Preconcentration of lead with Amberlite XAD-2 and Amberlite XAD-7 based chelating resins for its determination by flame atomic absorption spectrometry

P.K. Tewari, Ajai K. Singh *

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

Abstract

Four chelating matrices prepared by coupling Amberlite XAD-2 with chromotropic acid (AXAD-2-CA or 1), pyrocatechol (AXAD-2-PC or 2) and thiosalicylic acid (AXAD-2-TSA or 3) through azo spacer and impregnation of Amberlite XAD-7 with xylenol orange (AXAD-7-XO or 4) have been studied for enrichment of lead(II). All the four resins quantitatively sorb Pb(II) at pH 3.0-8.0 when the flow rate is maintained between 2 and 10 ml min^{1}. HNO$_3$ (0.5-4.0 M) instantaneously elutes Pb(II) from all the four chelating resins. The sorption capacity is in the range 16.0-186.0 |xmol g~^{1} and loading half time *(t$_{1/2}$)* between 3.2 and 15.5 min. The tolerance limits of electrolytes (NaCl, NaBr, NaNO$_3$, Na$_2$SO$_4$, Na$_3$PO$_4$) and cations (Ca and Mg) are reported. Phosphate interferes in the sorption with 3 and 4. The limit of detection and limit of quantification have been found to be in the ranges 2.44-7.87 and 2.76-8.64 ng ml ~ \ respectively. Lead has been determined in river (RSD ~ 2.6-12.8%) and tap (RSD ~ 1.8-7.2%) water samples.

Keywords: Amberlite XAD-2; Amberlite XAD-7; Lead; Atomic absorption spectrometry; Chelating resins; Preconcentration; Chromotropic acid; Pyrocatechol; Thiosalicylic acid; Xylenol orange

1. Introduction

Several methods extensively used for preconcentration include liquid-liquid extraction, ion exchange, solid phase extraction and chelating matrices. However, solvent extraction suffers with problems like handling of large sample volume, slow attainment of equilibrium, mutual solubility of two phases, poor selectivity and emulsion formation. The multistage extraction is required several times for quantitative recovery. Ion exchangers also lack selectivity. Consequently, in the last two decades use of chelating resins [1-4] for metal enrichment has increased very significantly. Their advantages include good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristics. The promis-

ing chelating resins are Chelex-100 [5,6], functionalised styrene-divinylbenzene copolymers [7-9] and polystyrene resins [10-12], poly(dithiocarbamate) resin [13-15], poly(acrylaminophosphonicdithiocarbamate) [16], polyurethane foam based chelators [17] and functionalised Amberlite XAD-2/4/7 resins [18-31].

Lead is a toxic metal, which accumulates in the vital organs of man and animals. Its cumulative poisoning effects are serious haematological damage, anaemia, kidney malfunctioning, brain damage etc. In natural water its typical concentration lies between 2 and 10 ng ml~ \ whereas, the upper limit recommended by WHO is less than 10 ngml^1. The flame atomic absorption spectrometry (FAAS) can be used to determine it at low concentration levels in diverse matrices but preconcentration becomes a necessity many times. The chelating resins have been used for its preconcentration [19-24,26-29,34-36]. However, interest in the selective chelating resins of high capacity for Pb continues. We have designed several Amberlite XAD-2/7 based chelating resins in the recent past [18-22,27-29,31] but not explored all of them for enrichment of lead. It was therefore thought worthwhile to explore sorption behaviour of four chelating resins viz. Amberlite XAD-2 immobilised with chromotropic acid (AXAD-2-CA or 1), pyrocatechol (AXAD-2-PC or 2) or thiosalicylic acid (AXAD-2-TSA or 3) and Amberlite XAD-7 impregnated with xylenol orange (AXAD7-2XO or 4) designed recently [27-29,31] for Pb(II). In the present paper the results of these investigations are reported and these resins are found promising for lead enrichment. The preconcentration coupled with FAAS determination method has been applied to determine lead in river and tap water samples.

2. Experimental

2.1. Instrumentation

The FAAS of Electronic Corporation India Ltd (Hyderabad, India), model 4139, with air-acetylene flame (air and acetylene flow rates of 10 and 2 1min^1, respectively) was used for measuring the concentration of lead. The UV-Visible spectrophotometer of Perkin- Elmer (Germany), model Lambda 3B was used for all spectrophotometric measurements. Elemental analyses were carried out in a Perkin-Elmer (Rotkreuz, Switzerland) elemental analyser, Model 240C and thermogravimetric analyses (TGA) were carried out in a Dupont (Wilmington, DE, USA) 2100 thermal analyser. A Nicolet (Madison, USA) FT-IR spectrometer model protege 460 was used to record IR spectra (in KBr) in the range of 400-4000 cm"1. The pH was measured with an Elico (Hyderabad, India) pH meter (Model LI-120 digital). The flow of solution through the column was maintained constant using a peristaltic pump (Watson-Marlow Model 101/U/R, Falmouth, UK). The sorption-desorption studies of lead(II) were generally carried out on columns of 1 cm diameter (Pharmacia, Bromma, Sweden). A mechanical shaker equipped with an incubator (Hindustan Scientific, New Delhi, India) with a speed of 200 rpm was used for metal ion-chelating resin equilibration.

2.2. Reagents and solutions

The stock solution of lead(II) was prepared by dissolving an appropriate amount of analytical reagent grade $Pb(CH_3COO)_2$-$3H_2O$ in deionised water acidified with acetic acid and standardised [33] before use. The working solution of Pb was obtained by the dilution of the stock solution with double distilled water. The pH was adjusted with 0.1 M HNO_3/NaOH or a buffer solution. For maintaining pH in the range 3.0-6.0 and 6.8-8.0, acetate and phosphate buffers were used, respectively. The dilute HNO_3 (up to 4.0 M) was used as an eluent for stripping off the metal from resin bed. Amberlite XAD-2 resin (surface area, 330 m^2 g~1; pore diameter, 90 A and bead size, 20-60 mesh) and Amberlite XAD-7 (surface area, 450 m^2 g~1 and bead size, 20-40 mesh) were procured from Aldrich (Milwaukee, USA). The chromotropic acid (Aldrich, Milwaukee, USA), pyrocatechol (CDH, India), thiosalicylic acid (Aldrich, Milwaukee, USA) and xylenol orange (BDH Chemicals Ltd, Poole, England) were used as received. The water samples analysed for lead content were collected from municipal tap water

supply (New Delhi, India) and from Ganges and Gomti rivers (Locations: Kanpur and Lucknow, India, respectively) and acidified with 2% HNO_3 immediately. They were filtered through 0.45 |im Millipore membrane and stored in glass bottles at room temperature. For cleansing of Amberlite XAD-2 and 7, procedures described earlier [27,31] were used.

2.3. Preparation and characterisation of chelating resins

The published procedures [27-29] were used for immobilising chromotropic acid (1), pyrocatechol (2) and thiosalicylic acid (3) on Amberlite XAD-2. Amberlite XAD-7 (0.2 g) was impregnated with xylenol orange by equilibrating the resin with a solution of dye (25 ml of concentration 50 |ig ml~^{1}) for 60 min at pH 1.9 as described earlier [31]. The impregnated resin (4) was rinsed with distilled water, air dried and stored for further use. The resins 1-3 were characterised by elemental analyses, TGA and IR spectra. The results were found to be similar to those reported earlier [27-29].

2.4. Recommended procedure for separation and preconcentration

The lead ions were preconcentrated by both column and batch methods.

2.4.1. Column method

The modified Amberlite XAD-2 or 7 (1 g, swollen for 24 h) was packed in a glass column (1.0 x 10.0 cm), treated with 50 ml of 4 M HCl or HNO_3 and washed with double distilled water until free from acid. A suitable aliquot of the solution containing Pb(II) in the concentration range of 0.025-1.0 ^gml^^{1} was passed through this column after adjusting its pH to optimum value (Table 1) at a flow rate of 2-4 ml min^{-1}. The metal from the resin bed was desorbed with 0.5-4.0 M HNO3 (10-25 ml) and the elutes were aspirated into the flame of FAAS standardised at 212 nm prior to the determination. The dilution with double distilled water was made before aspiration, if necessary in the case of concentrated elutes.

2.4.2. Batch method

A solution (100 ml) containing 0.1-250 \ig ml ~^{1} of Pb(II) was taken in a stoppered glass bottle (250 ml) after adjusting its pH to an optimum value (Table 1). The modified Amberlite XAD-2 or 7 (0.4 g) was added to it. The bottle was stoppered and shaken for 30 min. The resin was filtered, washed with double distilled water, shaken with 2 M HNO_3 (10-25 ml) for 20 min and filtered. The filtrate was aspirated into the flame of a prestandardised FAAS at 212 nm, after dilution if necessary.

Table 1
Optimum conditions for sorption and desorption of Pb(II) on chelating resins **1–4**

Experimental parameter	Chelating resin			
	1	2	3	4
PH	3.0-8.0	5.0-7.5	4.0	4.0
Flow rate (ml min^{-1})	2-10	2-8	2-8	2-3
HNO3 concentration for desorption (M)	1.0^.0	1.0	01.0-2.00	1.0
Sorption capacity of resin (junolg"^{1})	186.3	104.7	186.3	186.3
Loading half time, $t_{1/2}$ (min)	3.2	15.5	5.5	3.2
Average recovery (%)	97	94	93	91
Standard deviation[a]	0.041	0.036	0.070	0.046
Relative standard deviation (%)[a]	2.14	1.95	3.76	2.5

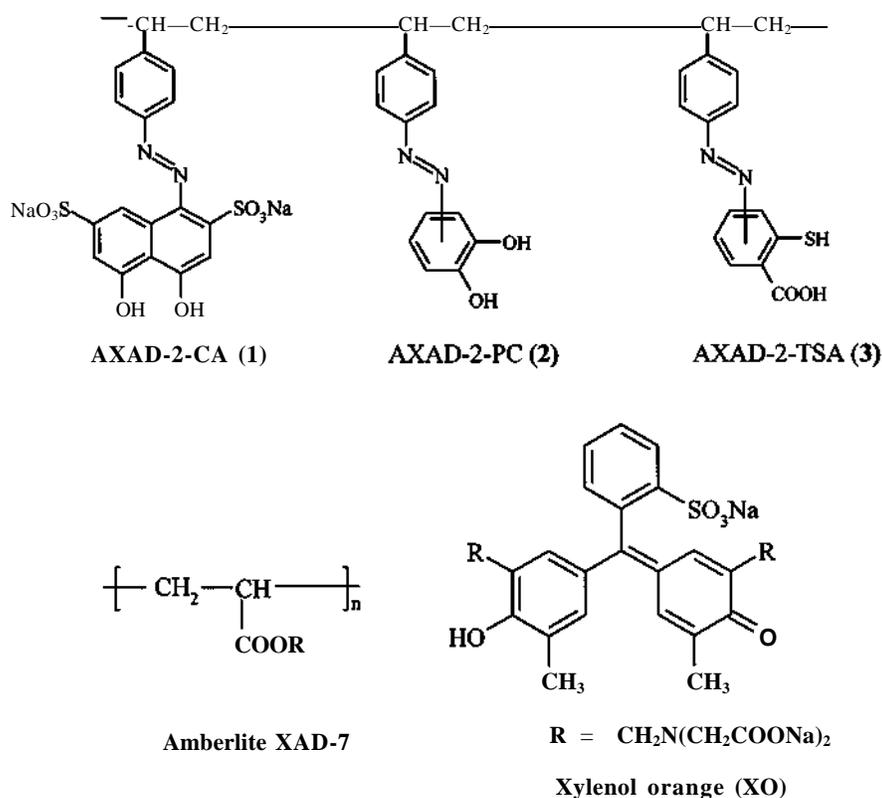[a] For six determinations of 2 ,ug ml^{-1}.

Fig. 1. Amberlite XAD-2 based resins 1 to 3, Amberlite XAD-7 and Xylenol Orange.

3. Results and discussion

The repeat units of functionalised Amberlite XAD-2 resins 1-3 are shown in Fig. 1. The structure of polymeric support (Amberlite XAD-7) used in the designing of resin 4 and the ligand (xylenol orange) loaded on it are also given in Fig. 1. IR spectra of 1-4 are characteristic and authenticate the modified resins [27-29,31]. In the IR spectra of 1-3, the -N=N- vibration appears at 1615-1629 cm^{-1} as reported earlier [27-29]. The other characteristic IR bands (in cm^{-1}) of the four resins are: 1: 1348 (>S=O stretching), 3503 and 1444 (OH vibrations); 2: 3545 (OH stretching), 1240 (C-O stretching) and 1352 cm^{-1} (O-H bending vibrations); 3: 1700 (>C=O stretching), 1255 (C-O stretching) and 1348 (O-H bending) and 4: 1639 (>C=O stretching) and 1152 (C-N stretching). On comparing the IR spectrum of each of these four resins saturated with Pb(II)

with that of the corresponding metal free resin a red shift of 7-12 cm^{-1} has been noticed in -N=N- vibration, OH (1 and 2), >S=O (1) and >C=O (3) bands. These observations suggest that chelation involving azo group is at least partly responsible for the sorption of Pb. The other functional groups involved in chelation with the azo group are -SO_3- (1), -OH (2) and -SH (3). In the sorption on 1 and 2, chelation of Pb(II) through two OH groups also seems to play a role. Similarly with 3 the chelate formation through -SH and -COOH groups appears to be partly responsible for the sorption.

3.1. Optimum conditions for sorption and desorption

A set of solutions of Pb(II) (volume: 100 ml of each; concentration between 0.01 and 0.2 |ig ml^{-1}) was taken. The pH of the set was varied

in range 2.0-9.0 and recommended procedure applied. The recovery (%) of Pb(II) as a function of pH is shown in Fig. 2. The optimum pH ranges along with maximum recovery values are given in Table 1. The acetate and phosphate buffer solutions (2-5 ml) were used to maintain the pH of the metal ion solutions in the range 3.0-6.0 and 6.8-8.0, respectively. Both buffers do not affect the sorption of Pb(II) and are suitable for pH adjustments except with 3 and 4, as phosphate interferes in the sorption with these resins. A flow rate of 2-10 ml min$\sim^1$ was found suitable for the sorption of lead(II) onto all the resins. An acid concentration between 0.5 and 4.0 M (HNO_3) was found suitable for its quantitative desorption. The higher concentration of acid (beyond 4.0 M) was not employed for desorption because the necessity of its partial neutralisation in the elute would reduce the preconcentration factor. The sorption capacity of each resin (per gram of resin) for Pb(II) was determined by column and batch methods. The resin was saturated with the metal ion under optimum conditions and the total metal sorbed was estimated with FAAS after stripping it off from the resin by HNO_3 of optimum concentration. The results are given in Table 1. The values of sorption capacity determined by the two methods for various batches of the resin are consistent (variation 1.0-3.0%). The standard and relative standard deviation (RSD) values for the preconcentration-coupled FAAS method are given in Table 1.
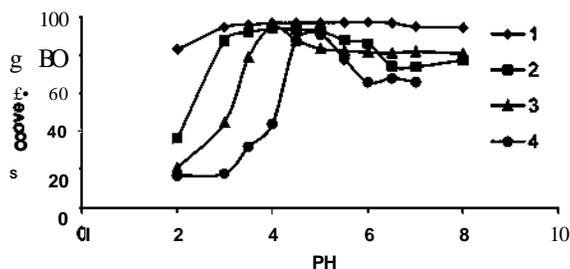
Table 2
Parameters at concentration limit

Experimental parameters	Chelating resin			
	1	**2**	**3**	**4**
Maximum volume of solution (l)	2.0	2.0	1.0	1.0
Concentration limit (ngml^1)	25	25	25	25
Breakthrough volume (ml)	10	8	10	10
Preconcentration factor	200	100	100	100

3.2. Calibration curves for working ranges

The calibration curves for Pb(II) were drawn after setting various parameters of FAAS (viz. wavelength, slit width, lamp current) at an optimum level and selecting the optimum concentration range (1.0-20.0 gml^1). The curves were found to be linear in the case of all the chelating resin. The linear equations along with regression (R^2) are as follows:

Resin 1 $A = 0.0246C + (+ 0.0008)$, $R^2 = 0.9984$

Resin 2 $A = 0.0243C + (+ 0.0022)$, $R^2 = 0.9975$

Resin 3 $A = 0.0221C + (+ 0.0016)$, $R^2 = 0.9987$

Resin 4 $A = 0.0227C + (+ 0.0119)$, $R^2 = 0.9945$

where A is absorbance corresponding to concentration C (ngml^{-1}) of Pb(II). The statistical calculations for each chelating resin are based on the average of triplicate readings for a standard solution of Pb(II).

3.3. Breakthrough volume of acid for elution

The efficacy of the eluent (2.0 M HNO_3) was studied by taking its different volumes (1-10 ml). It was found that 8-10 ml (Table 2) of acid was sufficient for quantitative recovery of the Pb(II) from all the four resins. Therefore, 10 ml of 2.0 M HNO_3 was used for the elution in all the further studies. The desorption was virtually instantaneous.

Fig. 2. Effect of pH on sorption of lead.

3.4. Limit of preconcentration and preconcentration factor

The lower limit of quantitative preconcentration was determined by loading a fixed amount of lead (50 |ig) onto 1 g of a resin using different feed volumes varying between 100 and 2000 ml. The maximum preconcentration factors achieved and corresponding lowest concentration below which recovery becomes non-quantitative are given in Table 2. The maximum volumes of lead(II) solution from which quantitative recoveries of metal can be made into 10 ml of 2.0 M HNO_3, are also reported in Table 2. The recovery of Pb(II) ion at a concentration below 25 ng ml~[1] (Table 2) becomes non-quantitative.

3.5. Limit of detection and quantification

The detection and quantification limit (LOD and LOQ) for Pb(II) were determined by passing a blank solution (5 l) through columns of all the modified Amberlite XAD-2/7 resins separately. The metal contents were desorbed from the column using 25 ml of 2.0 M HNO_3. The elutes were aspirated into the flame of AAS for metal ion monitoring. The detection limits (blank + 3 c, where *a* is standard deviation of blank estimation) for resins 1-4 are 4.06, 3.80, 4.87 and 2.44 ngml^[1], respectively, and the corresponding quantification limits (blank + 10<r) are 4.42, 4.19, 5.64 and 2.76 ngml^[1], respectively. On increasing the volume of blank solution these limits remain unchanged.

3.6. Effect of electrolytes and foreign ions

The effect of NaCl, NaBr, $NaNO_3$, Na_2SO_4 or Na_3PO_4 and Ca(II) and Mg(II) ions on the sorption of Pb(II) onto resins 1-4 was studied. A set of solutions (volume of 100 ml each) containing varying amount of electrolyte or cation (0.001-2.0 M) with Pb(II) (50 xg) was taken and recommended procedure applied. The Na_3PO_4 interferes in the sorption of lead on resins 3 and 4. The tolerance limits for all the electrolytes and cations with each resin are given in Table 3.

3.7. Lead sorption kinetics

To determine the rate of loading of Pb(II) ions on the four resins, batch experiments were carried out. The chelating resin beads (0.5 g) were stirred with a 50 ml of solution containing lead(II) ion (1000 ngml^[1]) at room temperature for 1, 5, 10, 20, 30, 40, 60, 80, 100, 120 and 180 min. The concentration of metal ions loaded onto the resin as well as present in the supernatant liquid was determined by the recommended procedure, after proper dilution. The loading half time needed to reach 50% of the total loading capacity was estimated from Fig. 3. The loading half time $(t_{1/2})$ values are reported in Table 1. The profile of lead uptake on these resins reflects good accessibility of the chelating sites in the resin.

3.8. Reusability of the resin

The reusability of the resin was tested by load-

Table 3
Tolerance limits of electrolytes and cations

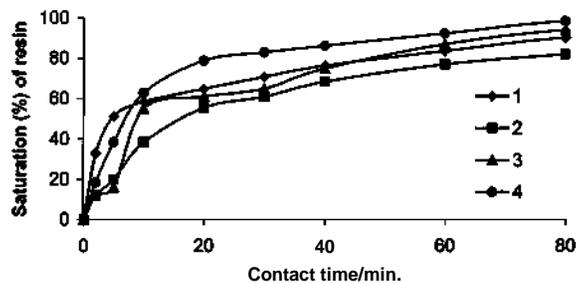| Modified resin	Electrolyte or cation (mol 1⁻)						
	NaCl	NaBr	$NaNO_3$	Na_2SO_4	Na_3PO_4	Ca^{2+}	Mg^{2+}
1	0.050	0.050	0.080	0.040	0.001	0.10	0.200
2	0.020	0.05	0.002	0.020	0.001	0.020	0.010
3	0.040	0.020	0.050	0.100	I	0.100	0.100
4	0.050	0.001	0.200	0.005	I	0.012	0.002

I = Interference.

Fig. 3. Kinetics of lead sorption on four chelating resins.

ing lead(II) ion several times on a column from a solution (100 ml) having a concentration of 40-500 (xgml^1 at a flow rate of 2-3 mlmin^1 and eluting it by the recommended procedure. It was found that the sorption capacity after 12 cycles of sorption and desorption does not vary more than 2% for any of the four matrices. Therefore, multiple use of the resin is feasible. Similar results are shown by batch method also. The sorption capacity of any of the four chelating resins does not change when it is treated with 100 ml of 6.0 M HNO$_3$ for 2 h. However, at further higher concentration of acid, xylenol orange bleeds from 4. The capacity of the resins 1-3 stored for more than 6 months under ambient conditions has been found practically unchanged. After loading river water samples also the resin cartridge can be regenerated fully with 2-4 M HNO$_3$ easily. Therefore, all the resins are suitable for repeated use.

4. Applications of the method

4.1. Determination of lead in tap water samples

The applicability of all the four resins was tested for tap water samples. The pH of 2 l of water sample (acidified with 2% HNO$_3$) was adjusted to the optimum level (Table 1) and the recommended procedure (column) applied. The standard addition of lead ions (5.0-250.0 |ig) to 2 l of water sample was made and the recommended procedure (column) was again applied. The results of both the estimations are given in Table 4 with RSD values and are consistent.

4.2. Determination of lead in river water samples

The sample solutions (1 l) were passed through the columns of chelating resins (after pH adjustments) with and without standard addition (5.0-250.0 |ig) and lead was determined as described in the recommended procedure. The results are given in Table 4 and indicate the suitability of the present resins for the preconcentration of lead from river water samples. The samples analysed after preconcentrations with different resins are not identical. They have been collected from the same site but at different times. Therefore, their lead contents have also been found to vary to some extent. The similarity of results obtained by direct and standard addition methods indicates that the reliability of the lead content data presented in Table 4 is reasonable.

5. Comparison with other metal ion collectors

The sorption capacity and preconcentration factor of thiosalicylic acid immobilised XAD-2 (3) are highest among all the four resins used in the present study. The loading half time with 4 in comparison to resins 1-3 is lower, which is usually the case with the chelating matrices made by physically coating the ligands onto the polymeric support.

The sorption capacity, preconcentration factor and loading half time of all four resins 1-4 are also compared with those of other important preconcentrating matrices used for lead enrichment (Table 5). All the resins except 4 exhibit better or comparable sorption capacities. 5-Amino-1,3,4-thiadiazole-2-thiol modified silica gel shows better capacity than 1 and 3. The preconcentration factors of only pyrocatechol violet modified Amberlite XAD-2, 7-dodecenyl-8-quinolinol loaded Amberlite XAD-4 and Chelex-100 are better than those of the present resins. The $t_{1/2}$ values of the present resins are also comparable with the other systems. The low matrix effects as evident from the river and tap water sample analyses and RSD values (except in the case of 3) are the additional advantages of the present resins.

Table 4
Determination of Pb(II) in water samples

Origin of sample	Method	Chelating resin							
		1		2		3		4	
		Pb (ngml^{-1})	RSD (%)	Pb (ngml^{-1})	RSD (%)	Pb (ngml^{-1})	RSD (%)	Pb (ngml^{-1})	RSD (%)
Ganges river, Kanpur	Direct	12.0	3.9	12.0	5.5	12.0	3.9	12.0	7.1
	SA	11.9	4.6	12.0	2.0	94.6	2.0	11.9	94
Gomti river, Lucknow	Direct	13.0	6.7	10.0	2.6	12.8	3.6	9.0	5.6
	SA	13.0	5.2	9.8	3.8	3.8	6.3	8.7	5.0
Tap water, New Delhi	Direct	7.1	1.9	6.4	2.1	7.2	1.9	6.1	1.8
	SA	7.0	1.4	6.6	2.2	7.1	1.4	6.0	1.6

SA, standard addition method; Direct, recommended procedure is directly applied; RSD (relative standard deviation) is for six determinations; SA results are after subtracting the amount of Pb added.

Table 5
Comparison of sorption capacity, preconcentration factor and loading half time $(t_{1/2})$ of resins **1–4** with other collectors of lead

Immobilised ligand	Parameter		
	Sorption capacity $(\mu mol\,g^{-1})$	Preconcentration factor	Loading half time $(t_{1/2})$, (min)
Support: Amberlite XAD-2			
Chromotropic acid (1)	186.3	200	3.2
Thiosalicylic acid (2)	89.3	100	4.5
Pyrocatechol (3)	104.7	100	15.5
Salicylic acid [18]	2.22	140	
Pyrocatechol violet [19]	6.56	23	
o-Vanillinthiosemicarbazone [20]	9.65	100	11
o-Aminophenol [21]	16.02	.02	16.02
Tiron [22]	60.3	25	4.0
Dithiocarbamate [23]		20	
Alizarin Red S [24]	1.5	40	
Pyrocatechol violet [26]		500	
Support: Amberlite XAD-4			
7-Dodecenyl-8-quinolinol [34]		500	
Support: Amberlite XAD-7			
Xylenol orange (4)	16.89	100	5.2
Dimethylglyoxalbis(4-phenyl-3-thiosemicarbazone) [35]		100	
Support: Polyacrylonitrile			
Aminophosphoric and dithiocarbamate [16]	27.6	200	
Support: Silica gel			
Acid Red 88 [32]	12.1		
5-Amino-1,3,4-thiadiazole-2-thiol [37]	130.0		
Support: Activated carbon			
8-Hydroxyquinoline [36]		100	
Cupferron [36]		100	
Other resins			
Chelex-100 [6]		1000	
Metalfix chelamine resin [38]		25	

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