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Determination of Lead in Solution by Solid Phase Extraction, Elution and Spectrophotometric Detection Using 4-(2-Pyridylazo)-Resorcinol

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Abstract

Lead (+2) was selectively adsorbed on a solid phase extraction (SPE) gel (molecular recognition technology, MRT), quantitatively extracted, and spectrophotometrically determined as the Pb(II)–PAR (4-(2-pyridylazo)-resorcinol) complex. The linear range was 0.01 to 0.75 mg L^{-1} and the detection limit was 6.4 μg L^{-1}. The MRT-SPE allows selective Pb(II) extraction from complex ion-rich matrices, which is difficult with other techniques. Interference from common matrix ions such as Fe^{2+}, Ni^{2+}, Cu^{2+} or Co^{2+} is minimized.

Keywords

Lead; 4-(2-pyridylazo)-resorcinol; Colorimetric; Interferences; Solid phase extraction

1.0 Introduction

Lead (+2), insidiously toxic to humans, is ubiquitous in nature. Once absorbed it is retained with a long half-life and may cause brain damage, anemia and kidney malfunction [1-3]. It has been widely used in manufacturing [4] in spite of its toxicity [2, 3] and stringent regulations on its use [5] because of its other desirable properties. Thus development of simple techniques for Pb(II) monitoring in industrial processes and products has gained wide interest.

Flame atomic absorption spectrometry, electrothermal atomic absorption, inductively coupled plasma mass spectrometry, inductively coupled plasma time of flight mass spectrometry, inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray fluorescence, electroanalytical, and spectrophotometric techniques are available for determination of Pb(II) in solution [6-9]. Spectrophotometry is preferred due to the high setup or operating costs of other techniques, particularly in developing countries [10]. It is also simple, fast, precise and accurate [11].

Spectrophotometry based on reaction with dithizone is most widely used for Pb(II) determination, but the method suffers from non-selectivity, dithizone photodecomposition and aqueous insolubility of the complex [12-14]. To overcome these limitations, several metallochromes have been proposed including xylenol orange [13], bromopyrogallol red [13], 4-(2-pyridylazo)-resorcinol (PAR) [13], arsenazo-TB [15], diethyldithiocarbamate [15], diphenylcarbazone [16] and 2-(2-thiazolylazo)-*p*-cresol [17]. Sensitivity, selectivity and speed vary among them. Most require extraction with a masking agent (organic solvent, surfactant or toxic cyanide) to increase the sensitivity or selectivity [10, 18]. PAR is the most suitable for routine spectrophotometric analysis not only for its speed and sensitivity but also because it works in the aqueous phase [13, 18]. Because matrix ions such as cadmium, cobalt, copper, silver, mercury, nickel and zinc interfere [18], separation is required before spectrophotometric determination [4].

Solvent extraction [18], co-precipitation [19], cloud point extraction [20], micro-extraction [4], solid-phase extraction [21] are commonly used to separate Pb(II) from the matrix. SPE offers simplicity, rapidity, and a high concentration factor [22] compared to the other extraction techniques. Several SPE materials, *e.g.* activated carbon [23], cellulose [24], Amberlite XAD resins [11], Chromosorb resin [25], Ambersorb resin [26], polyurethane foam [27], chitosan [28] and molecular recognition technology (MRT) gel [8, 29] have been proposed for Pb(II) separation. MRT gel showed excellent Pb(II) selectivity from biological and environmental samples [29, 30], and matrices high in metals [8, 31]. Its selectivity and speed are due to the macrocyclic molecular recognition chemistry [32].

This is the first report of the use of MRT-SPE for selective separation of Pb(II) in combination with spectrophotometric determination. Pb(II) is selectively retained by MRT-SPE, eluted, treated with PAR, and determined by UV-Vis spectrophotometry. The MRT-SPE gives simple single-step separation of Pb(II) from complex matrices and ensures its relatively interference-free determination. In addition, a color-chart based semi-quantitative Pb(II) determination appropriate for on-site analysis is described.

2.0 Experimental

2.1 Instrumentation

A Perkin Elmer Lambda 9000 spectrophotometer (USA) was used for UV-Vis spectrophotometric measurements. An SPS 5100 ICP-OES system (SII NanoTechnology; Chiba, Japan) Chiba, Japan) equipped with a radio frequency generator (40 MHz, 1.2 kW), one-piece extended torch in the axial view mode, glass cyclonic spray chamber and sea spray glass concentric nebulizer was used for metal analysis under the operating conditions: plasma gas flow, 15 L min^{-1}, auxiliary gas flow, 1.5 L min^{-1}; nebulizer gas flow, 0.75 L min^{-1}, integration time, 5 s. Argon was

used as the flow gas. Three replicate measurements were obtained and a polynomial fitted background correction was applied.

An HM-20P pH meter (DKK-TOA; Tokyo, Japan) was used for pH measurement. Ultrapure water (resistivity > 15.0 MΩ·cm) was produced by a Purelite PRB-002A (Organo; Tokyo, Japan) water purification system.

2.2 Reagents and materials

Standard solutions of Pb(II) or other elements, ultrapure grade KCl or NaCl, HNO_3 and 2-amino-2-(hydroxymethyl)-1,3-propanediol (Tris) were purchased from Wako Pure Chemical (Osaka, Japan). N-cyclohexyl-2-aminoethanesulfonic acid (CHES) and 4-(2-pyridylazo)-resorcinol (PAR) were procured from Dojindo Laboratories and Dojin Chemical, respectively, both located in Kumamoto, Japan. All other chemicals were reagent grade and used as received. The HNO_3 was used to prepare the wash solution or to adjust the solution pH. CHES and Tris were the buffer, and PAR was the chromogenic reagent. All solutions were prepared in ultrapure water.

The MRT-SPE, AnaLig Pb-02, was supplied by GL Sciences (Tokyo, Japan) but manufactured by IBC Advanced Technologies, Inc. (Utah, USA). It contains a proprietary polymer containing a host (usually a macrocycle) which recognizes specific electronic and spatial features of the guest, selectively forming a 'host-guest' complex. Binding is tailored to the target based on charge, size and shape [32].

Perfluoroalkoxy (PFA) tubes and micropipette tips from Nichiryo (Tokyo, Japan), and low-density polyethylene laboratory ware from Nalge (USA) were used. Laboratory ware was cleaned before use by: (a) soaking in Scat 20X-PF alkaline detergent (Nacalai Tesque; Kyoto, Japan) overnight, (b) rinsing with ultrapure water, (c) soaking in 4 M HCl overnight and (d) rinsing with ultrapure water.

2.3 Experimental process

2.3.1 Selective separation of Pb(II)

MRT-SPE material packed in polypropylene pipette tip (diameter 6 mm, length 45 mm) was used. The total process included: (a) rinsing with ultrapure water (3 mL at $3 \sim 4$ mL min^{-1}), (b) conditioning with 1 M HNO$_3$ (1 mL at $3 \sim 4$ mL min^{-1}), (c) sample loading (10 mL at 1 mL min^{-1}), (d) washing with 1 M HNO$_3$ and ultrapure water (1 mL + 2 mL at $3 \sim 4$ mL min^{-1}), and (e) elution with 4 M KCl (1.5 mL at 1 mL min^{-1}). Conditioning and washing were as recommended by the manufacturer [33]. The other steps were optimized as described later.

2.3.2 Standard procedure for spectrophotometric measurement

Spectrophotometric Pb(II) measurement followed separation: (a) collection of 1.5 mL of eluent in a 5 mL PFA tube, (b) addition of pH 9.4 CHES or Tris buffer, (c) addition of at least a 10-fold molar PAR excess, (d) allowing at least 3 min for color development, and (e) absorbance measurement at 525 nm.

3.0 Results and discussion

3.1 Selective separation of lead

3.1.1 Effect of MRT-SPE volume

Tip-type mini-columns packed with different amounts (5–25 mg) of the MRT-SPE material (AnaLig Pb-02) were evaluated. Under the optimized conditions a minimum of 20 mg MRT-SPE was required for quantitative Pb retention (Fig. 1a).

3.1.2 Effect of sample loading flow rate

Sample loading flow rates affect analyte retention. Pb(II) recoveries from the MRT-SPE at sample loading flow rates from 0.5–10 mL min^{-1} were evaluated at optimum conditions (Fig. 1b). Pb(II)-retention was quantitative up to 1 mL min^{-1}, then decreased gradually. Thus, 1 mL min^{-1} was chosen as the optimum sample loading flow rate.

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3.1.3   Selection of eluent

A good eluent requires minimum volume and has negligible effect on the analyte determination. Pb(II)-spiked aqueous samples were passed through the MRT-SPE and the retained lead was eluted with either EDTA (0.3 M), NaCl or KCl (4 M) (Fig. 1c). Although EDTA is the recommended eluent for this system [33] it interferes with the Pb(II)-PAR reaction. Thus, NaCl and KCl were tested (Hattori *et al.* [31]), and maximum recovery was achieved with 4 M KCl. Eluent flow of 1.5 mL at 1 mL min^{-1} gave complete Pb elution and was adopted in subsequent experiments.

3.1.4   Effect of pH

The Pb(II) retention rate on the Pb-02 MRT-SPE as a function of pH was evaluated. The HNO$_3$, ammonium acetate and Tris buffer (0.2 M) were used to attain the solution pH 1, 5 and 10 respectively. The pH-adjusted Pb(II)-spiked sample was passed through the MRT-SPE (2 mL × 5), and the adsorbed Pb(II) was later eluted (Fig. 2). The cumulative recovery rate (%) was highest at pH 1 (102 ± 4.3), followed by that at pH 5 (74.9 ± 3.3) and at pH 10 (3.7 ± 1.8). Therefore, 10% HNO$_3$ (1 mL) was added with each 10 mL loading to maintain the sample pH at *ca.* 1 for further experiments.

3.2 Spectrophotometric determination of Pb(II) with PAR

3.2.1   Optimization of variables

Maximum absorption of the Pb(II)-PAR complex was observed at 525 nm and pH 9.4, values comparable to those reported by Pollard *et al.* [34] and Dagnall *et al.* [13]. Although there are differences of opinion regarding the nature of Pb(II)-PAR complex [13, 34, 35], use of an 8–50 fold molar PAR excess has been recommended [13, 35] to promote complexation and reach maximum absorbance. A 10-fold PAR: Pb molar excess was used. At least three minutes of development time

was allowed before measurement, although the color of the complex appeared almost immediately and was stable for approximately 24 hours.

3.2.2   Interferences

The effect of potential interfering species in the determination of 0.03 mg L^{-1} of Pb(II) was examined by treating sample solutions containing different potential interferants under the optimal conditions. With a relative error of less than ±5%, the tolerance limits of the interfering species at various concentrations are shown in Table 1. Except for Bi(II) (>5 mg L–1), no species tested interferes with the determination at reasonable concentrations.

3.2.3   Analytical characteristics

Under the optimized conditions the calibration curve was linear from 0.01 to 0.75 mg L^{-1} with a correlation coefficient of 0.9981. The method's detection limit, calculated as three times the standard deviation of the blank ($n = 15$), was 6.4 µg L^{-1}. The reproducibility, as relative standard deviation, was 1.94% calculated from the measurements of 10 replicates containing 0.03 mg L^{-1} of Pb in solution.

3.3 Applications

3.3.1   Analysis of electroless nickel plating bath waste solution for Pb(II) content

Pb(II) is used as a stabilizer in commercial electroless nickel plating (ENP), widely applied to metal or plastic surfaces. Although their exact composition is proprietary, ENP bath solutions usually contain about 1000 μg L^{-1} of Pb and several g L^{-1} of other components including nickel sulfate (225 to 400), nickel chloride (30 to 60), and boric acid (30 to 45) [36]. Seven anonymous ENP bath samples received via the Japan Plating Industry Association were analyzed using the proposed technique and compared with the results obtained by ICP-OES (Table 2).

3.3.2 Analysis of food extracts for Pb(II) content

Food extracts were prepared for Pb(II) analysis according to the procedure of Li *et al.* [37]. The extract was then analyzed with the method developed. The results were verified by ICP-OES (Table 2).

3.3.3 Analysis of alloys for Pb(II) content

Sn-3.0Ag-0.5Cu is a solder alloy used in Japan by almost all major electric and electronic manufacturing companies. Three anonymous Sn-3.0Ag-0.5Cu solder alloy samples were treated accordingly as described by Bale *et al.* [38], and the results of analysis with the proposed technique were compared with those obtained by ICP-OES (Table 2).

3.3.4 Analysis of lead-plated handicraft materials for Pb(II) content

Lead plating is used to provide a polished look to handicrafts. Handicrafts (clay pottery, ceramic plate with a glossy pattern, and metal pot) were collected from local markets and treated with 4% acetic acid for 24 hours. The solution was analyzed for Pb(II) content followed by comparison with ICP-OES analysis (Table 2).

3.4 Comparison of the proposed technique with other SPE plus UV-Vis Spectrophotometric approaches

There have been a few reports of SPE Pb(II) extraction followed by complexation and spectrophotometric determination [11, 39]. Amberlite XAD resin SPE columns have been used in combination with PAR [11] or dithizone [39] for Pb(II) determination, but Fe^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+} interfere. In addition, the Amberlite XAD selectivity must be monitored carefully because it may extract several other ions simultaneously with Pb(II) [40, 41].

The proposed method represents improvements because: (a) Pb(II) is selectively extracted from ion-rich complex matrices due to the unique ion-selectivity of the MRT-SPE material and (b)

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the most common ions present in freshwater matrices (Fe^{2+}, Ni^{2+}, Cu^{2+} or Co^{2+}) cause almost no interference.

3.5 Scheme for color-chart based qualitative Pb(II) analysis using the proposed approach

A customized color chart was developed based on the Pb(II)-PAR reaction by mixing known concentrations of Pb(II) with PAR. The distinctive color produced depends on the Pb(II) concentration. It can be compared with a standard color chart for semi-quantitative Pb(II) determination. The scheme is shown in detail in Fig. 3.

Nine individuals measured the same Pb(II) solution with the color-chart based technique. The observed coefficient of variation was ±10%. The scheme is suitable for rapid on-site semi-quantitative Pb(II) determination from 0 to < 1 mg L^{-1}.

4.0 Conclusion

A spectrophotometric technique for determination of Pb(II) as the Pb(II)-PAR complex, preceded by separation using AnaLig Pb-02 MRT-SPE was developed. The MRT-SPE contains immobilized macrocyclic material and possesses unique Pb(II) selectivity. Collection of Pb(II) was quantitative at pH 1 and a sample loading flow rate of 1 mL min^{-1}, while 4 M KCl was used as the eluent. Addition of PAR in solution at pH 9.4 formed a colored complex, which was measured by UV-Vis spectrophotometry at 525 nm. The detection limit and relative standard deviation were 6.4 μg L^{-1} and 1.94 %. The method is also fairly free from interference from ions common in aqueous matrices, which facilitates the sensitive and rapid determination of Pb(II) in solution.

Acknowledgment

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Table 1: Effect of interfering species

Interfering species			Recovery (%)
Type	Name	Added Concentration (mg L^{-1})	
Metal ions	Ag	100	99 ± 3.5
	Al	100	100 ± 1.8
	Ba	10	100 ± 2.1
	Bi	5	68 ± 2.6
	Ca	1000	100 ± 1.9
	Cr(III)	100	100 ± 4.2
	Cu	100	92 ± 1.4
	Fe(II)	100	96 ± 2.6
	Fe(III)	100	98 ± 3.8
	K	1000	100 ± 2.1
	Ni	100	100 ± 3.7
	Mn	100	91 ± 3.4
	Mg	1000	100 ± 4.7
	Mo	100	100 ± 3.8
	Sn	100	100 ± 2.9
	Zn	100	98 ± 4.5
Surfactant	Sodium dodecyl sulfate	100	100 ± 4.8
	Zephiramine	100	100 ± 3.3
	Triton-X	100	96 ± 2.4
Organic acid	Acetic acid	40000	98 ± 3.6
	Glutamic acid	10000	100 ± 2.0
	Thiourea	10000	100 ± 2.2
	Ascorbic acid	10000	100 ± 3.4

Table 2: Application of the proposed technique to the analysis of real samples

Samples	proposed method (mg L^{-1})	ICP-OES method (mg L^{-1})
Analysis of electroless nickel plating (ENP) bath waste solution		
ENP sample-1	0.13 ± 0.07	0.12 ± 0.06
ENP sample-2	0.36 ± 0.13	0.31 ± 0.11
ENP sample-3	0.06 ± 0.04	0.07 ± 0.05
ENP sample-4	0.19 ± 0.09	0.18 ± 0.08
ENP sample-5	0.12 ± 0.05	0.16 ± 0.07
ENP sample-6	0.06 ± 0.02	0.06 ± 0.02
ENP sample-7	0.05 ± 0.02	0.05 ± 0.01
Analysis of food extracts		
Sample-1	31 ± 2.1	24 ± 1.4
Sample-2	0.89 ± 0.02	0.86 ± 0.07
Analysis of alloys		
Sample-1	230 ± 5.1	260 ± 5.2
Sample-2	130 ± 2.9	130 ± 2.6
Analysis of lead-plated handicraft materials		
Clay pottery	31 ± 4.31	24 ± 3.24
Ceramic plate	0.89 ± 0.12	0.86 ± 0.11
Metal pot	68 ± 3.60	72 ± 4.56

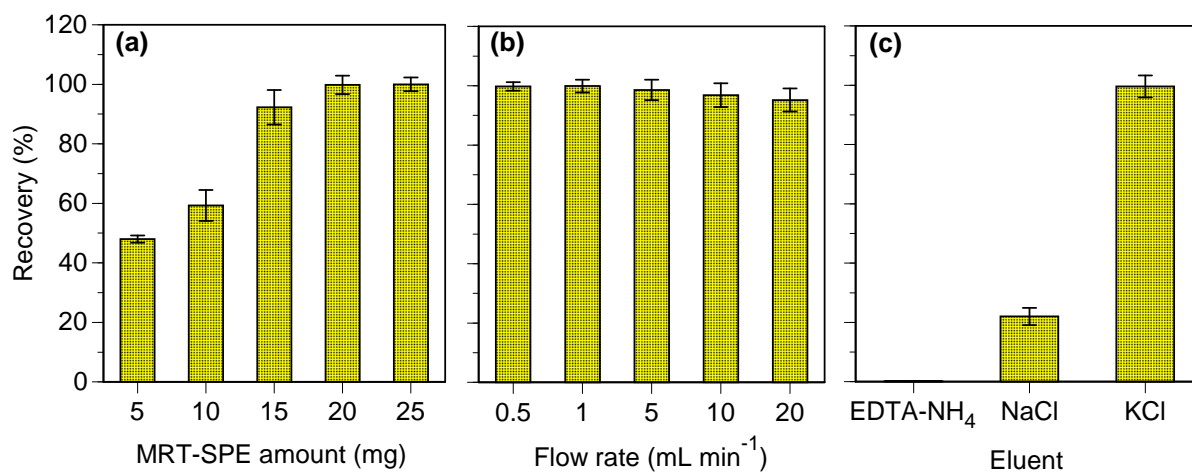*'BDL' – Below Detectable Limit*

Figure 1: Performance optimization of the MRT-SPE material: effect of (a) MRT-SPE amount, (b) sample loading flow rates, and (c) different eluents (EDTA-NH$_4$, 0.3 M; NaCl and KCl, 4 M). Sample solution: 0.03 mg L^{-1} Pb(II), volume: 10 mL ($n = 3$).
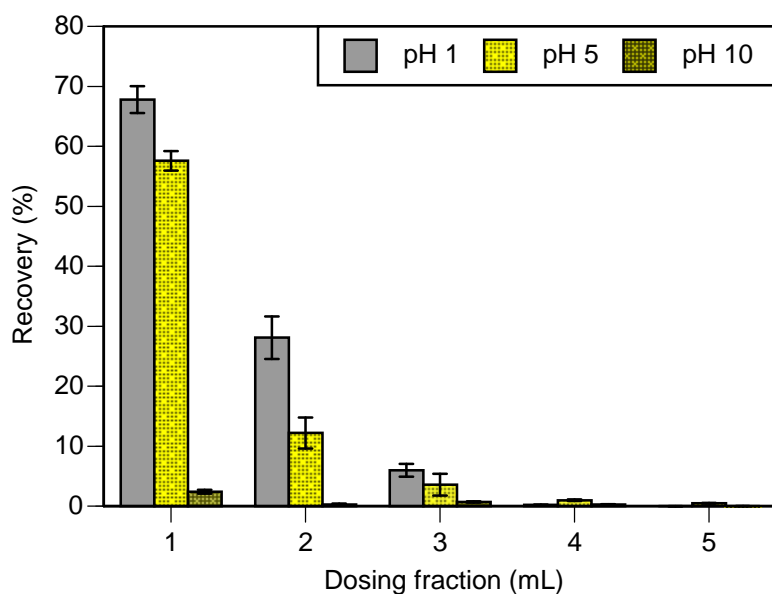
Figure 2: Effect of pH on the performance of MRT-SPE material. Sample solution: 0.03 mg L^{-1} Pb(II), volume: 10 mL (2 mL per dosing fraction), loading flow rate: 1 mL min^{-1}, eluent: 4 M KCl, eluent volume: 1.5 mL, elution flow rate: 1 mL min^{-1} ($n = 3$).
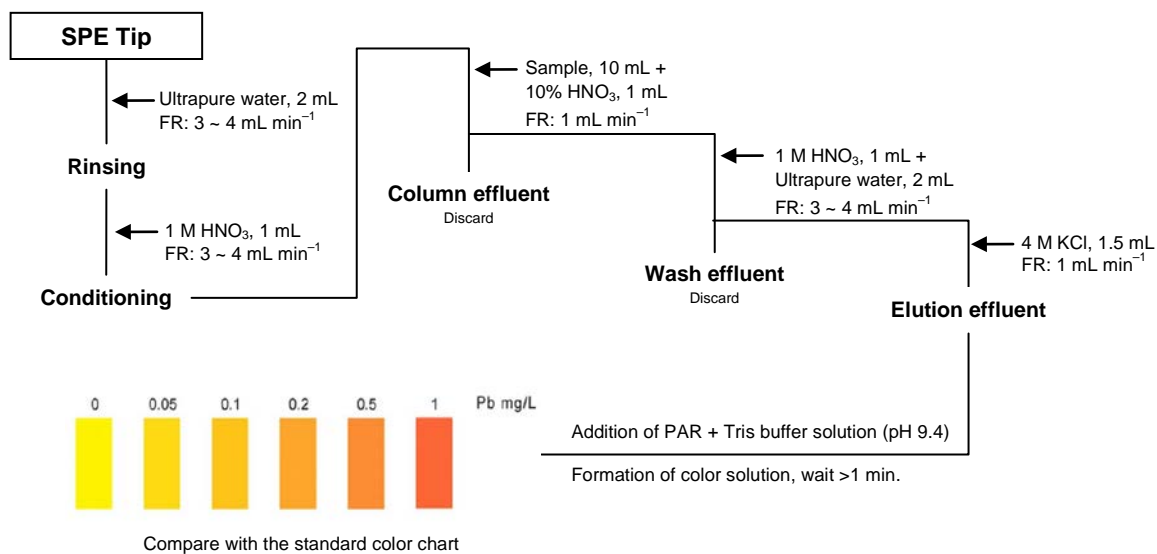
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Figure 3: Scheme for on-site semi-qualitative determination of Pb(II).