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6

7 **Electrochemical Boron-Doped Diamond Film Microcells**
8 **Micromachined with Femtosecond laser: Application to**
9 **the Determination of Water Framework Directive**
10 **Metals**

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1 *ABSTRACT*

2 Planar electrochemical microcells were micromachined in a microcrystalline boron-doped diamond
3 (BDD) thin layer using a femtosecond laser. The electrochemical performances of the new laser-
4 machined BDD microcell were assessed by differential pulse anodic stripping voltammetry
5 (DPASV) determinations, at the nanomolar level, of the four heavy metal ions of the European
6 Water Framework Directive (WFD): Cd(II), Ni(II), Pb(II), Hg(II). The results are compared with
7 those of previously published BDD electrodes. The calculated detection limits are 0.4, 6.8 5.5 and
8 2.3 nM, and the linearities go up to 35, 97, 48 and 5nM for, respectively, Cd(II), Ni(II), Pb(II) and
9 Hg(II). The detection limits meet with the environmental quality standard of the WFD for three of
10 the four metals. It was shown that the four heavy metals could be detected simultaneously in the
11 concentration ratio usually measured in sewage or runoff waters.

12 **KEYWORDS:** DPASV, laser micromachining; BDD; Planar microcell; heavy metal ions; Water
13 Framework Directive.

14 **1 Introduction**

15 With a concern for sustainable development and the eco-design of instruments installed in the natural
16 environment, the analytical methods involving toxic compounds must be banned, such as “heavy
17 metals”, in particular mercury impregnation or films, even if the quantities used are relatively low.
18 Indeed, substances such as cadmium or mercury have been classified as “priority hazardous
19 substances” in the Decision N° 2455/2001/EC ¹ and Directive 2008/32/CE ², for which Member
20 States should implement necessary measures with the aim of ceasing or phasing out emissions,
21 discharges, and losses into water of those priority hazardous substances which derive from human
22 activities. So it is preferable to banish these hazardous substances from our devices, rather than
23 quibble over low or negligible implemented quantities and to be vigilant about the potential toxicity
24 of any new substances used in our devices.

25 Furthermore, development of new devices using priority hazardous substances leads to a commercial
26 dead-end and a waste of time and money: they cannot be used in Europe and even in the other parts
27 of the world. Indeed, mercury is recognized as a chemical of global concern. U.S. Environmental

1 Protection Agency's Roadmap for Mercury (July 5, 2006) promotes reducing mercury in processes
2 and products, even where cost-effective substitutes do not exist. The overall goal of the Global
3 Mercury Partnership of the United Nations Environment Programme (Governing Council Decision
4 25/5, Nairobi, Kenya, 16-20 February 2009) is to reduce and eventually eliminate mercury use in
5 products and processes and raising awareness of mercury-free alternatives. Among these products,
6 electric and electronic devices are targeted. Because of these environment and regulatory concerns,
7 mercury-free electrodes have become more attractive.

8 So, electrodes made of boron doped diamond (BDD) are extensively investigated for environmental
9 and electroanalytical applications, because of their analytical properties, as low background current
10 and a wide potential window in aqueous solutions (~ -1.35 to $+2.3$ V versus the normal hydrogen
11 electrode)³ corrosion stability in aggressive media and resistance to biofouling⁴. Unfortunately, films
12 of BDD have to be prepared at high temperatures of about 800°C or above, using microwave assisted
13 plasma-enhanced chemical vapor deposition (MPECVD).

14 The microstructuring of deposited thin films in microcells is usually made by photolithographic
15 techniques that allow using photosensitive resins and selective chemical attacks (lift-off technique).
16 Photolithographic techniques are well established and used to achieve excellent resolution, a
17 magnitude order of one micrometer, but request several steps in a clean room environment, with each
18 of these steps introducing a risk of error. In addition, some materials, especially carbon materials, are
19 not chemically etched. These steps are time consuming; furthermore, they require preparations of
20 chemical reagents and their disposal, and each new design requires the manufacture of a new set of
21 masks, which complicates the process.

22 In this article we describe a new manufacturing process for electrochemical microcells
23 micromachined by a femtosecond laser, which starts from a thin film of carbon deposited on an
24 insulating layer of silicon.

25 Microelectrodes forming the microcell have sizes of a few hundred of micrometer, which is quite
26 feasible by laser machining. Achieving direct machining has a significant advantage over

1 conventional photolithography, because only one step is needed to make all electrochemical
2 microcells, the process is fast and without chemical reagent. Another characteristic of direct
3 machining is that the computer controls the path of the laser beam relative to the work-piece. This
4 helps one to obtain quickly and accurately repeatable structures and whether changes are needed and
5 can quickly be modified to change the program control of the laser accordingly.

6 These new electrochemical microcells micromachined by a femtosecond laser will be applied to
7 detection of metals cited in the Water Framework Directive (WFD) that governs European water
8 policy. WFD has been in place as the main European regulation for the protection of water resources
9 and the water environment since 2000 ⁵. One of its principal objectives is to achieve good chemical
10 and ecological status and to restore water bodies to a “good status” by 2015. Chemical status refers
11 to specific pollutants (e.g., priority substances or priority hazardous substances) for which
12 environmental quality standards (EQS) are proposed and defined for pollutants as minimum
13 requirements ⁶.

14 As the WFD implementation gradually comes into effect in European countries, the environmental
15 metrology market is bound to increase over the coming years. Consequently, faced with the
16 magnitude of this metrological challenge and the urgency of the situation, a paradigm shift is
17 required in order to imagine a new approach to the problem of water monitoring. Given this
18 situation, current research on microsensors is leading to the emergence of many measuring
19 principles. The Swift report (<http://www.swift-wfd.com>), published in December 2006, lists a wide
20 range of monitoring methods currently available or under development for supporting the WFD.

21 In this work the analytical characteristics of electrochemical microcells micromachined by a
22 femtosecond laser will be determined for cadmium, mercury, nickel, and lead using differential pulse
23 anodic stripping voltammetry (DPASV).

24 **2 Materials and Methods**

25 **2.1 Reagents**

26 Cadmium AAS standard solution in 2% nitric acid, at 1000 mg/L, mercury AA/ICP standard solution
27 for environmental analysis, in 9.4% nitric acid, at 995 mg/L, nickel AA standard solution in 0.9%

1 nitric acid, at 1000 mg/L, and lead ICP/DCP standard solution in 0.9% nitric acid, at 9954 mg/L,
2 used for BDD evaluation, sulphuric acid (H₂SO₄) 95-97%, and hydrogen peroxide (H₂O₂) 30% used
3 for cleaning, and potassium citrate used in the buffer were provided from Sigma-Aldrich (l'Isle
4 d'Abeau Chesnes, France). Nitric acid (HNO₃) 68% and hydrochloric acid (HCl) 37% were provided
5 from VWR International (Fontenay-sous-Bois, France).

6 **2.2 Microcell Preparation**

7 The work focused on achieving integrated planar electrochemical microcells made of a film of 300
8 nm of boron-doped microcrystalline diamond to 1300 ppm (BDD) deposited on an insulated silicon
9 wafer of 4" in diameter. BDD electrodes were purchased from Adamant Technologies (La Chaux-de-
10 Fonds, Switzerland). Polycrystalline boron-doped diamond (boron concentration higher than 1000-
11 1300 ppm) of 300 nm thickness was grown by MPECVD on silicon coated with a isolating layer of
12 silicon oxide and silicon nitride (Si/SiO₂/Si₃N₄) of 0.5 μm thickness. The electrodes were cut up
13 from the BDD wafer by micromachining ⁷. This one was conducted by IMPULSION SAS Company
14 using a femtosecond laser (5 kHz, 2.5 W, 800 nm, 150 fs); a scanner head; a set of XYZ moving
15 plates. The parameters used during processing are power, 150 mW; optic scanner, 80 mm; and speed,
16 10-20 mm/s. The design of microcells distributed on the wafer and the structure of each BDD
17 microcell, including the working electrode, counter electrode, and pseudo-reference electrode, are
18 shown, respectively, in Figure S1 and Photo 1.

19 **2.3 Electrochemical Measurements**

20 **2.3.1. Apparatus**

21 A PalmSens sensor PC interface (Eindhoven, The Netherlands) was used to apply differential
22 pulse voltammetry to the microcell. It was connected to a PC computer loaded with specific
23 software. The electrochemical cell was a 5 μL cell made of PEEK, provided by BVT Technologies
24 (Brno, Czech Republic). Instead of the conventional saturated calomel electrode (SCE), the device
25 used a pseudo-reference made of BDD. An O-ring seal defined the measuring volume, and the
26 electrical contacts were obtained by pressure on the front side of the BDD electrodes.

27 **2.3.2. Measuring Conditions**

1 Prior to the experiments and after each calibration concentration, the BDD microcells were cleaned
2 in a piranha mixture (H_2SO_4 (95-97%)/ HNO_3 (68%) [V/V=3:1]) at 200–215°C for 1.5 h,
3 subsequently heated to 80°C for 15 min in a mixture of H_2O_2 (30%)/ammonia (25%) [V/V=1:1] and
4 finally ultrasound cleaned in distilled water, then in ethanol, and finally dried with nitrogen. Piranha
5 mixture is very dangerous, being both strongly acidic and a strong oxidizer, it is extremely energetic
6 and potentially explosive if not handled with extreme caution. It should not be discharged with
7 organic solvent residues. Piranha mixture is prepared before use, applying the sulphuric acid first,
8 followed by the peroxide. Mix the solution in a hood with the sash between you and the solution.
9 Wear gloves and eye protection. Handle with care.

10 Daily, BDD microcells had to be cleaned and activated by 10 mL of Piranha solution, a mix of
11 H_2SO_4 (95-97%)/ H_2O_2 (30%) [V/V=7:3] for 5 min. BDD microcells were then rinsed with distilled
12 water, dried with nitrogen, and activated by cyclic voltammetry in 0.1 M HNO_3 . Finally, DPASV
13 was used for all determinations. Instrumental parameters and standard measuring conditions were
14 performed in 0.1 M potassium citrate/HCl buffer, at pH 2; deposition potential and time were -1.7 V
15 and 20 s; start and end potentials were -1.7 & 0.5 V; pulse amplitude & time are 50 mV & 0.01 s,
16 voltage step: 10 mV and sweep rate 0.05 V/s. The potential of accumulation was usually chosen at -
17 1.7 V and applied for 20 s. Preliminary studies showed that a short deposition time minimized
18 possible interactions between metals during the accumulation phase (data not shown). As previous
19 works, Mannivannan *et al.*⁸ showed that potentials and peak intensities are modified when metals
20 are mixed, and the calibration curves were determined with the four metals together. Indeed in our
21 case voltammograms obtained from the mixture of the four metals show potential peaks shifted, with
22 respect to the pure metals of 2.1%, 1.4%, 1.9%, respectively, for cadmium, lead, and nickel, except
23 for mercury whose potential is shifted nearly 50%.

24 The calibration curves were obtained by diluting the standard stock solution of the mixed four
25 metals (Cd, Hg, Pb, and Ni) in buffer covering the linearity range suspected. According to the
26 standard ISO 15839:2003⁹, the limit of detection (LD) was determined as the average blank value
27 plus three time the standard deviation of the voltammetric signal (peak current) of the lowest level
28 standard. Dividing the minimum detectable signal by the slope of the calibration curve provided the

1 minimum detectable concentration or limit of detection. The limit of linearity was determined by
2 performing standard additions of adequate concentrations on a blank solution, until nonlinearity of
3 the resulting graph was evident. The resulting calibration curves were validated for the linear model
4 according to the French standard method AFNOR XPT 90-210¹⁰. The fit of the Cochran test to the
5 linear model was performed with a risk of α error equal to 1%.

6 **3 Results and Discussion**

7 **3.1 Morphological Characterization of BDD Microcell**

8
9 SEM image of BDD surface (Photo S1) shows the microcrystalline structure. The mean crystal size
10 is in the range of 100 nm. Some large crystals appear. The SEM image of a micromachined groove is
11 presented in Photo 2; its width is around 50 μm . the BDD layer, insulating layer, and silicon
12 substrate clearly appear along the groove.

13 **3.2 Electrochemical Characterization of BDD Microcells**

14 The working potential window is an important electrode property for ASV because it dictates
15 which metal ions can be detected. For carbon electrodes, the anodic limit in most aqueous media is
16 determined by the potential at which oxygen evolution occurs and the cathodic limit is determined by
17 the potential at which hydrogen evolution commences. The reduction of dissolved oxygen is also a
18 parasitic cathodic reaction. The anodic potential limit is an important electrode property, particularly
19 for the analysis of the more electropositive metal ions. The cyclic voltammograms for 0.1 M HNO_3
20 solution performed with our BDD microcell (Figure S2) clearly shows that this one presents a low
21 background and a wide range of working potential, from -1.5 to $+1.5$ V (potential window of 3 V).
22 Electron transfer with the ferro/ferricyanide redox probe was tested. A voltammogram is presented in
23 Figure S3. The microcell shows an anodic–cathodic peak separation ΔE_p of 648 mV and a reversal
24 peak current ratio of 1. The electron transfer is quite limited, due to the rather low doping rate of the
25 microcrystallized BDD used.

1 3.3 Metal Detection Using DPASV

2 3.3.1 Optimization of Detection Conditions: Effect of pH

3 The measurement conditions were optimized of the four metals by varying the pH of 0.1 M citrate
4 buffer with 0.1 M HCl solution. The behavior of four metals versus pH is shown in Figure S4. In
5 more acid solutions, the lead and cadmium stripping peaks became increasingly sharper and more
6 intense. It appears that the best measurement condition is acidic pH (pH = 2) for cadmium, lead, and
7 nickel. But regarding nickel, the pH does not seem to affect the response, and for mercury the
8 response is slightly stronger at neutral pH. These results clearly indicate that the type of buffer used
9 have an effect on the DPASV peak current. Therefore, a 0.1 M citrate buffer (pH 2.0) was
10 determined to be the optimum buffer solution.

11 The calibration curves for the four metals, obtained with the BDD microcell, at pH 2 are shown in
12 Figure 1. The linear model was validated for the four metals, and the detection limits obtained for
13 these four metals are, respectively, Cd, 0.37 nM; Ni, 6.8 nM; Pb, 5.5 nM; and Hg, 2.3 nM. The
14 sensitivity is an important parameter for low detection limits; typically, a higher sensitivity will result
15 in a lower limit of detection. The sensitivities calculated from calibration curves are in decreasing
16 order equal to: Pb = 77 mA/M, Ni = 28 mA/M, Cd = 15 mA/M, and Hg = 9.3 mA/M. Another
17 important analytical parameter to be compared is the linear dynamic range, which is assessed from
18 calibration curves. The calibration curves are linear for all the metal ions, in a linear dynamic range
19 of two orders of magnitude for Cd (linear up to 35 nM) and Ni (linear up to 97 nM), and one order of
20 magnitude for Pb (linear up to 48 nM). Only mercury shows a relatively short linear range (linear up
21 to 5 nM), but the detection of this latter metal has to be optimized (see below). Variation coefficients
22 for Cd (20 nM), Pb (11 nM), Ni (38 nM), and Hg (0.55 nM) are respectively 11.4%, 3.2%, 0.8%, and
23 8.3%.

24 Comparing our results with those previously published about BDD electrodes shows the very low
25 detection limits obtained with BDD microcells, except for mercury detection (Table 1).

26 3.3.2 Metal Detection by DPASV

27 In order to achieve higher detection sensitivity, we have employed the DPASV technique. This one
28 increases the sensitivity by reducing capacitive current. A standard solution of (Cd^{2+} , Ni^{2+} , Pb^{2+} ,

1 Hg²⁺) was used to evaluate the ASV responses of BDD microcells. These four metals are the metals
2 identified as priority substances in the European Water Framework Directive (WFD). As the
3 concentration of one metal can exert influences on the detection of the other metals¹¹, the calibration
4 solution has been constructed to provide a concentration ratio of dissolved metals usually measured
5 in sewage or runoff waters. According to data from Table S1, measured dissolved concentrations of
6 Cd, Pb, and Ni are on average 15-50 times higher than those of mercury. Also, taking into account
7 these data and sensitivities of DPASV measurements for each metal, we used a standard mixed stock
8 solution with metal concentrations according to the following ratios 36/68/19/1 for, respectively,
9 Cd/Ni/Pb/Hg. A general electrochemical spectrum obtained at the concentrations of dissolved Cd
10 (21 nM), Ni (55 nM), Pb (1.1 nM), and Hg (0.55 nM) in 0.1 M potassium citrate/HCl buffer, pH 2, is
11 shown in Figure 2. Well-defined, and slightly asymmetric, stripping peaks are obtained for all the
12 metals. The peak-shape differences likely occur because of the manner in which the metal phase is
13 formed and subsequently oxidized at the working electrode. The stripping peak potentials versus our
14 pseudo-reference electrode, measured for the standard presented in Figure 2, are equal, respectively,
15 for cadmium, nickel, lead, and mercury, to (average \pm s; n=3): -1178 ± 25 mV (V%= 2.1%), -
16 974 ± 21 mV (V%= 2.3%), -254 ± 16 mV (V%= 6.3%), and 119 ± 20 mV (V%= 16.8%)
17 respectively. Variability is around 6-8% except for mercury where the peaks are small and potential
18 variability is 25%. On BDD electrodes, the metal deposition form particles with some metal atoms
19 having only metal-metal interactions and others having metal-diamond interactions. The
20 polycrystalline nature of BDD, in terms of site heterogeneity and non-uniform electrical
21 conductivity, gives a complex surface on which metal oxidation occurs. We attribute the asymmetric
22 peak shape to variable electron-transfer kinetics across the surface whereby deposits of varying size
23 are oxidized at different rates at different locations on the BDD surface. Consistent with this
24 supposition is the fact that the stripping peak widths for BDD became narrower with decreasing scan
25 rate³.

26 *Cadmium Detection*

27 Figure 1 shows the calibration plot for 0.07-35 nM Cd(II) using a 20 s deposition time. Although
28 cadmium calibration curve fits well to the linear model, at the error risk equal to 1%, the results seem

1 non-linear. This cadmium behavior using the BDD electrode has been already reported in the
2 literature¹²⁻¹³. This may be attributed to the way cadmium settles onto diamond surface, depending
3 on its concentration. This behavior, linked to nucleation and growth mechanisms during
4 accumulation step, is well-known for lead or mercury deposited onto the electrode surface, and it is
5 likely that cadmium behaves according to the same mechanism. At high cadmium concentrations, all
6 the active sites on the diamond surface are probably saturated by cadmium, and growth of these
7 nuclei is the principal deposition mechanism. At lower concentrations, the number of active sites on
8 diamond surface may be changing with cadmium concentration, resulting in this nonlinear
9 calibration. An alternative explanation for this nonlinear behavior may be competition, between
10 cadmium and the three other metal ions in the standard solution, for the active sites on the BDD
11 microcell surface. Indeed the calibration solution contains the four metals in the following ratios
12 36/68/19/1 for, respectively, Cd/Ni/Pb/Hg. According to Mannivanna *et al.*⁸, the sequence of events
13 during deposition and stripping from a solution containing both Pb and Cd could be as follows: 1) Pb
14 tends to preferentially deposit on BDD during the accumulation stage; 2) Cd then deposits across the
15 surface, directly on both BDD and Pb nanoparticles, which are already present on BDD; 3) during
16 the stripping potential sweep, the Cd that was deposited directly on the BDD surface is stripped at
17 the potential expected for Cd; 4) finally, at a more positive potential, the Cd that remains on the Pb
18 nanoparticles is stripped along with Pb itself^{8,11}.

19 The BDD microcell presented gives the lowest detection limit for cadmium (LD: 0.4 nM) if we
20 compared with data from Table 1. Indeed, El Tall *et al.*¹¹ found for cadmium a detection limit equal
21 to 3 nM, for a deposition time of 60 s at -1.7 V, in acetate buffer 10 mM and a linear signal up to
22 200 nM. Other authors found higher detection limits on BDD electrodes (Table 1).

23 *Lead Detection*

24 Figure 1 shows the calibration plot for 5-50 nM Pb(II) using a 20 s deposition time. The BDD
25 microcell gives a detection limit for lead (LD, 5.5 nM) among the lowest if compared with data from
26 Table 1. Indeed, El Tall *et al.*¹¹ found for cadmium and lead, LD equal to 3 nM and 8 nM,
27 respectively, for a deposition time of 60 s at -1.7 V, in acetate buffer 10 mM and a signal linear up to
28 200 nM. The deposition and anodic stripping detection by square-wave voltammetry of Pb on the

1 BDD electrode, in a 0.1 M HNO₃ solution, seem to be strongly enhanced by microwave activation.
2 According to Tsai *et al.*¹⁴, after a deposition time of 20 s, the LDs for Pb are equal to 0.1 nM and
3 1 nM, with microwave activation and without microwave activation, respectively. Recently, Chooto
4 *et al.*¹⁵ measured a LD of 1.5 nM for Pb on BDD by SWASV but after a deposition time of 7 min at
5 -1.3 V. Yoon *et al.*¹⁶ propose a simultaneous detection of Cd, Pb, Cu and Hg in a solution of 0.1 M
6 KNO₃ (pH 6) by DPASV on BDD electrode with a LD for Pb equal to 10 nM ($E_{\text{dep}} = -1.5 \text{ V}$; $t_{\text{dep}} =$
7 5 min, scan rate 50 mV/s).

8 *Nickel Detection*

9 For nickel determination, our BDD microcell displays a detection limit of 6.8 nM. Zhang &
10 Yoshihara measure Ni(II) ion concentrations in an electroless deposition bath using DPASV on a
11 BDD rotating disk electrode. Their detection limit was 33 nM, for a deposition time of 60 s. The
12 determination was carried out in alkaline solution (0.1 M NaOH + 0.1 M NH₄NO₃), and a
13 regeneration electrode, after the detection, was carried out in 0.1 M H₂SO₄¹⁷.

14 *Mercury Detection*

15 Concerning mercury, the microcells are not very sensitive (LD: 2.3 nM for 20 s of deposition time)
16 compared to Manivannan's team results where the LD is equal to 0.68 nM on the BDD electrode, but
17 with 20 min of deposition time¹⁸⁻¹⁹, and the detection limit reaches 0.05 nM using a rotating disk
18 electrode and a deposition time = 60 s²⁰. The same team, always on the BDD electrode calculate a
19 LD equal to 0.02 nM with a deposition time of 5 min²¹. One origin to this low sensitivity of the
20 BDD microcell under our operating conditions could be due to the presence of chloride ion in our
21 buffer solution. Indeed the chloride ion and chloride and mercuric ions are known to form an
22 insoluble calomel salt (Hg₂Cl₂) at the surface of the electrodes. This formation of calomel is a
23 problem in all the electrodes used so far, including BDD. Obviously we can change the buffer
24 composition, but chloride is an ubiquitous impurity and gold is an excellent metal which forms
25 amalgam with mercury. To overcome this problem one solution is to co-deposit gold on the BDD
26 electrode surface^{19,21}. Other publications give detection limits close to ours: 3.5 nM for a deposition
27 time of 5 min¹⁶ and 3.2 nM of mercurous ion by cyclic voltammetry on BDD electrodes modified

1 with iridium oxide film ²². Some improvements are necessary to optimize the response of these BDD
2 microcells to mercuric ions.

3 The detection limits of BDD microcells are good both for regulatory and toxicity purposes. WFD
4 proposes as minimum requirements Environmental Quality Standards (EQS) for Cd, Ni, Pb, and Hg
5 and they are respectively 0.7-2.2 nM, 341 nM, 35 nM, and 0.25 nM; and the Predicted Non Effect
6 Concentrations (PNEC) for water organisms are estimated to be: 1.9 nM, 8.5 nM, 1 nM, and
7 0.04 nM, respectively, for Cd, Ni, Pb, and Hg. Concerning regulatory purposes, the BDD microcell
8 reaches the EQSs for cadmium, nickel, and lead. The detection limit of mercury needs to be lowered.
9 With regard to aquatic organisms, toxicity thresholds (PNECs) are reached for cadmium and nickel
10 but not for lead or mercury.

11 **4 Conclusion**

12 Planar electrochemical microcells were micromachined in a microcrystalline BDD thin layer using
13 a femtosecond laser. They were designed for fitting in a flow-through cell. Sensing characteristics
14 obtained with these laser micromachined BDD microcells are the same order of magnitude as those
15 published in the bibliography, which are obtained with conventional electrochemical assemblies.

16 We showed how these microcells allow the detection of heavy metals in water, thus meeting the
17 demand of the European Water framework directive. The simplicity of the DPASV technique on
18 BDD microcells makes onsite monitoring of the heavy metal ions now a near-term reality.

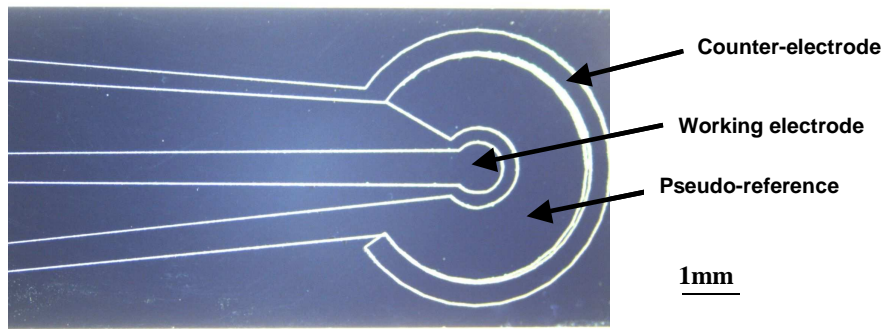
19 Obviously, some improvements of this microcell are still possible and even needed: in particular,
20 the potential for accumulation can be certainly optimized, the sensitivity to Hg ions must be
21 increased, and finally microcells should be tested in a microfluidic system that should allow one to
22 reduce the accumulation time and increase the sensitivity of the device.

23 These microcells have applications in electrochemical analysis not only in environmental water
24 samples (e.g., natural and drinking waters, wastewaters, industrial waters) but their applications can
25 be widened to biological samples for species directly detectable as electro-active species, heavy
26 metals, and neurotransmitters. Other compounds could be detected, after electrode functionalization
27 by synthetic or biological receptors.

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5

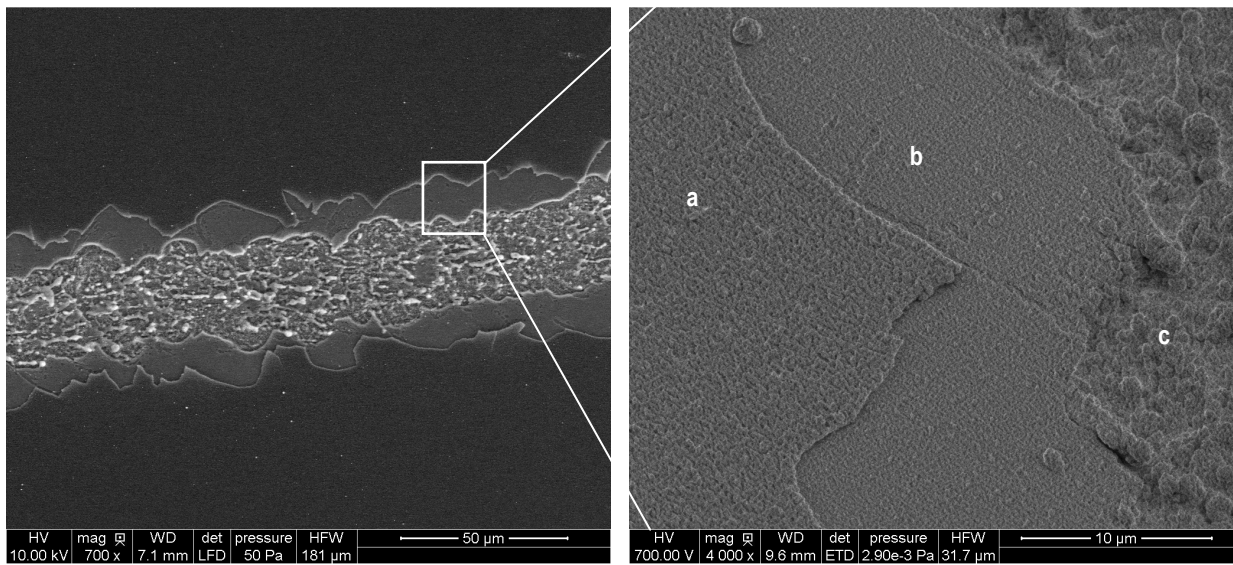


1

2 **Photo 1: the three electrodes cut up from the BDD wafer by laser-machining, the working electrode is in centre,**
 3 **then around it the "reference", and finally the counter electrode on the edge.**

4

5



6

7 **Photo 2: (Left) Femto laser micromachined groove; (Right) (a) BDD, (b) silicon nitride layers, and (c) silicon**
 8 **substrate, on the groove edge.**

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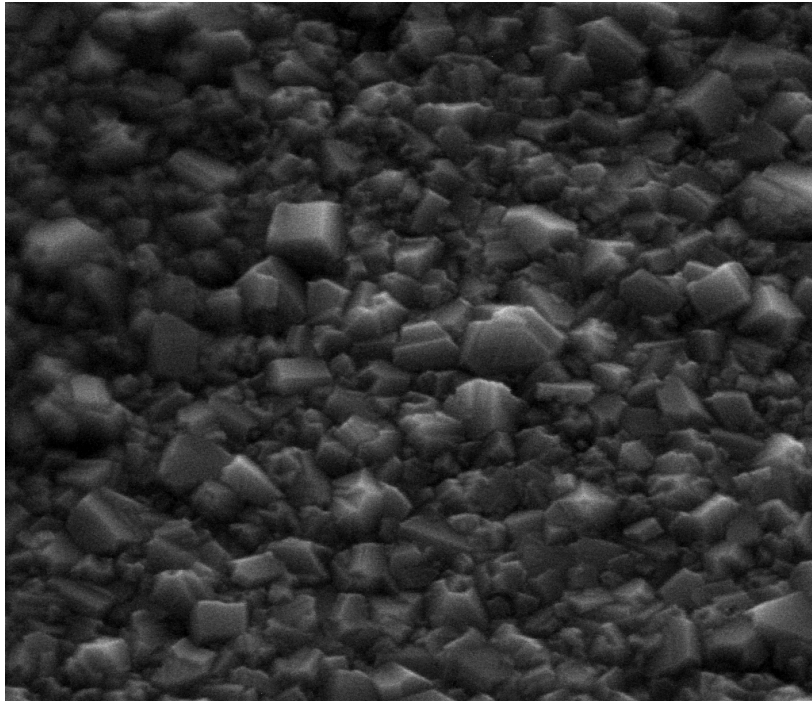
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2**Table 1: Comparison of our results on BDD microcell with the published performances in scientific literature on BDD electrodes**

Metal	Technique	Electrode	Doping (ppm)	Buffer	LD (nM)	Reference
Cd	DPASV	BDD	1 000 (10^{+20} cm^{-3})	0.1 M Acetate, pH 5.2	8.9	3
Cd	DPASV	BDD	810 ²³	0.1 M Acetate, pH 5.4	44	24
Cd	DPASV	BDD	10 000 ²⁵	0.2 M Acetate	355	8
Cd	DPASV	BDD	1300	0.01 M Acetate	3	11
Cd	DPASV	BDD	1300	0.1 M Acetate	8	11
Cd	DPASV	BDD	10 000 ²⁵	0.1 M KCl.	89	12
Cd	LSASV	Bi-BDD	1 000 (0.1%) Windsor Scientific	0.1 M HClO ₄ , pH 1.2	17	26
Cd	LSASV	BDD	0.1% in the source	0.1 M HClO ₄	89	27
Cd	DPASV	BDD	No specified	0.1 M Acetate, pH 6	31	16
Cd	DPASV	BDD	1 300	0.1 M Citrate/HCl, pH 2	0.4	Our result
Hg	DPASV	BDD	No specified	0.1 M Acetate, pH 6.0	3,5	16
Hg	DPASV	BDD	10 000 (ref ²⁵)	0.1 M KNO ₃ , pH 1	0,7	18-19
Hg	DPASV	BDD	No specified	1 M KCl, pH 4	0,05	20
Hg	ASV	IrOx- BDD	1 000 (0.1%) Windsor Scientific	0.1 M PO ₄ , pH 4	3,2	22
Hg	DPASV	BDD	10 000 ²⁵	1 M KCl, pH 4 + 4mg/L Au	0,02	21
Hg	DPASV	BDD	1 300	0.1 M Citrate/HCl pH 2	2.3	Our result
Ni	DPASV	BDD	10 000	0.1 M NaOH + 0,1 M NH ₄ NO ₃	33	17
Ni	DPASV	BDD	1 300	0.1 M Citrate/HCl pH2	6.8	Our result
Pb	DPASV	BDD	1 000 (10^{+20} cm^{-3})	0.1 M Acetate, pH 5.2	24	3
Pb	DPASV	BDD	810 ²³	0.1M Acetate, pH 5.4	24	24
Pb	DPASV	BDD	10 000 ²⁵	0.1 M KCl pH 1	4	28
Pb	DPASV	BDD	10 000 ²⁵	0.2 M Acetate pH 5	251	8
Pb	DPASV	BDD	1 300	0.01 M Acetate	8	11
Pb	DPASV	BDD	1 300	0.1 M Acetate	46	11
Pb	DPASV	BDD	10 000 ²⁵	0.1 M KCl.	48	12
Pb	LSASV	Bi-BDD	1000 (0.1%) Windsor Scientific	0.1 M HClO ₄ , pH 1.2	11	26
Pb	LSASV	BDD	10 000 ²⁵	0.2 M KCl pH 1	1998	29
Pb	SWASV	BDD	1 000 (10^{+19} - 10^{+20} cm^{-3})	0.1 M HNO ₃	101	14
Pb	SWASV	BDD	1 000 (0.1%) Windsor Scientific	0.2 M KNO ₃ + 0.05 M HNO ₃	1	15
Pb	DPASV	BDD	No specified	0.1 M Acetate,	10	16

				pH 6		
Pb	DPASV	BDD	1 300	0.1 M Citrate/HCl pH 2	5.5	Our result

1

2



HV	mag	WD	det	pressure	HFW	1 μ m
5.00 kV	50 000 x	10.3 mm	LFD	40 Pa	2.54 μ m	

Photo S1: Morphological aspect of BDD layer

1
2
3

1 Table S1: Dissolved metal concentrations measured in wastewater (*), runoff water (**), and
 2 rainwater (***)

Cd (nM)	Pb (nM)	Ni (nM)	Hg (nM)	References
2**	37**	49**	-	[1]
-	-	-	2.4-1.3**	[2]
3.3***	7.6***	50***	-	[3]
4.4***	24***	44***	-	[4]
0.8**	11**	-	0.23**	[5]
-	7.1***	7.7***	-	[6]
4.7**	19**	-	-	[7]
0.6*	8.2*	110*	-	[8]
0.2***	1.1**	5**	-	[9]
-	-	-	0.023**	[10]
89**	91**	-	-	[11]

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4 References cited

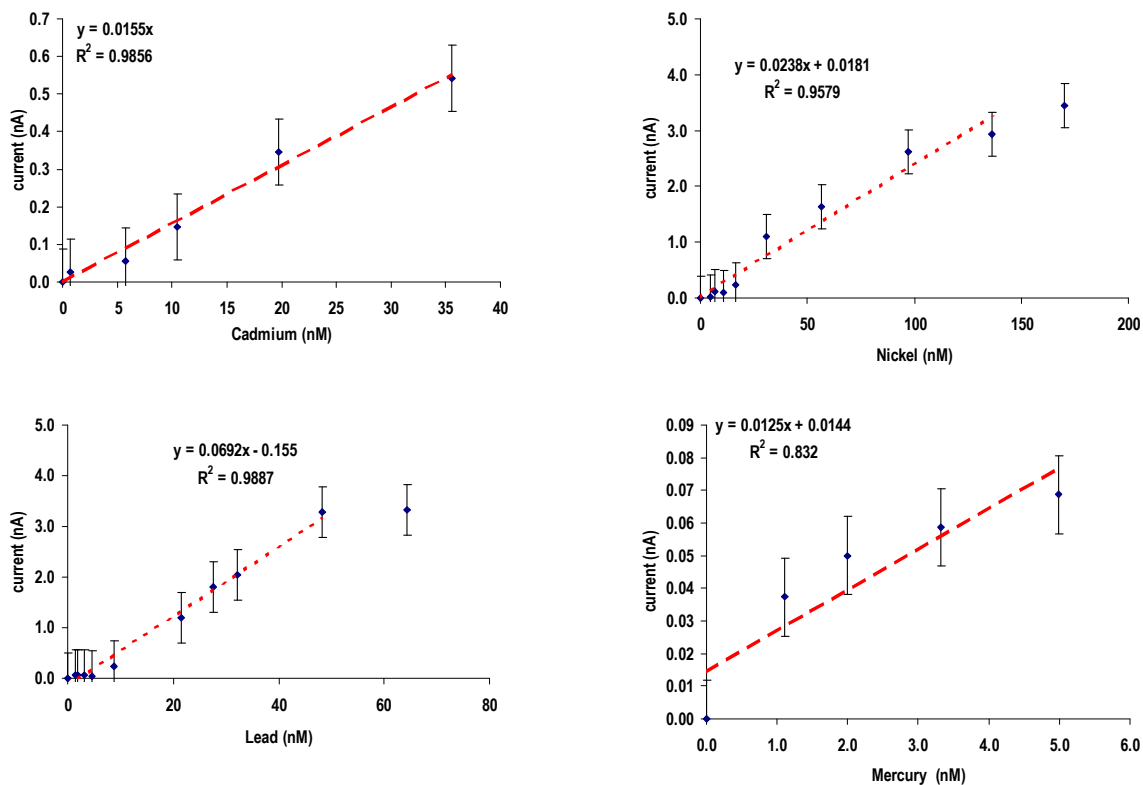
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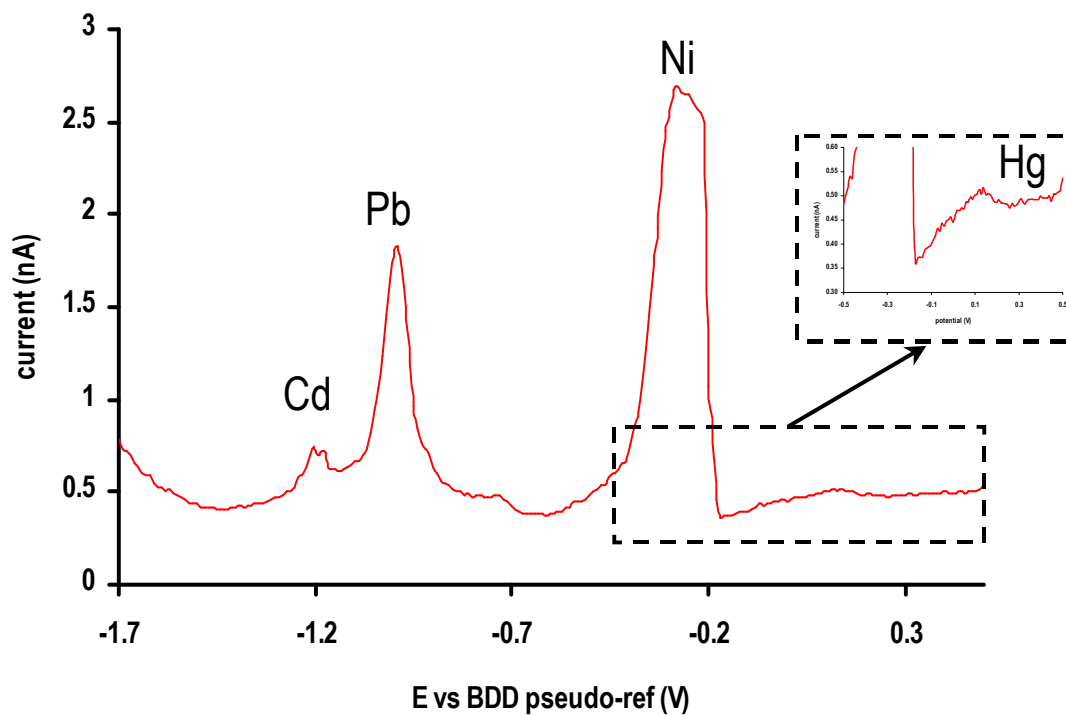
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2 **Figure 1: Calibration plots for Cd^{2+} , Ni^{2+} , Pb^{2+} , and Hg^{2+} ions at pH 2 in 0.1 M potassium citrate buffer:**
3 **concentration range on the micromachined BDD microcell. Operating conditions: $E_{\text{dep}} = -1.7$ V; $t_{\text{dep}} = 20$ s;**
4 **stripping at 50 mV/s.**

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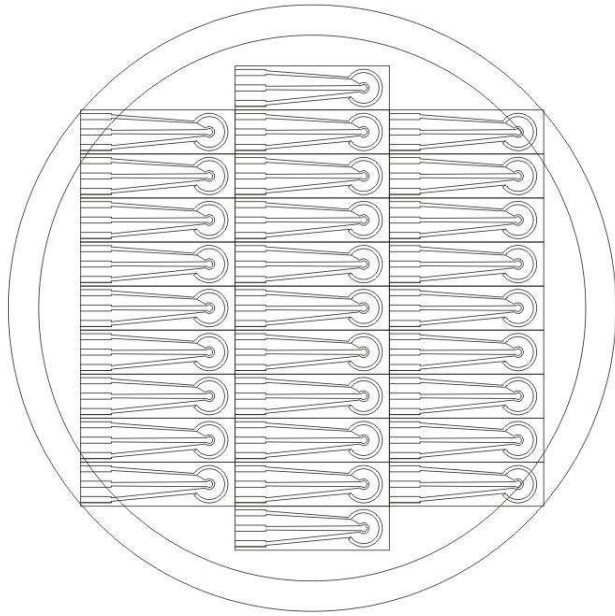
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3 Figure 2: DPASV obtained with the BDD micromachined microcell, on a standard solution of Cd
4 (20 nM), Ni (38 nM), Pb (11 nM), and Hg (0.55 nM) in 0.1 M potassium citrate/HCl buffer, pH 2;
5 deposition potential and time: -1.7 V and 20 s; start and end potentials: -1.7 and 0.5 V; pulse
6 amplitude and time: 50 mV and 0.01 s; voltage step: 10 mV; and sweep rate 0.05 V/s. The potential
7 is measured versus a pseudo-reference electrode made of BDD.

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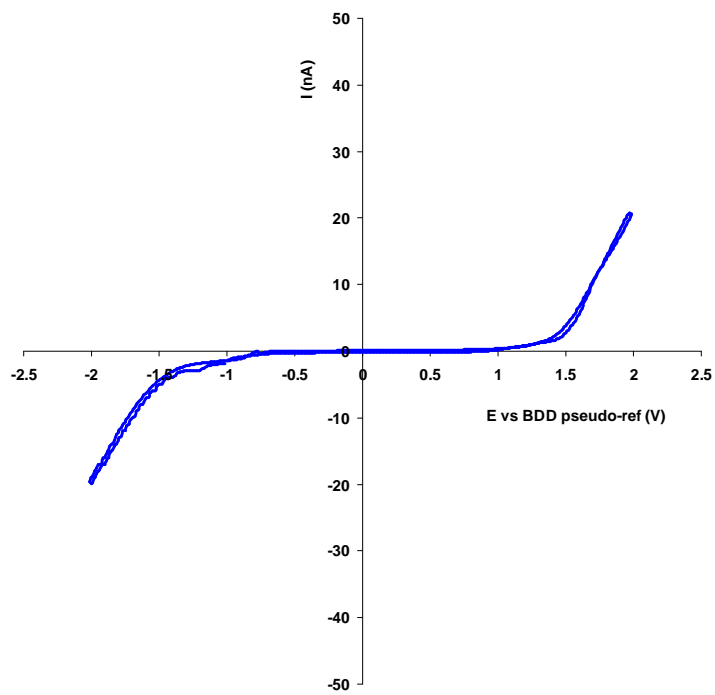
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Figure S1: Design of electrochemical microcells distributed on a wafer of silicon insulated (4" diameter)

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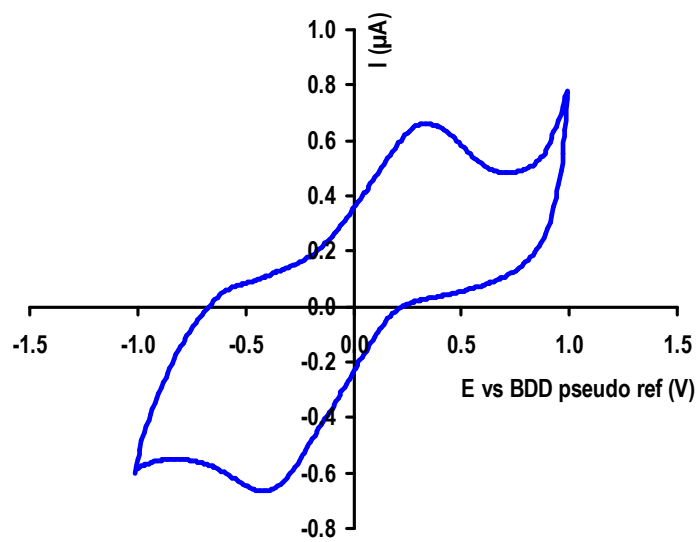


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Figure S2: cyclic voltammograms for 0.1 M HNO₃ performed with a BDD microcell

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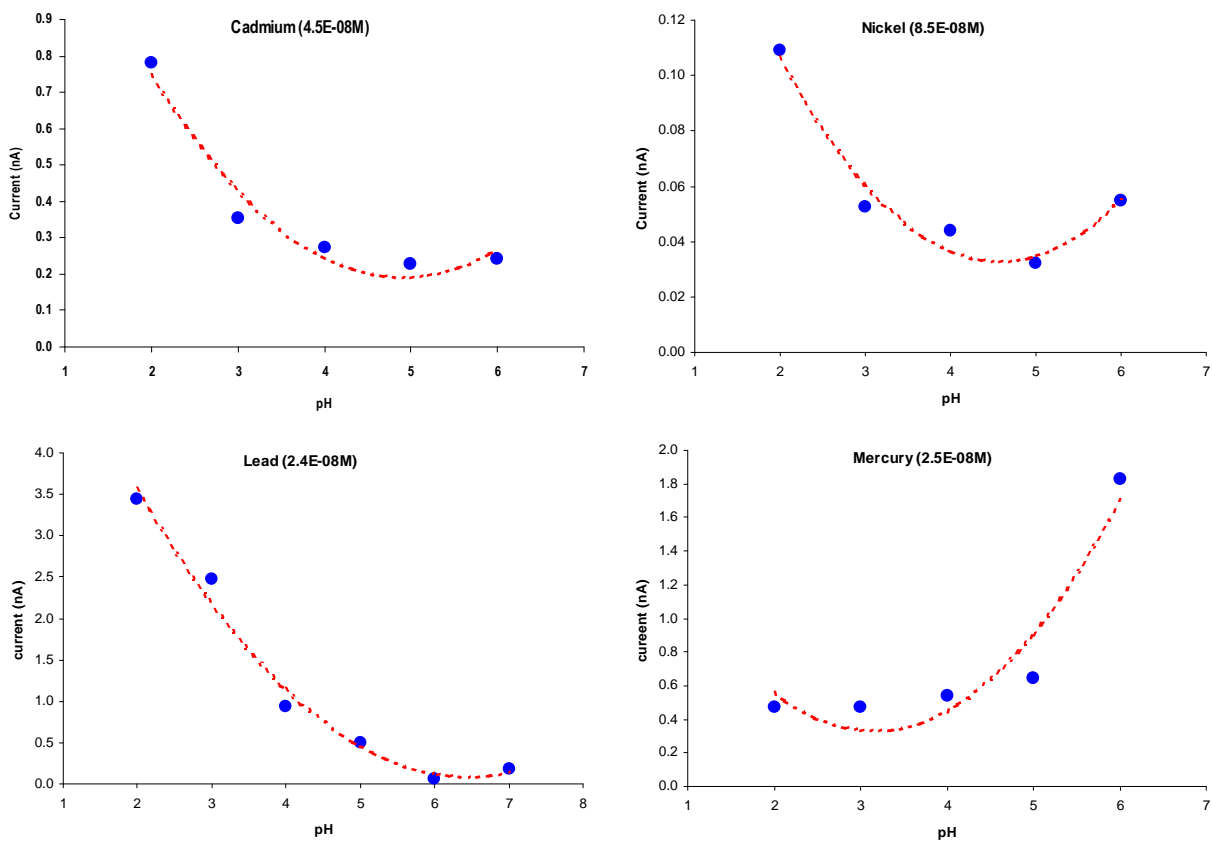


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2 **Figure S3: Cyclic voltammogram of 10 mM of ferro/ferricyanure in buffer solution (PBS 10 mM ; pH 7,4) with a**
3 **scanning speed of 0.1 V/s.**

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2 **Figure S4: pH effect on the metal stripping peak (height in nA) for cadmium (45 nM), nickel (85 nM), lead**
3 **(24 nM), and mercury (25 nM)**

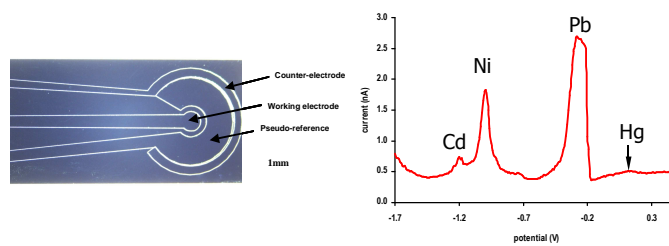
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Table of Contents Graphic



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