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Preconcentration of Heavy Metals and Matrix Elimination using Silica Gel Chemically Modified with 2,3-Dihydroxybenzaldehyde

Mesut Alan[a]; Derya Kara[a]; Andrew Fisher[b]
[a] Department of Chemistry, Art and Science Faculty, Balikesir University, Balikesir, Turkey [b] School of Earth, Ocean and Environmental Sciences, University of Plymouth, Plymouth, UK

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Preconcentration of Heavy Metals and Matrix Elimination using Silica Gel Chemically Modified with 2,3-Dihydroxybenzaldehyde

Mesut Alan and Derya Kara
Department of Chemistry, Art and Science Faculty, Balikesir University,
Balikesir, Turkey

Andrew Fisher
School of Earth, Ocean and Environmental Sciences, University
of Plymouth, Plymouth, UK

Abstract: Many direct methods cannot easily be used to measure analytes such as Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) ions in sea and river water since these elements are present at very low concentration and the sample has a very complex matrix. In this study a method was developed to preconcentrate these ions by solid phase extraction within a column system using a newly synthesised 2,3-dihydroxy benzaldehyde modified silica gel (SGDHB). Different parameters, such as pH, resin amount, eluent type, eluent volume, sample flow rate, preconcentration factors, and resin capacity were determined for the preconcentration of metal ions with the resin. Samples (125–500 ml) containing metal ions were passed through the column filled with SGDHB resin so that metal ions were retained on the column. The preconcentrated analytes were then eluted with 15 mL of 0.1 M HCl. The metal concentrations in the eluate were measured by FAAS. A sample and eluent flow rate of 1.12 and 0.56 ml/min respectively was used. Estimates of accuracy, precision, and detection limits were determined. In addition, analysis of the CRM LGC 6156 harbor sediment was undertaken, using the resin to isolate the analytes from potential interferences. Good agreement with certified values was obtained, indicating that the method is equally applicable to the analysis of water samples and to digests of solid materials.

Keywords: Solid phase extraction, Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) preconcentration, modified silica gel, FAAS

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Address correspondence to Derya Kara, Department of Chemistry, Art and Science Faculty, Balikesir University, Balikesir 10100, Turkey. E-mail: dkara@balikesir.edu.tr

INTRODUCTION

Preconcentration of trace elements holds an important place among the techniques used in modern analytical chemistry. Preconcentration has increased the possibilities of many analytical determinations because as well as the act of preconcentration, the use of resins also facilitates the eliminatination of the matrix effects which often significantly worsen the detection limits and other metrological parameters of the procedure and which can sometimes prevent the determination of one or more trace elements. Another advantage of preconcentration is that it enables large representative samples to be treated and thereby reduces the sampling error. Several methods have been used for preconcentration of trace amounts of metal ions present in aqueous solutions including both liquid–liquid extraction (LLE) and solid phase extraction (SPE) techniques (1–3). Solid phase extraction (SPE) has been increasingly used for preconcentration/separation of trace and ultra-trace amounts of inorganic and organic species from complex matrices. Many of these protocols have been described in recent reviews (4–6). The basic principle of SPE is the transfer of the analyte from the aqueous phase to bind to active sites of the adjacent solid phase. It has several advantages over other techniques, including stability and re-usability of the solid phase, the possibility of reaching high preconcentration factors, ease of separation and enrichment under dynamic conditions, no need for organic solvents which may be toxic or flammable and minimal costs due to low consumption of reagents. Various researchers (7) have highlighted the advantages of SPE over other preconcentration techniques and in particular over liquid–liquid extraction. Chelating resins have frequently been used as SPE materials as they provide good stability, high sorption capacity for metal ions and good flexibility in working conditions. Accordingly, several solid phase extractants have been prepared either by physical loading or chemical binding of selected chelating reagents on to different solid supports such as silica gel (8–10), activated carbon (11–13), cellulosic derivatives (14), clays(15), polyurethane foam (16), Amberlite XAD-4 (17–19), Amberlite XAD-2 (20, 21) and other chelating ion exchange resins (22).

Chelating ion-exchange resins are capable of preconcentrating some metal ions selectively from large volumes of aqueous samples and may easily be coupled on-line with atomic spectrometric detection systems to enhance their sensitivity. Examples of a chelating resin-based on-line matrix separation and preconcentration of metal ions followed by their determination using FAAS and inductively coupled plasma-mass spectrometry (ICP-MS) include papers by Nelms et al. (23–25). The selectivity of the solid phase extractors and preconcentrators depends mainly on the structure of the immobilized organic compound, the nature of the incorporated donor atoms (O, N, P, and S), the positioning of the functional groups along the surface of the solid support and the steric requirements of the complex formed after uptake of the desired metal ion (26).

This work aims to synthesize 2,3-dihydroxy benzaldehyde modified silica gel (SGDHB) where the chelating ligand is bound to the silica gel *via* the -C=N- covalent linkage by using a Schiff base reaction, and to use the product as a sorbent for the preconcentration of the heavy metals (Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II)) from aqueous solutions and from digests of solid materials.

EXPERIMENTAL

Instrumentation

A flame AAS instrument (AA 929, Unicam, Cambridge, UK) furnished with an air-acetylene flame (3:7, gas flow rate ratio) as the atomizer was used for monitoring Cu, Pb, Ni, Zn, and Cd at 324.7, 283.3, 232.0, 213.9, and 228.8 nm, respectively throughout the experiments. For FT-IR analysis, samples were ground into a powder with FTIR-grade potassium bromide (KBr) and pressed into disks. Fourier transform infrared absorbance spectra were taken with a Perkin Elmer BX 2 spectrometer. The elemental analysis of the resin was measured using a LECO CHNS 932 analyzer (LECO Corp., St Joseph, MI. USA).

Reagents and Solutions

All the reagents were of analytical grade and were used without further purification. De-ionized water was used throughout. Multi-element stock solutions containing 100 mg L^{-1} of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) were prepared from their nitrate salts. Hydrochloric acid, toluene, 3-aminopropyltrimethoxysilane, 2,3-dihydroxy benzaldehyde, and methanol were purchased from Fluka (Gillingham, Dorset, UK). Silica gel 60 for column chromatography used was of 70–230 mesh and 0.063–0.20 mm particle size and was obtained from Merck (Poole, Dorset, UK). A pH meter (Nel pH 890) was also used to adjust solutions to the required pH. The peristaltic pump was a Watson Marlow 323 SD peristaltic pump (Falmouth, UK). The column was a glass tube (0.7 cm × 10 cm Aldrich C 3669) packed with modified silica gel resin (2 g). Transport lines were made using 1.25 mm i.d. tygon tubing. All glassware used was washed with 10% nitric acid for one day and rinsed with deionized water before use. A harbor sediment sample, LGC 6156 (Laboratory of the Government Chemist, Teddington, London, UK) was used in the experiments for method validation.

Synthesis of the 2,3-Dihydroxy Benzaldehyde Modified Silica Gel (SGDHB) Resin

The precursor was prepared as described previously in the literature (27). Silica gel (3 g) was treated by refluxing it in 50 mL of 6 M HCl for 3 h. It was then washed with distilled water until the washings were neutral and was dried at 180°C for 24 h. Activated silica gel (3 g) was suspended in 100 mL of 10% v/v 3-aminopropyltrimethoxysilane in dry toluene. The mixture was refluxed through a calcium chloride tower for 3 h without stirring. The resulting product, aminopropyl silica gel (AP-gel), was filtered off and washed repeatedly with methanol. This product was mixed with 5 g of 2,3-dihydroxy benzaldehyde dissolved in 60 mL of ethanol. The mixture was refluxed for 8 h without stirring. The product obtained (SGDHB) was filtered off, washed with small portions of methanol, and was placed in a Soxhlet extractor and extracted with 95% ethanol in order to dissolve the free 2,3-dihydroxy benzaldehyde. The product was then separated from the liquid phase and dried in an oven at 50°C. No stirring was required to obtain a chelating resin with a suitable pore size to pack the column. If stirring is performed, a smaller pore size is obtained which hinders the flow of sample (27). A reaction scheme for this synthesis is given in Fig. 1.

Recommended Procedure for Preconcentration and Determination of Metal Ions

Batch Method

The effect of pH on the retention capability was determined using a batch system. The sample solution (50 ml) containing 5 mg L^{-1} of one of the five metal ions was taken in a glass stoppered bottle (150 ml). The pH was adjusted and buffered to values in the range 2.0 to 7.0 using either acetic

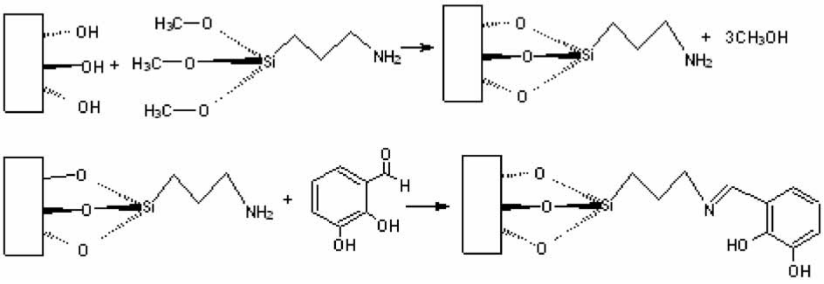

Figure 1. Reaction scheme for the preparation of SGDHB resin.

acid-sodium acetate, ammonium acetate-acetic acid, or boric acid-sodium borate buffer solutions. Then a 0.5 g of SGDHB was added to the bottle and the mixture was shaken for 1 hour at 25°C. After filtration, the supernatant was analyzed for the analytes using FAAS. The optimum pH value was determined to be pH 6.7.

Column Method

The 2 g of SGDHB was slurry packed with de-ionized water into a glass column (Aldrich C 3669, 0.7 cm × 10 cm) and allowed to swell for 24 h. It was thoroughly washed with double distilled water and then with pH 6.7 ammonium acetate buffer (0.1 mol/L). A suitable aliquot (25 ml) of the solution containing Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) in the concentration range 0.040–10.0 mg L^{-1} was passed through this column after adjusting its pH to an optimum value 6.7 at a flow rate range of 0.56–4.28 mL min^{-1}. The stripping of the metal ions from the column was carried out by 0.1 mol L^{-1} HCl (15–25 mL) at a flow rate in the range of 0.56–4.28 mL min^{-1}. The concentration of metal ions in the eluate was measured by FAAS.

Analysis of Sediment and water Samples

2.5 g of the certified harbor sediment sample (LGC 6156) was weighed accurately into a 100 ml beaker and *aqua regia* (22.5 mL of concentrated hydrochloric acid and 7.5 mL of concentrated nitric acid) was added (28). The container was covered with a watch glass and the mixture was heated on a hot plate at 95°C almost to dryness. Then 10.0 mL of *aqua regia* were added to the residue and the mixture was again evaporated almost to dryness. After cooling, the resultant mixture was filtered through a Whatman No: 41 filter paper into a pre-cleaned volumetric flask. The sample was diluted to 50 mL with DDI water. A 20 mL aliquot of this solution was added to sufficient 5-sulfosalicylic acid dihydrate (4% m/v in the final volume) to prevent precipitation of $Fe(OH)_3$ and to form stable complexes with the Fe (29), hence preventing it from being retained on the resin. The sample was then neutralized using NaOH solution (1 mol/L), buffer solution added and diluted again to 100 ml. The proposed method was applied to this solution.

In order to validate the methodology, the method proposed for these five metal ions was applied to natural waters. River water was collected from Susurluk River in Susurluk, Balikesir and sea water was collected from the Marmara Sea near the Bandirma Coast. The water samples were filtered through 0.45 μm pore size millipore cellulose acetate membrane filters and acidified to pH 2.0 with 0.1 mol L^{-1} HNO_3 and stored in a pre-cleaned polyethylene bottle. The samples were analyzed within 2 weeks of collection.

After adjusting the pH to 6.7, the standard preconcentration procedure was applied to an aliquot (200 ml) of each sample.

RESULTS AND DISCUSSION

Synthesis and Characterization of SGDHB

The synthetic route of SGDHB is described schematically in Fig. 1. After the reaction, the silica gel particles became red-brown and the color did not change after a Soxhlet extraction with ethanol. The results of elemental analysis of the SGDHB were 3.1% N, 20.27% C, and 13.26% H, indicating that the Schiff base modification yield is 76.4% after amino-silica gel calculated based on nitrogen value. The elemental analysis result for nitrogen yields a result that is in complete concordance with the theoretical result for the nitrogen of the compound produced by the first reaction in Fig. 1. The IR spectrum of the SGDHB was compared with that of the silica gel and 2,3-dihydroxy benzaldehyde (Fig. 2). The infrared spectrum of the reagent (KBr pellet) is complicated because the SiO_2 portion of the molecule produces numerous bands, the overlap of which makes detailed assignments difficult. The band at 1731 cm^{-1} for C=O stretching coming from 2,3-dihydroxy benzaldehyde had disappeared from the spectrum of the synthesised resin (SGDHB), produced by a reaction 2,3-dihydroxy benzaldehyde and amino-silica gel, confirming the presence of only the enol-imine tautomer in SGDHB. The infrared spectrum of the SGDHB showed bands at 1633 cm^{-1} for C=N, 800–700 cm^{-1} (benzene) and 3400 cm^{-1} (aromatic OH), respectively.

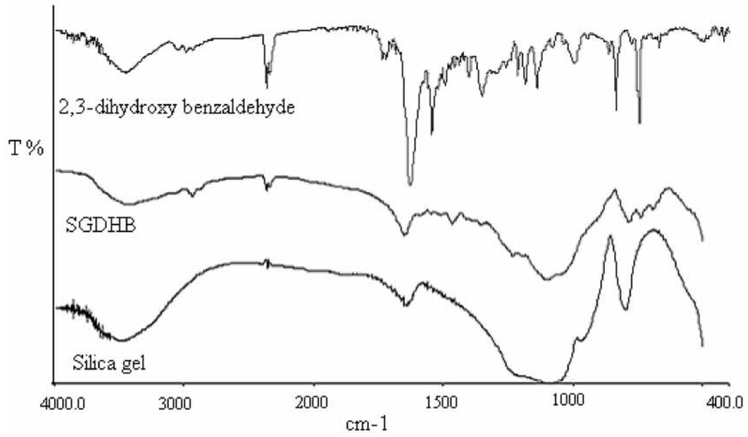

Figure 2. The IR spectra of silica gel, 2,3-dihydroxy benzaldehyde and SGDHB.

Optimization

Among the chemical variables studied that could potentially affect the determination and preconcentration of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) with SGCHB, the pH was the most important. The range of pH investigated was between 2 and 7 using the batch system at 25°C. The results are shown in Fig. 3. These results showed that absorbance values of metal ions do not change between pH values of 6 and 7 indicating that maximum metal retention occurred. The optimum pH value was selected as 6.7 for all subsequent experiments using SGDHB. The metal ions may possibly be bound to the SGDHB at two different sites. One possible site may be between one nitrogen and one hydroxide whilst the other possible binding site for metals may be between the two hydroxide groups. Figure 3 demonstrates that some Pb(II) and Cd(II) is sorbed onto the SGDHB below pH 4 while sorption of Zn(II), Cu(II), and Ni(II) is very low. This possibly indicates that the complex formation constants of Pb(II) and Cd(II) with SGDHB are higher than the complex formation constants of Zn(II), Cu(II), and Ni(II). The amount of resin packed in the column was also changed between 0.5 and 2.5 g to investigate the effect on quantitative recovery of 5 mg L^{-1} of Cu (II), Zn(II), Cd(II), Ni(II), and 20 mg L^{-1} of Pb (II) in a 50 mL solution at pH 6.7. The amount of 2.0 g of SGDHB resin was selected as the optimum for quantitative recovery. Different concentrations of HCl and HNO_3 were used to investigate the effect of different eluents on the desorption of the Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II). A lower concentration of acid was used for elution since the column life time was extended. This was concluded

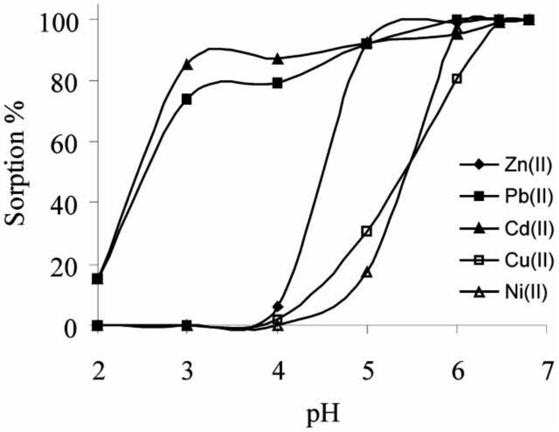

Figure 3. The pH effect on the sorption of Pb(II), Cd(II), Cu(II), Zn(II), and Ni(II) ions on the SGDHB. 5 mg L^{-1} of Cd(II), Cu(II), Zn(II), and Ni(II) and 20 mg L^{-1} Pb(II). 0,5 g resin (n = 3), batch method.

because a significant decrease in resin efficiency was observed after repeated use of high acid concentrations. Complete desorption of these metal ions took place with 0.1 M HCl and therefore this was selected as eluent in subsequent column experiments. A lower percentage of analytes were stripped from SGDHB when 0.1 M HNO_3 was used as eluent and this was attributed to it probably being due to the effect of the nitrate counter ion. Therefore, the effect of the volume of 0.1 M HCl for quantitative recovery of the metal ions was investigated in the range of 5–25 mL. Quantitative recovery values were obtained using a volume greater than 10 mL of eluent solution. Therefore 15 mL of eluent solution was selected as the volume of eluent in subsequent experiments. The optimization of the sample flow rate is very important for preconcentration experiments. Higher sample flow rate and higher retention yield are wanted in preconcentration experiments because this will give the highest preconcentration factor in the shortest time. However, the kinetics of the retention may limit the rate at which the sample can be pumped through the resin. The sample flow rate was changed between 0.56 and 4.28 mL min^{-1} and the signal was recorded with the FAAS system at pH 6.72 without any preconcentration step. The recovery values for Ni(II) and Pb(II) decreased at sample flow rates greater than 3.37 mL min^{-1}. The sorption of the other metal ions (Cu, Cd, and Zn) was quantitative at sample flow rates between 0.56 and 4.28 mL min^{-1} (Fig. 4). These results show that SGDHB resin is capable of retaining these metal ions at high flow rates. All subsequent experiments were performed at a sample flow rate of 1.15 mL min^{-1}. The effect of the flow rate of the eluent

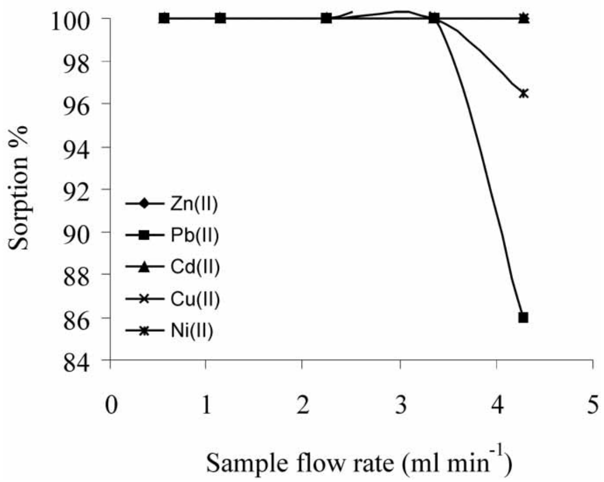

Figure 4. The effect of sample flow rates on the recovery of the metal ions (5 mg L^{-1} of Cd(II), Cu(II), Zn(II), and Ni(II) and 20 mg L^{-1} Pb(II). 0,5 g resin (n = 3), column method.).

solution (0.1 M HCl) was studied between 0.56 and 4.28 mL min^{-1}. The recovery values for metal ions decreased at eluent flow rates greater than 1.15 mL min^{-1} so therefore the value of 0.56 mL min^{-1} was selected as an optimum value for the flow rate of the eluent solution.

Effect of Inert Electrolytes

Chloride, nitrate, sulphate, and phosphate ions etc. found in natural water samples have the capability to complex with many metal ions. Therefore, in their presence, the efficiency of the immobilized ligand to bind metal ions may be hampered resulting in the reduction of overall extraction (30). Also, extensive studies have revealed that the magnitude of the electolyte effect is highly dependent upon the charges of the participants in an equilibrium (31). Therefore, an investigation of the electrolyte effect in water samples is very important on the sorption of metal ions. Thus the effect of inert electrolytes, i.e. NaCl, Na_2SO_4, $NaNO_3$, $Na_2C_2O_4$, KI, $NaClO_4$, NaF, KH_2PO_4, $MgSO_4$, NH_4CH_3COOH, $Ca(NO_3)_2$ (under the condition that the conjugate bases of weak acids were brought to the optimal pH values of 6.72 with acid) on the recovery of the metal ions were investigated in the column system. Table 1 shows the upper concentration limits for these inert electrolytes for which the recoveries of the metal ions are quantitative. This demonstrates that the column was efficient at retaining the analytes,

Table 1. Tolerance limits of electrolytes

	Metal ions									
	Pb(II)		Zn(II)		Ni(II)		Cu(II)		Cd(II)	
Electrolyte	mol/L	R%	mol/L	R%	mol/L	R%	mol/L	R%	mol/L	R%
NaCl	0.4	100	0.4	100	0.4	96.4	0.4	100	0.4	100
Na_2SO_4	0.01	99.9	0.025	99.6	0.05	99.9	0.1	99.9	0.05	99
$NaNO_3$	0.1	100	0.1	100	0.05	100	0.05	100	0.05	100
$Na_2C_2O_4$	0.05	100	0.025	100	0.01	100	0.1	100	0.005	100
KI	0.05	100	0.1	97.5	0.1	100	0.1	100	0.1	100
$NaClO_4$	0.025	100	0.1	100	0.1	100	0.1	100	0.005	100
NaF	0.1	100	0.1	99	0.1	100	0.1	100	0.1	100
KH_2PO_4	0.025	100	0.1	100	0.1	100	0.1	100	0.05	100
$MgSO_4$	0.05	100	0.1	100	0.02	100	0.1	100	0.005	100
CH_3COONH_4	0.01	100	0.1	100	0.05	100	0.1	100	0.05	100
$Ca(NO_3)_2$	0.1	100	0.1	99	0.05	100	0.1	100	0.1	100

pH = 6.7, 1 mg L^{-1} of Cd(II), Cu(II), Zn(II), Ni(II), and 2.5 mg L^{-1} of Pb(II), 2 g SGDHB, sample flow rate 1.12 mL min^{-1}, column system, n = 3.

whilst effectively separating potentially interfering matrix constituents. The developed method can therefore be applied to natural samples containing high salinity.

Maximum Retention Capacity of 2,3-Dihydroxy Benzaldehyde Modified Silica Gel (SGDHB) Resin

The sorption capacity of the chelating resin was determined by the batch process by equilibrating about 0.05 g of the resin with individual solutions of 50 mL of 25 mg L^{-1} metal ion solution for 4 h at pH 6.7 (for Cd, Ni, Pb, and Zn) and at pH 6.3 (for Cu(II)) at 25°C. The maximum retention capacity of Cu(II) was determined at pH 6.3 because 25 mg L^{-1} of Cu(II) precipitates at higher pH values. The loading capacity of the resin for each metal ion was calculated from the difference between the metal ion concentrations in the solutions before and after sorption. The maximum retention capacities for these metals on this resin are compared with other modified silica gel resins in Table 2. As shown, the maximum retention capacity values of this resin are very high and compare favorably with other modified silica gel resins reported in the literature. The thioacetamide functionalized silica gel reported previously had higher capacity for some analytes (Cu, Cd, and Pb) and similarly, o-dihydroxybenzene functionalized silica gel had higher capacity for some elements (Cu, Ni, and Pb) than the resin reported here. However, the resin reported here was applicable to more analytes.

Table 2. Comparison of capacity values of SGDHB with other modified silica immobilized resins reported in the literature

Resin	Cu(II) (mmol/g)	Zn(II) (mmol/g)	Cd(II) (mmol/g)	Ni(II) (mmol/g)	Pb(II) (mmol/g)	Reference
o-Dihydroxy benzene	0.348	0.168	0.032	0.178	0.082	(30)
Acid red 88	0.012	0.016	0.11	0.011	—	(32)
Salicylaldoxime	0.08	0.04	—	0.04	—	(33)
3-Methyl-1-pentyl-4-stearoyl-5-pyrazolone	0.042	—	—	0.048	—	(34)
Thioacetamide	0.257	—	0.111	—	0.095	(35)
1,8-dihydroxy anthraquinone	—	0.180	0.070	—	0.076	(36)
SGDHB	0.132	0.133	0.070	0.040	0.040	This work

Measurement of Preconcentration Factors

Preconcentration factors for a given volume of the sample solution passing through the column depend upon the original sample volume and the volume of acid solution required to quantitatively elute the metal retained on the resin. The recoveries and the enrichment factors are listed in Table 3. The preconcentration factor obtained may theoretically be very high if extremely large volumes of sample are pumped through the resin. However, this suffers the obvious drawback of taking a substantial amount of time. An experimental technique is not really viable if it takes several hours to prepare one sample. As a result, a compromise between time and the enrichment factor is necessary. As a result, preconcentration factors of 10–20 are commonplace. In this work, volumes of sample ranging from 125–500 mL were used, depending on the analyte and on the enrichment factor required to obtain a range of concentrations suitable for the sample type.

Method Validation

In order to evaluate the performance of the method, the linearity and the detection limits were determined. This was followed by an assessment of the accuracy and repeatability. Standards and blanks were prepared with ultra-pure water. Linearity was demonstrated for all elements with correlation coefficients better than 0.998. Detection limits were determined by analysing replicate blanks (n = 15). Limits of detection (3s) were Cu = 2.45 μg L^{-1}, Ni = 3.06 μg L^{-1}, Zn = 2.35 μg L^{-1}, Pb = 9.50 μg L^{-1}, and Cd = 1.95 μg L^{-1} for the proposed method.

Analysis of the Synthetic Metal Mixture Solution

The proposed method was applied to a synthetic sample containing 5.0 μg Cu(II), Zn(II), Cd(II), Ni(II) and 10.0 μg Pb(II) in 50 mL and to a

Table 3. The determination of preconcentration factors

Metal ions	Sample volume (mL)	Concentration (μg/mL)	Eluent volume (mL)	Recovery (%)	Preconcentration factor
Cu(II)	250	0.040	15	100.0	17
Cd(II)	125	0.10	20	94.5	6.25
Ni(II)	250	0.080	15	103.7	17
Pb(II)	500	0.080	20	99.0	25
Zn(II)	250	0.040	15	100.0	17

pH = 6.7, 2 g SGDHB, sample flow rate 1.12 mL min^{-1}, column system, n = 3.

synthetic sample containing 5.0 μg Cu(II), Zn(II), Cd(II), Ni(II), and 10.0 μg Pb(II) in 50 mL of 0.4 mol/L NaCl. The metal concentrations expected and found are listed in Table 4. From this, it can be seen that, in both experiments, recovery was close to 100%. This corroborates the data in Table 1 and demonstrates further the ability of the resin to retain the analytes in the presence of high concentrations of concomitant ions.

Application of the Method to Real Water Samples

The proposed method was then applied to real water samples. Unfortunately, the proposed method used FAAS as a detection system, which does not have sufficiently low LOD to analyze a certified, unpolluted seawater sample. Therefore, the metal determinations were confirmed using a spike recovery procedure. The results shown in Table 5 prove that the polluted seawater and river water samples may be analyzed for the metal(II) ions with an adequate precision, in this case with a maximum RSD of 5.37%. As shown in Table 5, the Cd concentration in un-spiked sea water and the Cd and Pb concentration in un-spiked river water could not have been determined using this method because these samples contain concentrations of these analytes that are lower than LOD values of FAAS. The resin was used for several hundred sample loading/elution cycles and no significant loss of performance was observed, thus demonstrating the stability and robustness of the resin.

Table 4. Analysis of synthetic metal mixture solution (in water and in 0.40 mol/L NaCl aqueous solution)

	In water		In salted mixture solution (containing 0.40 mol/L NaCl)	
Metal ion	Experimentally determined concentration (μg/mL)	Recovery (%)	Experimentally determined concentration (μg/mL)	Recovery (%)
Cu(II)	0.100 ± 0.007	100	0.105 ± 0.005	105
Cd(II)	0.098 ± 0.011	98	0.093 ± 0.017	93
Ni(II)	0.100 ± 0.009	100	0.099 ± 0.012	99
Pb(II)	0.198 ± 0.015	99	0.205 ± 0.007	102.5
Zn(II)	0.102 ± 0.013	102	0.105 ± 0.017	105

pH = 6.7, 5.0 μg of Cd(II), Cu(II), Zn(II), Ni(II), and Pb(II) at 50 ml, 2 g SGDHB, sample flow rate 1.12 mL min^{-1}, column system, (n = 5).

Table 5. Determination of metal ion concentration found in water samples

Trace element	Seawater μg L^{-1}	Spike seawater[a]	Found μg L^{-1}	Recovery (%)	River water μg L^{-1}	Spike river water[a]	Found μg L^{-1}	Recovery (%)
Cu	12.48 ± 0.56	53.9 ± 1.06	41.42	104	13.09 ± 0.38	56.69 ± 1.78	43.6	109
Ni	19.84 ± 0.25	57.1 ± 0.82	37.26	93.2	20.91 ± 0.73	60.64 ± 1.46	39.73	99.3
Pb	16 ± 0.86	216.3 ± 4.01	200.3	100	nd	201.9 ± 3.98	—	101
Cd	nd	38.41 ± 0.75	38.41	100	nd	38.54 ± 0.68	—	96.4
Zn	53.32 ± 0.96	83.06 ± 1.75	29.74	99.3	169.1 ± 2.15	203.9 ± 4.52	34.8	104

[a] The spikes of 40 μg L^{-1} of Cu, Cd and Ni, 200 μg L^{-1} Pb and 30 μg L^{-1} Zn has been added to sea water and river water samples. pH = 6.7, 2 g SGDHB, sample flow rate 1.12 mL min^{-1}, (n = 3).

Analysis of the Sediment Sample LGC 6156

In order to evaluate the accuracy and precision of the technique, certified sediment reference material (LGC 6156) was analyzed. The concentration of the measured analytes; Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) in acid digests of solid certified samples may be too low to measure directly by FAAS and hence their determination may require a preconcentration step. The proposed method was therefore adopted to determine these metals. Some of these samples contain a high concentration of iron, which may saturate the column and hence lead to low recovery of the analytes. Alternatively, at some pH values the iron may precipitate leading to co-precipitation of the other ions. To obtain reliable results, the Fe must therefore be prevented from both being retained on the column and from precipitating. Therefore sufficient 5-sulfosalicylic acid dihydrate (4% m/v in the final volume of 100 ml) was added to the samples to prevent precipitation of $Fe(OH)_3$ and to form stable complexes with the Fe, hence preventing it from being retained on the resin. The samples were then analyzed using the proposed method. The results obtained were in good agreement with the certified values and the precisions (RSDs) for the analytes examined were in the ranges 2.31 to 4.0%. The results are summarized in Table 6. The results have been compared with certified values using the student *t*-test. The test results in Table 6 indicate that there was no significant difference between experimental results and certified results at the 95% confidence limits. Although the concentrations of the analytes present in the sample digests were sufficiently high to be measured directly, i.e. without the need for preconcentration on the resin, the aim was to demonstrate that the resin could be used for matrix elimination/preconcentration from digests of solid materials. Other environmental samples e.g. lesser polluted sediments and soils, vegetation etc.,

Table 6. The analysis of certified material LGC 6156

Metal ion	Certified value ($mg\ kg^{-1}$)	Found ($mg\ kg^{-1}$)	% RSD	$\lvert \bar{x} - \mu \rvert$	$ts/\sqrt{(N)}$
Cu(II)	2400 ± 122	2362 ± 88	3.72	38	60
Cd(II)	2.9 ± 0.5	2.86 ± 0.066	2.31	0.04	0.1
Pb(II)	1685 ± 140	1641 ± 47	2.86	44	74.7
Zn(II)	3530 ± 195	3449 ± 103	2.98	56	162
Ni(II)	161 ± 13	158 ± 6.32	4.0	3	10.04

pH = 6.7, 2 g SGDHB, sample flow rate 1.12 $mL\ min^{-1}$, 2.5 g of LGC 6156, column system, (n = 3). (If the difference between experimental and certified results $\lvert \bar{x} - \mu \rvert$, is smaller than the computed value of $ts/\sqrt{(N)}$, no significant difference between experimental and certified results has been accepted at the 95% confidence level).

could be analyzed in a similar manner, safe in the knowledge that analyte ions are retained and potential interferences are removed. This experiment demonstrated that as well as providing a robust and reliable method for the determination of trace analytes, the resin is equally applicable to the determination of trace analytes in digests of solid materials.

CONCLUSIONS

This Schiff base modified chelating resin facilitates the determination of trace analytes and the efficient separation of matrix elements found in natural samples such as seawater. The successful determination of five elements in natural water samples and a solid certified sample was achieved with a minicolumn packed with the chelating resin. The system is very simple to construct, the sample volume required is small (unless preconcentration is required) and the number of reagents used is also small. The results obtained demonstrate good reproducibility. The combination of the preconcentration of analytes and the elimination of matrix substances using a mini-column packed with newly synthesised 2,3-dihydroxy benzaldehyde modified silica gel (SGDHB) by FAAS methods was found to be a versatile technique with considerable promise for the determination of trace elements in a wide variety of samples.

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