Original Paper

Solid-phase extraction of Zn(II), Cu(II), Ni(II) and Pb(II) on poly(vinyl chloride) modified with 3-ferrocenyl-3-hydroxydithioacrylic acid, and their subsequent determination by electrothermal atomic absorption spectrometry

Jackson K. Kiptoo[1], J. Catherine Ngila[2], Ned D. Silavwe[3]

[1] Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology, Nairobi, Kenya
[2] School of Chemistry, University of KwaZulu Natal, Westville Campus, Durban, South Africa
[3] Department of Chemistry, University of Botswana, Gaborone, Botswana
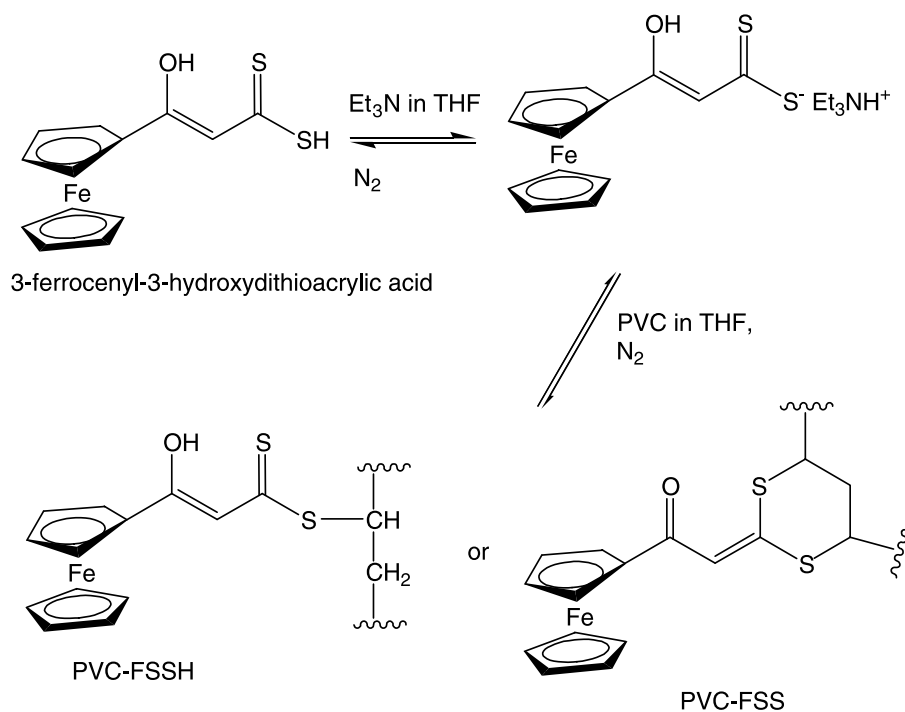
Abstract. A new chelating resin based on poly(vinyl chloride) functionalized with 3-ferrocenyl-3-hydroxydithioacrylic acid has been synthesized and characterized. The resin was used as a packing material in an off-line mini-column solid-phase extraction system for preconcentration of Zn, Ni, Cu and Pb in water samples prior to their determination using electrothermal atomic absorption spectrometry. Analytical parameters such as pH, flow rate and sample breakthrough volume were optimized. The breakthrough volume for 0.2 μg of analyte using 0.1 g of adsorbent was 60–100 mL, permitting enrichment factors of at least 60. The proposed procedure, validated using a riverine water reference material (SLRS-3), was applied to environmental water samples. The potential for use of the chelating resin to separate interfering ions such as Na, K, Mg and Ca is also explored.

Keywords: 3-ferrocenyl-3-hydroxydithioacrylic acid; poly(vinyl chloride); trace metal enrichment; ETAAS

Correspondence: Jackson K. Kiptoo, Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology, P.O. Box 62000-00200, Nairobi, Kenya, e-mail: kiptoojac@yahoo.com

The direct determination of trace metals in water systems remains a challenge to analytical chemists because of their low concentrations. Although advances in electronic instrumentation has provided powerful analytical tools for trace metal determination such as electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma-mass spectrometry (ICP-MS), matrix interferences is a major limitation. Therefore, separation and preconcentration techniques remain important complimentary steps in trace metal analysis. Trace metal enrichment methods in common use include ion exchange [1], coprecipitation [2], liquid–liquid extraction [3], and recently solid phase extraction (SPE) [4–7]. SPE techniques have been widely used for trace metal preconcentration and sample cleanup because they permit higher enrichment factors with higher sample throughput, while utilizing minimal or no organic solvents [8]. Due to the need to meet certain specific ecological and environmental challenges, new chelating resins are being developed. In recent years, ligands trapped in or chemically bonded to solid supports have been successfully used to selectively preconcentrate trace metals [9, 10]. Dithiocarbarmates (DTCs) have lately attracted interest as chelating agents because of their thermodynam-

Fig. 1. Reaction scheme for the modification of PVC with 3-ferrocenyl-3-hydroxydithioacrylic acid and the possible structures of modified PVC (FSSH-PVC and FSS-PVC)

ically stable metal complexes and selectivity against alkali and alkaline earth metals [11], hence are suitable for trace metal preconcentration as well as for sample cleanup. However, DTCs are known to be unstable in acidic media and readily convert to the amine and carbon disulphide [12]. Consequently, dithiocarbamic acids are generally isolated as salts instead of the free forms. On the other hand, a number of dithiocarboxylates can be converted to the acidic forms and isolated without significant decomposition [13]. Due to their greater stability, therefore, dithiocarboxylates may be more suitable chelating materials for separation and preconcentration of trace metal ions.

In the present study, a new chelating agent based on poly(vinyl chloride) (PVC) functionalized with 3-ferrocenyl-3-hydroxydithioacrylic acid ($FSSH_2$) (Fig. 1) was prepared and investigated as a sorbent for SPE enrichment of trace metals in water samples with subsequent determination by ETAAS.

Experimental

Apparatus and reagents

Characterization analyses were performed using the following instruments: A Vario EL CHNOS elemental analyzer (Hanau, Germany) a PerkinElmer System 2000 Fourier-Transform Infrared spectrometer (PerkinElmer Inc., Wellesley, USA), Bruker DMX-600 NMR Spectrometer (Germany) Shimadzu UV-2101PC UV-Visible Scanning Spectrophotometer (Shimadzu Corporation,

Kyoto, Japan), and a Varian SpectrAA 220 FS (Varian Inc., Victoria, Australia) flame atomic absorption spectrometer (FAAS) using air-acetylene fuel system and equipped with a deuterium background correction. A Shimadzu AA-6800 graphite furnace atomic absorption spectrometer, (Shimadzu Corporation, Kyoto, Japan) equipped with a deuterium background correction with pyrolytic graphite tube atomizer and appropriate hollow cathode lamps was used for trace metal determination. The analytical wavelengths used for zinc, nickel, copper and lead were 213.9, 232.0, 324.8, and 283.3 nm, respectively. Other conditions were similar to those recommended by the manufacturer. Sodium and potassium were determined using a Sherwood flame photometer, model 410 (Sherwood Scientific Ltd., Cambridge, UK) using air-butane fuel system. A multi-channel Gilson Miniplus 3 peristaltic pump (Gilson International, France) furnished with silicone tubes was used to pump the solutions through the column during the preconcentration and elution steps, while pH was determined using a HANNA digital pH meter (HANNA Instruments Inc., Portugal).

High purity water used in this work was obtained by passing distilled water through a reverse osmosis system (Milli-Q water system, Millipore, USA). Standard stock solutions ($1000\ mg\ L^{-1}$) of Zn, Ni, Cu and Pb (SAARCHEM, South Africa) were diluted appropriately with high purity water to obtain the working solutions. Tetrahydrofuran (THF), ethanol, PVC and triethylamine used in the synthesis of modified PVC (Aldrich, USA) were of analar grade. Other reagents; sodium acetate, nitric acid, hydrochloric acid, acetic acid and ammonia were of spectral purity (Fluka, Switzerland).

Synthesis and characterization of PVC-FSSH ester

$FSSH_2$ was prepared following a procedure similar to the one described by Buchweitz et al. [14], while functionalization of PVC with $FSSH_2$ was done using a procedure earlier reported for substitution reactions between similar compounds and PVC [15, 16]. A solution containing 1.0 g of $FSSH_2$ in 50 mL of THF was added into a 500 mL Buchner flask equipped with a gas inlet and a magnetic

stirrer. Triethylamine ($460 \, \mu L$) was then added dropwise with stirring, followed by 0.2 g of PVC. The mixture was stirred at room temperature overnight under nitrogen atmosphere. The volume of the resultant solution was reduced to about 5 mL using a rotary evaporater. The product was precipitated with 50 mL of ultrapure water and finally washed 3 times with 10 mL portions of ultrapure water. The precipitate was redissolved in 5 mL of THF followed by precipitation and washing with 2 M HCl. The product was dried *in vacuo*, ground with a mortar and pestle, and finally sieved through a 100 mesh sieve ($150 \, \mu m$ aperture). The resin was characterized to determine its elemental composition and functionality using elemental analyzer, FTIR, UV-Vis as well as its Water regain capacity. Water regain values for PVC and the modified PVC were determined using a procedure described by Pramanik et al. [17].

Preparation of mini-column

The SPE columns were prepared by slurry-packing 0.1 g (in ultrapure water) of the resin into glass columns of dimensions 50×2 mm i.d. Both ends of the column were fitted with small pieces of glass wool (soaked overnight in 10% nitric acid) to retain the resin in the column. Before use, the column was washed with 2 M HCl and ultrapure water to remove any metal contaminants.

Preconcentration procedure

The column was first preconditioned with 10 mL of 0.1 M Na_2CO_3 and then washed with 10 mL of high purity water. Sample and standard aliquots at appropriate pH were pumped through the mini-column using peristaltic pumps to control flow rates. The column was then washed with 10 mL of ultrapure water. The retained metal was finally eluted with 2 M HCl and the eluate was analysed using ETAAS. Some preliminary studies were performed to establish the optimal conditions for trace metal enrichment. The conditions optimized were sample pH, flow rates, eluent type and volume, and sample breakthrough volume. For this purpose, model solutions containing $20 \, ng \, mL^{-1}$ each of Zn, Ni, Cu and Pb in acetate buffer (0.1 M sodium acetate/acetic acid) were used. The pH was adjusted using 2 M HCl or 2 M NaOH.

Sample preparation

The wastewater samples were filtered through a $0.45 \, \mu m$ membrane filter paper. An aliquot of the filtered sample (50 mL) was put into a 250 mL conical flask and digested with 5 mL mixture of concentrated nitric acid (65%) and perchloric acid (70%). When digestion was complete, 10 mL of 0.5 M HCl was added to redissolve the residue and the resultant solution quantitatively filtered into a 50 mL volumetric flask. The pH was adjusted to 7 using a mixture of 10% w/v NaOH and acetate buffer (0.1 M). Finally, ultrapure water was used to bring the volume to the mark and then subjected to the SPE procedure. Another sample aliquot (50 mL) was subjected to the procedure without acid digestion.

Results and discussion

Characterization of the resin

The reaction between $FSSH_2$ and PVC (Fig. 1) yielded a brown microcrystalline solid (Yield $\approx 80\%$). $FSSH_2$ is first converted into the more reactive ionic form using triethylamine (Et_3N). The greater reactivity of this form is due to the fact that $Et_3NH^+Cl^-$ is a better leaving group than HCl. In our synthesis we tried reacting $FSSH_2$ and PVC alone, as well as in the presence of sodium hydroxide, sodium carbonate and Triethylamine. Triethylamine gave the highest yield.

The elemental composition of PVC, $FSSH_2$ and FSSH-PVC was determined using FAAS (Fe) and elemental analyzer (C, S and H). The presence of iron and sulphur in PVC-FSSH is an indication of modification of PVC with the ligand containing the two elements, which are absent in PVC. However, the lower observed values of iron (13.7%) and sulphur (14.8%) in the modified PVC compared to the expected values of 16.9 and 19.3%, respectively, shows that not all the chlorine atoms of PVC are substituted. The amounts of iron and sulphur found correspond to a Fe:S mole ratio of 1:1.88, which is close to the 1:2 ratio expected due to the incorporation of the $C_{13}H_{11}OS_2Fe$ unit. Although the presence of the ferrocenyl group is not expected to improve the metal chelating property of the resin, it serves as an extra chemical marker for purposes of characterization based on Fe. The amount of iron, obtained after conventional acid digestion with determination using relatively simple instrumentation such as FAAS can be equated to the amount of active sites in the chelating agent. Assuming that all iron is due to the incorporation of the ligand in the PVC matrix without structural changes, the modified PVC contains 2.4 mmol of binding sites per gram. This agrees well with the value of 2.3 mmol calculated based on the sulphur content.

The FTIR spectrum of the free ligand, $FSSH_2$ shows absorptions of the $-SH$ group ($2520 \, cm^{-1}$), which are absent in the modified PVC as expected. The very strong absorption at $1240 \, cm^{-1}$ assigned to $\nu(C=S)$ stretching is in agreement with that reported in the literature for $FSSH_2$ [14]. This functionality is also present in the modified PVC and confirms the incorporation of the ligand in PVC with retention of O,S donor set. In order to establish the nature of bonding between the chelating resin and metal ions, a Cu complex was prepared by addition of $CuCl_2$ to a solution of PVC-FSSH (in THF) followed by precipitation with ultrapure water. The FTIR spectrum of this complex did not show an absorption band at around $1240 \, cm^{-1}$, showing that the ester binds metal ions through the O,S-bonding mode. In addition, the strong UV-Vis absorptions (in THF) at 335, 402 and 545 nm of $FSSH_2$ which are shifted to 373, 475 and 487 nm in

the modified PVC, is consistent with results from our investigations on the transformation of a dithiocarboxy (−CSSH) moiety to the dithioester (−CSSR). PVC is transparent in this region.

The ^{1}H-NMR spectrum (in CDCl$_3$) of the FSSH$_2$ showed signals at $\delta = 15.34$ ppm for the chelated proton (s, 1H), at $\delta = 6.59$ ppm for vinylic proton (s, 1H), $\delta = 5.16$ ppm for free thiol proton (s, 1H), $\delta = 4.86/4.64$ ppm for the substituted cyclopentadienyl ring protons (m, 4H) and $\delta = 4.27$ ppm for the unsubstituted cyclopentadienyl ring protons (m, 5H). No signal was observed at $\delta \approx 15$ ppm as expected for a chelated proton in the ^{1}H-NMR spectrum of modified PVC, while the region between $\delta = 1$ and 7 ppm was too crowded (due to the polymeric nature of PVC) to allow for accurate assignment of peaks. However, the absence of a peak at $\delta \approx 15$ ppm suggests that modified PVC may contain one or both of the structures shown in Fig. 1. FSSH-PVC is expected to exhibit a peak at $\delta \approx 15$ ppm in ^{1}H-NMR spectrum and a peak around 1230–1260 cm^{-1} in the IR spectrum due to ν(C=S). On the other hand FSS-PVC is expected to exhibit a peak around 1610 due to ν(C=O) and no peak due to ν(C=S). The absence of a peak at $\delta \approx 15$ ppm supports the presence of FSS-PVC, while the presence of a peak at 1240 cm^{-1}, in the same region as reported in the literature [13, 14, 18], supports the presence of FSSH-PVC. Alternatively, this situation may indicate the presence of FSSH-PVC where the enol is not chelated, but possibly hydrogen bonded to a chlorine atom in the polymer chain. It is important to note, however, that in the presence of the two structures, the O,S donor set is available for metal complexation and the bonding modes are therefore expected to be similar.

The interaction between water and a chelating resin is necessary to allow for the uptake of metal ions from water samples by the resin. This interaction is quantified using water regain value, W calculated as, $W = (m_w - m_d)/m_d$, where, m_w is the weight of air-dried resin after equilibration with water and m_d is the weight of the oven-dried (100 °C) resin. A high W value indicates improved wettability (with water) and is expected to improve metal retention since the water sample has to interact with the resin matrix. Water regain values were 2.17 and 26.11 mmol g^{-1} for PVC and PVC-FSSH, respectively. This values show about ten times improvement in hydrophilicity upon modification of PVC.

The capacity of the sorbent towards the metal ions was determined using a column method. This was done by passing a large excess of the respective metal ion standard solutions (20 mL of 10 μg mL^{-1}, pH 7) through the column at a flow rate of 0.5 mL min^{-1}. The adsorbed metal was then eluted with 2.0 mL of 2 M HCl and determined by FAAS. Column capacities at pH 7 were 7.09, 12.33, 28.83 and 38.37 μg g^{-1} towards Zn, Ni, Cu and Pb, respectively.

Effect of sample pH

In order to investigate the effect of pH on sorption efficiencies, model solutions of the metal ions with pH adjusted to the range 4–9 were subjected to the proposed SPE procedure. The column is first reconditioned with sodium carbonate to convert the −OH group to −O$^-$Na$^+$ which is more reactive (easier to exchange Na$^+$ than covalent −H). A final wash with ultrapure water serves to remove excess sodium carbonate and other impurities, and prepare the column to accept the analyte. Figure 2 gives the percentage recoveries of the metals from model solutions. Recoveries were calculated as the ratio of the amount of metal in the eluate solution to the amount of metal in the initial feed solution. It is noted (Fig. 2) that the recoveries of Zn, Ni and Cu were sensitive to pH, unlike that of Pb whose recoveries were fairly constant at the various pH values. This is indicative of the stronger stability of Pb complexes and may be explained in terms of the hard–soft acid/base theory. Recoveries were quantita-
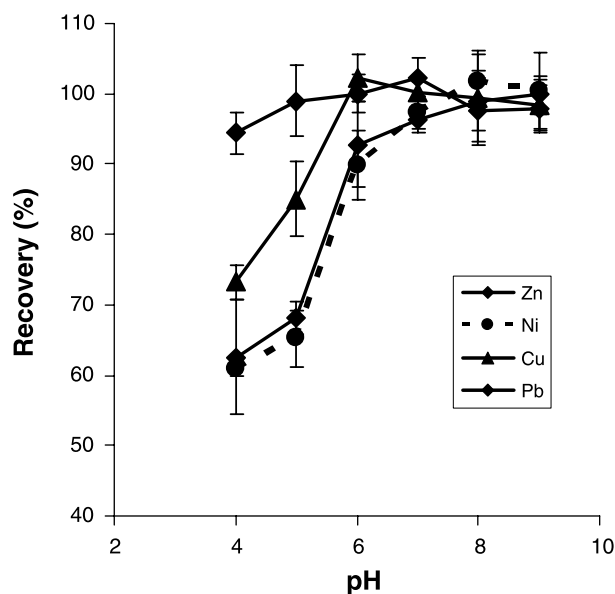
Fig. 2. Effect of pH on the recoveries (%) of Zn, Ni, Cu and Pb. Sample flow rate 0.5 mL min^{-1}; elution flow rate 1.0 mL min^{-1}; sample volume 50 mL; elution volume 1.0 mL

tive (>95%) for all the elements at pH ≥ 7. Therefore pH 7 was chosen as the optimum pH.
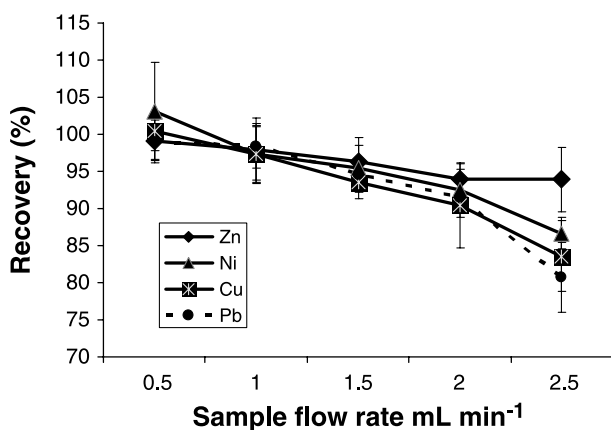
Choice of eluent type and elution volume

Different concentrations of HNO_3 and HCl were investigated as elution solvents. Aqueous solutions of HCl (2.0 M) and HNO_3 (1.0 M) gave good recoveries (>95%). Nitric acid is an oxidizing agent even at low concentrations, hence is not a good choice for the stability of the chelating agent. Thus 2.0 M HCl was used as the eluent of choice. Experiments on elution volume showed recoveries to be quantitative up to a minimum volume of 1.0 mL.
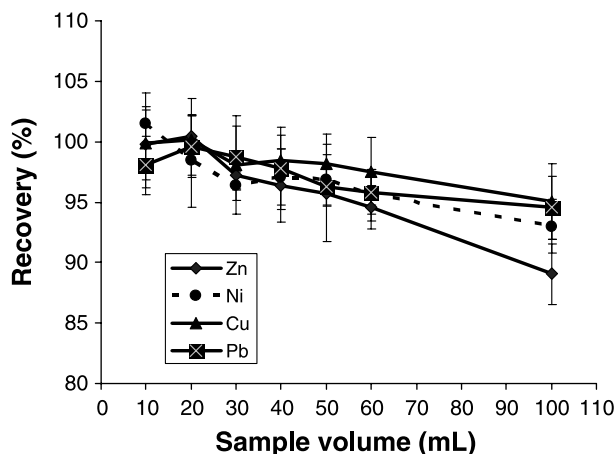
Effect of sample and eluent flow rates

The sample and eluent flow rates are other critical factors affecting enrichment efficiency of a SPE procedure. Sample flow rates of 0.5–2.5 mL min^{-1} were investigated for sample loading. Figure 3 illustrates the effect of sample flow rate on recoveries (%) for the four elements. Elution rate was optimized by considering recoveries of copper at different flow rates. Recoveries were found to be quantitative at sample and eluate flow rates up to 1.0 mL min^{-1}. In this work, loading and elution flow rates of 0.5 and 1.0 mL min^{-1}, respectively, were adopted in the general procedure.

Effect of sample volume

Sample breakthrough volume is one of the most important factors affecting the magnitude of enrichment

Fig. 4. Effect of sample volume on recoveries of Zn, Ni, Cu and Pb. Sample flow rate 0.5 mL min^{-1}; elution flow rate 1.0 mL min^{-1}; elution volume 1.0 mL

factors attainable. This parameter was determined using model solutions of 10–100 mL containing 0.2 μg of the metal ions. Figure 4 shows the recoveries (%) of the trace metals as a function of sample volume. The analytes were quantitatively retained (≥95%) up to a maximum of 60 mL of sample (for Zn and Ni) and up to 100 mL (Cu and Pb). Since the final volume of elution was 1.0 mL, preconcentration factors of between 60 and 100 for the metal ions were achieved. Preconcentration factors were calculated as the ratio of the concentration of metal in the eluate solution after enrichment and the concentration in the feed solution by direct aspiration.

Limits of detection (LOD)

The regression equations obtained by subjecting calibration standards in the range 0–2 (Zn), 0–20 (Ni), 0–10 (Cu) and 0–20 (Pb) μg L^{-1} to the SPE procedure under the optimal conditions is shown in Table 1. Blank determinations were obtained by performing the SPE procedure using a 0.1 M acetate buffer in high purity water (pH adjusted to 7). The detection limits

Fig. 3. Effect of sample flow rate on the recoveries (%) of Zn, Ni, Cu and Pb at pH 7. Elution flow rate 1.0 mL min^{-1}; elution volume 1.0 mL; sample volume 50 mL

Table 1. Regression equations and limit of detection

Metal	Regression equation	LOD$_{instr}$ (μg L^{-1})	LOD$_{method}$ (ng L^{-1})
Zn	Abs = 0.1312Conc + 0.0400	0.07	1.17
Ni	Abs = 0.0011Conc + 0.0069	2.49	41.50
Cu	Abs = 0.0049Conc + 0.0138	0.59	5.92
Pb	Abs = 0.0078Conc + 0.0527	5.10	51.04

LOD$_{instr}$ Instrumental limit of detection; *LOD$_{method}$* method detection limit.

of the instrument (LOD$_{instr}$) were calculated based on mean ± three times the standard deviation of ten runs of the blank ($\bar{X}_{Blank} + 3s$), while the detection limits of the method (LOD$_{method}$) were obtained by dividing the LOD$_{instr}$ by the sample breakthrough volume.

Removal of interfering ions

It is well recognized that high concentrations of Na, K, Ca and Mg may limit direct determination of trace elements, especially by ICP-MS [19]. Therefore, the separation of these ions may be necessary. The potential of removal of these metal ions in model solutions was examined by determining the metal concentrations before and after performing the SPE procedure. Model solutions (20 mL) containing 2500–50000 µg mL^{-1} of Na and 500–5000 µg mL^{-1} each of K, Mg and Ca were separately subjected to the column procedure. Table 2 gives the results of the determinations of Na,

K, Mg and Ca in the original model solutions and in the eluates after following the SPE procedure. Sodium and potassium were determined using flame photometry, while magnesium and calcium were determined using FAAS. Under the optimized preconcentration conditions, the concentrations of Na, K, Mg and Ca were significantly reduced in the eluates, with removal efficiencies >99%. These results are in close agreement with those reported with DTC based modified chelating resins [20], and generally emphasize the selectivity of the developed resin against alkali and alkali earth metal ions. Recovery studies on model solutions containing the above concentrations of the interfering ions and spiked with 0.2 µg of the trace metals showed that these concentrations were well tolerated (recoveries >95%).

Application to real samples and method validation

The developed SPE procedure was used to determine Zn, Ni, Cu and Pb in borehole water (BH), river water (RW) and brewery wastewater (BW) samples, all collected from different locations within Gaborone City, Botswana. The samples were filtered through a 0.45 µm membrane filter paper and pH adjusted to 7. 50 mL aliquots of the filtered samples were then subjected to the SPE procedure under optimal conditions. The results presented in Table 3 are the mean concentrations ($n = 3$). It can clearly be seen that the SPE procedure improves detection limits as well as the precision of the results. This is especially true in the case of river water samples where the metals could be detected only after enrichment. This trend was not observed with the brewery wastewater samples. The

Table 2. Interference studies: removal of Na, K, Mg and Ca in model solutions by SPE procedure

Element	Model solution (µg mL^{-1})	Eluent (µg mL^{-1})
Na	2500	<LOD
	10000	0.32 ± 0.04
	50000	0.45 ± 0.04
K	500	<LOD
	1000	<LOD
	5000	<LOD
Mg	500	0.12 ± 0.02
	1000	0.13 ± 0.01
	5000	0.64 ± 0.01
Ca	500	0.11 ± 0.01
	1000	0.20 ± 0.02
	5000	0.33 ± 0.02

<LOD Less than instrumental limit of detection.

Table 3. Concentrations (µg L^{-1}) of trace metals in environmental samples and a certified reference material

Sample		Zn	Ni	Cu	Pb
BH	A	1.05 ± 0.07	1.94 ± 0.38	5.44 ± 0.37	<LOD
	B	1.28 ± 0.06	1.86 ± 0.16	4.76 ± 0.28	0.038 ± 0.01
	C	1.49 ± 1.08	2.29 ± 0.17	5.97 ± 0.30	0.043 ± 0.01
RW	A	<LOD	<LOD	<LOD	<LOD
	B	0.63 ± 0.08	0.29 ± 0.01	0.41 ± 0.02	0.05 ± 0.008
	C	0.79 ± 0.08	0.78 ± 0.06	0.62 ± 0.02	0.089 ± 0.01
BW	A	12.72 ± 0.84	1.17 ± 0.43	3.59 ± 0.72	<LOD
	B	7.94 ± 0.63	0.27 ± 0.01	1.61 ± 0.05	0.22 ± 0.04
	C	15.99 ± 1.06	1.37 ± 0.18	2.45 ± 0.13	1.45 ± 0.13
SLRS-3	Found	1.22 ± 0.13	0.55 ± 0.06	1.19 ± 0.08	0.084 ± 0.01
	Certified	1.04 ± 0.09	0.83 ± 0.08	1.35 ± 0.07	0.068 ± 0.007

A Direct aspiration, *B* after column enrichment and *C* acid digested sample followed by column enrichment, *SLRS-3* Riverine water reference material.

Table 4. Comparative data from other metal chelating sorbents employed in solid phase extraction systems

Chelating agent	Support	Analyte	PF	LOD	Detection	Ref.
Pyrocatechol	Amberlite XAD-2	Cd, Co, Ni	21–48	0.27–1.29 μg L^{-1}	FAAS	[21]
Pyrocatechol violet	Amberlite XAD-1180	Pb, Fe	100	0.20–0.37 μg L^{-1}	FAAS	[22]
Alizarin red	Naphthalene	Pb	40	53 μg L^{-1}	ICP OES	[23]
8-quinolinole	Metal alkoxide glass	Cd, Co, Ni	27–55	4.0–89 ng L^{-}	ICP-MS	[24]
Acrylic acid	PTFE fibres	Ni	23	0.25 μg L^{-1}	FAAS	[25]
2-aminotiazole	Silica	Cu, Fe	10	0.1–3.2 μg L^{-1}	FAAS	[26]
Calix[4]arene-*o*-vanillinsemicarbazone	Chloromethylated polystyrene	U	143	6.14 μg L^{-1}	ETAAS	[27]
		Th	153	4.29 μg L^{-1}	ICP-AES	[27]
2-(2-thiazolylazo)-p-cresol	Polyurethane foam	Pb	16	0.25 μg L^{-1}	FAAS	[28]
Chromosorb 106	1-(2-pyridylazo)-2-naphthol	Cd, Pb	250	0.19–0.32 μg L^{-1}	FAAS	[29]
3-ferrocenyl-3-hydroxydithioacrylic acid	Poly(vinyl chloride)	Zn, Ni, Cu, Pb	60–100	1.17–51.04 ng L^{-1}	ETAAS	this work

concentrations of Zn, Ni and Cu obtained after enrichment were lower than those from direct analysis. However, precisions (standard deviations) were improved (Table 3), which may be attributed to elimination of matrix interferences. The lower concentration values for brewery wastewater for the metals obtained after the SPE procedure may be explained by considering the competing ligands present in the sample. The brewery wastewater samples are expected to contain strong complexing ligands, mainly protein materials. Thus the metals in the wastewater may be present in strongly complexed forms that cannot be retained in the column. As expected, the total dissolved metal content (Table 3) obtained after acid digestion is higher than the dissolved metal content (Table 3A and B). Acid digestion serves to convert any complexed metal species to 'free metal ion' or labile forms that can be retained by the resin, and consequently a larger amount of metal is retained by the chelating agent in the column. Generally, these observations provide opportunities for trace metal speciation using the developed procedure.

The proposed SPE procedure was validated by applying it to the determination of Zn, Ni, Cu and Pb in a Riverine Water reference Material, SLRS-3 (National Research Council, Ottawa, Canada). The results are listed in Table 3. The results show a fairly good agreement between the observed and certified values, and hence the proposed procedure can be applied to the determination of these metals in similar water systems. The preconcentration factors and limits of detection obtained by this method are comparable to those obtained using other chelating sorbents recently reported in the literature (Table 4). Furthermore, the sorbent used in this work is quite promising for the removal of interfering ions such as Na, K, Ca and Mg.

Conclusion

A solid phase extraction procedure using PVC modified with 3-ferrocenyl-3-hydroxydithioacrylic acid as sorbent, was used prior to ETAAS detection of Zn, Cu, Ni and Pb in model solutions and environmental water samples. The simple off-line system has been shown to be beneficial due to improved detection limits and precision. The preconcentration factors and detection limits obtained are comparable to those reported in the literature using other chelating sorbents (Table 4). Furthermore, its ability to remove some common interfering cations (Na, K, Mg, Ca) in model solutions was excellent (removal efficiencies >99%), demonstrating the potential benefits of the procedure in the analysis of trace metal ions in high salt water samples.

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