

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

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

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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 HNO_3 matrix with pre–added
39 Ni, Cu and other interfering elements (1000 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

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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]. 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 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⁻¹) 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⁻¹ to µg L⁻¹ were prepared by dilution on a weight basis. Ultrapure reagent grade HNO₃
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 Ω cm⁻¹ 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⁻¹; (c) operational pH range – <0 to 9.5; and (d) binding capacity
139 – 0.1 to 0.3 mmol g⁻¹.

140 Synthetic metal-waste solutions simulating the waste discharge from ENP baths were
141 prepared in a 2 M HNO₃ matrix containing either 100 or 1000 μ g L⁻¹ of Pb and 1000 mg L⁻¹
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 HNO₃, 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 HNO₃ was used to remove metals adsorbed on the silica support of the SPE-MRT;
164 lead cannot be eluted by HNO₃. The third washing with ultrapure water was used to prevent
165 acidification and/or precipitation of EDTA due to the contact with HNO₃. 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 HNO₃ (pH ≤ 3) or with ammonium acetate solution (pH 5–9). Almost complete

178 retention of lead (%), 96.1 ± 3.2 for Pb-01 and 98.8 ± 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⁻¹. 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⁻¹, followed by gradual decrease in
189 the retention rate with increases in the flow rate. Analyte recoveries (%) of 92.5 ± 6.2 for Pb-
190 01 and 95.0 ± 2.5 for Pb-02 were observed at the high flow rates (5–100 mL min⁻¹),
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⁻¹ 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⁻¹ of Pb²⁺ 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⁻¹ 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⁻¹ 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 μg
230 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 ± 2.3 and 94.9 ± 1.8
236 after treatment with Pb–01 and Pb–02, respectively. The Pb recoveries (%) were 75.7 ± 3.2
237 for Pb–01 and 93.8 ± 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 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 g L^{-1}), nickel chloride (30 to 60 g L^{-1}), and boric acid (30 to 45 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 ± 1.8 and 104 ± 4.7 , respectively, for the freshly prepared ENP
249 bath solution, while it was 87.6 ± 3.6 and 97.6 ± 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⁻¹; 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

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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 ⁻¹)	Argon 15.0
Auxiliary gas flow (L min ⁻¹)	Argon 1.50
Nebulizer gas flow (L min ⁻¹)	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

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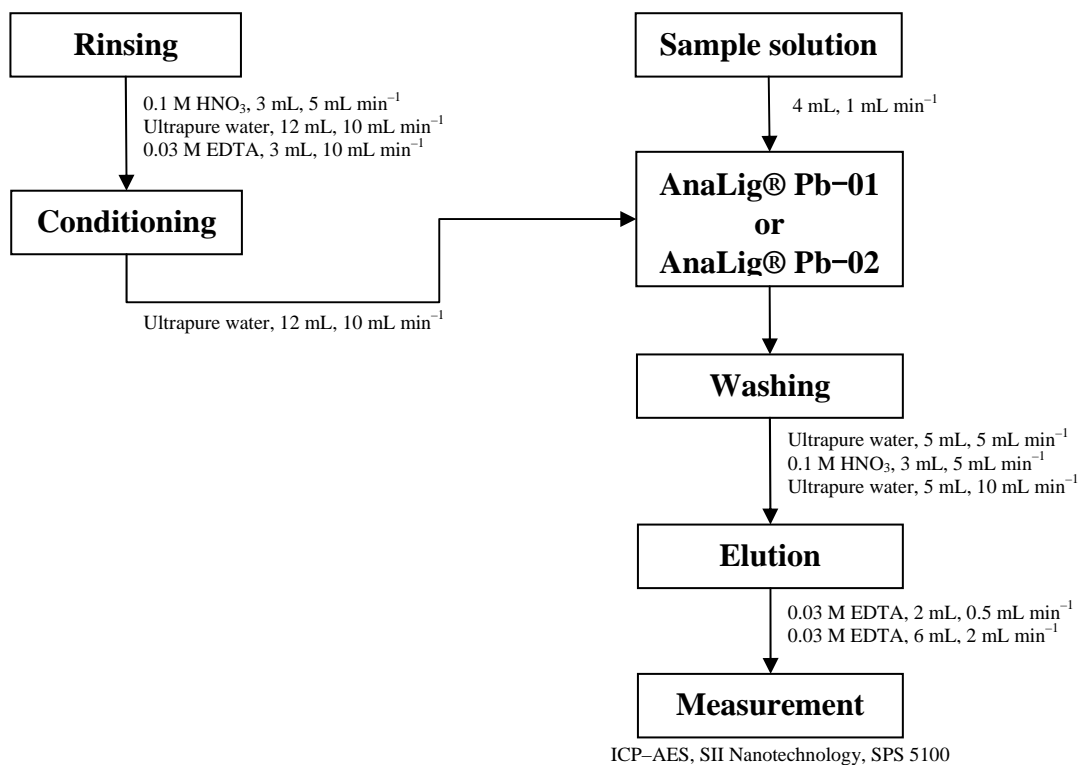


Figure 1: Schematic diagram of the experimental setup

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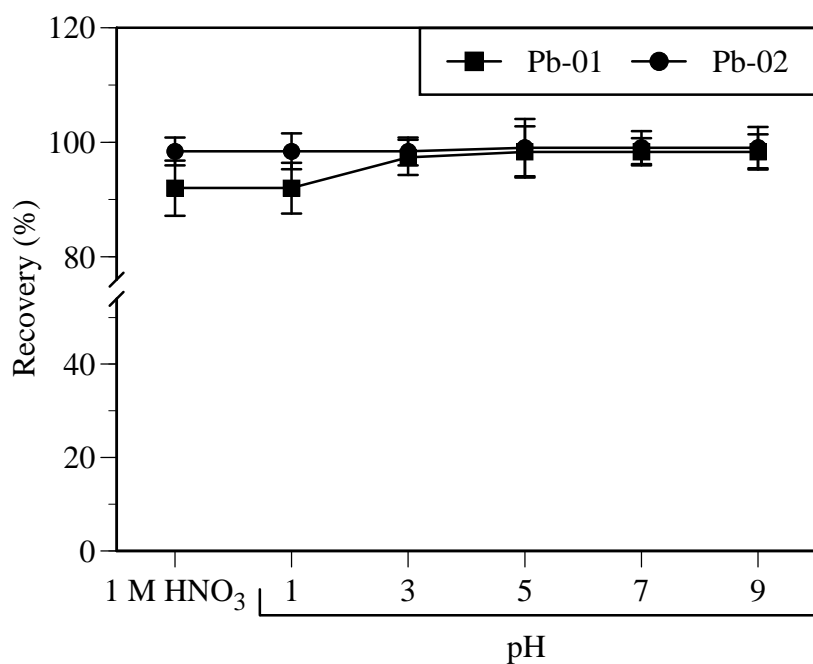
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440 Figure 2: Effect of pH on the performance of SPE–MRT cartridges. Sample solution: 100 μg
441 L^{-1} Pb, volume: 4 mL, loading flow rate: 1 mL min^{-1} , eluent: 0.03 M EDTA, elution flow
442 rate: 2 mL at 0.5 mL min^{-1} and 6 mL at 2 mL min^{-1}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

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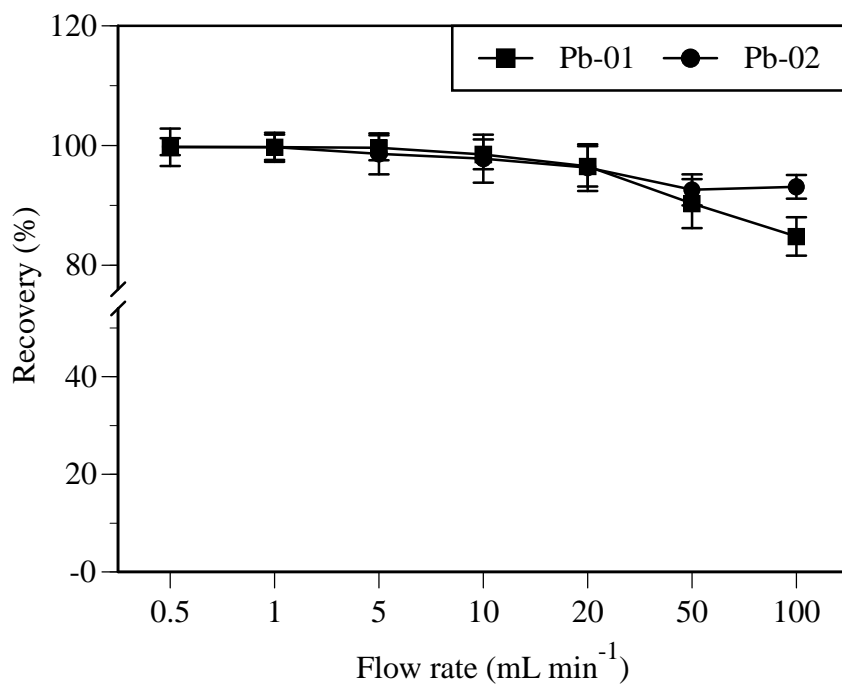
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455 Figure 3: Effect of flow rate on the performance of SPE–MRT cartridges. Sample solution:

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

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

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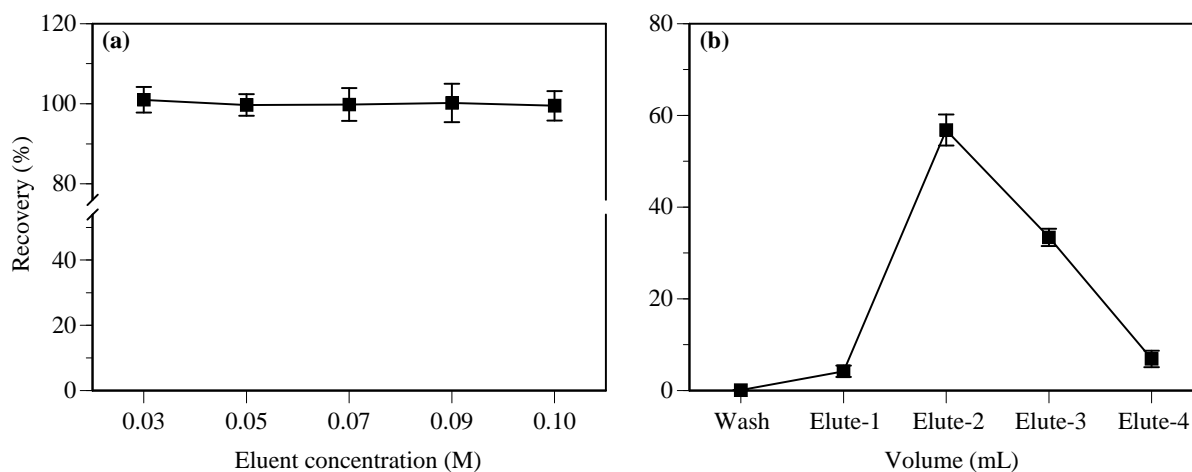
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467 Figure 4: Effect of (a) eluent concentration and (b) eluent volume on the performance of Pb-
 468 02 SPE-MRT cartridge. Sample solution: $100 \mu\text{g L}^{-1}$ Pb, volume: 4 mL, loading flow rate:
 469 1.0 mL min^{-1} , eluent: (a) 0.03–0.10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

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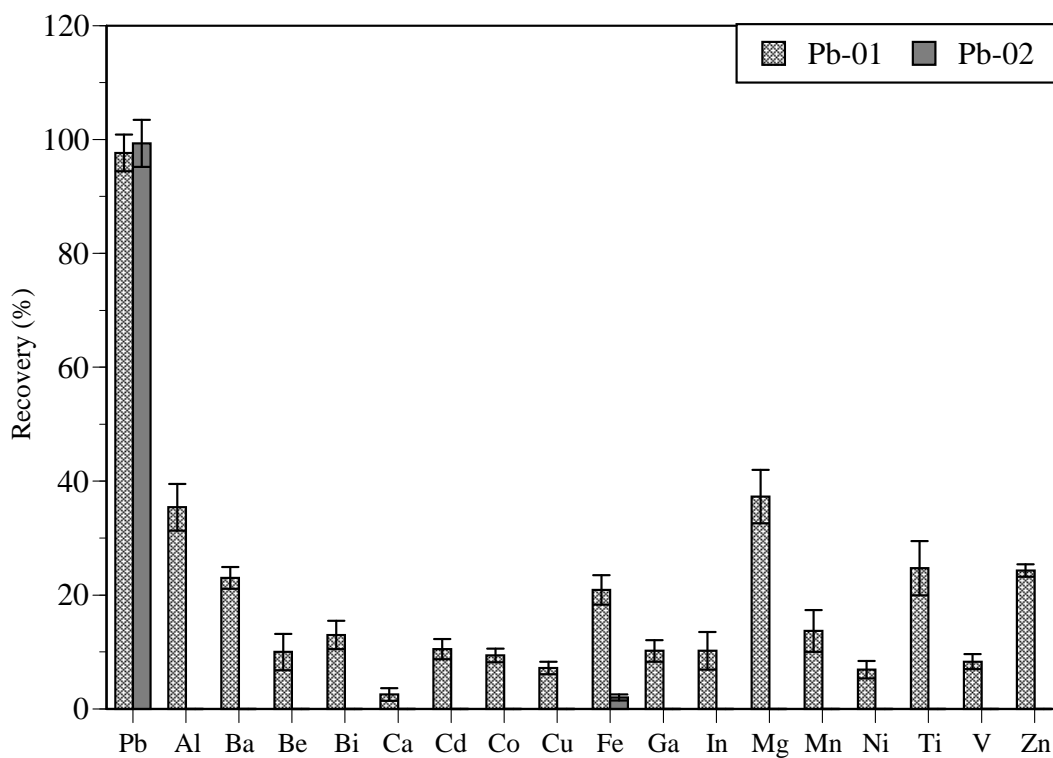
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485 Figure 4: Effect of coexisting ions on the performance of SPE-MRT cartridges. Sample
 486 solution: $100 \mu\text{g L}^{-1}$ (Pb and other elements), volume: 4 mL, loading flow rate: 1 mL min^{-1} ,
 487 eluent: 0.03 M EDTA, and elution flow rate: 2 mL at 0.5 mL min^{-1} and 6 mL at 2 mL min^{-1}
 488 ($n = 3$).

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