

Separation of lead from high matrix  
electroless nickel plating waste solution  
using an ion-selective immobilized macrocycle  
system

著者	Rahman Ismail M. M., Furusho Yoshiaki, Begum Zinnat A., Ronald Neil Izatt, Akhmad Sabarudin Bruening, Hasegawa Hiroshi
journal or publication title	Microchemical Journal
volume	98
number	1
page range	103-108
year	2011-05-01
URL	<a href="http://hdl.handle.net/2297/26264">http://hdl.handle.net/2297/26264</a>

doi: 10.1016/j.microc.2010.12.005

1 **Separation of Lead from High Matrix Electroless Nickel Plating Waste**  
2 **Solution Using an Ion–Selective Immobilized Macrocyclic System**

3  
4  
5  
6  
7 Ismail M. M. Rahman<sup>1,2\*</sup>, Yoshiaki Furusho<sup>3\*</sup>, Zinnat A. Begum<sup>1</sup>, Neil Izatt<sup>4</sup>, Ronald  
8 Bruening<sup>4</sup>, Akhmad Sabarudin<sup>5,6</sup>, Hiroshi Hasegawa<sup>1\*</sup>

9  
10 <sup>1</sup>*Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa*  
11 *920–1192, Japan*

12 <sup>2</sup>*Department of Chemistry, Faculty of Science, University of Chittagong, Chittagong 4331,*  
13 *Bangladesh*

14 <sup>3</sup>*GL Sciences Inc., Nishishinjuku 6-22-1, Shinjuku, Tokyo 163-1130, Japan*

15 <sup>4</sup>*IBC Advanced Technologies Inc., 856 East Utah Valley Drive, American Fork, UT 84003*  
16 *USA*

17 <sup>5</sup>*Division of Nanomaterial Science, EcoTopia Science Institute, Nagoya University, Furo-cho,*  
18 *Chikusa-ku, Nagoya 464-8603, Japan*

19 <sup>6</sup>*Department of Chemistry, Faculty of Science, Brawijaya University, Jl. Veteran Malang 65145*  
20 *Indonesia*

21  
22  
23  
24  
25 \*Author(s) for correspondence

26 E-mail: I.M.M.Rahman@gmail.com (I.M.M. Rahman); furusho@gls.co.jp (Y. Furusho);  
27 hhiroshi@t.kanazawa-u.ac.jp (H. Hasegawa).

28 TEL/Fax: +81-76-234-4792

29 **Abstract**

30 Separation of trace levels of lead from concentrated–matrix electroless nickel plating  
31 (ENP) waste solutions is required to meet the increasingly stringent environmental  
32 regulations. A solid phase extraction (SPE) system using a molecular recognition technology  
33 (MRT) gel was used for the selective separation of trace levels of lead (Pb) from the waste  
34 discharge of ENP operations, followed by subsequent analysis with inductively coupled  
35 plasma optical emission spectrometry (ICP–OES). Two SPE–MRTs, AnaLig® Pb–01 and  
36 AnaLig® Pb–02, packed in 3 mL polypropylene cartridges were used to treat the synthetic  
37 metal–waste solutions that were used to simulate the typical metal mixture in ENP bath waste.  
38 The fortified solutions contained 100–1000  $\mu\text{g L}^{-1}$  of Pb in an  $\text{HNO}_3$  matrix with pre–added  
39 Ni, Cu and other interfering elements (1000  $\text{mg L}^{-1}$ ). After the sample treatment, the SPE–  
40 MRT cartridges were washed with water and 0.1 M nitric acid, followed by elution with 0.03  
41 M EDTA. The matrix elements (e.g., Ni, Cu) were completely removed at the washing step,  
42 while the ‘captured’ Pb was quantitatively eluted, as determined by ICP–OES measurements.  
43 The detection limit of the proposed method was 2.6  $\mu\text{g L}^{-1}$ . ‘Real’ samples from commercial  
44 ENP operations were used to assess the validity of this method, and almost quantitative Pb  
45 recovery was observed. The excellent Pb selectivity of the SPE–MRT system indicates the  
46 potential of the proposed technique for trace–level Pb separation from the Pb–containing high  
47 matrix aqueous waste discharge.

48

49 **Keywords**

50 Solid phase extraction, Molecular Recognition Technology, lead separation, non–  
51 destructive, ion–selective, electroless nickel plating solution

52

53

## 54 **1.0 Introduction**

55       Lead (Pb) is ubiquitous in nature and has been and continues to be extensively used in  
56 industrial processes such as the smelting of lead, the recycling of lead batteries, the  
57 manufacturing of lead paints, and electroless nickel plating [1]. In recent years, there has  
58 been increased concern over the content of lead in the environment due to its high persistence  
59 [1, 2]. Humans are exposed to lead through contaminated drinking water and food [3, 4], and  
60 lead remains in the system for a long period of time because of its long half-life when  
61 absorbed [2]. Lead is toxic to humans, causing hematological damage, brain damage, anemia,  
62 and kidney malfunctioning [1, 2, 5]. Therefore, the World Health Organization (WHO)  
63 recommends that Pb concentrations be below  $10 \mu\text{g L}^{-1}$  in natural water systems [6].

64       Electroless nickel plating (ENP) technology is a widely applied industrial technique for  
65 the surface modification of solids such as metal or plastic. In the ENP technique, an auto-  
66 catalytic reaction is used to deposit a coating of nickel on the plating surface [7, 8]. An ENP  
67 bath is essentially a meta-stable system due to the autocatalytic nature. Therefore, tiny  
68 particles of nickel or/and nickel phosphate, generated as by-products in the plating bath,  
69 initiate a rapid propagation of Ni colloidal particles, resulting random bath decomposition [9,  
70 10]. A significant increase in operation costs thus may occur with the generation of large  
71 amounts of environmentally hazardous waste [9, 11]. A trace amount of a special kind of  
72 chemical known as a stabilizer is usually added to overcome the problems related to bath  
73 decomposition [8, 9].  $\text{Pb}^{2+}$  ion is a commonly used stabilizer material in commercial ENP  
74 operations [8, 11]. Recently, stringent environmental regulations were imposed by  
75 government authorities to reduce the amount of toxic materials released into the environment  
76 by restricting the concentrations of certain toxic substances allowed in a manufactured  
77 product and providing for the recyclability of the manufactured product. The Restriction of  
78 Hazardous Substances (RoHS) directive [12] and the End of Life Vehicle (ELV) directive

79 [13] specify the limit for Pb in an electroless nickel deposit at less than  $1.0 \text{ mg L}^{-1}$ . Therefore,  
80 the separation of trace amounts of lead from ENP bath solutions is required to protect the  
81 environment.

82 Inductively coupled plasma optical emission spectrometry (ICP-OES) is a good  
83 technique for the determination of trace metal concentrations in aqueous waste solutions.  
84 However, low sensitivity at trace level concentrations and high levels of matrix make the  
85 accurate analytical measurement of Pb concentrations difficult [14]. Hence,  
86 separation/preconcentration steps in combination with the analytical technique are required to  
87 avoid the matrix effect [1]. Co-precipitation [15], liquid-liquid extraction [16], cloud point  
88 extraction [17], micro-extraction [1], and solid-phase extraction [18] are some commonly  
89 used techniques for the separation and preconcentration of trace amounts of Pb.

90 Solid phase extraction (SPE) is usually considered to be superior to traditional  
91 extraction techniques with respect to simplicity, rapidity, and the ability to attain a high  
92 concentration factor when the level of the ion being removed is present at trace levels [18,  
93 19]. The main requirements for such trace level binding and concentration for analytical- or  
94 process-scale separation using SPE materials are as follows: highly selective and efficient  
95 extraction of the targeted metal ion in the matrix range requiring separation, fast and  
96 quantitative retention and easy recovery of the retained analytes, repeated usability, and  
97 accessibility [20-22]. Two methodologies have been commonly performed for solid phase  
98 extraction of Pb: one based on chemical reactions, either the synthesis of a selective ligand  
99 [23] or the covalent coupling of Pb to a support material [24, 25], and the other involves  
100 functionalization of the solid support itself [26, 27]. Several SPE materials, *e.g.*, activated  
101 carbon [28], cellulose [29], amberlite XAD resins [30], chromosorb resin [31], ambersorb  
102 resin [32, 33], polyurethane foam [34], and chitosan [27], have been used for the  
103 separation/preconcentration of Pb. However, most of the mentioned SPE systems have

104 difficulty in separating out trace levels of Pb when there are high concentrations of other 2+  
105 transition or post-transition elements (such as Ni and Cu) in the matrix [35, 36], such as in  
106 ENP waste solutions or other industrial wastes. Hence, SPE materials with sufficiently high  
107 and selective affinity to trace levels of Pb are required to treat such waste solutions.

108 Molecular recognition technology (MRT) offers non-destructive, selective, and fast  
109 separation of an analyte of interest. Macrocycles, covalently attached to the inert silica or  
110 polymeric support materials, are used as the SPE material in MRT. In SPE-MRT, separation  
111 of the target analyte is performed based on the combination of size, configuration, electronic  
112 interaction, charge, wetting, and other factors. The technique also shows excellent selectivity  
113 in binding the analyte of interest even in highly concentrated matrix solutions [37]. The SPE-  
114 MRT technique has been successfully applied for the separation/preconcentration of lead  
115 from biological and environmental samples [35, 36, 38, 39].

116 In this work, two MRT materials, AnaLig® Pb-01 and AnaLig® Pb-02, were used for  
117 the adsorption and separation of lead from high matrix ENP bath solutions containing large  
118 amounts of Ni, Cu, and other similar interfering 2+ transition metal ions, and the separated  
119 samples were subsequent analyzed by ICP-OES. This is the first-ever report focusing the  
120 non-destructive separation of trace amounts of lead from high matrix ENP bath waste  
121 solutions. The separation technique also has the potential to be used for the separation of Pb  
122 from high matrix industrial waste solutions to meet the environmental safety regulations.

## 123 **2.0 Experimental**

### 124 ***2.1 Reagents and materials***

125 Standard stock solutions (1000 mg L<sup>-1</sup>) of Pb and other elements from Plasma CAL,  
126 SCP Science, Canada, were used. Working standards of metal solutions in the range of mg  
127 L<sup>-1</sup> to µg L<sup>-1</sup> were prepared by dilution on a weight basis. Ultrapure reagent grade HNO<sub>3</sub>  
128 (PlasmaPURE Plus, SCP Science, Canada) was used to prepare the washing solution and the

129 high matrix sample solution. Ethylenediaminetetraacetic acid (EDTA) from Dojindo  
130 Laboratories, Japan, was dissolved in electronic industrial reagent grade ammonia water  
131 (29%) purchased from Kanto Chemicals, Japan, to prepare a 0.03 M solution. Ultrapure water  
132 (18.3 M $\Omega$  cm<sup>-1</sup> resistivity) prepared by an Elix 3/Milli-Q Element system (Nihon Millipore,  
133 Tokyo, Japan) was used throughout and is referred to as ultrapure water hereafter.

134 The lead-selective SPE-MRT materials, AnaLig® Pb-01 and AnaLig® Pb-02, were  
135 purchased from GL Sciences Inc., Japan. The SPE sorbents are proprietary polymeric organic  
136 materials, and the sorption ability is attributable to molecular recognition and macrocyclic  
137 chemistry. The specifications of the sorbent particles are as follows: (a) mesh size – 60 to  
138 100; (b) density – 0.4 g mL<sup>-1</sup>; (c) operational pH range – <0 to 9.5; and (d) binding capacity  
139 – 0.1 to 0.3 mmol g<sup>-1</sup>.

140 Synthetic metal-waste solutions simulating the waste discharge from ENP baths were  
141 prepared in a 2 M HNO<sub>3</sub> matrix containing either 100 or 1000  $\mu$ g L<sup>-1</sup> of Pb and 1000 mg L<sup>-1</sup>  
142 or higher of either Cu or Ni.

143 The ‘real’ ENP bath solutions used to assess the validity of the technique were  
144 obtained from Nikko Metal Plating Co., Ltd., Japan (now merged with Nikko Shoji Co, Ltd.,  
145 Japan).

146 Low-density polyethylene laboratory ware from Nalge, USA, was used throughout.  
147 For cleaning, the bottles and laboratory ware were soaked in an alkaline detergent (Scat 20X–  
148 PF, Nacalai Tesque, Japan) overnight, rinsed with ultrapure water, soaked in 4 M HCl  
149 overnight, and rinsed again with ultrapure water. Perfluoroalkoxy tubes and micropipette tips  
150 (Nichiryo, Japan) were cleaned according to the procedure described by Sohrin et al. [40].

## 151 ***2.2 Column separation procedure***

152 SPE materials packed in 3 mL polypropylene cartridges were used in this experiment.  
153 MetaPREP® APS-1 (M & S Instruments, Japan), an automated-robotic system, was used for

154 sample loading and treatment. The whole procedure was computer-controlled and ran  
155 through five steps: rinsing, conditioning, collection, washing, and elution.

156 In the rinsing and conditioning steps, 0.1 M HNO<sub>3</sub>, ultrapure water, and 0.03 M  
157 EDTA were passed through the SPE-MRT cartridge, followed by conditioning with water.  
158 Then, the sample solution was passed through the cartridge. The cartridge effluent was  
159 collected. The next step was washing, which was conducted with the target to remove  
160 residual matrix solution from the cartridge because such residual matrix could affect the  
161 accurate measurement of Pb. The first washing with ultrapure water aimed to remove  
162 elements that were retained in the void volume of the SPE material. The second washing with  
163 0.1 M HNO<sub>3</sub> was used to remove metals adsorbed on the silica support of the SPE-MRT;  
164 lead cannot be eluted by HNO<sub>3</sub>. The third washing with ultrapure water was used to prevent  
165 acidification and/or precipitation of EDTA due to the contact with HNO<sub>3</sub>. Low background  
166 levels of Ni and Cu combined with the concentrated Pb levels in the eluent after SPE-MRT  
167 pretreatment were achieved after the washing steps. In the next step, the analyte adsorbed on  
168 the SPE-MRT cartridge was eluted with 0.03 M EDTA in ammonia solution, and the eluent  
169 was subsequently analyzed using an SPS 5100 ICP-OES system (SII NanoTechnology Inc.,  
170 Japan). The operating conditions of ICP-OES is shown in Table 1. The separation process is  
171 shown schematically in Fig. 1. The average of triplicate measurements was used in all  
172 calculations.

### 173 **3.0 Results and discussion**

#### 174 ***3.1 Effect of pH***

175 Retention of Pb on the Pb-01 and Pb-02 SPE-MRT cartridges was studied as a  
176 function of pH. The pH values of the samples were adjusted either with 1.0, 0.1, 0.01, or  
177 0.001 M HNO<sub>3</sub> (pH ≤ 3) or with ammonium acetate solution (pH 5–9). Almost complete



178 retention of lead (%),  $96.1 \pm 3.2$  for Pb-01 and  $98.8 \pm 0.4$  for Pb-02, in the studied pH range  
179 (Fig. 2) was observed. Hence, the MRT materials showed high affinities for Pb with minimal  
180 or no affect from the solution pH. A sample pH of 1 or lower was maintained for further  
181 experiments to avoid any risk of precipitation during sample preparation or binding of  
182 analytes to the silica gel support itself.

### 183 *3.2 Effect of sample loading flow rate*

184 The retention of an analyte to a sorbent material depends on the sample loading flow  
185 rate. The effect of the sample loading flow rate on the recovery percentage was analyzed  
186 under optimum conditions. The solution was passed through the cartridge using flow rates in  
187 the range of 0.5–100 mL min<sup>-1</sup>. As shown in Fig. 3, the retention of Pb on the MRT gel  
188 cartridges was quantitative up to a flow rate of 1 mL min<sup>-1</sup>, followed by gradual decrease in  
189 the retention rate with increases in the flow rate. Analyte recoveries (%) of  $92.5 \pm 6.2$  for Pb-  
190 01 and  $95.0 \pm 2.5$  for Pb-02 were observed at the high flow rates (5–100 mL min<sup>-1</sup>),  
191 indicating the constant lead-retaining capability of the MRT gel during the initial loading  
192 period. Based on this experiment, a sample loading flow rate of 1 mL min<sup>-1</sup> was selected to  
193 achieve maximum quantitative extraction of the analyte.

### 194 *3.3 Effect of eluent concentration and volume*

195 To achieve a high enrichment factor during the separation process, the eluent should  
196 be selected based on its capacity to elute the analyte with a minimum volume without  
197 affecting the accurate determination of the target analyte [41]. Either EDTA or NTA is  
198 recommended as the eluent for Pb-01 and Pb-02. We prefer to use EDTA as the eluent  
199 because the stability constant of Pb-EDTA is larger than that of Pb-NTA. To determine the  
200 effect of the eluent concentration on the elution of the analyte, a series of fortified aqueous  
201 samples each containing 5 µg L<sup>-1</sup> of Pb<sup>2+</sup> were passed through the SPE-MRT cartridges, and  
202 the extracted analytes were eluted using 0.03–0.10 M EDTA. ICP-OES analysis followed

203 elution (Fig. 4a). The Pb recovery rate remained almost constant with increasing EDTA  
204 concentrations, indicating the complete elution of Pb at all concentration ranges examined;  
205 0.03 M was selected as the eluent concentration for the subsequent experiments. An eluent  
206 flow rate of 2.0 mL min<sup>-1</sup> enabled complete elution of Pb from the SPE–MRT cartridges,  
207 which may be due to the faster rate of complex formation between EDTA and Pb. The eluent  
208 volume required for complete elution of the ‘captured’ Pb from the SPE–MRT system was  
209 studied (Fig. 4b). The SPE–MRT cartridges were loaded with 2 mL of 0.03 M EDTA each  
210 time, and the combined recovery (%) of all the fractions was 101 ± 2.1. Hence, 8 mL of 0.03  
211 M EDTA was selected as the eluent.

### 212 ***3.4 Effect of coexisting ions***

213 The Pb selectivity of the SPE–MRT cartridges in the presence of other coexisting ions  
214 was examined by treating sample solutions containing 20 elements at concentrations of 100  
215 µg L<sup>-1</sup> each under the optimal conditions (Fig. 5). The elements were added individually to  
216 the synthetic sample solutions, and the final solutions were allowed to equilibrate for 24 h  
217 before use. The study was carried out in a non–competitive environment by applying 4 mL of  
218 ion–fortified sample at the optimized flow rate with subsequent collection using an  
219 appropriate eluent. As observed, the recovery rates (%) of Pb were 97.6 ± 3.2 with Pb–01 and  
220 99.3 ± 4.1 with Pb–02, whereas the recovery rates of other elements were less than 37%.  
221 Therefore, both Pb–01 and Pb–02 have excellent selectivity and stronger affinity for Pb than  
222 for other elements in acidic matrices. The recovery of Pb was fairly free from interference  
223 resulting from the coexisting ions.

### 224 ***3.5 Analytical characteristics***

225 ICP–OES was used to measure the concentrations of Pb in the treated solutions from  
226 the Pb–01 and Pb–02 SPE–MRT cartridges. Using the optimized conditions, a calibration  
227 graph was obtained. The data was explained by the following equation:  $y = 98.3x + 20.7$ , with

228 a correlation coefficient of 0.993. The detection limit (LOD) of the proposed technique,  
229 calculated as three times the standard deviation of the Pb analysis was approximately 2.6  $\mu\text{g}$   
230  $\text{L}^{-1}$ .

### 231 ***3.6 Separation of Pb from synthetic high matrix metal–waste solution***

232 The synthetic metal–waste samples (4 mL), emulating typical metal mixtures in  
233 aqueous ENP bath discharge and termed ‘model’ ENP solutions hereafter, were loaded onto  
234 SPE–MRT cartridges followed by elution with 0.03 M EDTA (8 mL). The recoveries (%) of  
235 Pb from the Cu–matrix ‘model’ ENP solution were found to be  $87.1 \pm 2.3$  and  $94.9 \pm 1.8$   
236 after treatment with Pb–01 and Pb–02, respectively. The Pb recoveries (%) were  $75.7 \pm 3.2$   
237 for Pb–01 and  $93.8 \pm 4.7$  for Pb–02 from the Ni–matrix ‘model’ ENP solution.

### 238 ***3.7 Method validation using ‘real’ ENP bath solutions***

239 The Pb separation efficiencies of the Pb–01 and Pb–02 SPE–MRT cartridges when  
240 using a matrix with a high level of background Ni were determined using ‘real’ ENP bath  
241 solutions. ‘Real’ ENP bath solutions usually contain about  $1000 \mu\text{g L}^{-1}$  of Pb and several g  
242  $\text{L}^{-1}$  of Ni and other components. Although the exact compositions of the ENP bath solutions  
243 of particular companies are proprietary, typical components include nickel sulfate (225 to 400  
244  $\text{g L}^{-1}$ ), nickel chloride (30 to 60  $\text{g L}^{-1}$ ), and boric acid (30 to 45  $\text{g L}^{-1}$ ). The plating operation  
245 is typically conducted at temperatures of 44 to 66 °C and pHs of 2 to 4.5 [42].

246 Two different sample types were available for analysis: freshly prepared and old.  
247 After the separation treatment with the Pb–01 or Pb–02 SPE–MRT cartridges, the Pb  
248 recovery (%) was about  $88.7 \pm 1.8$  and  $104 \pm 4.7$ , respectively, for the freshly prepared ENP  
249 bath solution, while it was  $87.6 \pm 3.6$  and  $97.6 \pm 4.1$  for the old ENP bath solution.

## 250 **4.0 Conclusions**

251 Immobilized macrocyclic material containing SPE materials (AnaLig® Pb-01 and  
252 AnaLig® Pb-02) known as MRT gel was used for the separation/preconcentration of Pb from  
253 ENP bath solutions followed by ICP-OES analysis. Quantitative collection of Pb was  
254 achieved using the following optimized conditions: a) pH range: 0–1; b) sample loading flow  
255 rate: 1 mL min<sup>-1</sup>; and c) eluent: 0.03 M EDTA. Of the two SPE-MRT cartridges available for  
256 Pb separation, Pb-02 showed better Pb-selectivity in the presence of competing ions when  
257 using the ENP bath solutions. Therefore, Pb-02 is a better candidate for the selective  
258 separation of Pb from high matrix industrial waste solutions. The non-destructive nature and  
259 excellent ion selectivity of SPE materials are the major focal points of the proposed  
260 separation process.

261

## 262 **Acknowledgment**

263 This research was partially supported by Grants-in-Aid for Scientific Research  
264 (K222042) from Ministry of the Environment, Japan.

265

266

267

268

269

270

271

272

273

274

275

276

277

278

279 **References**

- 280 [1] S. Dadfarnia, A.M. Salmanzadeh, A.M.H. Shabani, A novel  
281 separation/preconcentration system based on solidification of floating organic drop  
282 microextraction for determination of lead by graphite furnace atomic absorption  
283 spectrometry, *Anal. Chim. Acta* 623 (2008) 163-167.
- 284 [2] M. Ikeda, Z.W. Zhang, C.S. Moon, Y. Imai, T. Watanabe, S. Shimbo, W.C. Ma, C.C.  
285 Lee, Y.L.L. Guo, Background exposure of general population to cadmium and lead in  
286 Tainan city, Taiwan, *Arch. Environ. Con. Tox.* 30 (1996) 121-126.
- 287 [3] D.R. Lynarn, L.G. Plantanido, J.F. Cole, *Environmental Lead*, Academic Press, New  
288 York, 1975.
- 289 [4] P.J. Peterson, Lead and vegetation, in: J.O. Nriagu (Ed.) *Biochemistry of Lead in the*  
290 *Environment*, Elsevier, Amsterdam 1978, pp. 357-384.
- 291 [5] A.A. Ensafi, A.Z. Shiraz, On-line separation and preconcentration of lead(II) by solid-  
292 phase extraction using activated carbon loaded with xylenol orange and its  
293 determination by flame atomic absorption spectrometry, *J. Hazard. Mater.* 150 (2008)  
294 554-559.
- 295 [6] F. Solsona, Guidelines for drinking water quality standards in developing countries  
296 (OPS/CEPIS/PUB/02.77), Pan American Health Organization, Pan American Sanitary  
297 Bureau, Regional Office of the World Health Organization, Lima, 2002.
- 298 [7] W. Riedel, *Electroless Nickel Plating*, ASM International Finishing Publications,  
299 Stevenage, Hertfordshire, UK, 1991.
- 300 [8] G.O. Mallory, J.B. Haydu, *Electroless Plating-Fundamentals and Applications*, in,  
301 American Electroplaters and Surface Finishers Society, Orlando, FL, 1990.
- 302 [9] W.J. Cheong, B.L. Luan, D.W. Shoesmith, The effects of stabilizers on the bath  
303 stability of electroless Ni deposition and the deposit, *Appl. Surf. Sci.* 229 (2004) 282-  
304 300.

- 305 [10] X. Yin, L. Hong, B.H. Chen, T.M. Ko, Modeling the stability of electroless plating  
306 bath--diffusion of nickel colloidal particles from the plating frontier, *J. Colloid Interf.*  
307 *Sci.* 262 (2003) 89-96.
- 308 [11] K. Wang, L. Hong, Z.L. Liu, Exploring the water-soluble phosphine ligand as the  
309 environmentally friendly stabilizer for electroless nickel plating, *Ind. Eng. Chem. Res.*  
310 48 (2009) 1727-1734.
- 311 [12] Anonymous, RoHS Regulations-Government Guidance Notes, in, Department for  
312 Business, Innovation & Skills, Eco-design and Product Regulation Unit,  
313 Environmental & Technical Regulation Directorate, London, UK, 2010.
- 314 [13] Anonymous, Council Directive 2000/53/EC on End of Life Vehicles, in, Environment  
315 Directorate, European Commission, Brussels, Belgium, 2003.
- 316 [14] Y.A. Zolotov, N.M. Kuz'min, Preconcentration of Trace Elements (*Comprehensive*  
317 *Analytical Chemistry*), Elsevier Science, Amsterdam, 1990.
- 318 [15] D.S.K. Peker, O. Turkoglu, M. Soylak, Dysprosium(III) hydroxide coprecipitation  
319 system for the separation and preconcentration of heavy metal contents of table salts  
320 and natural waters, *J. Hazard. Mater.* 143 (2007) 555-560.
- 321 [16] J. Wang, E.H. Hansen, FI/SI on-line solvent extraction/back extraction  
322 preconcentration coupled to direct injection nebulization inductively coupled plasma  
323 mass spectrometry for determination of copper and lead, *J. Anal. Atom. Spectrom.* 17  
324 (2002) 1284-1289.
- 325 [17] J. Chen, S. Xiao, X. Wu, K. Fang, W. Liu, Determination of lead in water samples by  
326 graphite furnace atomic absorption spectrometry after cloud point extraction, *Talanta*  
327 67 (2005) 992-996.
- 328 [18] M. Ghaedi, F. Ahmadi, A. Shokrollahi, Simultaneous preconcentration and  
329 determination of copper, nickel, cobalt and lead ions content by flame atomic  
330 absorption spectrometry, *J. Hazard. Mater.* 142 (2007) 272-278.
- 331 [19] E. Hosten, B. Welz, Evaluation of an immobilised macrocyclic material for on-line  
332 column preconcentration and separation of cadmium, copper and lead for  
333 electrothermal atomic absorption spectrometry, *Anal. Chim. Acta* 392 (1999) 55-65.
- 334 [20] R.A. Nickson, S.J. Hill, P.J. Worsfold, Analytical perspective. Solid phase techniques  
335 for the preconcentration of trace metals from natural waters, *Anal. Proc.* 32 (1995)  
336 387-395.
- 337 [21] H. Hasegawa, I.M.M. Rahman, S. Kinoshita, T. Maki, Y. Furusho, Non-destructive  
338 separation of metal ions from wastewater containing excess aminopolycarboxylate

- 339 chelant in solution with an ion-selective immobilized macrocyclic material,  
340 *Chemosphere* 79 (2010) 193-198.
- 341 [22] I.M.M. Rahman, Z.A. Begum, M. Nakano, Y. Furusho, T. Maki, H. Hasegawa,  
342 Selective separation of arsenic species from aqueous solutions with immobilized  
343 macrocyclic material containing solid phase extraction columns, *Chemosphere* 82  
344 (2011) 549–556.
- 345 [23] D. Prabhakaran, M.S. Subramanian, Selective extraction and sequential separation of  
346 actinide and transition ions using AXAD-16-BTBED polymeric sorbent, *React. Funct.*  
347 *Polym.* 57 (2003) 147-155.
- 348 [24] D. Prabhakaran, M.S. Subramanian, A new chelating sorbent for metal ion extraction  
349 under high saline conditions, *Talanta* 59 (2003) 1227-1236.
- 350 [25] M. Kumar, D.P.S. Rathore, A.K. Singh, Amberlite XAD-2 functionalized with *o*-  
351 aminophenol: synthesis and applications as extractant for copper(II), cobalt(II),  
352 cadmium(II), nickel(II), zinc(II) and lead(II), *Talanta* 51 (2000) 1187-1196.
- 353 [26] J.P. Bernal, E.R.D.S. Miguel, J.C. Aguilar, G. Salazar, J. De Gyves, Adsorption of  
354 metallic cations on silica gel-immobilized 8-hydroxyquinoline, *Separ. Sci. Technol.*  
355 35 (2000) 1661 - 1679.
- 356 [27] A.O. Martins, E.L. da Silva, M.C.M. Laranjeira, V.T. de Fávère, Application of  
357 chitosan functionalized with 8-hydroxyquinoline: Determination of lead by flow  
358 injection flame atomic absorption spectrometry, *Microchim. Acta* 150 (2005) 27-33.
- 359 [28] A.A. Ensafi, T. Khayamian, M.H. Karbasi, On-line preconcentration system for  
360 lead(II) determination in waste water by atomic absorption spectrometry using active  
361 carbon loaded with pyrogallol red, *Anal. Sci.* 19 (2003) 953-956.
- 362 [29] M. Soylak, R.S. Cay, Separation/preconcentration of silver(I) and lead(II) in  
363 environmental samples on cellulose nitrate membrane filter prior to their flame atomic  
364 absorption spectrometric determinations, *J. Hazard. Mater.* 146 (2007) 142-147.
- 365 [30] M. Soylak, L.A. Kariper, Selective preconcentration/separation of copper(II), iron(III),  
366 and lead(II) as their *N*'-benzoyl-*N,N*-diisobutylthiourea chelates on Amberlite XAD-  
367 16 resin, *J. AOAC Int.* 93 (2010) 720-724.
- 368 [31] Y. Bakircioglu, D. Bakircioglu, N. Tokman, A novel preconcentration method for  
369 determination of iron and lead using Chromosorb-103 and flame atomic absorption  
370 spectrometry, *Anal. Chim. Acta* 547 (2005) 26-30.

- 371 [32] I. Narin, M. Soylak, The uses of 1-(2-pyridylazo) 2-naphtol (PAN) impregnated  
372 Ambersorb 563 resin on the solid phase extraction of traces heavy metal ions and their  
373 determinations by atomic absorption spectrometry, *Talanta* 60 (2003) 215-221.
- 374 [33] S. Baytak, A.R. Türker, Determination of lead and nickel in environmental samples  
375 by flame atomic absorption spectrometry after column solid-phase extraction on  
376 Ambersorb-572 with EDTA, *J. Hazard. Mater.* 129 (2006) 130-136.
- 377 [34] N. Burham, Separation and preconcentration system for lead and cadmium  
378 determination in natural samples using 2-aminoacetylthiophenol modified  
379 polyurethane foam, *Desalination* 249 (2009) 1199-1205.
- 380 [35] Y. Furusho, M. Ono, M. Yamada, K. Ohashi, T. Kitade, K. Kuriyama, S. Ohta, Y.  
381 Inoue, S. Motomizu, Advanced solid phase extraction for inorganic analysis and its  
382 applications, *Bunseki Kagaku* 57 (2008) 969-989.
- 383 [36] A. Sabarudin, N. Lenghor, Y. Liping, Y. Furusho, S. Motomizu, Automated online  
384 preconcentration system for the determination of trace amounts of lead using Pb-  
385 selective resin and inductively coupled plasma-atomic emission spectrometry,  
386 *Spectrosc. Lett.* 39 (2006) 669-682.
- 387 [37] R.M. Izatt, J.S. Bradshaw, R.L. Bruening, B.J. Tarbet, M.L. Bruening, Solid phase  
388 extraction of ions using molecular recognition technology, *Pure Appl. Chem.* 67  
389 (1995) 1069-1074.
- 390 [38] X.P. Yan, M. Sperling, B. Welz, Application of a macrocycle immobilized silica gel  
391 sorbent to flow injection on-line microcolumn preconcentration and separation  
392 coupled with flame atomic absorption spectrometry for interference-free  
393 determination of trace lead in biological and environmental samples, *Anal. Chem.* 71  
394 (1999) 4216-4222.
- 395 [39] M. Hattori, Y. Takaku, T. Shimamura, Novel rapid separation of lead using highly  
396 selective resin for measurement of precise lead isotope ratio and its application to  
397 geochemical reference samples, *Bunseki Kagaku* 57 (2008) 113-121.
- 398 [40] Y. Sohrin, S.-i. Iwamoto, S. Akiyama, T. Fujita, T. Kugii, H. Obata, E. Nakayama, S.  
399 Goda, Y. Fujishima, H. Hasegawa, K. Ueda, M. Matsui, Determination of trace  
400 elements in seawater by fluorinated metal alkoxide glass-immobilized 8-  
401 hydroxyquinoline concentration and high-resolution inductively coupled plasma mass  
402 spectrometry detection, *Anal. Chim. Acta* 363 (1998) 11-19.
- 403 [41] D. Chen, C. Huang, M. He, B. Hu, Separation and preconcentration of inorganic  
404 arsenic species in natural water samples with 3-(2-aminoethylamino)



405 propyltrimethoxysilane modified ordered mesoporous silica micro-column and their  
406 determination by inductively coupled plasma optical emission spectrometry, *J. Hazard.*  
407 *Mater.* 164 (2009) 1146-1151.

408 [42] G.D. Bari, Nickel plating, in: F. Reidenbach (Ed.) *ASM Handbook*. Vol. 5, Surface  
409 Engineering, ASM International, Materials Park, Ohio, U.S.A, 1994, pp. 201-212.

410

411 Table 1. Operating conditions of ICP–OES

---

Spectrometer	SPS 5100 (SII Nanotechnology)
RF generator	40 MHz, 1.2 kW
Plasma gas flow (L min <sup>-1</sup> )	Argon 15.0
Auxiliary gas flow (L min <sup>-1</sup> )	Argon 1.50
Nebulizer gas flow (L min <sup>-1</sup> )	Argon 0.75
Spray chamber	Glass cyclonic spray chamber
Nebulizer	Sea spray glass concentric nebulizer
Torch	One–piece extended torch in the axial view mode
Integration time/s	5
Replicates	3
Background correction	Polynomial fitted

---

412

413

414

415

416

417

418

419

420

421

422

423

424

425

426

427

428

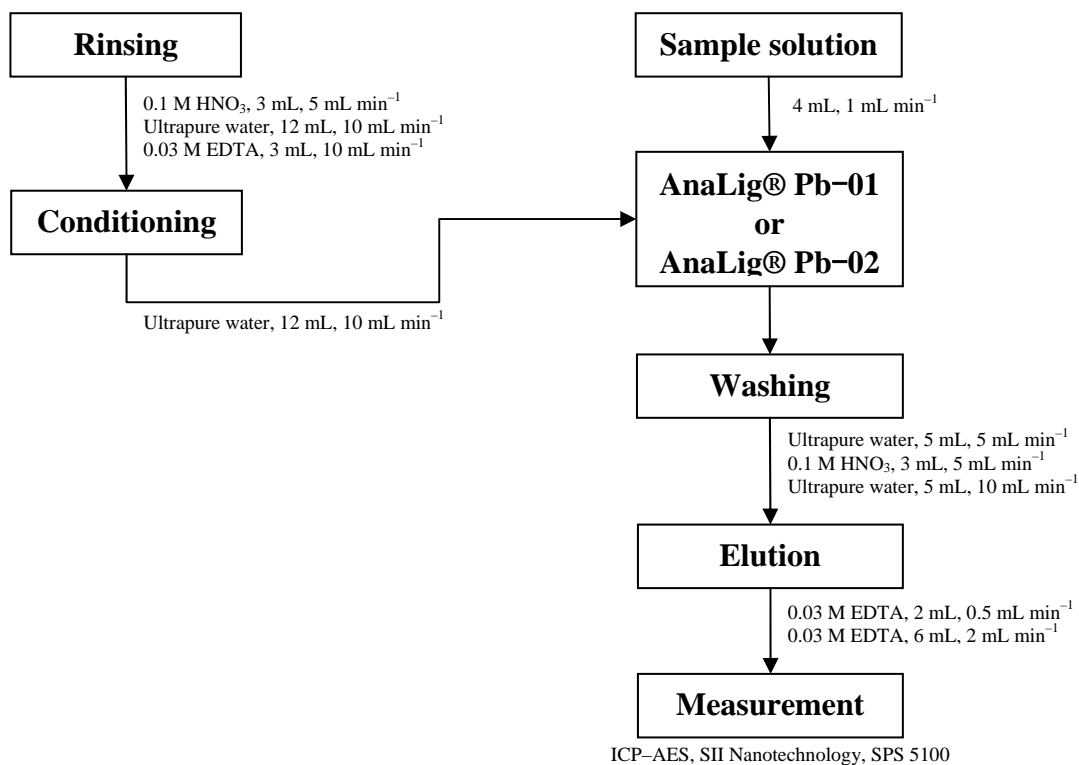


Figure 1: Schematic diagram of the experimental setup

429

430

431

432

433

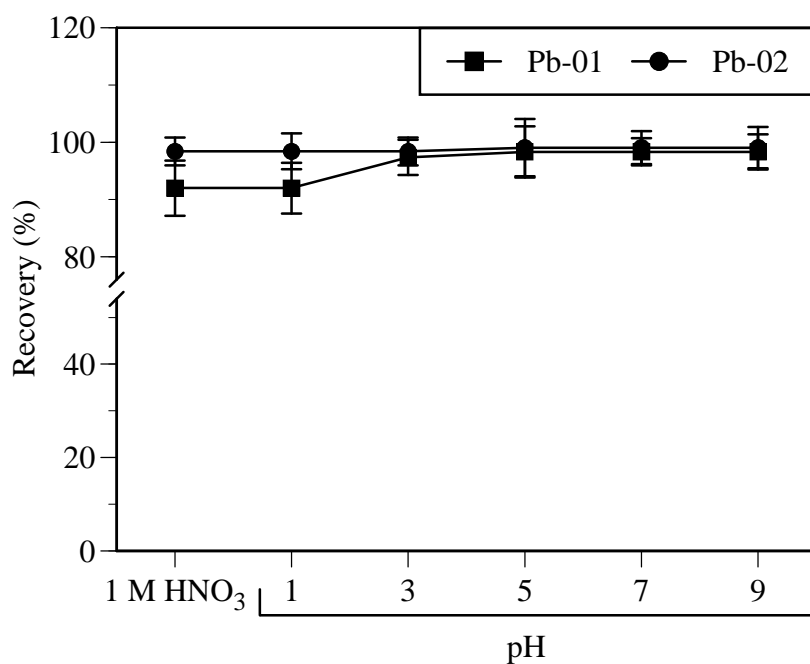
434

435

436

437

438



439

440 Figure 2: Effect of pH on the performance of SPE–MRT cartridges. Sample solution: 100  $\mu\text{g}$   
441  $\text{L}^{-1}$  Pb, volume: 4 mL, loading flow rate: 1  $\text{mL min}^{-1}$ , eluent: 0.03 M EDTA, elution flow  
442 rate: 2 mL at 0.5  $\text{mL min}^{-1}$  and 6 mL at 2  $\text{mL min}^{-1}$  ( $n = 3$ ).

443

444

445

446

447

448

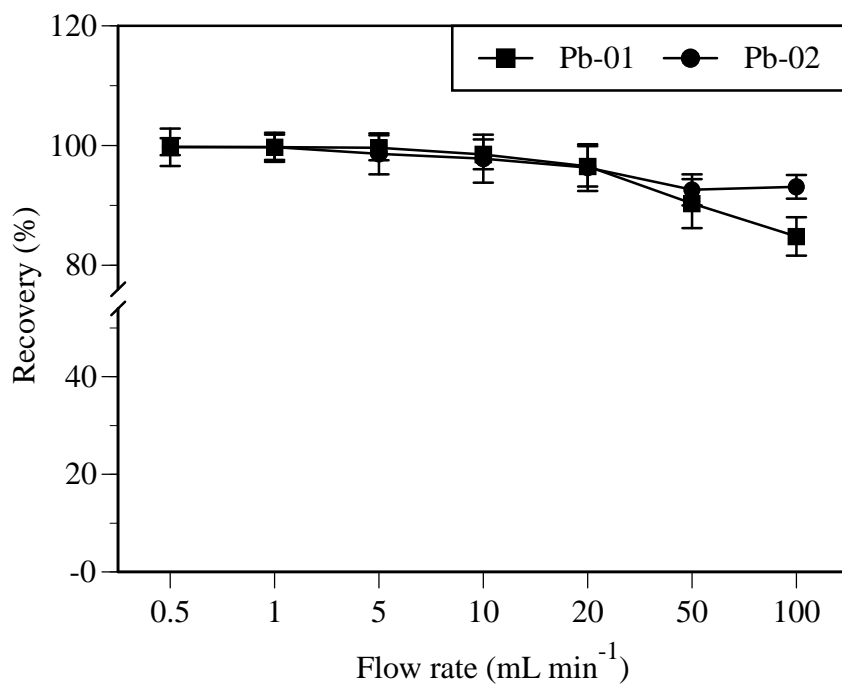
449

450

451

452

453



454

455 Figure 3: Effect of flow rate on the performance of SPE–MRT cartridges. Sample solution:

456  $100 \mu\text{g L}^{-1}$  Pb, volume: 4 mL, eluent: 0.03 M EDTA, elution flow rate: 2 mL at  $0.5 \text{ mL min}^{-1}$

457 and 6 mL at  $2 \text{ mL min}^{-1}$  ( $n = 3$ ).

458

459

460

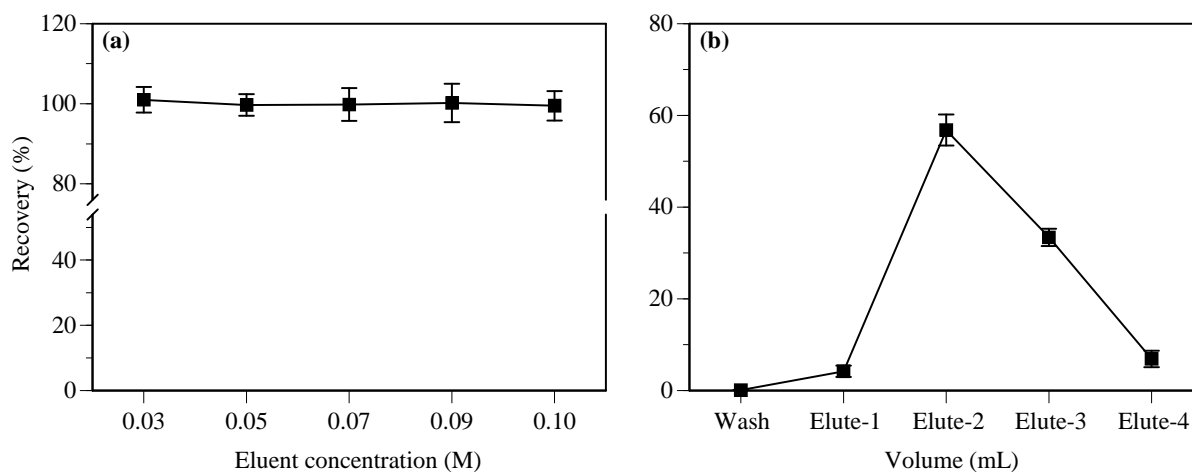
461

462

463

464

465



466

467 Figure 4: Effect of (a) eluent concentration and (b) eluent volume on the performance of Pb-  
 468 02 SPE-MRT cartridge. Sample solution:  $100 \mu\text{g L}^{-1}$  Pb, volume: 4 mL, loading flow rate:  
 469  $1.0 \text{ mL min}^{-1}$ , eluent: (a) 0.03–0.10 M EDTA (b) 0.03 M EDTA, elution flow rate: 2 mL at  
 470  $0.5 \text{ mL min}^{-1}$  and 6 mL at  $2.0 \text{ mL min}^{-1}$  ( $n = 3$ ).

471

472

473

474

475

476

477

478

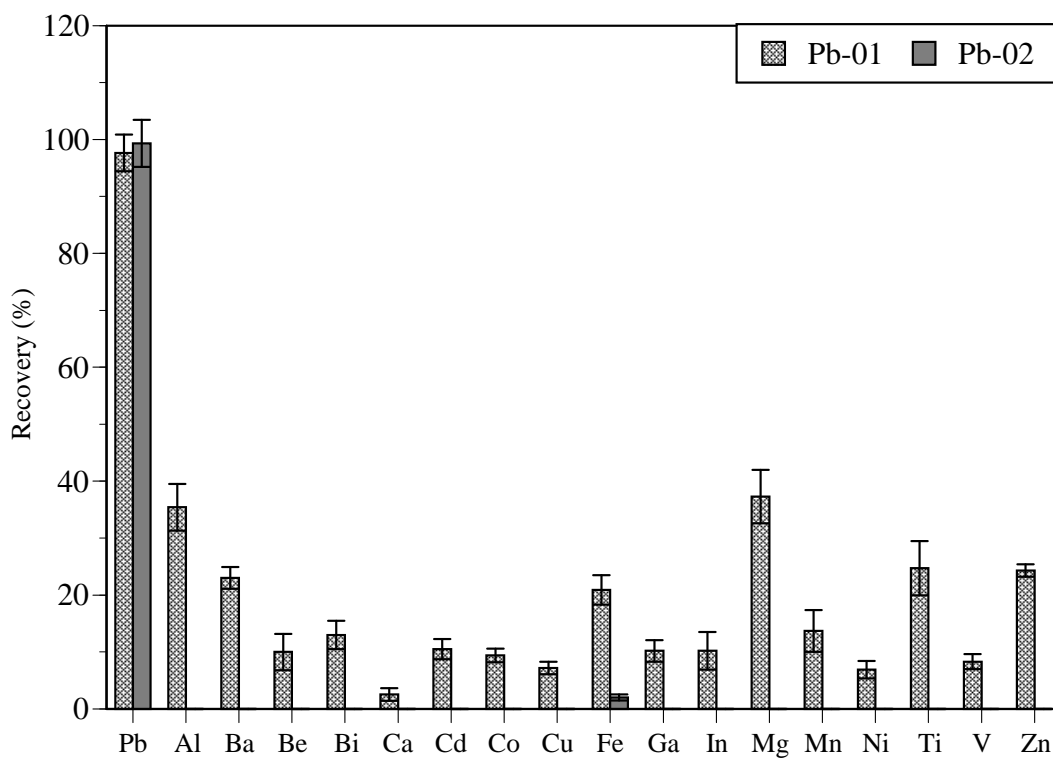
479

480

481

482

483



484

485 Figure 4: Effect of coexisting ions on the performance of SPE-MRT cartridges. Sample

486 solution:  $100 \mu\text{g L}^{-1}$  (Pb and other elements), volume: 4 mL, loading flow rate:  $1 \text{ mL min}^{-1}$ ,

487 eluent: 0.03 M EDTA, and elution flow rate: 2 mL at  $0.5 \text{ mL min}^{-1}$  and 6 mL at  $2 \text{ mL min}^{-1}$

488 ( $n = 3$ ).

489