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1 Reversible microfluidics device for precious metal electrodeposition and depletion yield 2 studies

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12 Abstract

13 A new low-cost reversible Glass-NOA[®]-PDMS microfluidic device was designed for the study of
14 recovery yield of precious metals present in acid media mimicking leach liquors for long-term
15 recycling objectives. It offers the unique advantage of allowing easy washing of the microchannel
16 and renewal of the electrode surface by simply repositioning the microband electrodes which
17 allows this type of device to have a relatively much longer lifespan than irreversibly closed ones.
18 It consists in a re-usable microchip with four graphite microbands electrodes, prepared by screen
19 printing, to set-up an original amperometric device for both depletion and yield quantification.
20 One upstream working electrode is devoted to the depletion of the metallic ions through their
21 electrolysis by electrodeposition while the second downstream working microelectrode is used as
22 real-time detection electrode to evaluate the depletion efficiency. The dimensions of the depletion

23 electrode and of the channel were optimized thanks to numerical simulations for a given range of
24 flow velocities. First, the performances of the device were assessed experimentally according to
25 flow rate and applied potential under continuous flow, and then compared to theoretical
26 predictions using an electrochemical probe, ferrocenemethanol. The proof of concept was then
27 demonstrated for precious metal, by electroreduction of Pd(II) and Au(III) from acidic leach
28 liquors under continuous flow, with a depletion yield of up to 89% and 71% respectively.

29 **Keywords**

30 Precious metals – Microfluidic – Depletion – Electrodeposition

31 **1. Introduction**

32 Printed circuit boards (PCBs) are known as an integral part of our technological devices
33 (smartphones, computers...). As their use has become more and more important in the recent
34 decades, the amount of waste is increasing and becomes an ecological, economic and strategic
35 challenge [1,2]. Indeed, waste PCBs are a major source of strategic metals [3], such as platinum
36 group metals (PGM), rare earth elements or other expensive species. Their recovery is crucial,
37 especially since some of them are defined as critical (supply risks, high cost) by the European
38 Commission [4] since 2014, such as Platinum (Pt) or Palladium (Pd). Their recycling is generally
39 carried out in a three steps process [5]: (i) a mechanical grinding to reduce PCBs to powders and
40 separate ferrous and non-ferrous metals, (ii) pyrolysis at 1000°C to remove the organic
41 constituents and (iii) a hydrometallurgical treatment to selectively remove metals in ionic form in
42 leaching solutions. These treatments are thus promising in terms of strategic metals recovery rate,
43 but purification methods are still time-consuming and need to be optimized to ensure high purity
44 of recycled materials, especially in their metallic form.

45 Thanks to microfluidics [6], the change in scale from an industrial process to microchannel
46 results in a modification of the mechanical properties of fluids. This allows leading to high
47 conversion for organic synthesis, for example, and high purity of the products [7,8]. In addition,
48 the low manufacturing cost of microreactors permits them to be parallelized, allowing for
49 processing a large quantity of samples, thus competing with current industrial macro-processes
50 [9]. Even if diagnosis is one of the main application of microfluidics (for environmental [10] and
51 biological [11] survey), the use of such miniaturized tools for the treatment of large amounts of
52 liquid is also feasible.

53 Microfluidic coupled to the integration of electrodes within microchannels has been previously
54 used to remove potential interfering agents from real samples but also to increase the selectivity
55 towards a target (such as oxalic acid or nitric oxide) during its electrochemical detection [12,13].
56 The developed setups are composed of a four-electrodes cell, where two working electrodes
57 (WE) are placed perpendicularly to a single microchannel containing the solution under
58 continuous flow. Watanabe et al. [12] used a large WE (WE_{DEP} , depletion electrode) in order to
59 remove the electroactive analyte (ferricyanide) from the solution and checked the depletion yield
60 by measuring ferricyanide concentration thanks to the second WE (WE_{det} , detection electrode)
61 positioned downstream. The importance of main parameters on the depletion yield has been
62 discussed by the authors such as ratio of electrode width to channel height, flow velocity and
63 applied potentials. The authors stated that their setup was not suitable to complete the depletion
64 up to 100 % due to the height of the channel which was larger than the convection-diffusion layer
65 of the sample. Indeed, the thin-layer regime at the electrode must be achieved under mass
66 transport control for complete depletion [14–16]. More recently, similar strategy was adopted for
67 the assessment of global antioxidant capacity and for the depletion of hydrogen peroxide (up to

68 95%) [13]. In this last case, the selectivity of nitric oxide detection was enhanced by positioning a
69 NO-sensor downstream of the depletion electrode. It should be noted that the devices described in
70 the literature for this type of application are sealed and do not offer any possibility of easy and
71 quick reuse in case of pollution of the depletion electrodes and their regeneration.

72 Reversibly bonded chips reported in the literature are generally used for other applications such
73 as coupling of electrophoresis with electrochemical detection or surface patterning for bio-
74 molecule analysis [17]. Several strategies for the reversible bonding of the different parts of the
75 microdevices were used such as magnetism, vacuum or spontaneous conformal contact between
76 PDMS and glass [18] or other materials (metals, acrylate plate [19]). They offer the main
77 advantage of facilitating the washing and the renewability of channels. We propose in this study
78 an original microfluidic device to address the issue of recovering Au and Pd dissolved in acidic
79 media (as AuCl_4^- and PdCl_4^{2-} respectively), mimicking leach liquors from the waste PCBs
80 recycling process. For this purpose, a re-usable new reversible Glass-NOA[®]-PDMS microchip
81 with four graphite microbands electrodes adapted from previously developed one by our group
82 [20], was designed to set-up an original amperometric recovery device for both depletion and
83 yield quantification. The device reported here offers the unique advantage of being a micro
84 sandwich system with a reversible bond composed of two parts without the need for a magnetic
85 or other device to maintain perfect adhesion, allowing easy washing of the microchannel and
86 renewal of the electrode surface by simply repositioning the microband electrodes. This
87 configuration permits enhancing its lifetime. First, to optimize the performance of the proposed
88 microdevice, ferrocene methanol was used as a model. Then, the method efficiency for precious
89 metallic species were discussed and compared to theoretical predictions.

90 **2. Materials and methods**

91 *2.1. Chemicals*

92 Standard solution of Gold Standard for ICP TraceCERT® 1000 mg/L (5% HCl) and Palladium
93 Standard for ICP TraceCERT® 10000 mg/L (10% HCl with HNO₃⁻ traces), ferrocene methanol
94 (noted as FcMeOH, 97%), sodium phosphate dibasic (99%), sodium phosphate monobasic (99%)
95 were purchased from Sigma-Aldrich (Germany). HCl (37%) was purchased from Acros Organics
96 (France). Graphite powder (2-15µm microcrystal grade 99.9995%) was obtained from Alfa Aesar
97 (Germany), PDMS RTV 615 kit was obtained from Mentiv (France), PDMS Sylgard 184 kit
98 from Dow Corning (Germany), SU8 2075 from Microchem (USA), and Norland Optical
99 Adhesive 81® (noted as NOA81®) from Epotecny (France) and were used for fabrication of
100 microchannels and microelectrodes. Ultrapure water was obtained from a Purelab Flex System
101 (18.2 MΩ.cm Veolia, France).

102 *2.2. Solutions*

103 The artificial leach liquors were prepared by dilution of appropriate amounts of metallic standard
104 solutions with HCl in ultrapure water so as to obtain a 0.1 mol L⁻¹ HCl solution. 200 µmol L⁻¹
105 FcMeOH was prepared in 0.2 mol L⁻¹ phosphate buffer (pH 6.7) with sonication for at least 2
106 hours to complete solubilization.

107 *2.3. Microelectrode and microchip fabrication*

108 The microfabrication process, developed in our lab, has been previously described [20]. Briefly,
109 for the electrode fabrication, PDMS substrates containing microchannels of desired width are
110 prepared by soft-lithography technic. A pattern is molded by UV exposure of spin-coated SU-8
111 on a silicon wafer with a photomask containing the design of the electrodes. Electrode pattern

112 were printed on Kimolek® Paper with a Filmstar® photoplotter (Bernier Electronik, France).
113 PDMS is spread on the surface of the mold prior to degassing and reticulating at 70°C for 1h. A
114 mix of graphite powder and PDMS (C-PDMS, 1:1, w/w) is spread in the microchannels and
115 polished by hand to remove the excess. The resulting electrodes are placed in an oven at 70°C for
116 3h before use. For the microchannel fabrication, a PDMS mold containing the positive pattern is
117 prepared by the same technic. The mold is applied on top of a glass substrate previously covered
118 with NOA®81. After UV exposure, the open-channel is revealed by properly demolding the
119 PDMS mold. The two parts are then assembled so as to close the chip, forming a spontaneous
120 conformal contact between the open-channel (NOA81®) and the electrode (C-PDMS on PDMS
121 substrate). The scheme and a picture of the setup are shown in Figure 1. In such a device, WE_{DEP}
122 is the working electrode dedicated to the depletion process (and also to the recovery of the
123 metals), WE_{det} is the working electrode dedicated to the determination of the considered species
124 and thus to the evaluation of the recovery efficiency.

125

126 **Figure 1 – (a) Scheme of microchannel with four integrated C/PDMS microbands**
127 **electrodes. WE_{DEP} is dedicated to the depletion process (and thus to the recovery), WE_{det} is**
128 **dedicated to the determination of the considered species and thus to the evaluation of the**
129 **recovery efficiency. Dimensions in μm (unless specified). * upper part of the setup (NOA81®**
130 **microchannel; ** lower part of the setup (C-PDMS electrodes in PDMS substrate) (b)**
131 **Photography of the experimental setup**

132 *2.4. Electrochemical measurement and depletion*

133 Chronoamperometric (CA) and cyclic voltammetric (CV) measurements were performed with an
134 Autolab PGSTAT 128N potentiostat (Metrohm), in a four electrodes cell (two WE coupled to one
135 reference electrode RE and one counter electrode CE). The CVs were performed at 25 mV s⁻¹ for
136 each electrode to determine the potential required for CA, with RE connected to the 100 μm strip

137 electrode and the CE connected to the 1000 μm strip electrode. The WE dedicated to the
138 depletion (WE_{DEP}) was located upstream (500 μm width) along the flow direction, and the one
139 dedicated to detection for control (WE_{det}) was positioned downstream (50 μm width). The flow of
140 the solution along the microchannel was insured by a flow controller (MFCSTM-EZ and flow rate
141 sensor S, Fluigent, France), applying a negative pressure (0 to -345 mbar) from the outlet of the
142 channel to prevent detachment of the reversibly sealed chip. The depletion yield for FcMeOH, Pd
143 and Au were estimated by measuring in CA the difference in oxidation charge generated on the
144 WE_{det} with and without polarization of WE_{DEP} , after subtraction of charges measured with a
145 blank sample (phosphate buffer or HCl alone). The depletion yield for FcMeOH was also
146 evaluated from steady-state currents in CV.

147 The dimensions of the channels and of the electrode as well as the estimation of the depletion
148 yield were first optimized by performing numerical simulations using COMSOL Multiphysics
149 5.3, through a similar approach as previously described [13]. Briefly, a laminar flow was
150 considered in a rectangular microchannel by assuming a parabolic velocity profile in a two-
151 dimension. The electrochemical reactions were supposed to be limited by mass transport and the
152 diffusion-convection equation was solved numerically by finite elements. As a boundary
153 condition, concentration of the analyte was imposed to 0 mol L⁻¹ at the polarized electrode
154 surface. The diffusion coefficient of the analyte was assumed equal to $7.6 \cdot 10^{-6}$ cm² s⁻¹, which is
155 the one of FcMeOH used as a model [21]. Simulations provided an optimal size of WE_{DEP} versus
156 the channel height, within the range of flow velocities that could be used experimentally.
157 According to the configuration and geometry of the microdevice described in Figure 1, depletion
158 yields up to 95 % were expected for flow rate lower than 2 $\mu\text{L min}^{-1}$. The device was then applied
159 to the recovery of Pd(II) and Au(III).

160 3. Results and discussion

161 3.1. Electrochemical behavior of FcMeOH under continuous flow

162 The electrochemical behavior of FcMeOH has been studied in the present configuration by CV
163 on both WEs without flow (static mode) and under continuous flow (from 1 to 5 $\mu\text{L min}^{-1}$), as
164 shown on Figure 2. The oxidation current for both WEs (WE_{DEP} and WE_{det}) increase with the
165 flow rate due to convection induced by continuous flow, leading to a steady-state mass transport
166 to the electrodes and the observation of limiting currents. As expected in convective regimes,
167 limiting currents increase linearly with the cubic root of flow rate (see inserts). At the highest
168 flow rate (5 $\mu\text{L min}^{-1}$, *i.e.* 2.1 mm s^{-1}), the faradic current started from about 0.1V and reached a
169 limiting value only for potential values higher than 0.5V due mainly to ohmic drop. According to
170 these voltammograms the potential on both electrodes should be comprised between +0.5 and
171 +1.0 V to ensure a constant oxidation current under continuous flow (for 1 to 5 $\mu\text{L min}^{-1}$) for
172 optimal operating conditions. Indeed, to guarantee an optimum depletion efficiency (see sections
173 below), the process needs to be performed at potential values that do not lead to a drastic current
174 variation.

175 **Figure 2 – Cyclic voltammograms of 200 $\mu\text{mol L}^{-1}$ FcMeOH in 0.2 mol L^{-1} phosphate buffer**
176 **at (a) WE_{DEP} and (b) WE_{det} , in static mode (full line) and under continuous flow (from 1 to**
177 **5 $\mu\text{L min}^{-1}$). Scan rate: 25 mV s^{-1} . Inserts correspond to the plots of limiting currents as a**
178 **function of cubic root of flow rate.**

179 3.2. FcMeOH depletion

180 Cyclic voltammograms (CV) were performed at WE_{det} with and without polarization of WE_{DEP} at
181 a constant potential of +1.0 V. Figure 3-a shows the mean values of limiting currents, noted as
182 $I_{\text{lim,WEdet}}$, monitored under these conditions at WE_{det} as a function of flow rate. The depletion

183 yield (Figure 3-b) was determined from these data by calculating the ratio between limiting
184 currents at WE_{det} (corrected from residual currents) with and without polarization of WE_{DEP}:

$$Depletion\ yield_{CV}\ (%) = \left(1 - \frac{I_{lim, WE_{det}}\ with\ WE_{DEP}^{ON}}{I_{lim, WE_{det}}\ with\ WE_{DEP}^{OFF}} \right) \times 100 \quad eq.1$$

185 As expected theoretically, the depletion yield decreases by increasing the flow rate: the higher the
186 flow, the shorter the residence time of redox species near the depletion electrode. However,
187 experimental depletion yields were lower (by a factor ranging between 1.2 to 2) than the ones
188 predicted by simulation, as shown in Figure 3-b.

189 **Figure 3 – (a) Limiting currents measured by cyclic voltammetry (from data in Fig. 2) at**
190 **WE_{det} without (OFF) and with (ON) polarization of WE_{DEP}. (b) Corresponding depletion**
191 **yield evaluated from eq.1 as a function of flow rate. WE_{DEP} is biased at 1.0 V when**
192 **polarized (ON).**

193 The depletion process was also evaluated by chronoamperometry (CA). More precisely,
194 consecutive potential steps (ON) and (OFF) were performed at WE_{DEP}, while maintaining WE_{det}
195 at a constant potential of 1 V for oxidizing remaining FcMeOH (Figure 4). Note that polarization
196 of WE_{DEP}, at 1 V and 0 V corresponds to the activation (ON) and deactivation (OFF) of the
197 depletion process, respectively. As expected, polarization of WE_{DEP} at +1,0V leads (i) to the
198 increase of currents characteristic of FcMeOH oxidation and (ii) to a decrease of currents at
199 WE_{det} due to FcMeOH depletion. With this configuration of device and electrode material, the
200 time delay to reach steady-state currents was estimated about 10 s.

201 **Figure 4 – (a) Potential steps applied to WE_{DEP} for successive activations (1 V) and**
202 **deactivations (0 V) of the depletion process. WE_{det} is continuously polarized at 1 V. (b)**
203 **Corresponding chronoamperograms monitored at WE_{det} (full line) and WE_{DEP} (dashed**
204 **line). 200 μmol L⁻¹ FcMeOH in 0.2 mol L⁻¹ phosphate buffer and flow rate of 1 μL min⁻¹.**

205 Then, similar experiments were conducted on a longer time scale. Figure 5-a shows
206 chronoamperograms obtained at WE_{det} for low flow rate (1 μL min⁻¹, *i.e.* 0.4 mm s⁻¹) with or

207 without polarization of WE_{DEP}. First, a potential of 0 V was applied to WE_{det} during 30 s for
 208 stabilization of the baseline followed by a potential step to 1.0 V during 60 s. This procedure was
 209 applied either in presence of FcMeOH or in PBS to consider the influence of residual currents
 210 into the evaluation of the charges developed at WE_{det}, noted as Q_{WE_{det}}. Experiments were also
 211 carried out for other flow rates. Thus Figure 5-b shows the evolution of Q_{WE_{det}} during the second
 212 step as a function of flow rate, with or without polarization of WE_{DEP}. These data allowed
 213 evaluating in Figure 5-c the corresponding depletion yields (with subtraction of charge measured
 214 in PBS) according to the equation

$$Depletion\ yield_{CA}\ (\%) = \left(1 - \frac{Q_{WE_{det}}\ with\ WE_{DEP}^{ON}}{Q_{WE_{det}}\ with\ WE_{DEP}^{OFF}} \right) \times 100 \quad eq.2$$

215

Figure 5 – (a) Chronoamperometry at WE_{det} (30 s at 0 V and 60 s at 1.0 V) without depletion (curves 1 and 2, WE_{DEP} OFF) and with depletion (curves 3 and 4, WE_{DEP} polarized at 1 V) at 1 μL min⁻¹ flow rate. (b) Experimental charge Q_{WE_{det}} developed at WE_{det} during the second step as a function of flow rate. (c) Depletion yield evaluated by eq. 2 from experimental data (cross points, dashed line) and simulations (solid curve) as a function of flow rate (200 μmol L⁻¹ FcMeOH in 0.2 mol L⁻¹ phosphate buffer).

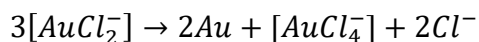
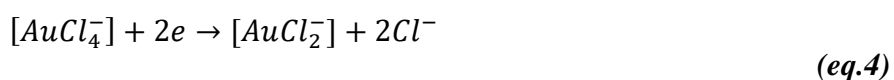
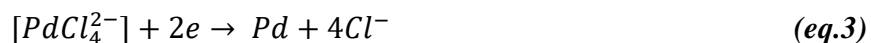
216 In comparison to data obtained by CV (Figure 3-b) the same behavior was observed as a function
 217 of flow rate. A maximal depletion yield of 76.4% at the lowest flow rate 1 μL min⁻¹. The
 218 discrepancy between experimental and simulated data was similar. Indeed, the experimental
 219 depletion yields were lower than the predicted ones with: 76.4±3.3 % versus 99.6 at 1 μL min⁻¹
 220 and 41.1±7.0 % versus 73.4 % at 4 μL min⁻¹. As for data obtained by CV, this can be attributed to
 221 the composite material C-PDMS of the electrodes that does not lead to a well-defined active
 222 surface, perfectly planar, homogeneous, with no cavity or deformation. As shown by SEM [20],
 223 the C-PDMS electrodes cannot be considered as planar for simulations. Also, the ohmic drop can

224 reduce the performances of the depletion process if steady-state current at WE_{DEP} , related to
225 mass-transport limitation, is not reached at the applied potential. The larger the WE_{DEP} ; the higher
226 the influence of ohmic drop on depletion yield. However, according to our previous experiments,
227 the potential of 1.0 V that was applied at both electrodes was sufficiently high to overcome the
228 ohmic drop and to implement a process fully limited by mass transport. Therefore, only surface
229 defaults and inactive areas of the C-PDMS electrodes could explain the deviations observed from
230 numerical simulations.

231 Compared to the previously mentioned literature [13], performance of this microdevice is lower.
232 In our case, the electrode material and aspect lead to significant differences since simulation did
233 not consider the exact shape and nature of the material, and thus cannot reach the same level of
234 efficiency than other metal electrode material. But since this system is of low fabrication cost, C-
235 PDMS electrode material is of interest to counteract the onerous and technically laborious
236 development of platinum electrodes. Also the eventual electrode passivation after successive runs
237 and its potential pollution are overcompensated by the originality of this reversible system.
238 Indeed, in case of major pollution of the electrodes during depletion processes, the device can be
239 re-used as many times as portions of the band electrodes have not been exposed to the electrolyte
240 solution. This is clearly an advantage compared to previously developed irreversibly closed
241 depletion systems. In the case of FcMeOH study, no passivation was observed for the duration of
242 the study on the different electrode areas used as continuous monitoring of blank samples was
243 performed between each analysis so as to check the electrode and eventually renew the
244 electroactive surface to avoid potential deterioration of the system.

245 *3.4. Electrochemical reduction of chlorocomplexes of gold and palladium*

246 The electrochemical activity of the different metal complexes has been previously examined on
247 glassy carbon electrode in HCl solution [22,23], with electrodeposition occurring for potential
248 value of 0 V for Pd and 0.35 V for Au. Pd and Au in HCl solution can be reduced and metals can
249 be deposited according to the following reactions:



250 Their electrodeposition on C-PDMS microelectrode within a microchannel occurs similarly but at
251 different potentials (about -0.3 V and -0.5 V/C-PDMS for Au and Pd, respectively, Figure 6). The
252 difference in values is due to the use of the pseudo-reference C-PDMS and to the nature of the C-
253 PDMS electrodes. The stripping processes take place at around 0.26 and 0.30 V/C-PDMS for Au
254 and Pd respectively, with behaviors similar to those described on glassy carbon electrodes. At 1
255 $\mu\text{L min}^{-1}$, the voltammograms on both WE_{DEP} and WE_{det} for Au and Pd do not show a wave-
256 shaped signal, except for Au on WE_{det} (Figure 6-a). Indeed, the presence of a metal deposit on C-
257 PDMS electrode such as Pd catalyzes hydroxonium ions reduction, leading to the overlapping of
258 reduction signals and possibly to some interferences, as it will be discussed later.

259
260 **Figure 6 – Cyclic voltammograms of (a) 500 $\mu\text{mol L}^{-1}$ Au in 0.14 mol L^{-1} HCL and (b) 1000**
261 **$\mu\text{mol L}^{-1}$ Pd in 0.1 mol L^{-1} HCl on WE_{det} and WE_{DEP} at 25 mV s^{-1} (static mode)**

262 *3.5. Au and Pd electrodeposition as a function of applied potential and flow rate*

263 Experiments were performed by chronoamperometry within the microchannel under constant
264 flow rate (1 $\mu\text{L min}^{-1}$) for different potentials. The deposition yields of both metals were

265 evaluated separately. Three potential steps were successively applied at WE_{DEP} and at WE_{det}: (i) 0
266 V for 30 s to evaluate the current baseline, (ii) a constant potential between -0.4 and -1.2 V for 60
267 s to reduce metal ions and finally (iii) +0.5 V for more than 100 s to fully oxidize the metal
268 deposits.

269 Figure 7 shows the chronoamperograms obtained at WE_{det} with the corresponding oxidation
270 charges (third step) at both WE_{DEP} and WE_{det} as a function of the applied potential for metal
271 reduction.

Figure 7 – (a) Chronoamperograms (i & ii) of 1000 μmol L⁻¹ Pd in 0.1 mol L⁻¹ HCl and 500 μmol L⁻¹ Au in 0.14 mol L⁻¹ HCL at WE_{det} under 1 μL min⁻¹ flow rate with WE_{DEP} polarized at various potential and (b) oxidation charges corresponding to the third step measured at WE_{det} and on WE_{DEP} as a function of the reduction potential applied to WE_{DEP} during the second step.

272
273 The depletion yield as a function of flow rate for both metals is given in Figure 8. The same
274 experiment than figure 7 was performed but without activation of WE_{DEP} so as to estimate the
275 depletion yield, calculated from the oxidation charges Q developed at WE_{DEP} and WE_{det} during
276 the third step as follows:

$$Depletion\ yield_{CA}\ (\%) = \left(1 - \frac{Q_{WE_{det}}\ with\ WE_{DEP}^{ON}}{Q_{WE_{det}}\ with\ WE_{DEP}^{ON}} \right) \times 100 \quad eq.5$$

277 Note that the calculation of the depletion yield was not based on cathodic charges because the
278 metal reductions are prone to interferences from solvent reduction. The highest depletion yields
279 were obtained for the lowest flow rates, as previously observed for FcMeOH, namely 68.2 and
280 44.6 % for Au and Pd, respectively at 1 μL min⁻¹.

281 **Figure 8 – Depletion yield estimated from Eq. 5 for Pd and Au as a function of the flow rate.**
282 **(500 $\mu\text{mol L}^{-1}$ Au in 0.14 mol L^{-1} HCl, 1 mmol L^{-1} Pd in 0.1 mol L^{-1} HCl, 200 $\mu\text{mol L}^{-1}$**
283 **FcMeOH in phosphate buffer 0.2 mol L^{-1} , first step (0 to 30 s): $\text{WE}_{\text{det}} = 0$ V/C-PDMS;**
284 **second step (30 to 90 s): $\text{WE}_{\text{det}} = -1$ V, -1.2 V and $+1$ V/C-PDMS for Au, Pd and FcMeOH,**
285 **respectively, and third step (90 to 200 s): $\text{WE}_{\text{det}} = 0.5$ V/C-PDMS (for Pd and Au, only).**
286 **WE_{DEP} is set at the same potential than WE_{det} when activated.**

287 *3.6. Depletion yield as a function of metal concentration and mechanism of deposition*

288 The previously described results allowed setting the optimum parameters for the depletion of
289 precious metals as follows: reduction potential values of -1.0 and -1.2 V for Au and Pd,
290 respectively and minimal flow rate of $1 \mu\text{L min}^{-1}$. The evaluation of the depletion yield as a
291 function of the metal concentration in acidic solution was then performed (Figure 9) using the
292 same procedure as in Figure 8 for concentrations ranging between 25 and $500 \mu\text{mol L}^{-1}$ for Au
293 and for concentrations ranging between 25 to $1000 \mu\text{mol L}^{-1}$ for Pd.

294 **Figure 9 – Depletion yield of Au and Pd as function of their concentration for flow rate of 1**
295 **$\mu\text{L min}^{-1}$. Same conditions as in Figure 8.**

296 The data showed that the depletion yield decreased with the increase in concentration for both
297 metals, with values of up to 89% for Pd ($25 \mu\text{mol L}^{-1} / 2.7 \text{ mg L}^{-1}$) and 71 % for Au ($25 \mu\text{mol L}^{-1}$
298 $/ 4.9 \text{ mg L}^{-1}$). These results are promising since they are obtained for concentrations close to the
299 expected ones in real leach liquors from waste printed circuits boards recycling processes (9.4 to
300 94.0 mg L^{-1} for Pd and 5.1 to 50.8 mg L^{-1} for Au) [24].

301 Simulations performed under similar conditions predicted a depletion yield of 89% at $2.6 \mu\text{L min}^{-1}$,
302 which is higher than the experimental one. The difference between theoretical and experimental
303 values can be attributed to several factors as discussed for FcMeOH, but other issues can also
304 affect the process in the case of the metal deposition. Indeed, for Au the deposition of the metal
305 occurs through its reduction into $\text{Au}(+I)$ (as described by eq. 4) followed by the formation of
306 $\text{Au}(0)$ by dismutation. This phenomenon occurs after adsorption of gold complexes onto active

307 sites, leading to the formation of multiple entities assimilated to nanoparticles [22]. The
308 deposition of Au occurs in parallel to the formation of Au(+III), thus a fraction of the sample
309 doesn't turn into solid and it is removed from the system without any treatment and being
310 recovered. For Pd, the mechanism of growth of metallic deposit is discussed in the literature since
311 it does not seem to correspond to a simple model where the ion is reduced on existing nuclei sites
312 [25]. Depending on the applied potential, the growth of Pd can be described by different models
313 [26] and only for high overpotential reduction value, bulk Pd deposit is observed [27]. In our
314 case, the applied potential during the reduction step of chronoamperometric experiment
315 corresponds to high overpotential, which is in favor of the formation of bulk metals. Moreover,
316 since this potential value is high, reduction of the solvent overlaps the metal reduction and this
317 leads to loss of performances of the electrode, explaining the impossibility to reach high
318 depletion yield. The fact is that as soon as the deposition process begins for a given metal, the
319 formation of the metal on the C/PDMS electrodes can induce a change in the reduction of metal
320 complexes. This was evaluated by measuring the mean current of reduction of each metal on C-
321 PDMS electrode previously modified with the same metal deposit. As illustrated in Figure 10, the
322 mean current of metal ion reduction obtained by chronoamperometry on C-PDMS or on metal
323 modified C-PDMS electrode are represented as a function of the applied potential (with blank
324 subtraction).

325 **Figure 10 – Mean current value obtained by chronoamperometry as a function of the**
326 **potential for (a) 1000 $\mu\text{mol L}^{-1}$ Pd in 0.1 mol L^{-1} HCl and (b) 500 $\mu\text{mol L}^{-1}$ Au in 0.14 mol L^{-1}**
327 **HCl at WE_{DEP} C-PDMS electrode (open square) and WE_{DEP} C-PDMS modified electrode**
328 **(solid square). Metal deposits were performed at -1 V/C-PDMS on WE_{DEP} for 120s without**
329 **flow. The same experiments with WE_{det} let to similar results (data not shown).**

330 In the case of Au, the current related to the reduction of the metal complex is higher on Au-
331 modified electrode than on C-PDMS for all the considered potential range. This can be attributed

332 to a higher active surface or to a thermodynamically more favourable deposition on Au
333 substrates. Thus, thin layered gold modification of C-PDMS electrode material is recommended
334 to enhance the performances of the process. In the case of Pd, the current related to Pd reduction
335 is clearly lower on Pd-modified electrode than on C-PDMS electrode for all the considered
336 potential range. This can be explained by the fact that Pd acts as a catalyst at such a high
337 reduction potential for the hydroxonium reduction. The reduction of Pd is thus overlapping with
338 that of protons. This leads to a decrease of the deposition rate and potentially explains why the
339 depletion yield cannot be larger. All these results demonstrate also why the depletion yield for Au
340 is much higher than for Pd (Figure 8).

341 **4. Conclusion**

342 The depletion of precious metals on home-made reversibly bonded microchips was demonstrated
343 with the integration of graphite/PDMS microelectrodes within microfluidic channels. It offers the
344 unique advantage of allowing easy washing of the microchannel and renewal of the electrode
345 surface by simply repositioning the microband electrodes which allows this type of device to
346 have a relatively much longer lifespan than irreversibly closed ones. After characterization of
347 process performances with a model electroactive probe (FcMeOH), this device was applied for
348 the electrodeposition of Au and Pd, with a depletion yield of up to 89% for Pd and 71% for Au.
349 These values were obtained for low metal concentration ($25 \mu\text{mol L}^{-1}$), which is in the range of
350 those expected from leach liquors of PCBs wastes, undergoing a hydrometallurgical treatment.
351 In order to further increase the depletion yield, other experimental parameters can be explored,
352 such as the electrode size so as to increase the overall active surface and to overcome surface
353 defaults. Such a microchip thus opens the way for real leach liquor treatment from the waste
354 electric equipment recycling industry or for wastewater purification. To do so, a focus is

355 therefore recommended on the optimization of the confinement on which this process is based, so
356 as to increase the depletion yield. Indeed, this setup can be implemented on industrial scale
357 provided that the confinement is ensured and optimized. It can also be used as a promising tool
358 for the depletion of contaminant species whose removal rests on their electrochemical reactivity,
359 such as organic pollutants or inorganic ions.

360

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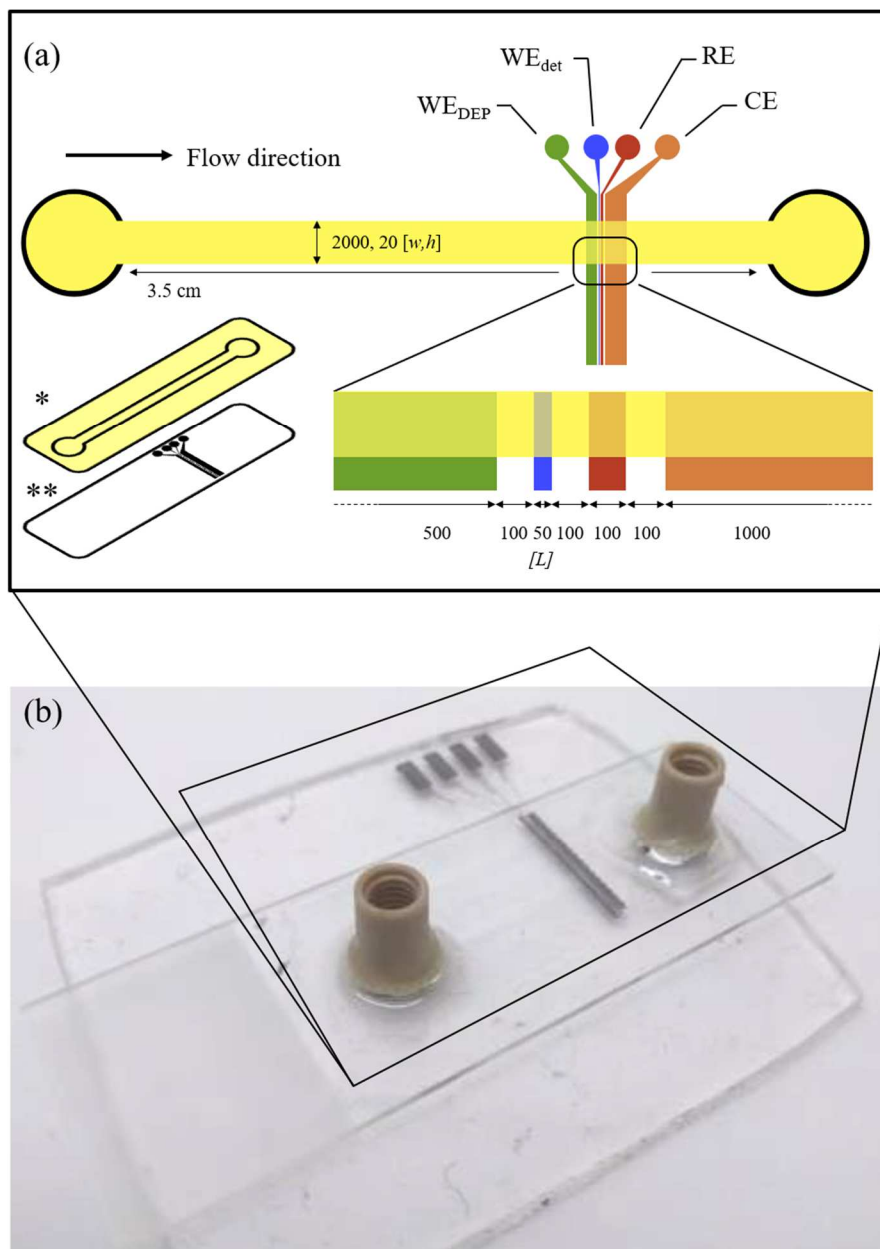


Figure 1 – (a) Scheme of microchannel with four integrated C/PDMS microbands electrodes. WE_{DEP} is dedicated to the depletion process (and thus to the recovery), WE_{det} is dedicated to the determination of the considered species and thus to the evaluation of the recovery efficiency. Dimensions in μm (unless specified). * upper part of the setup (NOA81® microchannel; ** lower part of the setup (C-PDMS electrodes in PDMS substrate) (b) Photography of the experimental setup

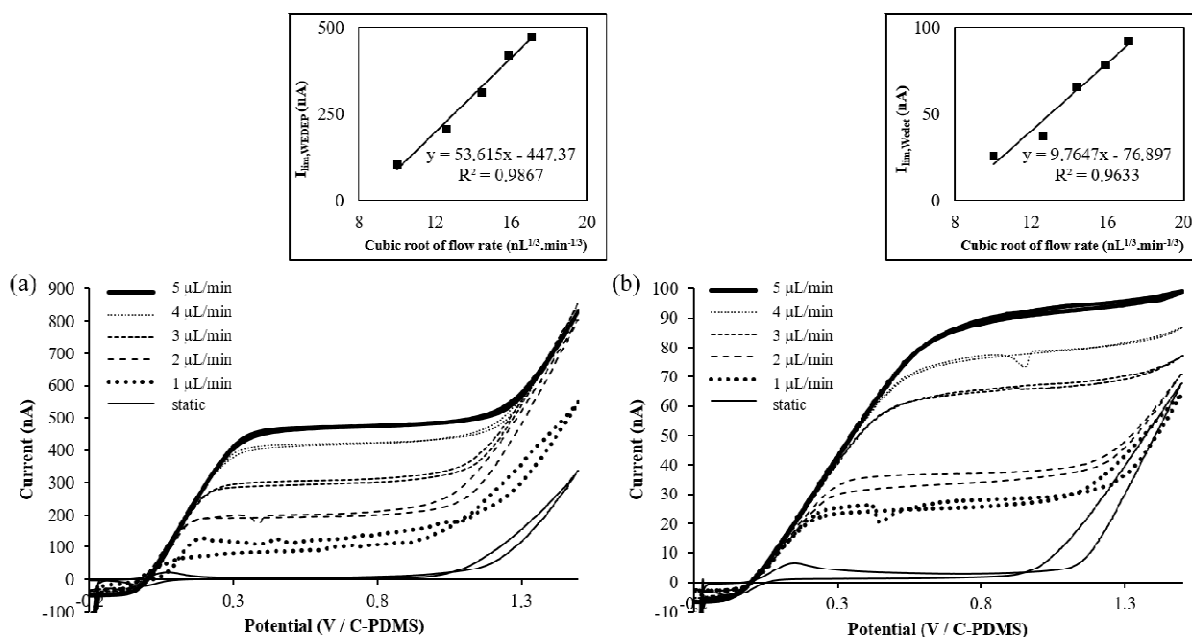


Figure 2 – Cyclic voltammograms of $200 \mu\text{mol.L}^{-1}$ FcMeOH in 0.2 mol.L^{-1} phosphate buffer at (a) WE_{DEP} and (b) WE_{DET}, in static mode (full line) and under continuous flow (from 1 to 5 $\mu\text{L} \cdot \text{min}^{-1}$). Scan rate: $25 \text{ mV} \cdot \text{s}^{-1}$. Inserts correspond to the plots of limiting currents as a function of cubic root of flow rate.

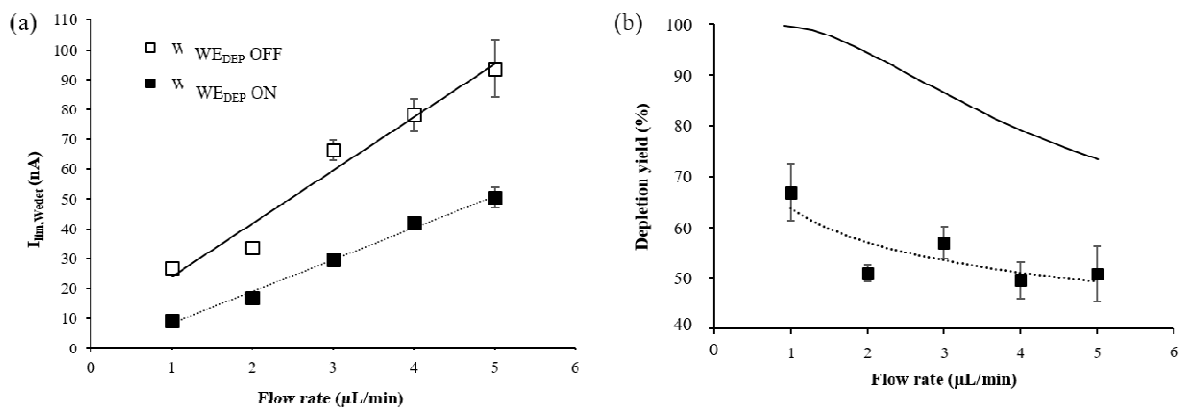


Figure 3 – (a) Limiting currents measured by cyclic voltammetry (from data in Fig. 2) at WE_{det} without (OFF) and with (ON) polarization of WE_{DEP} . (b) Corresponding depletion yield evaluated from eq.1 as a function of flow rate. WE_{DEP} is biased at 1.0 V when polarized (ON).

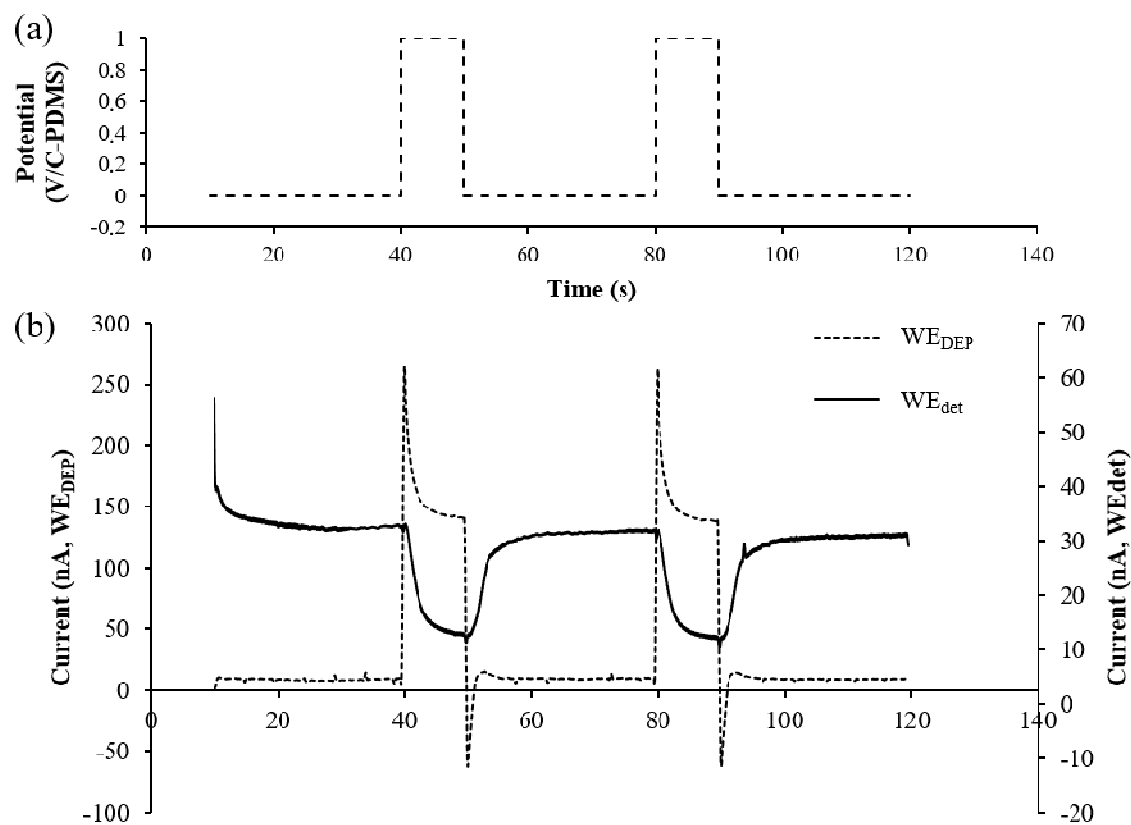


Figure 4 – (a) Potential steps applied to WE_{DEP} for successive activations (1 V) and deactivations (0 V) of the depletion process. WE_{det} is continuously polarized at 1 V. (b) Corresponding chronoamperograms monitored at WE_{det} (full line) and WE_{DEP} (dashed line). 200 $\mu\text{mol.L}^{-1}$ FcMeOH in 0.2 mol.L^{-1} phosphate buffer and flow rate of 1 $\mu\text{L.min}^{-1}$.

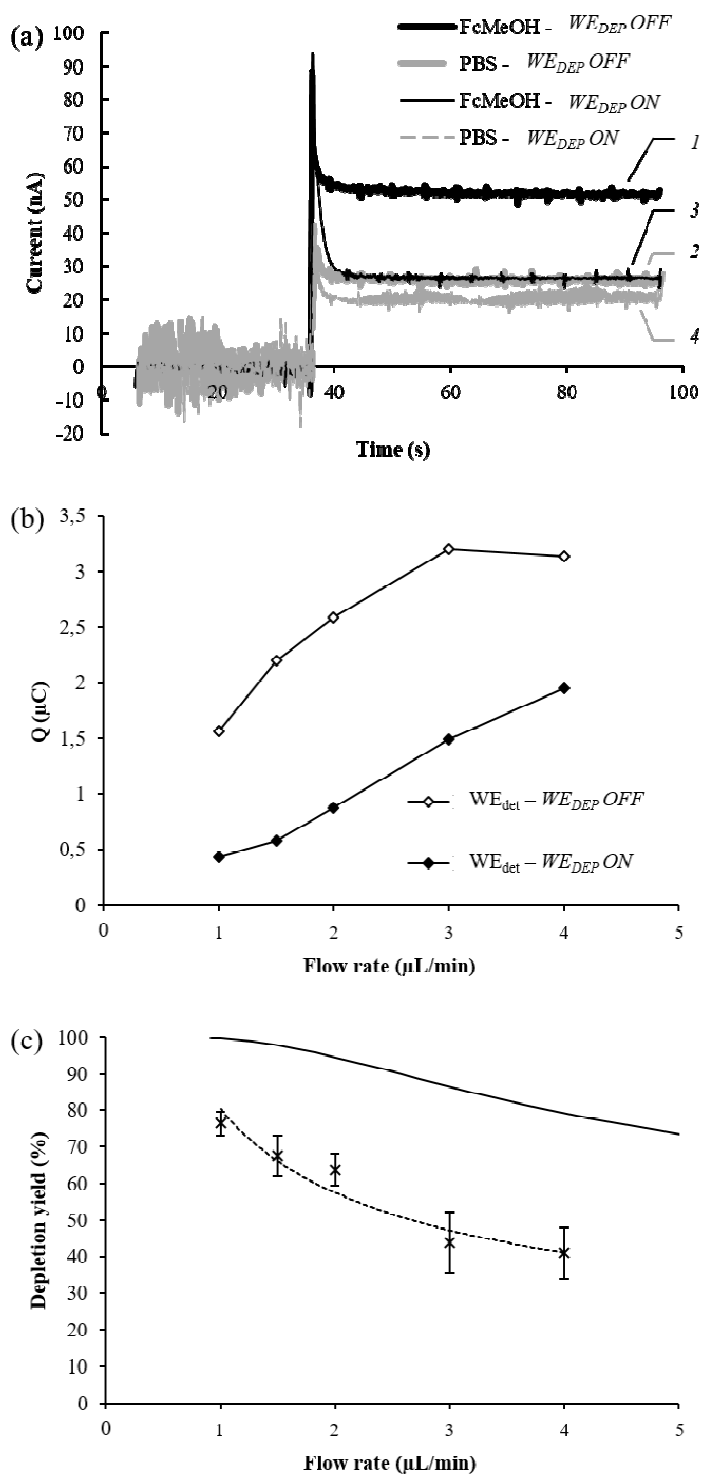


Figure 5 – (a) Chronoamperometry at WE_{det} (30 s at 0 V and 60 s at 1.0 V) without depletion (curves 1 and 2, WE_{DEP} OFF) and with depletion (curves 3 and 4, WE_{DEP} polarized at 1 V) at $1 \mu\text{L}\cdot\text{min}^{-1}$ flow rate. (b) Experimental charge $Q_{WE_{det}}$ developed at WE_{det} during the second step as a function of flow rate. (c) Depletion yield evaluated by eq. 2 from experimental data (cross points, dashed line) and simulations (solid curve) as a function of flow rate ($200 \mu\text{mol}\cdot\text{L}^{-1}$ FcMeOH in $0.2 \text{ mol}\cdot\text{L}^{-1}$ phosphate buffer).

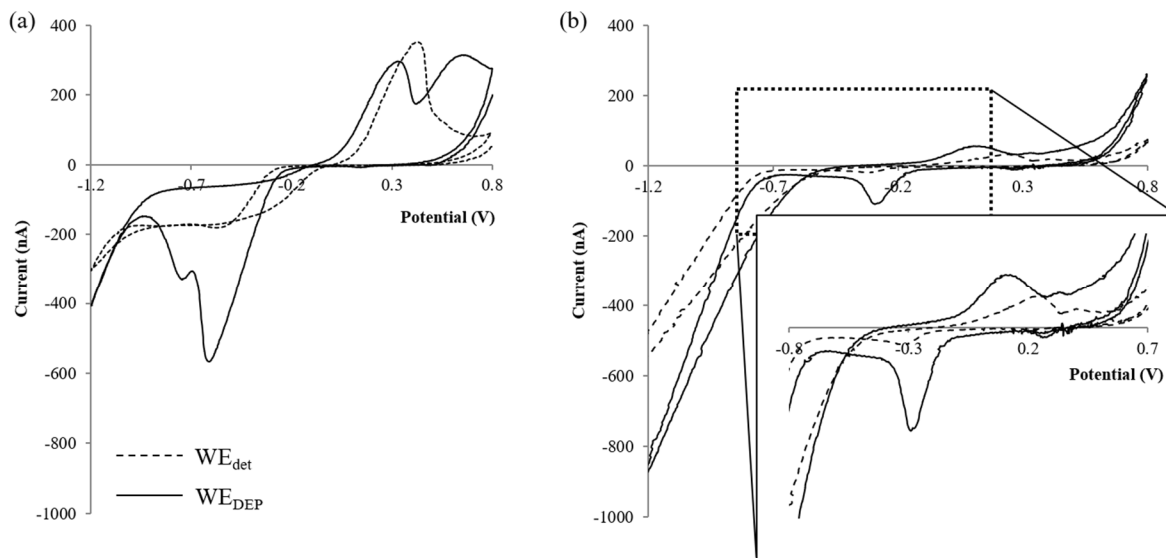


Figure 6 – Cyclic voltammograms of (a) 500 $\mu\text{mol.L}^{-1}$ Au in 0.14 mol.L $^{-1}$ HCl and (b) 1000 $\mu\text{mol.L}^{-1}$ Pd in 0.1 mol.L $^{-1}$ HCl on WE_{det} and WE_{DEP} at 25 mV/s (static mode)

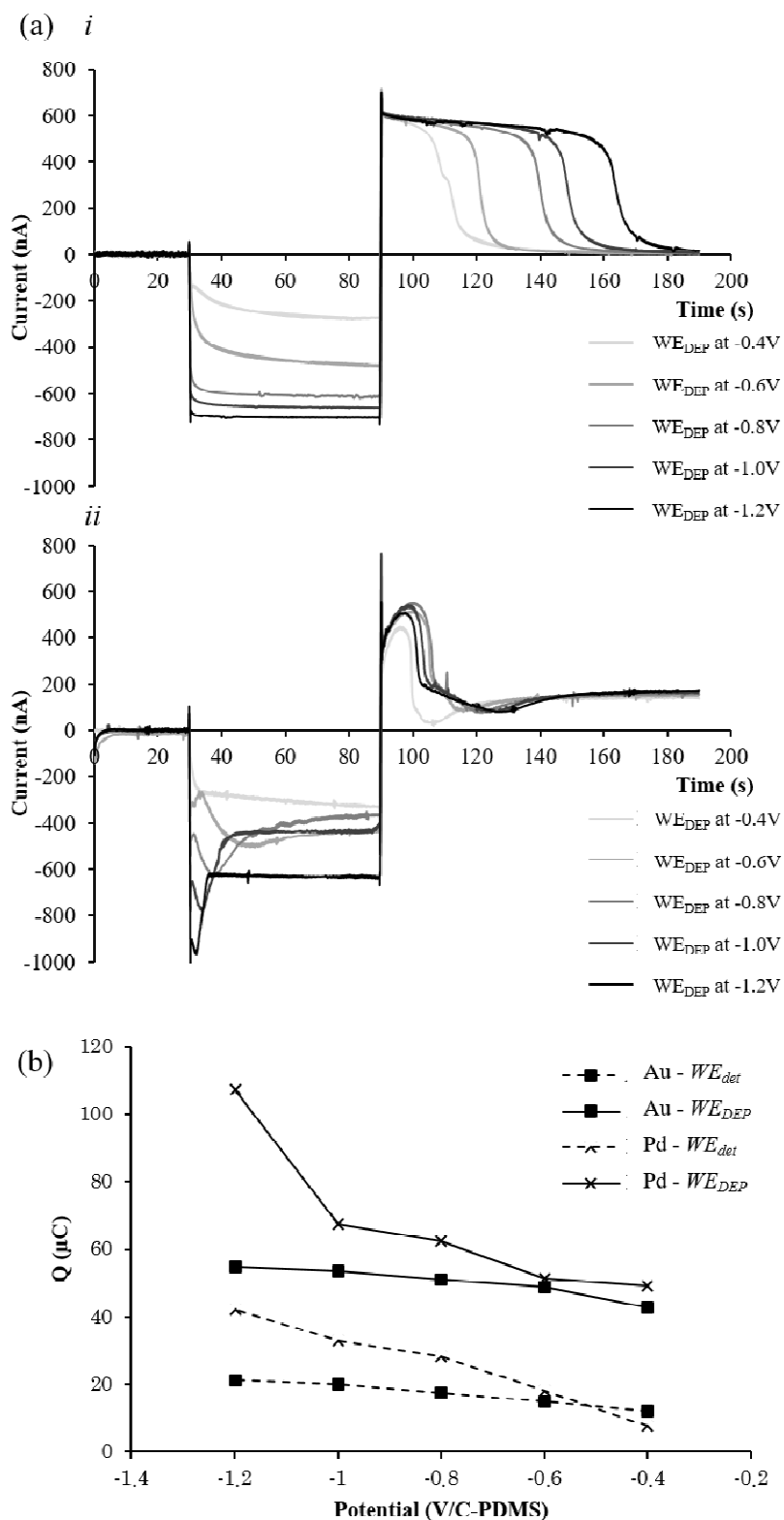


Figure 7 – (a) Chronoamperograms (i & ii) of $1000 \mu\text{mol.L}^{-1}$ Pd in 0.1 mol.L^{-1} HCl and $500 \mu\text{mol.L}^{-1}$ Au in 0.14 mol.L^{-1} HCL at WE_{det} under $1 \mu\text{L.min}^{-1}$ flow rate with WE_{DEP} polarized at various potential and (b) oxidation charges corresponding to the third step measured at WE_{det} and on WE_{DEP} as a function of the reduction potential applied to WE_{DEP} during the second step.

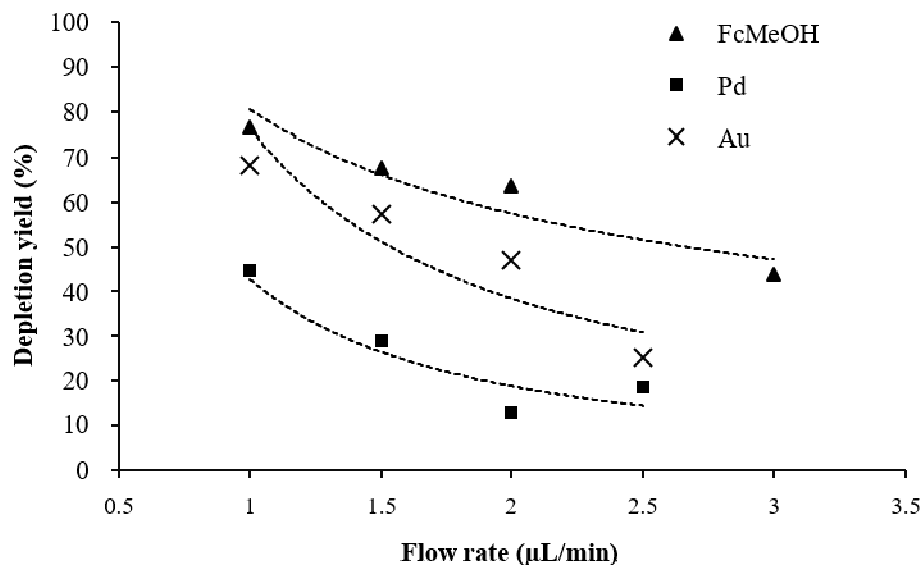


Figure 8 – Depletion yield estimated from Eq. 5 for Pd and Au as a function of the flow rate. (500 $\mu\text{mol.L}^{-1}$ Au in 0.14 mol.L^{-1} HCl, 1 mmol.L^{-1} Pd in 0.1 mol.L^{-1} HCl, 200 $\mu\text{mol.L}^{-1}$ FcMeOH in phosphate buffer 0.2 mol.L^{-1} , first step (0 to 30 s): $WE_{\text{det}} = 0$ V/C-PDMS; second step (30 to 90 s): $WE_{\text{det}} = -1$ V, -1.2 V and $+1$ V/C-PDMS for Au, Pd and FcMeOH, respectively, and third step (90 to 200 s): $WE_{\text{det}} = 0.5$ V/C-PDMS (for Pd and Au, only). WE_{DEP} is set at the same potential than WE_{det} when activated.

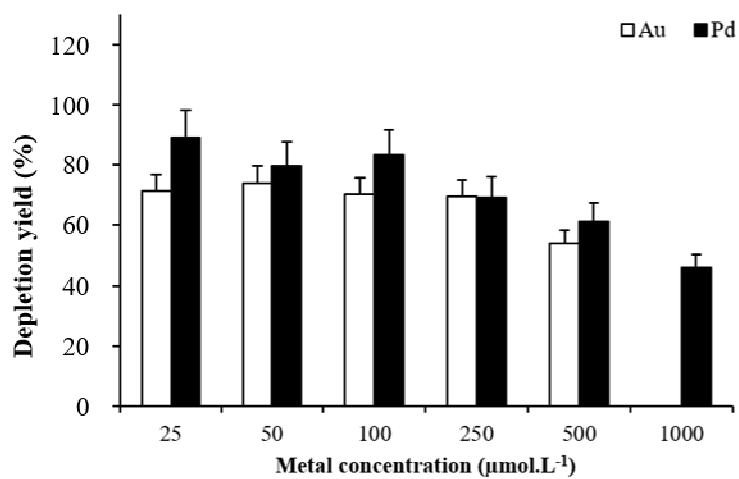


Figure 9 – Depletion yield of Au and Pd as function of their concentration for flow rate of 1 µL.min⁻¹. Same conditions as in Figure 8.

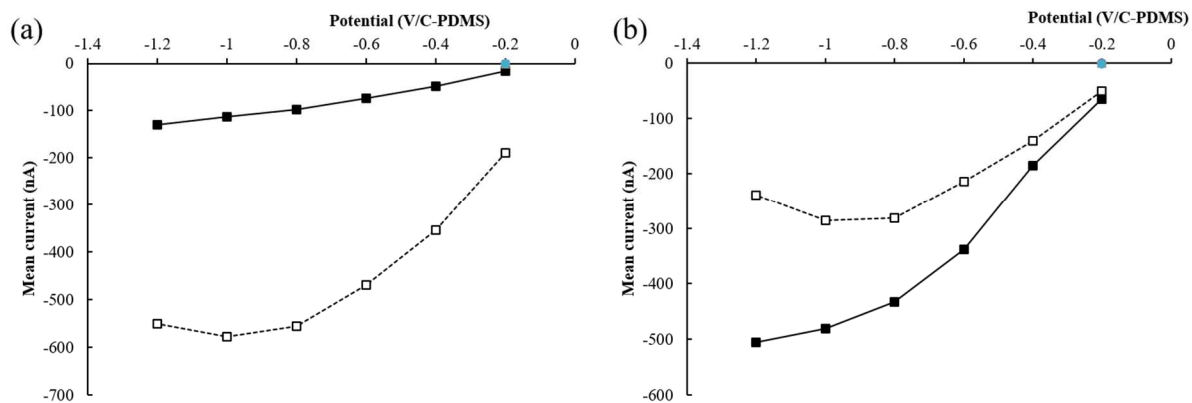


Figure 10 – Mean current value obtained by chronoamperometry as a function of the potential for (a) 1000 $\mu\text{mol.L}^{-1}$ Pd in 0.1 mol.L⁻¹ HCl and (b) 500 $\mu\text{mol.L}^{-1}$ Au in 0.14 mol.L⁻¹ HCl at WE_{DEP} C-PDMS electrode (open square) and WE_{DEP} C-PDMS modified electrode (solid square). Metal deposits were performed at -1 v:C-PDMS on WE_{DEP} for 120s without flow. The same experiments with WE_{det} let to similar results (data not shown).