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Separation of Lead from High Matrix Electroless Nickel Plating Waste Solution Using an Ion–Selective Immobilized Macrocycle System

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Abstract

Separation of trace levels of lead from concentrated–matrix electroless nickel plating (ENP) waste solutions is required to meet the increasingly stringent environmental regulations. A solid phase extraction (SPE) system using a molecular recognition technology (MRT) gel was used for the selective separation of trace levels of lead (Pb) from the waste discharge of ENP operations, followed by subsequent analysis with inductively coupled plasma optical emission spectrometry (ICP–OES). Two SPE–MRTs, AnaLig® Pb–01 and AnaLig® Pb–02, packed in 3 mL polypropylene cartridges were used to treat the synthetic metal–waste solutions that were used to simulate the typical metal mixture in ENP bath waste. The fortified solutions contained 100–1000 µg L^{-1} of Pb in an HNO_3 matrix with pre–added Ni, Cu and other interfering elements (1000 mg L^{-1}). After the sample treatment, the SPE–MRT cartridges were washed with water and 0.1 M nitric acid, followed by elution with 0.03 M EDTA. The matrix elements (e.g., Ni, Cu) were completely removed at the washing step, while the 'captured' Pb was quantitatively eluted, as determined by ICP–OES measurements. The detection limit of the proposed method was 2.6 µg L^{-1}. 'Real' samples from commercial ENP operations were used to assess the validity of this method, and almost quantitative Pb recovery was observed. The excellent Pb selectivity of the SPE–MRT system indicates the potential of the proposed technique for trace–level Pb separation from the Pb–containing high matrix aqueous waste discharge.

Keywords

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

1.0 Introduction

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

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

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

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

Solid phase extraction (SPE) is usually considered to be superior to traditional extraction techniques with respect to simplicity, rapidity, and the ability to attain a high concentration factor when the level of the ion being removed is present at trace levels [18, 19]. The main requirements for such trace level binding and concentration for analytical– or process–scale separation using SPE materials are as follows: highly selective and efficient extraction of the targeted metal ion in the matrix range requiring separation, fast and quantitative retention and easy recovery of the retained analytes, repeated usability, and accessibility [20-22]. Two methodologies have been commonly performed for solid phase extraction of Pb: one based on chemical reactions, either the synthesis of a selective ligand [23] or the covalent coupling of Pb to a support material [24, 25], and the other involves functionalization of the solid support itself [26, 27]. Several SPE materials, *e.g.*, activated carbon [28], cellulose [29], amberlite XAD resins [30], chromosorb resin [31], ambersorb resin [32, 33], polyurethane foam [34], and chitosan [27], have been used for the separation/preconcentration of Pb. However, most of the mentioned SPE systems have difficulty in separating out trace levels of Pb when there are high concentrations of other 2+ transition or post–transition elements (such as Ni and Cu) in the matrix [35, 36], such as in ENP waste solutions or other industrial wastes. Hence, SPE materials with sufficiently high and selective affinity to trace levels of Pb are required to treat such waste solutions.

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

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

2.0 Experimental

2.1 Reagents and materials

Standard stock solutions (1000 mg L^{-1}) of Pb and other elements from Plasma CAL, SCP Science, Canada, were used. Working standards of metal solutions in the range of mg L^{-1} to µg L^{-1} were prepared by dilution on a weight basis. Ultrapure reagent grade HNO_3 (PlasmaPURE Plus, SCP Science, Canada) was used to prepare the washing solution and the high matrix sample solution. Ethylenediaminetetraacetic acid (EDTA) from Dojindo Laboratories, Japan, was dissolved in electronic industrial reagent grade ammonia water (29%) purchased from Kanto Chemicals, Japan, to prepare a 0.03 M solution. Ultrapure water (18.3 MΩ cm^{-1} resistivity) prepared by an Elix 3/Milli–Q Element system (Nihon Millipore, Tokyo, Japan) was used throughout and is referred to as ultrapure water hereafter.

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

Synthetic metal–waste solutions simulating the waste discharge from ENP baths were prepared in a 2 M HNO_3 matrix containing either 100 or 1000 µg L^{-1} of Pb and 1000 mg L^{-1} or higher of either Cu or Ni.

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

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

2.2 Column separation procedure

SPE materials packed in 3 mL polypropylene cartridges were used in this experiment. MetaPREP® APS‒1 (M & S Instruments, Japan), an automated‒robotic system, was used for sample loading and treatment. The whole procedure was computer–controlled and ran through five steps: rinsing, conditioning, collection, washing, and elution.

In the rinsing and conditioning steps, 0.1 M HNO_3, ultrapure water, and 0.03 M EDTA were passed through the SPE–MRT cartridge, followed by conditioning with water. Then, the sample solution was passed through the cartridge. The cartridge effluent was collected. The next step was washing, which was conducted with the target to remove residual matrix solution from the cartridge because such residual matrix could affect the accurate measurement of Pb. The first washing with ultrapure water aimed to remove elements that were retained in the void volume of the SPE material. The second washing with 0.1 M HNO_3 was used to remove metals adsorbed on the silica support of the SPE–MRT; lead cannot be eluted by HNO_3. The third washing with ultrapure water was used to prevent acidification and/or precipitation of EDTA due to the contact with HNO_3. Low background levels of Ni and Cu combined with the concentrated Pb levels in the eluent after SPE–MRT pretreatment were achieved after the washing steps. In the next step, the analyte adsorbed on the SPE–MRT cartridge was eluted with 0.03 M EDTA in ammonia solution, and the eluent was subsequently analyzed using an SPS 5100 ICP–OES system (SII NanoTechnology Inc., Japan). The operating conditions of ICP-OES is shown in Table 1. The separation process is shown schematically in Fig. 1. The average of triplicate measurements was used in all calculations.

3.0 Results and discussion

3.1 Effect of pH

Retention of Pb on the Pb–01 and Pb–02 SPE–MRT cartridges was studied as a function of pH. The pH values of the samples were adjusted either with 1.0, 0.1, 0.01, or 0.001 M HNO_3 ($pH \leq 3$) or with ammonium acetate solution (pH 5–9). Almost complete retention of lead (%), 96.1 ± 3.2 for Pb–01 and 98.8 ± 0.4 for Pb–02, in the studied pH range (Fig. 2) was observed. Hence, the MRT materials showed high affinities for Pb with minimal or no affect from the solution pH. A sample pH of 1 or lower was maintained for further experiments to avoid any risk of precipitation during sample preparation or binding of analytes to the silica gel support itself.

3.2 Effect of sample loading flow rate

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

3.3 Effect of eluent concentration and volume

To achieve a high enrichment factor during the separation process, the eluent should be selected based on its capacity to elute the analyte with a minimum volume without affecting the accurate determination of the target analyte [41]. Either EDTA or NTA is recommended as the eluent for Pb–01 and Pb–02. We prefer to use EDTA as the eluent because the stability constant of Pb–EDTA is larger than that of Pb–NTA. To determine the effect of the eluent concentration on the elution of the analyte, a series of fortified aqueous samples each containing 5 µg L^{-1} of Pb^{2+} were passed through the SPE–MRT cartridges, and the extracted analytes were eluted using 0.03–0.10 M EDTA. ICP–OES analysis followed elution (Fig. 4a). The Pb recovery rate remained almost constant with increasing EDTA concentrations, indicating the complete elution of Pb at all concentration ranges examined; 0.03 M was selected as the eluent concentration for the subsequent experiments. An eluent flow rate of 2.0 mL min^{-1} enabled complete elution of Pb from the SPE–MRT cartridges, which may be due to the faster rate of complex formation between EDTA and Pb. The eluent volume required for complete elution of the ‘captured’ Pb from the SPE–MRT system was studied (Fig. 4b). The SPE–MRT cartridges were loaded with 2 mL of 0.03 M EDTA each time, and the combined recovery (%) of all the fractions was 101 ± 2.1. Hence, 8 mL of 0.03 M EDTA was selected as the eluent.

3.4 Effect of coexisting ions

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

3.5 Analytical characteristics

ICP–OES was used to measure the concentrations of Pb in the treated solutions from the Pb–01 and Pb–02 SPE–MRT cartridges. Using the optimized conditions, a calibration graph was obtained. The data was explained by the following equation: $y = 98.3x + 20.7$, with a correlation coefficient of 0.993. The detection limit (LOD) of the proposed technique, calculated as three times the standard deviation of the Pb analysis was approximately 2.6 µg L^{-1}.

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

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

3.7 Method validation using 'real' ENP bath solutions

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

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

4.0 Conclusions

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

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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

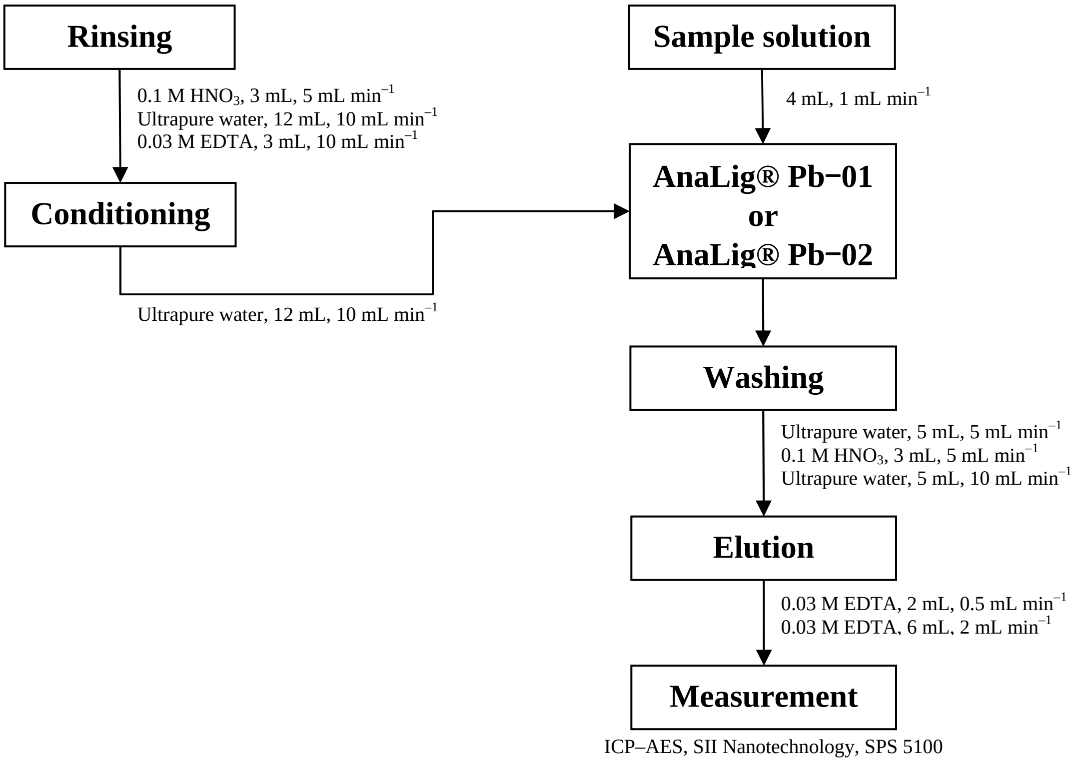

Figure 1: Schematic diagram of the experimental setup

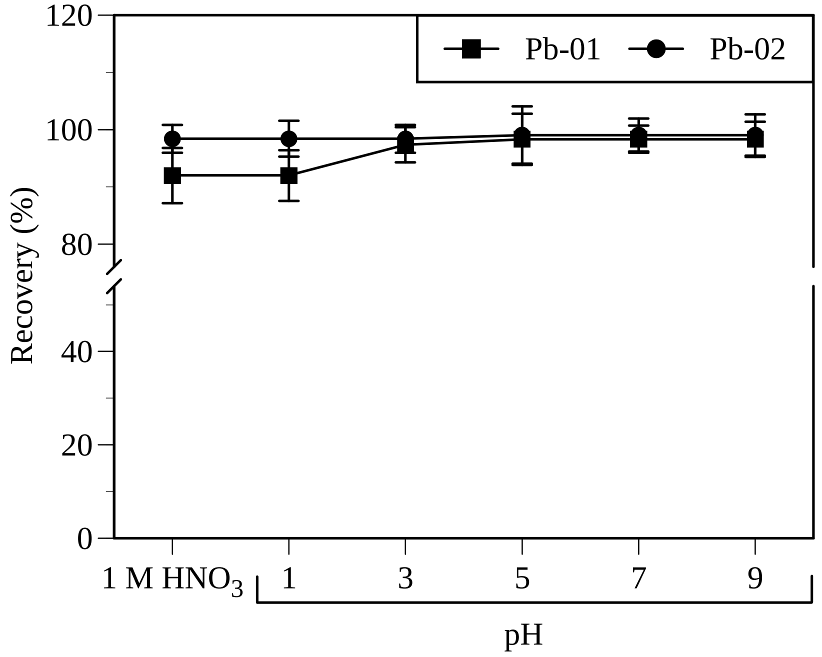

Figure 2: Effect of pH on the performance of SPE–MRT cartridges. Sample solution: 100 µg L^{-1} Pb, volume: 4 mL, loading flow rate: 1 mL min^{-1}, eluent: 0.03 M EDTA, elution flow rate: 2 mL at 0.5 mL min^{-1} and 6 mL at 2 mL min^{-1} (*n* = 3).

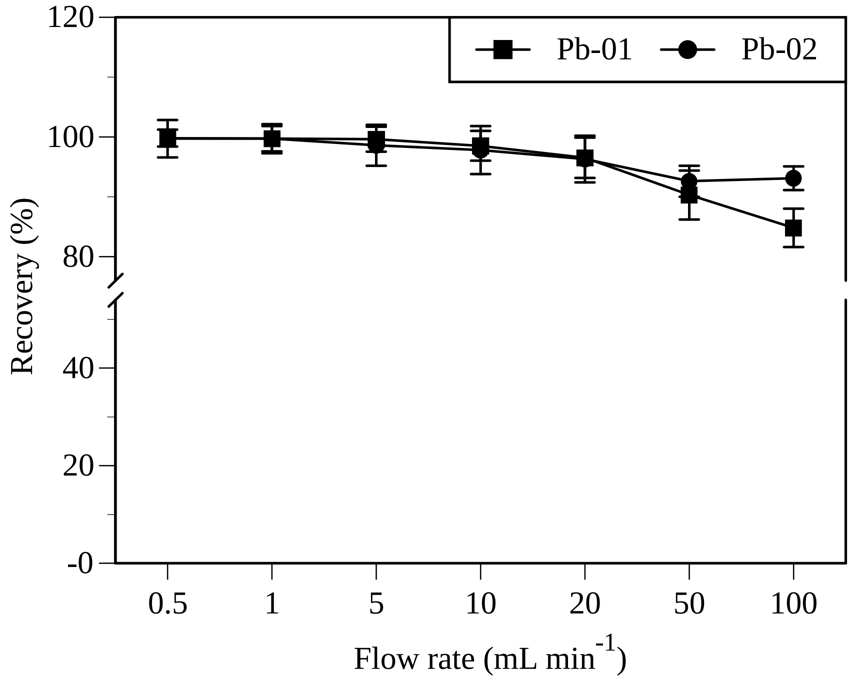

Figure 3: Effect of flow rate on the performance of SPE–MRT cartridges. Sample solution: 100 µg L^{-1} Pb, volume: 4 mL, eluent: 0.03 M EDTA, elution flow rate: 2 mL at 0.5 mL min^{-1} and 6 mL at 2 mL min^{-1} ($n = 3$).

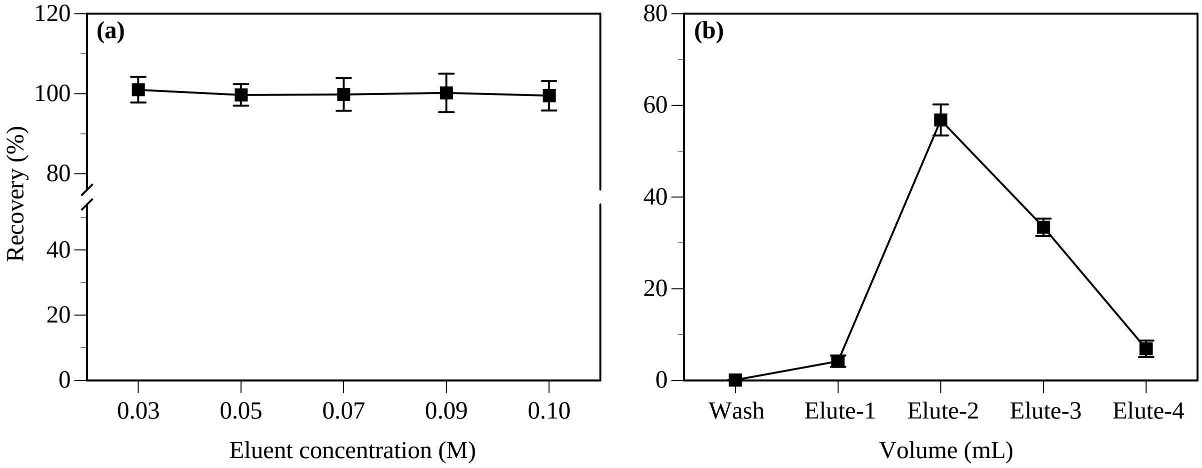

Figure 4: Effect of (a) eluent concentration and (b) eluent volume on the performance of Pb–02 SPE–MRT cartridge. Sample solution: 100 µg L^{-1} Pb, volume: 4 mL, loading flow rate: 1.0 mL min^{-1}, eluent: (a) 0.03–0.10 M EDTA (b) 0.03 M EDTA, elution flow rate: 2 mL at 0.5 mL min^{-1} and 6 mL at 2.0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

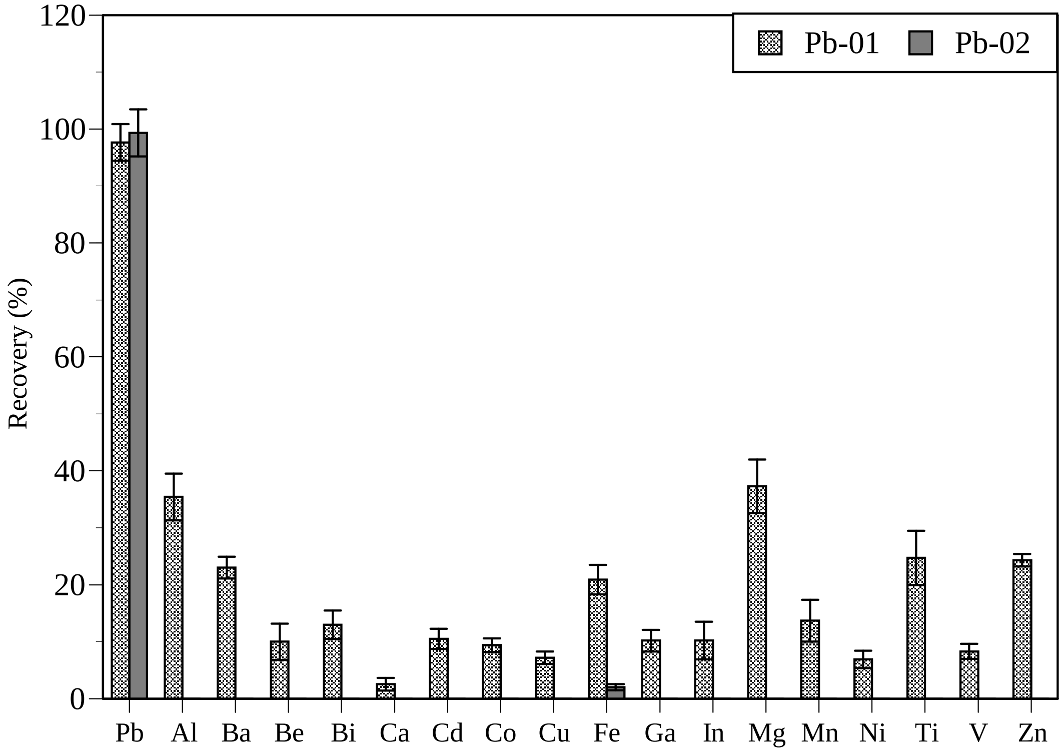

Figure 4: Effect of coexisting ions on the performance of SPE–MRT cartridges. Sample solution: 100 µg L^{-1} (Pb and other elements), volume: 4 mL, loading flow rate: 1 mL min^{-1}, eluent: 0.03 M EDTA, and elution flow rate: 2 mL at 0.5 mL min^{-1} and 6 mL at 2 mL min^{-1} (*n* = 3).