour and the amount of metal deposited did not saturate the working electrode during the deposition step.

#### *3.4.2. Eluent composition, volume and concentration*

A constant  $\text{Cl}^-$  concentration is necessary in the eluting solution to keep constant the potential of the Ag/AgCl pseudo-reference during the deposition and stripping steps [31]. Elution with 0.50 or 1.0 mol  $\text{L}^{-1}$  HCl did not affect the charge related to the stripping, indicating that 0.50 mol  $\text{L}^{-1}$  contained a high enough  $[\text{H}^+]$  to protonate the complexing sites of IDA, thus releasing the metals. The increase in HCl concentration from 0.50 to 1.0 mol  $\text{L}^{-1}$  moved the stripping peaks to less negative potentials because of the greater proportions of chloro-complexes. To minimize the influence of these chloro-complexes on the stripping potential, the eluting solution was composed of 0.50 mol  $\text{L}^{-1}$   $\text{HNO}_3$  in 0.10 mol  $\text{L}^{-1}$  NaCl. The volume of this solution was varied from 200 to 400  $\mu\text{L}$  and, at the eluent volume of 300  $\mu\text{L}$ , the analytical signal approached a stationary value for both 5 and 25  $\mu\text{g L}^{-1}$   $\text{Cd}^{2+}$  standard solutions (Figure 5). Elution volumes larger than 400  $\mu\text{L}$  decreased the charge for both the 5 and 25  $\mu\text{g L}^{-1}$   $\text{Cd}^{2+}$  solutions, a fact that may be explained by the leaching of the deposited metals by the flow of the eluting solution through the electrochemical cell. As the solution used for elution was not degassed, dissolved  $\text{O}_2$  may have caused some oxidation of deposited metals, especially at higher concentrations of metals.

### 3.5. Figures of merit

Using the parameters defined in the method development, calibration curves were constructed for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  separated in individual solutions (Table 2). The calibration curves exhibited satisfactory linearity ( $r^2 > 0.98$ ) (Figure 2S) from 5 to 100  $\mu\text{g L}^{-1}$ . The limits of detection (LOD) and quantification (LOQ) were computed as  $\text{LOD} = 3 S_d/m$  and  $\text{LOQ} = 10 S_d/m$ , where  $m$  is the slope of the calibration curve and  $S_d$  is the standard deviation of nine replicates of the 10  $\mu\text{g L}^{-1}$  solution. The LOD for the three metals was lower than the maximum concentration levels (MCL) established by the

United States Environmental Protection Agency (USEPA) [45] for tap and drinking waters. The MCL for  $\text{Cd}^{2+}$  is  $5 \mu\text{g L}^{-1}$ , which corresponds to the first point of our calibration curves, and thus is within the linear calibration range. The LOQ of  $2.2 \mu\text{g L}^{-1}$  for  $\text{Pb}^{2+}$  is suitable for monitoring the quality of tap water because the action level established by USEPA for this metal is  $15 \mu\text{g L}^{-1}$  [45]. For  $\text{Cu}^{2+}$  the LOQ of  $1.7 \mu\text{g L}^{-1}$  by the proposed method is significantly lower than the MCL of  $1300 \mu\text{g L}^{-1}$  [45].

Repeatability of measurements was evaluated from the RSD of charge values obtained from nine measurements of a  $10 \mu\text{g L}^{-1}$  solution containing a mixture of the three metals. The values of RSD were 7.4%, 5.7% and 4.7% for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , respectively. This sequence of measurements (Figure 3S) demonstrated the absence of memory effects, and so was the appropriate procedure to be used for eluting and reconditioning the column.

### 3.6. Interferences

To investigate the potential interference from ions commonly found in water, a  $5 \mu\text{g L}^{-1}$   $\text{Cd}^{2+}$  solution was prepared in the presence of these ions and the charge signal was compared with that of the pure  $\text{Cd}^{2+}$  solution. The concentration of some of these ions was chosen on the basis of the MCL for “Class 3” waters, defined by the Brazilian Council for the Environment (CONAMA) [46] as the class of waters that can be used for human consumption after conventional or advanced treatment [46]. Table 3 shows that the interference from all cations was below 10%. Positive interference of  $\text{Cl}^{-}$  was observed as its concentration increased from  $12.5$  to  $250 \text{ mg L}^{-1}$ , suggesting that the complexing column retained the chloro complexes of  $\text{Cd}^{2+}$  more efficiently than their aquo complexes. Thus, it is crucial to keep the chloride concentration constant

throughout the analysis by conditioning the sample and standard solutions with 0.01 mol L<sup>-1</sup> MES buffer (pH 6.0) in 0.10 mol L<sup>-1</sup> NaCl. Another positive interference was for fulvic acid, which also forms weak complexes with Cd<sup>2+</sup>. One can speculate that these complexes access more efficiently the IDA sites in the porous structure of the column than does hydrated Cd<sup>2+</sup>. On the other hand, the signal for Cd<sup>2+</sup> in the presence of humic acid was smaller than the RSD of the measurements at the studied concentration level, indicating that the possible interference caused by the formation of slow-diffusing complexes was circumvented by the extraction and matrix exchange promoted by the poly(GMA-co-EDMA)-IDA column.

### 3.7. Simultaneous determination of Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup>

The low level of interference of Cu<sup>2+</sup> (+2.3%) and Pb<sup>2+</sup> (+3.2%) on the Cd<sup>2+</sup> signal suggested that the method would be able to perform simultaneous determination of these metals. Interference in doing so would be caused either by preferential complexation of one metal in the column, or by incomplete elution [47]. To investigate the simultaneous determination of the three metals, calibration curves were constructed in the range of 5 to 100 µg L<sup>-1</sup> for the three metals mixed in the same solution (Figure 6). The slope and intercept do not differ significantly from those for the metals in individual solutions (Tables 2 and 4, Fig 2S), thus indicating that at low concentrations the calibration curves for each metal is independent of the other two. The LOD and LOQ did not differ significantly from those obtained with the individual solutions (Table 4), and the chronopotentiograms of 0.50 to 2.0 µg L<sup>-1</sup> solutions (Figure 4S) confirm the realistic values obtained from the statistical computation based on the standard deviation of peak areas of the 10 µg L<sup>-1</sup> and the slope of the calibration curve.

### 3.8. Applications

The method was applied to tap, filtered and fresh water samples (Figure 7). Copper was found at high concentration in the tap water collected at the university (Table 5). This finding was expected because  $\text{CuSO}_4$  is often used for control of algal blooms in the water reservoir that supplies the district where the university is located [48], confirming the results obtained previously by square-wave stripping voltammetry [49]. Our results have demonstrated that the municipal water treatment system is not able to remove  $\text{Cu}^{2+}$  completely from the tap water from the Guarapiranga dam. After conventional purification in domestic active-charcoal carbon filters the concentration of  $\text{Cu}^{2+}$  dropped down to values below the LOD of the method. The water supplied by the Cantareira system (Guarulhos) is less liable to algal bloom, thus resulting in lower concentrations of  $\text{Cu}^{2+}$  (Table 5). The dam water from the Sumaré municipality did not exhibit detectable concentrations of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  or quantifiable concentrations of  $\text{Cu}^{2+}$  (Figure 7). The accuracy of the method was evaluated by spiking the samples with CONAMA “Class 3” MCL concentrations of the metals ( $10 \mu\text{g L}^{-1}$  of  $\text{Cd}^{2+}$ ,  $33 \mu\text{g L}^{-1}$  of  $\text{Pb}^{2+}$  and  $13 \mu\text{g L}^{-1}$  of  $\text{Cu}^{2+}$ ). The concentrations were computed by external calibration curves obtained with the same screen-printed sensor. Recoveries between 75.5 and 117.3% were found, indicating that the proposed method provide accurate results in water matrixes of different origins.

## 4. Conclusion

We demonstrated that monolithic columns based on poly(GMA-co-EDMA) can be designed for online SPE of metals using a low-pressure SI analyzer assembled with two conventional syringe pumps, one selection valve and one injection valve. This robust system automated all the SPE steps of column loading, washing, elution and

reconditioning. The use of a monolith for SPE circumvented the difficulties in obtaining a dense and stable packing of small particles inside short columns. The rigid structure of the monolith minimizes variations of bed volumes that are reported for columns filled with IDA-modified polymer particles upon changes in pH.

Despite the low capacity of the prepared column, which prioritized permeability over the density of complexing sites, analytical curves prepared using individual or mixed metals gave similar slopes, indicating that there was no competition between the analytes for the binding sites of the column. Additionally, the proposed method has potential application to automate molecular absorption or flame atomic absorption spectrometry measurements, usually less sensitive than stripping chronopotentiometric detection.

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**Figure 1.** Sequential injection analyzer for online SPE. B1 = 0.050 mol L<sup>-1</sup> MES (pH 6.0) in 0.010 mol L<sup>-1</sup> NaCl; B2 = 0.010 mol L<sup>-1</sup> NH<sub>4</sub>OH/NH<sub>4</sub>Cl (pH = 10); E = 0.50 mol L<sup>-1</sup> HNO<sub>3</sub> in 0.10 mol L<sup>-1</sup> NaCl; S = sample or standard; SP<sub>1</sub> and SP<sub>2</sub> = syringe pumps 1 (2.50 mL) and 2 (1.0 mL); SV<sub>1</sub> and SV<sub>2</sub> = 3-way solenoid valves, position In and Out; RV = 8-port rotary selection valve in the sampling position; HC = 780 µL holding coil; IV = 6-port, 2-way, injection valve in the loading position (injection is made by valve rotation, so that ports 3 and 4, 1 and 2, and 5 and 6 are internally connected); MC = monolithic column; EFC = electrochemical flow cell; POT = potentiostat; W = waste. Solid lines represent external connections of SV, RV and IV, whereas broken lines represent the internal connections.

**Figure 2.** SEM images of poly(GMA-co-EDMA) monolith 5. (a) 50× magnification of the top head of the column; (b) 250× magnification of the interface between monolith and inner tube wall; (c) 2000× magnification of the bulk of the poly(GMA-co-EDMA) with measurements the size of some flow-through pores; (d) 10,000× magnification of the bulk of the GMA-co-EDMA polymer with measurements of the size of some globules and clusters.

**Figure 3.** Breakthrough (a and c) and elution curves (b and d) in poly(GMA-co-EDMA) (a and b) and poly(GMA-co-EDMA)-IDA (c and d) columns. Breakthrough curves were obtained for a 0.020 mol L<sup>-1</sup> CuSO<sub>4</sub> solution in water. After saturation of the complexing sites, the columns were washed with deionized water and then the retained Cu<sup>2+</sup> was eluted with 1.0 mol L<sup>-1</sup> HNO<sub>3</sub>. After elution, the columns were reconditioned in 0.010 mol L<sup>-1</sup> NH<sub>4</sub>OH/NH<sub>4</sub>Cl (pH = 10) and washed with water. Flow rate = 2.5 µL s<sup>-1</sup>. Monitoring wavelength = 790 nm.

**Figure 4.** Influence of the sample volume on the charge obtained for a 100 µg L<sup>-1</sup> Cd<sup>2+</sup> solution: (a) 250, (b) 500, (c) 750, (d) 1000, (e) 1250, (f) 1500 and (g) 2000 µL.

Experimental conditions: eluent solution = 500  $\mu\text{L}$  of 0.50  $\text{mol L}^{-1}$   $\text{HNO}_3$  in 0.10  $\text{mol L}^{-1}$   $\text{NaCl}$ ; flow rate = 10  $\mu\text{L s}^{-1}$ ; deposition potential =  $-1.0$  V; end potential =  $-0.45$  V; oxidizing current = 2  $\mu\text{A}$

**Figure 5.** Charge as a function of the volume of eluent for  $\text{Cd}^{2+}$  solutions of different concentrations. Sample volume: 1500  $\mu\text{L}$ ; eluent solution: 0.50  $\text{mol L}^{-1}$   $\text{HNO}_3$  in 0.10  $\text{mol L}^{-1}$   $\text{NaCl}$ ; flow rate: 10  $\mu\text{L s}^{-1}$ ; deposition potential:  $-1.0$  V; end potential:  $-0.45$  V; oxidizing current: 2  $\mu\text{A}$

**Figure 6.** Blank subtracted chronopotentiograms for construction of a calibration curve from a mixture of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  at concentrations of (a) 5, (b) 10, (c) 20, (d) 40, (e) 60, (f) 80 and (g) 100  $\mu\text{g L}^{-1}$  prepared in 0.010  $\text{mol L}^{-1}$  MES buffer (pH 6.0) in 0.10  $\text{mol L}^{-1}$   $\text{NaCl}$ . Chronopotentiograms were obtained after loading 1500  $\mu\text{L}$  of solution on the poly(GMA-co-EDMA)-IDA column, and elution with 300  $\mu\text{L}$  of 0.50  $\text{mol L}^{-1}$   $\text{HNO}_3$  in 0.10  $\text{mol L}^{-1}$   $\text{NaCl}$  at flow rate of 10  $\mu\text{L s}^{-1}$ . Deposition potential:  $-1.0$  V, end potential:  $-0.1$  V, oxidizing current: 2  $\mu\text{A}$

**Figure 7.** Blank subtracted chronopotentiograms of (a) Tap water sample collected at the campus of the University of São Paulo (USP), (b) Drinking water obtained after filtration of the tap water from USP in a domestic activated-charcoal filter, (c) tap water collected at the municipality of Guarulhos, furnished by the Cantareira Dam, and (d) fresh water sample from a dam located in the municipality of Sumaré. All the samples were spiked with 10  $\mu\text{g L}^{-1}$  of  $\text{Cd}^{2+}$ , 33  $\mu\text{g L}^{-1}$  of  $\text{Pb}^{2+}$  and 13  $\mu\text{g L}^{-1}$  of  $\text{Cu}^{2+}$ . Experimental conditions described in the caption of Figure 6.

**Table 1.** Composition, backpressures and permeability of tested monoliths

| Monolith | Composition in wt % |      |      |      |                      |     |     |    |      | Permeability<br>( $10^{-14} \text{ m}^2$ ) | Ref  |
|----------|---------------------|------|------|------|----------------------|-----|-----|----|------|--------------------------------------------|------|
|          | GMA                 | EDMA | CH   | DOD  | $\text{H}_2\text{O}$ | TOL | PRO | BD |      |                                            |      |
| 1        | 22.5                | 7.5  | 28   | -    | -                    | 42  | -   | -  | -    |                                            | [37] |
| 2        | 18.75               | 6.25 | 6.8  | 68.2 | -                    | -   | -   | -  | 5.78 |                                            | [36] |
| 3        | 18                  | 12   | 23.3 | 46.7 | -                    | -   | -   | -  | 21.0 |                                            | [17] |
| 4        | 12                  | 8    | 26.7 | 53.3 | -                    | -   | -   | -  | -    |                                            | [17] |
| 5        | 30                  | 10   | -    | -    | 5                    | -   | 35  | 20 | 43.3 |                                            | [35] |

DOD = dodecanol, CH = cyclohexanol, TOL = toluene, PRO = n-propanol, BD = 1,4 butanediol

**Table 2.** Intercept, slope, linear correlation, limits of detection (LOD) and quantification (LOQ) for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  in individual solutions

| Metal Ion        | Intercept ( $\mu\text{C}$ ) | Slope/ $10^3$ ( $\mu\text{C L } \mu\text{g}^{-1}$ ) | $R^2$ | LOD ( $\mu\text{g L}^{-1}$ ) | LOQ ( $\mu\text{g L}^{-1}$ ) |
|------------------|-----------------------------|-----------------------------------------------------|-------|------------------------------|------------------------------|
| $\text{Cd}^{2+}$ | $0.01 \pm 0.03$             | $13.2 \pm 0.7$                                      | 0.99  | 1.0                          | 3.3                          |
| $\text{Pb}^{2+}$ | $0.006 \pm 0.03$            | $6.7 \pm 0.2$                                       | 0.99  | 0.7                          | 2.2                          |
| $\text{Cu}^{2+}$ | $-0.4 \pm 0.2$              | $84 \pm 4$                                          | 0.99  | 0.5                          | 1.8                          |

**Table 3.** Effect of potential interfering specie on the peak area of a  $5 \mu\text{g L}^{-1}$   $\text{Cd}^{2+}$  solution

| Interfering species | Concentration ( $\text{mg L}^{-1}$ ) | Deviation in Cd(II) peak area (%) |
|---------------------|--------------------------------------|-----------------------------------|
| $\text{Al}^{3+}$    | 0.2                                  | +8.5                              |
| $\text{Fe}^{3+}$    | 5                                    | +8.1                              |
| $\text{Mg}^{2+}$    | 120                                  | -0.3                              |
| $\text{Cu}^{2+}$    | 0.013                                | +2.3                              |
| $\text{Pb}^{2+}$    | 0.033                                | +3.2                              |
| $\text{Ca}^{2+}$    | 0.2                                  | +18                               |
| $\text{Cl}^-$       | 250                                  | +172                              |
| $\text{Cl}^-$       | 12.5                                 | -0.35                             |
| Fulvic acid         | 5                                    | +17                               |
| Humic acid          | 5                                    | +3.7                              |

**Table 4.** Intercept, slope, linear correlation, limits of detection (LOD) and quantification (LOQ) for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  mixed in the same solution

| Metal Ion        | Intercept ( $\mu\text{C}$ ) | Slope/ $10^3$ ( $\mu\text{C L } \mu\text{g}^{-1}$ ) | $R^2$ | LOD ( $\mu\text{g L}^{-1}$ ) | LOQ ( $\mu\text{g L}^{-1}$ ) |
|------------------|-----------------------------|-----------------------------------------------------|-------|------------------------------|------------------------------|
| $\text{Cd}^{2+}$ | $0.02 \pm 0.02$             | $12.1 \pm 0.3$                                      | 0.99  | 1.2                          | 3.8                          |
| $\text{Pb}^{2+}$ | $0.01 \pm 0.02$             | $5.5 \pm 0.5$                                       | 0.98  | 1.4                          | 4.7                          |
| $\text{Cu}^{2+}$ | $-0.1 \pm 0.2$              | $89 \pm 4$                                          | 0.99  | 0.51                         | 1.7                          |

**Table 5.** Concentrations found in water samples ( $n = 3$ ) and recovery of metals after spiking the samples with  $10 \mu\text{g L}^{-1}$  of  $\text{Cd}^{2+}$ ,  $33 \mu\text{g L}^{-1}$  of  $\text{Pb}^{2+}$  and  $13 \mu\text{g L}^{-1}$  of  $\text{Cu}^{2+}$

| Sample                                         | Cd(II) | Pb(II) | Cu(II)     |
|------------------------------------------------|--------|--------|------------|
| Tap water (USP) ( $\mu\text{g L}^{-1}$ )       | -      | -      | $95 \pm 4$ |
| Recovery (%)                                   | 94.4   | 98.0   | 104        |
| Tap water (Guarulhos) ( $\mu\text{g L}^{-1}$ ) | -      | -      | $16 \pm 2$ |
| Recovery (%)                                   | 82     | 87.5   | 117.3      |
| Filtered water (USP)                           | -      | -      | -          |
| Recovery (%)                                   | 89.6   | 97     | 75.5       |
| Dam water (Sumaré) ( $\mu\text{g L}^{-1}$ )    | -      | -      | -          |
| Recovery (%)                                   | 116.6  | 110.2  | 107.5      |

### Highlights

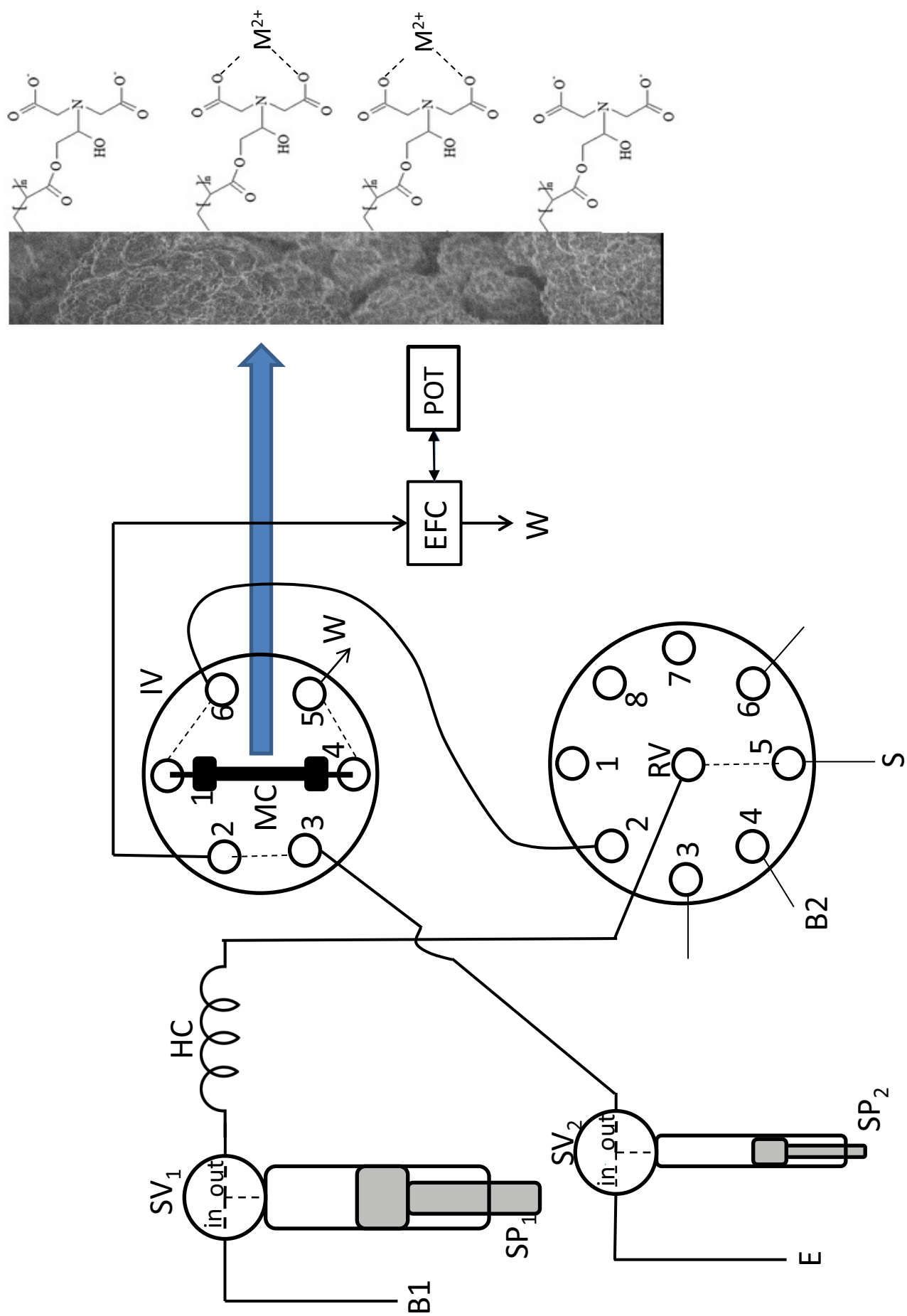
Automated solid phase extraction of metals from waters in monolithic columns

Porous monolith prepared with permeability suitable for sequential injection analyzes

Modification with iminodiacetate afforded the polymer with complexing groups

The column retained metals at pH 6.0 and released them upon acidification

Copper quantified in tap waters of the metropolitan area of São Paulo City



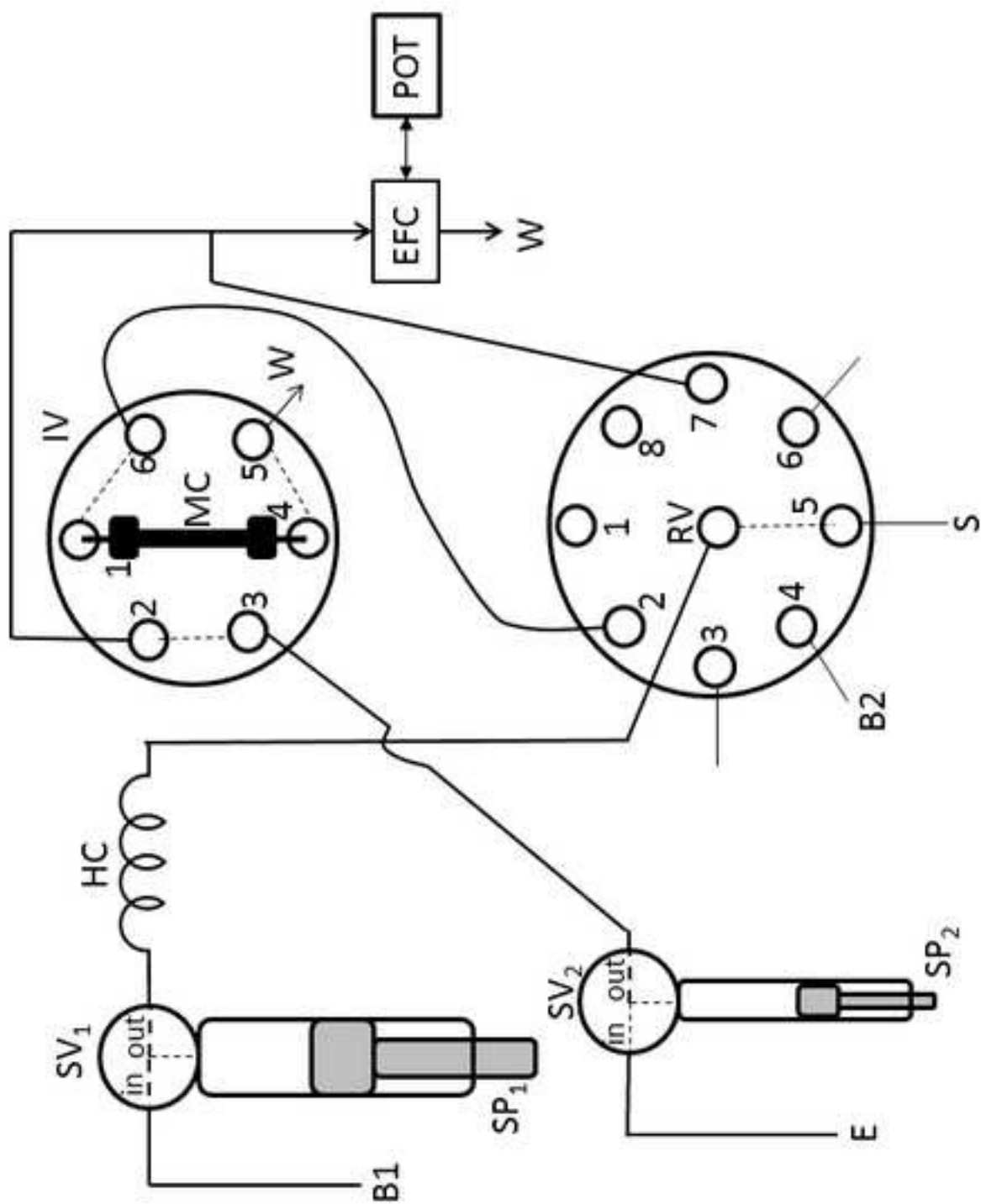


Figure 1

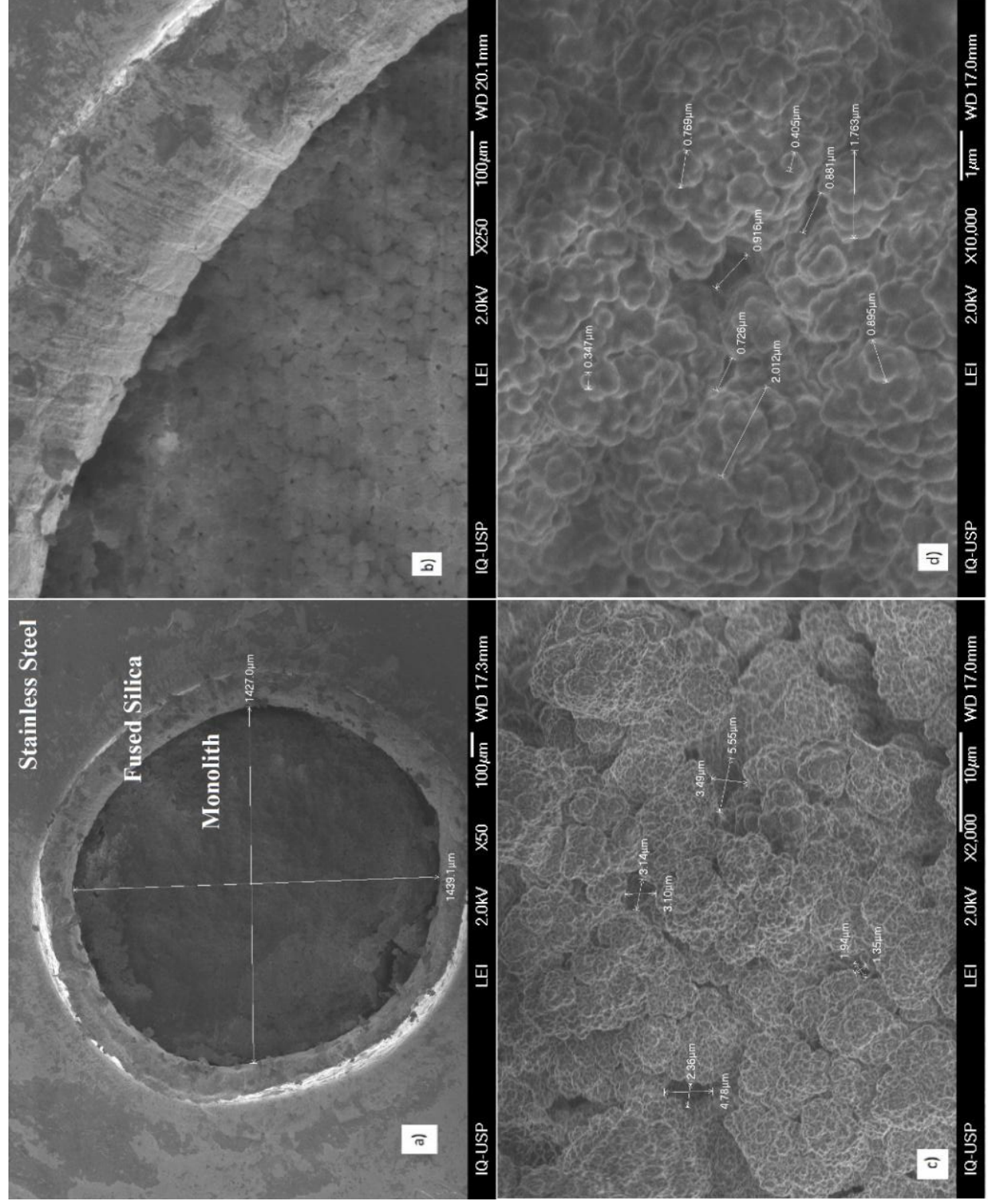
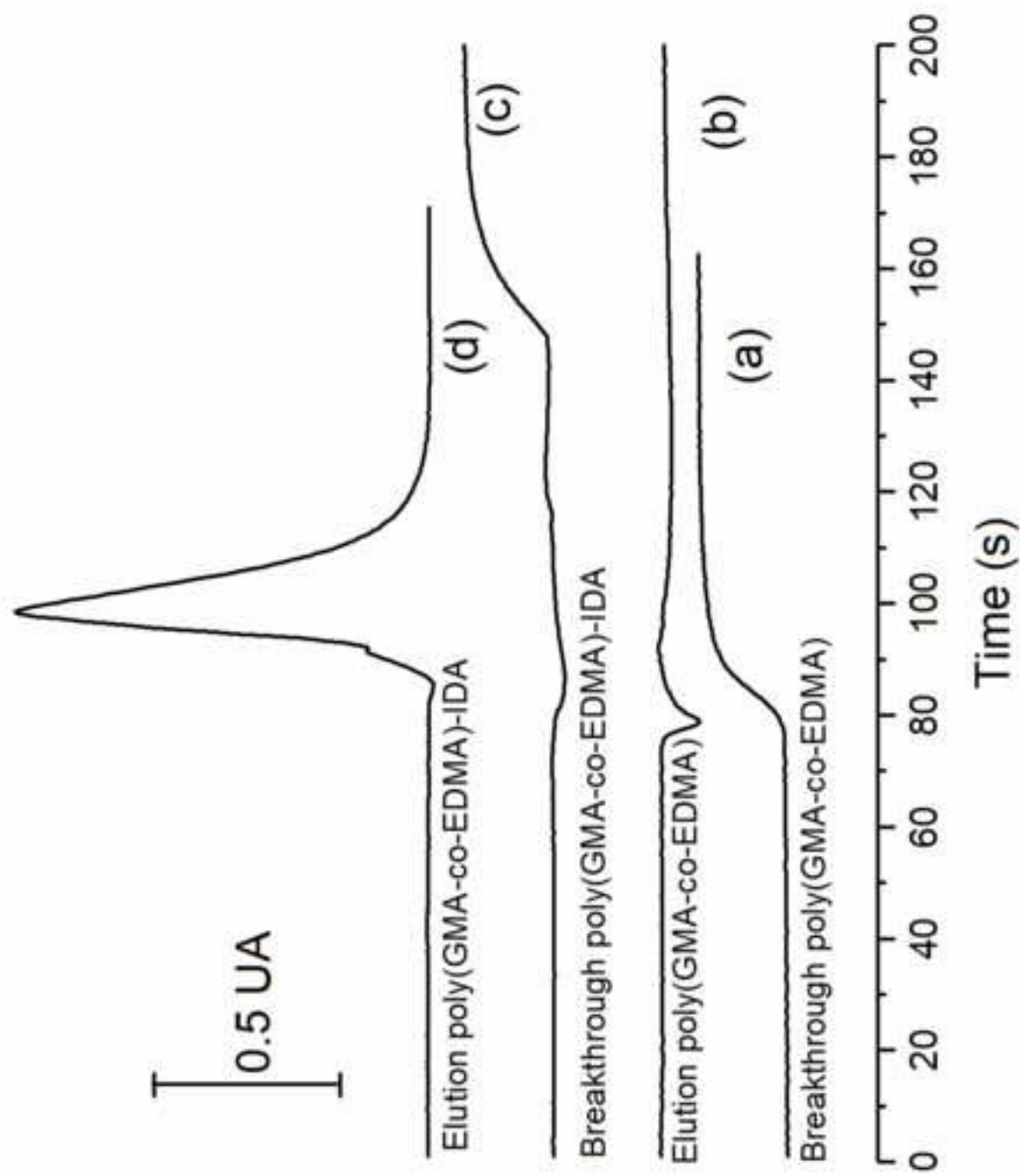


Figure 2



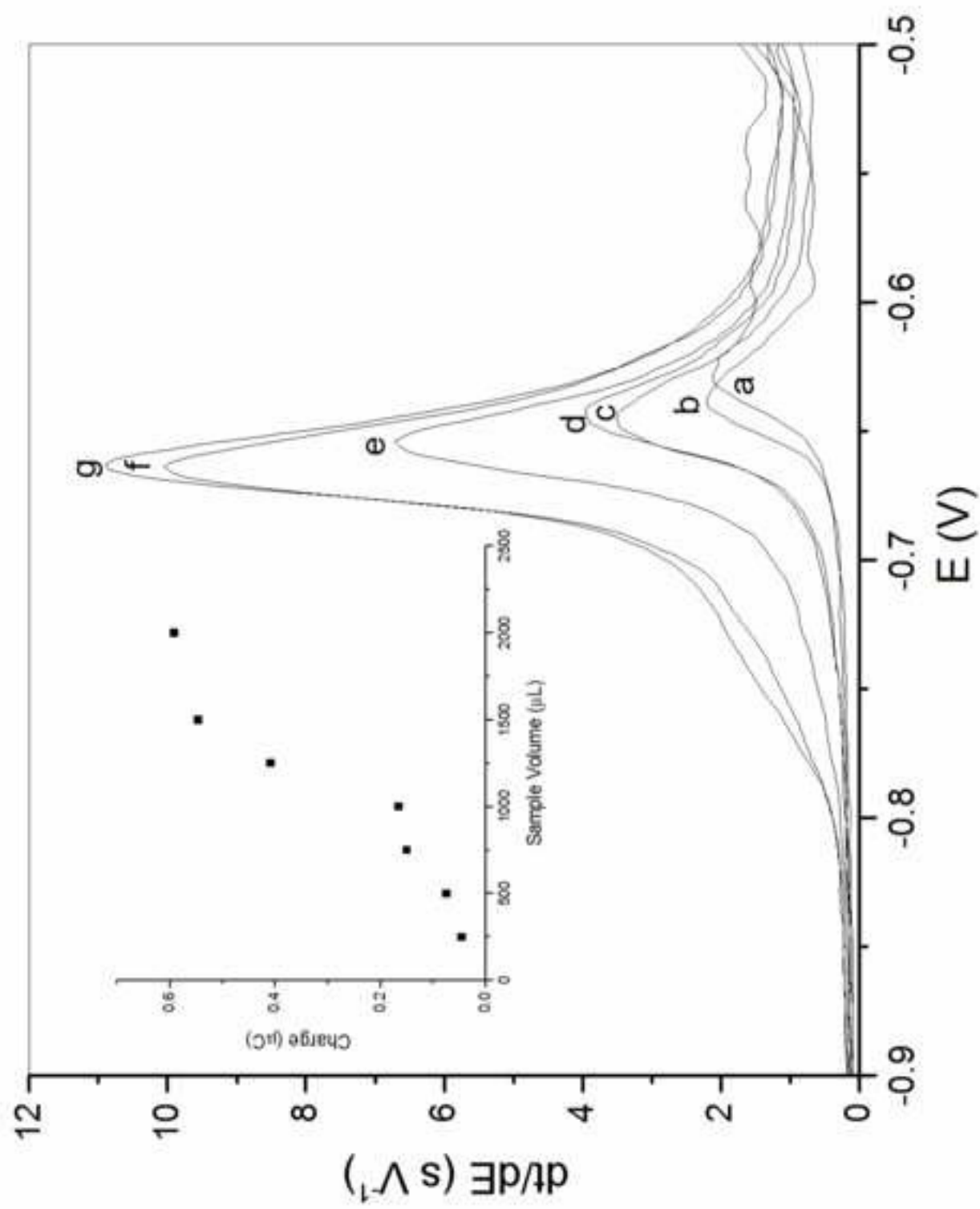


Figure 4

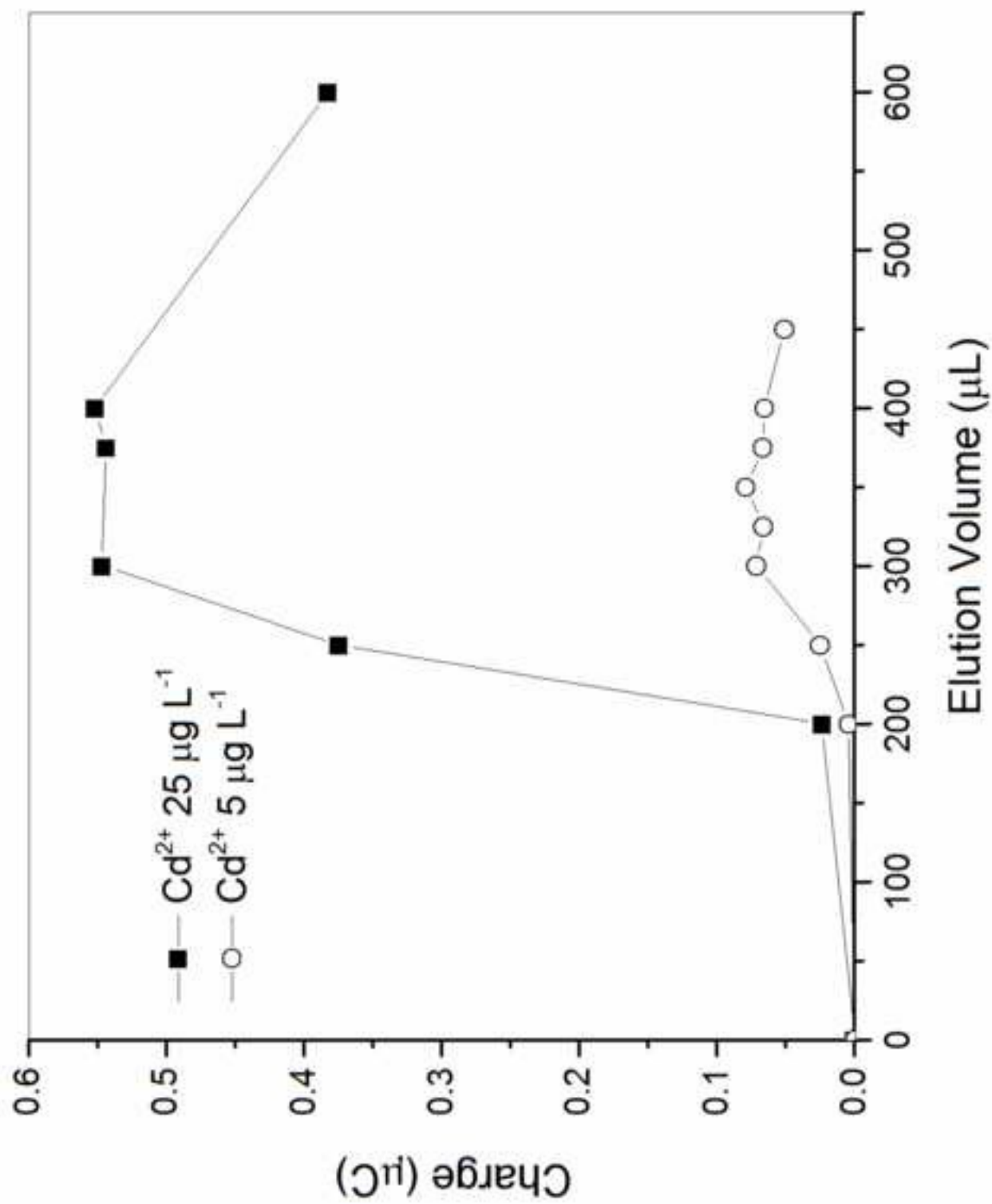


Figure 5

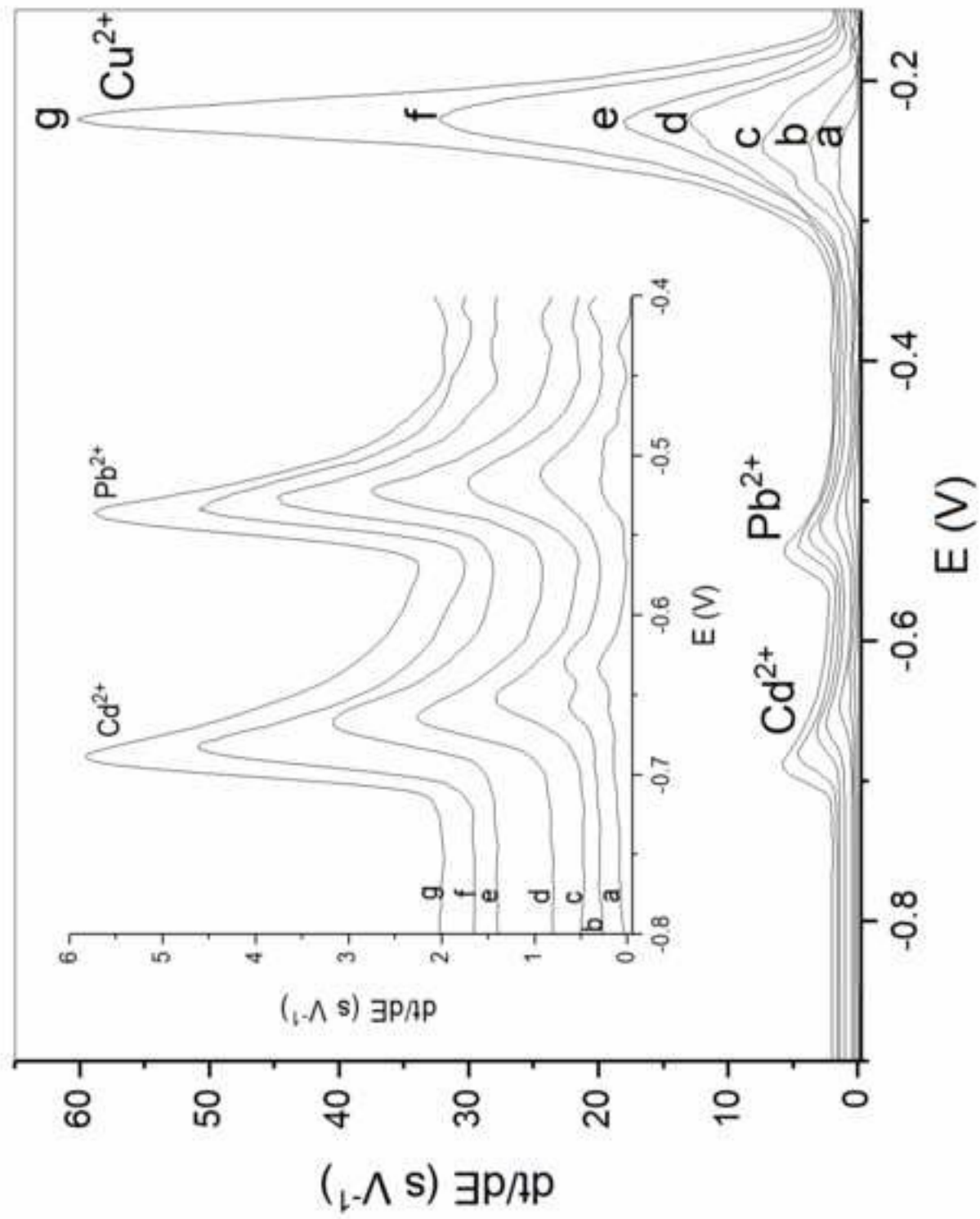


Figure 6

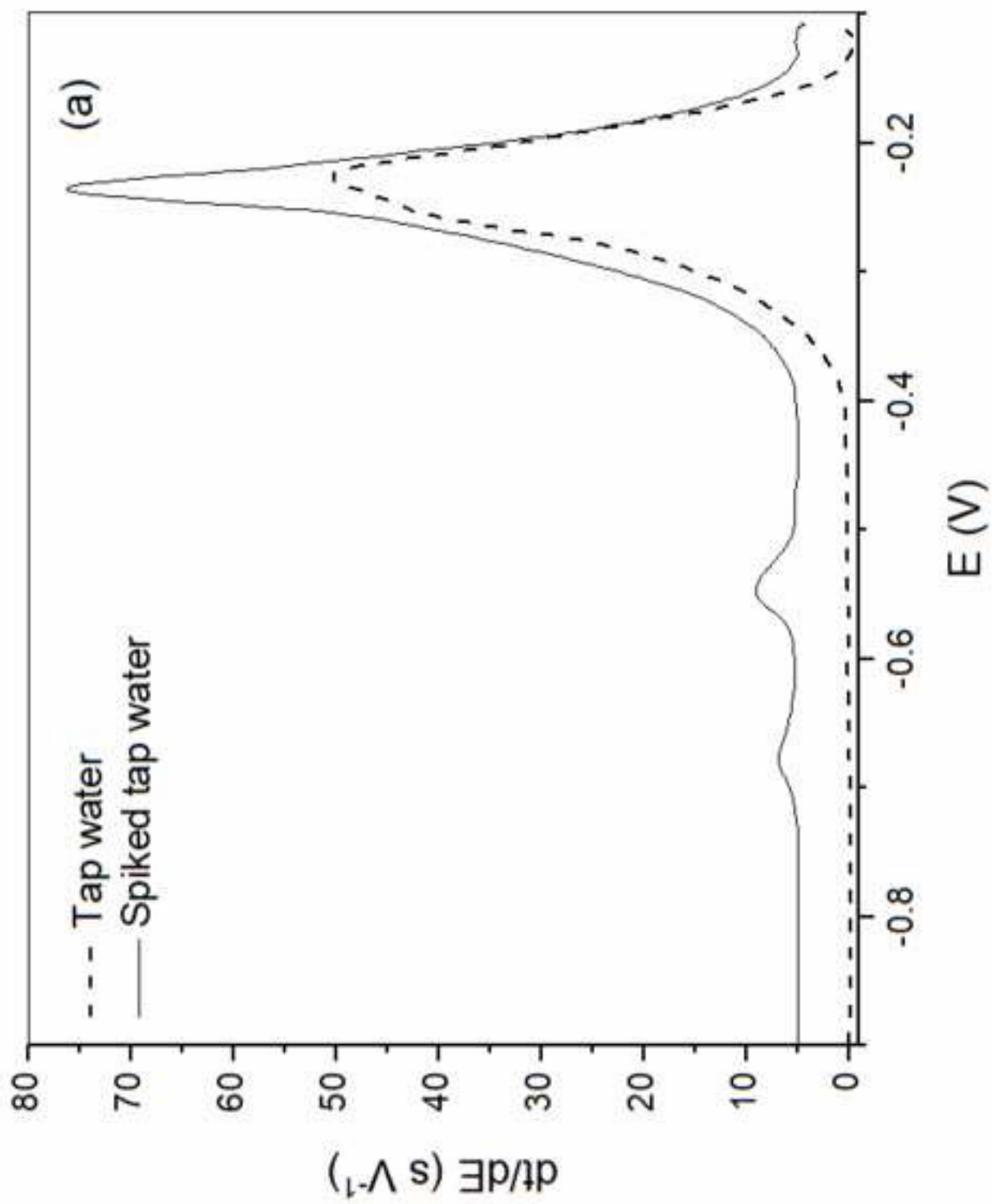


Figure 7a

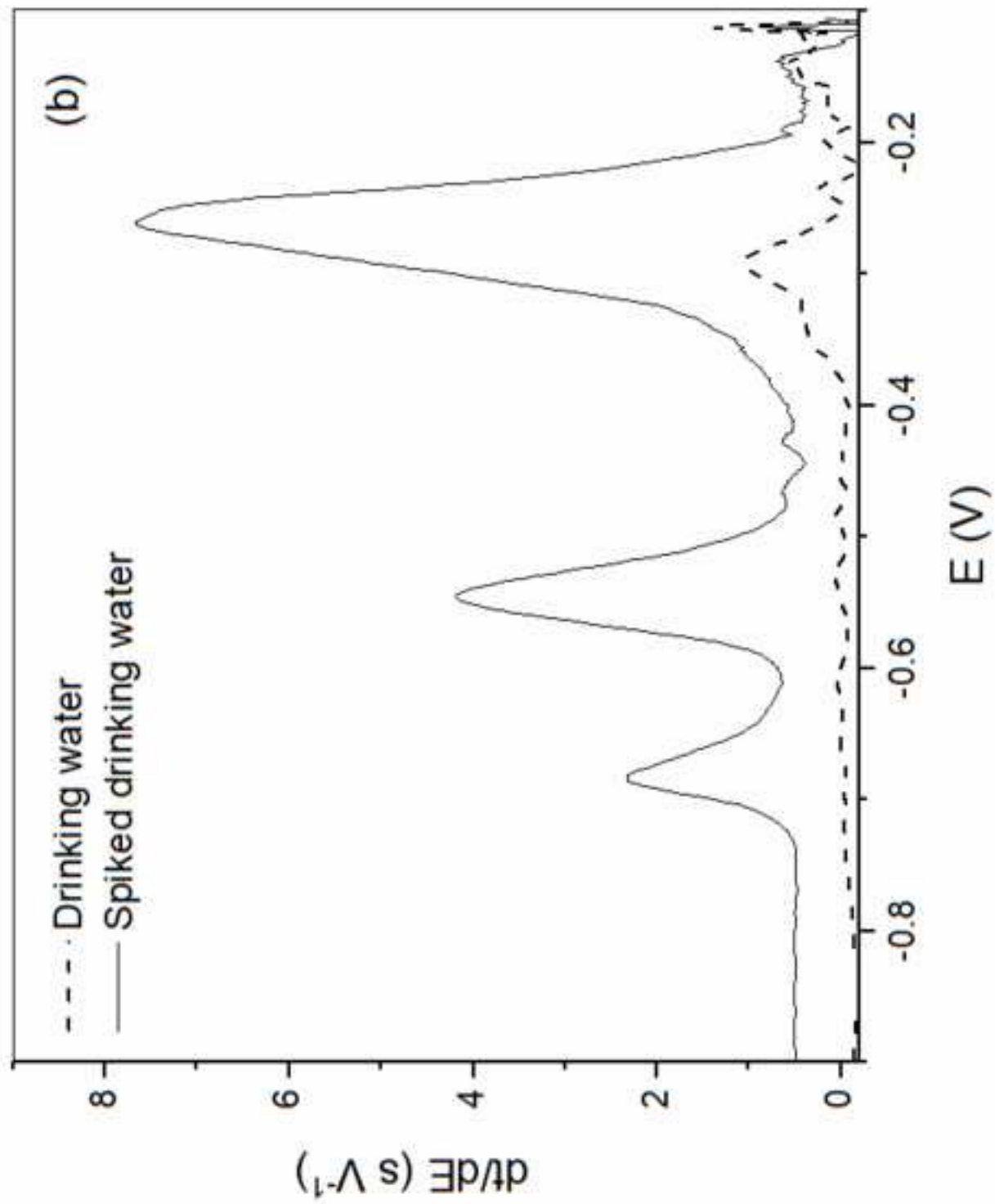


Figure 7b

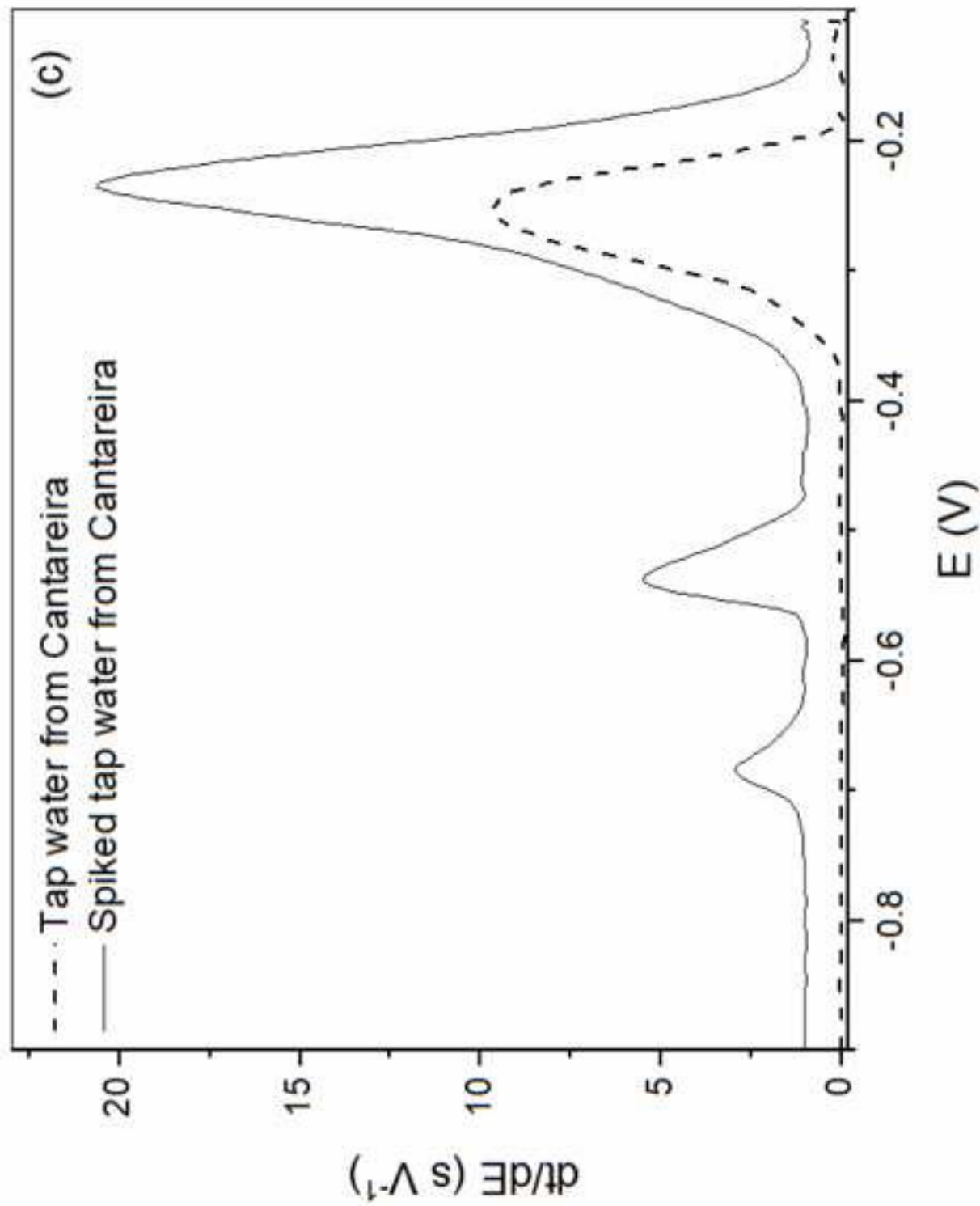


Figure 7c

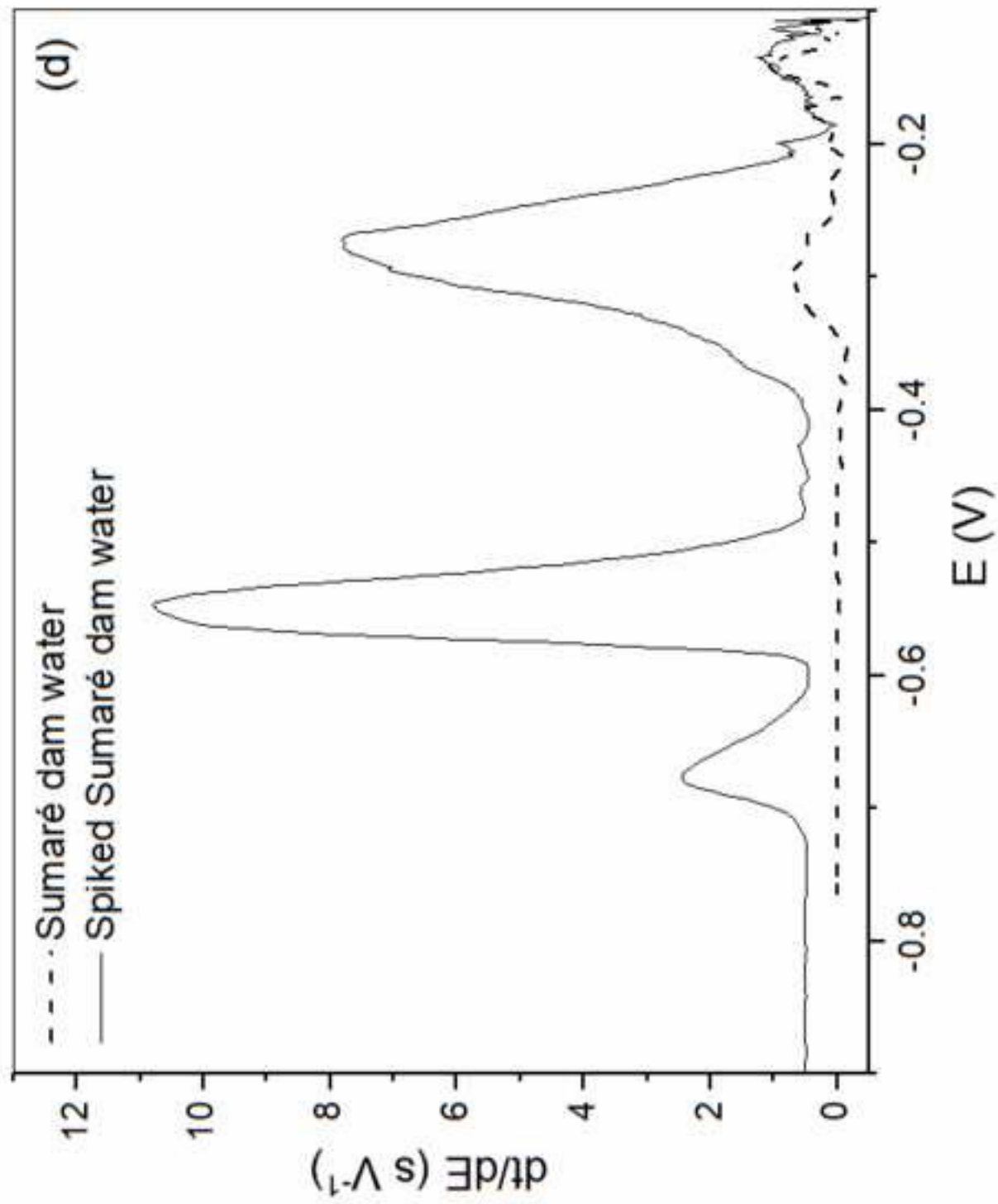


Figure 7d