Determination of trace heavy metals in soil and sediments by atomic spectrometry following preconcentration with Schiff bases on Amberlite XAD-4

Derya Kara [a],*, Andrew Fisher [b], Steve J. Hill [b]

[a] Department of Chemistry, Art and Science Faculty, Balikesir University, 10100 Balikesir, Turkey
[b] School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, UK

ARTICLE INFO

ABSTRACT

A matrix separation and analyte preconcentration system using Amberlite XAD copolymer resins functionalized by Schiff base reactions coupled with atomic spectrometry has been developed. Three different functionalized Amberlite XAD resins were synthesized using 4-phenylthiosemicarbazide, 2,3-dihydroxybenzaldehyde and 2-thiophenecarboxaldehyde as reagents. These resins could be used to preconcentrate transition and other trace heavy metal analytes from nitric acid digests of soil and sediment samples. Analyte retention was shown to work well at pH 6.0. After treatment of the digests with sodium fluoride and buffering to pH 6, samples that contain extremely large concentrations of iron were analysed for trace analytes without the excess iron overloading the capacity of the resin. The analytes Cd, Co, Cu, Ni and Pb were preconcentrated from acid extracts of certified soil/sediment samples and then eluted with 0.1 M HNO_3 directly to the detection system. Flame atomic absorption spectrometry was used as a means of detection during the studies. The efficiency of the chelating resin and the accuracy of the proposed method were evaluated by the analysis of soil (SO-2) and sediment (LGC 6157 and MESS-3) certified reference materials.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The analysis of solid material usually requires a dissolution/digestion stage prior to introduction to most atomic spectrometric techniques. This normally involves use of an acid digestion procedure, the constituents of which would depend largely on the sample type and of the level of digestion required. Transforming the solid material into a liquid form so that it may be introduced more easily to the analytical instrumentation has the drawback of diluting the analytes present. Typically, such digestions lead to dilution factors of between 25 and 100. Other dissolution procedures, e.g. fusions add substantial amounts of solid material to the mixture and may therefore require even greater dilutions (e.g. by a factor of 1000) so that the sample is not too viscous.

Dilutions of 100 or greater will often place many of the most toxic metals near or even below the limit of detection by flame atomic absorption spectrometry (FAAS) and by inductively coupled plasma-atomic emission spectrometry (ICP-OES) which, for many analytes, have a limit of detection of approximately 0.01 mg L^{-1}.

Given a dilution factor of 100, this would correspond to a concentration of 1 mg kg^{-1} in a solid sample. For other, less sensitive analytes, e.g. lead, the limit of detection may be substantially higher, e.g. 10 mg kg^{-1}. For material such as foodstuffs, vegetation and some soils and sediments these concentrations would be regarded as being toxic and hence potentially hazardous to health. Although other analytical instrumentation is more sensitive, it may be either prohibitively expensive for universal use, e.g. ICP-MS or may be extremely slow, e.g. electrothermal AAS that may take typically 5–8 min to analyse one sample in triplicate.

There is therefore a need to develop simple, robust and reliable preconcentration techniques that are applicable to as many toxic analytes as possible so that relatively inexpensive but rapid analytical techniques can be used to analyse such samples. A large number of such preconcentration techniques have been developed. Many of these have been used for analyte preconcentration from aqueous samples and have involved ion-exchange [1,2], coprecipitation [3], solvent extraction [4,5] or adsorption [6,7].

Of the various preconcentration methods, solid-phase extraction (SPE) is one of the most effective multi-element methods because of its simplicity, rapidity and ability to attain a high concentration factor. XAD resins [8–12], activated carbon [6,13], silica gel [14,15], ion-exchange resins [16,17], chelating resins [12,18,19]

* Corresponding author. Tel.: +90 266 612 10 00; fax: +90 266 612 12 15.
E-mail address: dkara@balikesir.edu.tr (D. Kara).

and various polymers have all been used as solid-phase materials. Schiff bases are an important class of ligands that are obtained by condensation of aldehydes with amines. Schiff base functionalized polymeric matrices have been synthesized by the formation of a C=N bond on the different matrices and have been used for preconcentration of metals in several previous studies [8,9,14,18,20–24].

Despite the advances in analytical instrumentation, the search for specific analytical reagents and techniques is still far from being completed. Improvements have been attained through the coupling together of powerful analytical techniques which has been fueled by the pursuit towards speciation analysis. Flow injection (FI) is a powerful tool to extend the capabilities of analytical techniques. The coupling of a FI system to a FAAS is well established and has obvious advantages, such as improvement of the action of the pneumatic nebulizer (i.e. samples with very high dissolved solids loading may be analysed for longer periods before burner blockage becomes problematic) lower consumption of samples and masking reagents, reduced contamination risk, and increased sample throughput [25,26]. The applicability of the FI–FAAS coupling is again extended by using mini-columns containing chemical materials for improving selectivity by discarding the matrix and preconcentrating the analyte, thereby improving detection limits. A comprehensive discussion about on-line preconcentration in FI–FAAS systems can be found in the excellent text written by Fang [27]. Most proposed analytical applications involved the use of selective column materials or at least an enhancement of selectivity by appropriate adjustment of reaction conditions.

The aim of this study was to develop a resin-based preconcentration procedure that was sufficiently robust to enrich several analytes simultaneously from acid digests of solid materials whilst being relatively selective, hence preventing the active sites of the resin from being swamped by major constituents within the sample. An on-line procedure was developed since these are regarded as being less prone to contamination, are more rapid and are often cheaper. Three Schiff base modified resins were prepared and their analytical performance compared. These resins do not require the use of complexing materials such as diethydithiocarbamate and also do not require organic solvents to assist in the elution of the analytes. These factors offer two important advantages; i.e. the smaller the number of reagents added to the system the less likelihood there is of contamination and, since the use of organic solvents can lead to trouble during the analysis (in terms of smoke production, plasma perturbation in the case of ICP instrumentation, etc.), their absence also circumvents potential problems. In addition, many organic solvents are potentially harmful for the environment and hence should be used only when absolutely necessary. Bulut et al. [10] also managed to overcome the problems associated with the use of organic solvents, but had to resort to the use of an evaporation stage which, inevitably, led to an increase in time required per analysis and, as with all sample manipulation steps, added to the potential for analytical error. As a consequence of the evaporation stage, the method described in reference 10 was a batch (off-line) method. These are regarded as being generally reliable but, since samples and reagents are open to the atmosphere, they also have the potential to become contaminated more easily than on-line methods that are enclosed. Previous publications using similar resins concentrated very much on environmental waters, e.g. riverine and seawaters [8,9]. These applications were shown to be very successful with major ions such as Ca, Mg and Na proving not to be problematic since they had very limited retention on the resins. The present study has focused more on the analysis of solid environmental samples, such as soils and sediments. Here, there are additional elements that have the potential to be troublesome. Included in this list is iron. This may be present at very high concentrations (typically 2–5%) in this sample type and hence has the

real potential to overwhelm the active sites on the resins, leading to analyte breakthrough and error. The present study therefore has a different focus than previous similar papers. In addition, since analytes tend to be at somewhat higher concentrations in soils and sediments compared with waters, it enables the use of other, less expensive techniques such flame atomic absorption spectrometry. This therefore makes the method described more applicable to laboratories that cannot yet afford high cost instrumentation such as ICP-MS and, to a lesser extent, ICP-OES.

2. Experimental

2.1. Reagents and solutions

Multi-element stock solution containing $100 \, mg \, L^{-1}$ of Cd, Co, Cu, Ni and Pb were prepared from $10,000 \, mg \, L^{-1}$ stock standard solutions (BDH, Aristar, Poole, UK). From this solution, an intermediate multi-elemental stock solution containing $1 \, mg \, L^{-1}$ of each analyte was prepared. Other diluted standard solutions were prepared daily from this $1 \, mg \, L^{-1}$ standard. Buffer solution (1 M, pH 6.0) were prepared using pure acetic acid and ammonia solution (BDH).

All reagents used were of the highest available purity. Doubly deionized water (18.2 MΩ cm) obtained from a Primar water system (Elga, Buckinghamshire, UK) was used throughout. Nitric acid for sample digestion was obtained from BDH. The chelating reagents, 4-phenylthiosemicarbazide, 2,3-dihydroxybenzaldehyde and 2-thiophenecarboxaldehyde and Amberlite XAD-4 were purchased from Fluka (Gillingham, Dorset, UK). Three certified reference materials were used in this study: a soil sample (soil SO-2) (Canada Centre for Mineral and Energy Technology) and two sediment sample (LGC 6156) (LGC Teddington, UK) and (MESS-3) (National Research Council Canada).

2.2. FAAS system

A GBC 902 atomic absorption spectrometer (Dandenong, Victoria, Australia) furnished with appropriate hollow cathode lamps, and an air-acetylene flame ($9.0/3.0 \, L \, min^{-1}$) as the atomiser was used as the detector throughout. The wavelengths (nm) selected for the determination of the analytes were as follows: Cd 228.8, Co 240.7, Cu 324.8, Ni 232.0 and Pb 283.3. The flow rate of the peristaltic pump was adjusted to be between 0.4 and $2.4 \, mL \, min^{-1}$.

2.3. Procedures

A schematic diagram of the on-line preconcentration system is presented in Fig. 1. The system consists of a Gilson Minipuls 3 peristaltic pump (Anachem Ltd., Luton, UK), a four-way valve and a mini-column (5 cm × 3 mm, Omnifit, Cambridge, UK), packed with the Schiff base functionalized Amberlite XAD-4. The peristaltic pump was connected to the sample uptake capillary and to the mini-column via the four way rotary valve. This valve also had a loop fitted that could be filled with the nitric acid eluent. Transport lines were made using 0.3 mm i.d. PTFE tubing.

The FI system was operated as follows: during the 60 s sample loading period, with the valve in the 'fill' position, a sample (standard or blank) at known pH buffered with acetic acid–ammonia was pumped at $0.8 \, mL \, min^{-1}$ (via the peristaltic pump) through the mini-column. The metals were adsorbed on the resin within the mini-column and the sample matrix was allowed to pass through to the detector. Then, with the valve in the 'fill' position, de-ionized water was pumped at $0.8 \, mL \, min^{-1}$ through the mini-column for a period of 1.5 min to wash the non-adsorbed metal ions and the remnants of the matrix from the system. After preconcentration, the
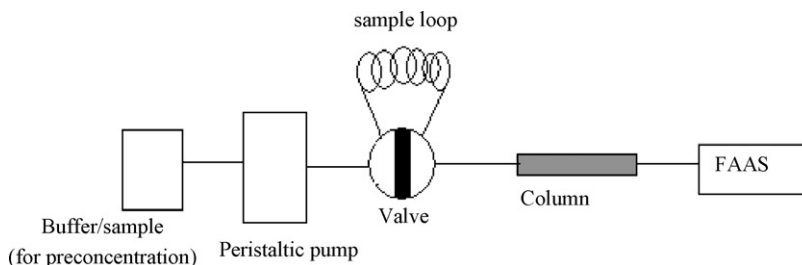
Fig. 1. Schematic diagram of the on-line flow injection FAAS system.

Table 1
Experimental parameters for on-line preconcentration FI–FAAS.

Buffer pH	6.0
Buffer flow time	30 s
Buffer flow rate	2.4 mL min^{-1}
Volume of buffer used	1.2 mL
Sample flow time	60 s
Sample flow rate	0.8 mL min^{-1}
Volume of sample used	0.4 mL
Washing time	1.5 min
Washing rate	0.8 mL min^{-1}
Volume of wash solution used	1.2 mL
Elution solution	0.1 M HNO$_3$
Elution flow rate	2.4 mL min^{-1}
Eluent loop volume	60 μL

60 μL loop was filled with 0.1 M HNO$_3$ and, on turning the valve, this was pumped in a stream of water at a rate of 2.4 mL min^{-1} by the peristaltic pump to the FAAS instrument. After measuring the metal ions, buffer solution was passed at 2.4 mL min^{-1} for 30 s through the mini-column to re-equilibrate it prior to the next sample.

3. Results and discussion

3.1. Method validation

The optimum values for the FI–FAAS system and experimental factors are given in Table 1. 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. The Cu(II), Cd(II), Co(II), Ni(II) and Pb(II) calibration solutions were run under the optimum chemical and flow conditions using the manifold shown in Fig. 1. Standards and blanks were prepared with ultra-pure water. The analytical curves obtained had a correlation coefficient of 0.9999. The analytical figures of merit of these

resins for five elements are indicated in Table 2. The detection and the quantification limits were calculated as 3 s/slope and 10 s/slope respectively ($n = 15$ runs of blanks). These results are satisfactory considering the relatively short preconcentration time employed. LODs were found to be independent of the sample matrix. An investigation into the effect of artificial sea water (1270 ppm Mg^{2+}, 400 ppm Ca^{2+}, 10,750 ppm Na^{2+}, 400 ppm K$^+$, 5100 ppm SO$_4^{2-}$, 600 ppm CO$_3^{2-}$, 16,610 ppm Cl$^-$, 620 ppm NO$_3^-$) on the signal of each analyte was undertaken. After passing the sample through the mini-column, the resin was washed with ultra-pure water for 1.5 min at a flow rate of 0.8 mL min^{-1} to remove the sample matrix from the column. No significant differences in signal were obtained between samples containing interfering ions and those without them. The only potential interferant that would swamp the active sites and hence lead to low preconcentration factors or worse still incomplete or irreproducible retention of the analytes is iron. It was therefore decided that the preconcentration procedure be applied to sediments/soils, since these sample types have huge iron concentrations. This would demonstrate that the resins were efficient at retaining the analytes, effectively separating them from potentially interfering matrix constituents.

3.2. Analysis of certified samples

To demonstrate the robustness of the method and to extend its applicability to other types of sample and detection systems, the proposed method was applied to the determination of heavy metals in solid CRMs; a soil sample (soil SO-2) and two sediment sample (LGC 6156 and MESS-3) by the on-line FI–FAAS method. The concentration of the analytes; Cd, Co, Cu, Ni and Pb in acid digests of solid certified samples may be too low to measure directly by FAAS and their determination may therefore require a preconcentration step. The proposed method was therefore adopted to determine

Table 2
Analytical figures of merits obtained for Cu, Cd, Ni and Pb by FI–FAAS with on-line preconcentration.

Resins	Metal ion	Linear working range (mg L^{-1})	Detection limit (mg L^{-1}) (without preconcentration)	Quantification limit (mg L^{-1}) (without preconcentration)	Enrichment factor	Detection limit (μg L^{-1}) (with preconcentration)
Resin 1	Cu(II)	0.10–0.50	0.038	0.127	13.3	2.86
	Cd(II)	0.05–0.20	0.016	0.050	13.3	1.20
	Co(II)	0.20–1.0	0.002	0.007	13.3	0.15
	Ni(II)	0.4–2.0	0.048	0.160	13.3	3.60
	Pb(II)	0.10–0.30	0.084	0.280	13.3	6.31
Resin II	Cu(II)	0.10–0.50	0.017	0.057	13.3	1.27
	Cd(II)	0.05–0.20	0.010	0.033	13.3	0.75
	Co(II)	0.20–1.0	0.033	0.110	13.3	2.48
	Ni(II)	0.4–2.0	0.115	0.380	13.3	8.63
	Pb(II)	0.10–0.30	0.097	0.320	13.3	7.20
Resin III	Cu(II)	0.10–0.50	0.032	0.100	13.3	2.40
	Cd(II)	0.05–0.20	0.024	0.080	13.3	1.80
	Co(II)	0.20–1.0	0.044	0.147	13.3	3.30
	Ni(II)	0.4–2.0	0.032	0.100	13.3	2.40
	Pb(II)	0.10–0.30	0.059	0.196	13.3	4.43

Table 3
Analysis of certified reference materials with on-line FI–FAAS.

Reference materials	Metals	Certified values	Functionalized aldehydes onto the Amberlite XAD-4		
			4-Phenylthio semicarbazide	2,3-Dihydroxy benzaldehyde	2-Thiophene carboxaldehyde
LGC 6156 (mg/kg)	Cu	2400 ± 122	nd	nd	nd
	Cd	2.9 ± 0.5	2.48 ± 0.24	2.21 ± 0.13	3.06 ± 0.40
	Ni	161 ± 13	nd	nd	nd
	Co	28.3 ± 2.8	24.2 ± 0.81	23.89 ± 1.21	27.6 ± 1.83
	Pb	1685 ± 8	nd	nd	nd
Soil SO-2 (mg/kg)	Cu	7 ± 1	8.67 ± 0.40	6.96 ± 0.33	6.93 ± 0.68
	Cd	–	–	–	–
	Ni	8 ± 2	7.86 ± 1.60	9.17 ± 1.86	8.33 ± 1.55
	Co	9 ± 2	6.74 ± 0.80	7.40 ± 0.60	8.69 ± 1.48
	Pb	21 ± 4	21.9 ± 1.88	20.4 ± 1.55	19.8 ± 2.44
MESS-3 (mg/kg)	Cu	33.9 ± 1.6	nd	nd	nd
	Cd	0.24 ± 0.01	<LOD	<LOD	<LOD
	Ni	46.9 ± 2.2	39.92 ± 1.6	43.8 ± 3.2	48.2 ± 0.07
	Co	14.4 ± 2.0	10.15 ± 0.82	14.4 ± 0.61	13.9 ± 1.0
	Pb	21.1 ± 0.7	18.6 ± 1.90	17.7 ± 1.6	17.5 ± 2.7

these metals. Solid samples were weighed (approx. 0.250 g) into pre-cleaned glass beakers, and then aqua regia (5 mL) added. The beakers were then covered with clean watch glasses and placed on a hotplate and boiled for at least 1.5 h. If the sample neared dryness, a further volume (2 mL) of aqua regia was added. Sediment and soil samples usually contain high concentrations of iron, which could potentially saturate the column and hence lead to low recovery of the analytes. Alternatively, at some pH values the iron may precipitate which may also lead to the coprecipitation of analyte ions [28]. Therefore, to obtain reliable results, the Fe must be prevented from being retained on the column and from precipitating. Sufficient NaF (1% m/v in the final volume of 25 mL) was therefore 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 [8,9]. The samples were then filtered to remove undigested material and diluted to volume with ammonium acetate buffer to give a pH of 6.0, prior to being analysed 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 0.14–20.36%. The results are summarised in Table 3. Those analytes that were at a sufficiently high concentration such that preconcentration was not necessary (Cu, Ni and Pb in LGC 6156 and Cu in MESS-3) were not determined because they could be measured directly using FAAS. The results of the experiments demonstrated that as well as providing a robust and reliable method for the determination of ultra-trace analytes, these resins are equally applicable to the determination of trace analytes in digests of solid materials.

When a comparison of more than two treatment or sample means is required, the null hypothesis to be tested is usually that the t-treatment or sample means are the same, and that the alternative hypothesis is that they are not [29]. Analysis of variance (ANOVA) is a useful technique for making decisions about hypotheses. In ANOVA it is actually the variation in the t-treatment or sample responses that is used to decide whether or not treatment effects are significant. The one-way ANOVA statistical method was applied to the results obtained using the resins to decide whether or not there are any significant effects between the different resins and whether those effects are significant [29]. The SPSS 10.0 for windows program (Woking, Surrey, UK) was therefore used as a chemometric package programme. According to the ANOVA analysis, the effect of resins on the preconcentration of the elements were not found to be significant ($P > 0.01$), i.e. there was no significant difference between the results obtained and the certified values.

4. Conclusions

The resins were quick and simple to prepare using a series of three reactions over a two-day period. All of the resins were found to be stable, with several hundred sample loading/elution cycles being undertaken before any loss of performance was observed. The presence of ammonium acetate buffer at pH 6.0 enabled concomitant matrix elements, e.g. Ca, Mg, Na, etc. to be removed prior to analyte elution whilst simultaneously enabling analyte retention. Thus, the matrix removal capabilities of these resins are adequate at the pH values studied. Potential interferences from the presence of high concentrations of Fe were overcome by the addition of sodium fluoride.

These Schiff base modified chelating resins have been shown to facilitate the determination of trace analytes and their efficient separation from matrix elements found in aqua regia digests of soil and sediment samples using FI–FAAS as a detection system. Although FAAS is an inexpensive technique for the determination of metal ions, it often has inadequate detection limits and is therefore frequently not fit for purpose. In these cases a preliminary preconcentration step is required to bring the analyte concentration to a level where an FAAS instrument may determine it. The determination of five elements in soil/sediment certified samples by on-line FI–FAAS were successfully achieved with a mini-column packed with the chelating resins. The system was very simple to construct, the sample volume required is small (unless a preconcentration is required) and the number of reagents used is also small. The results obtained demonstrated good reproducibility. The combination of the preconcentration of analytes and the elimination of matrix substances using a mini-column packed with Schiff base functionalized Amberlite XAD-4 resins was found to be a versatile technique with considerable promise for the determination of trace elements in a wide variety of samples. The samples tested were soils and sediments and despite the very high concentrations of iron present, results were in good agreement with certified values. The same procedure is equally applicable to other sample types, e.g. food and vegetation where the potential interference from iron is very much reduced. The need to use expensive and more complex instrumentation may also be avoided, although clearly, this analyte preconcentration approach could also be used with more sophisticated instruments if available. High speed, ease of use and the potential for automation, selectivity and relative freedom from interference make this method suitable for trace metal determination in digests of many solid samples.

Acknowledgements

References

[1] P. Carrero, L. Gutiérrez, C. Rondón, J.L. Burguera, M. Burguera, Y. Petit de Peña, Flow injection determination of bismuth in urine by successive retention of Bi(III) and tetrahydroborate(III) on an anion-exchange resin and hydride generation atomic absorption spectrometry, Talanta 64 (2004) 1309–1316.

[2] J. Wang, E.H. Hansen, Coupling on-line preconcentration by ion-exchange with ETAAS: a novel flow injection approach based on the use of a renewable microcolumn as demonstrated for the determination of nickel in environmental and biological samples, Anal. Chim. Acta 424 (2000) 223–232.

[3] H. Chen, J. Jin, Y. Wang, Flow injection on-line coprecipitation-preconcentration system using copper(II) diethyldithiocarbamate as carrier for flame atomic absorption spectrometric determination of cadmium, lead and nickel in environmental samples, Anal. Chim. Acta 353 (1997) 181–188.

[4] A.N. Anthemidis, G.A. Zachariadis, C.G. Farastelis, J.A. Stratis, On-line liquid–liquid extraction system using a new phase separator for flame atomic absorption spectrometric determination of ultra-trace cadmium in natural waters, Talanta 62 (2004) 437–443.

[5] J. Wang, E.H. Hansen, Development of an automated sequential injection on-line solvent extraction-back extraction procedure as demonstrated for the determination of cadmium with detection by electrothermal atomic absorption spectrometry, Anal. Chim. Acta 456 (2002) 283–292.

[6] R.A. Gil, S. Cerutti, J.A. Gásquez, R.A. Olsina, L.D. Martinez, Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination, Talanta 68 (2006) 1065–1070.

[7] Y. Li, Y. Jiang, X.P. Yan, Further study on a flow injection on-line multiplexed sorption preconcentration coupled with flame atomic absorption spectrometry for trace element determination, Talanta 64 (2004) 758–765.

[8] D. Kara, A. Fisher, S.J. Hill, Comparison of some newly synthesized chemically modified Amberlite XAD-4 resins for the preconcentration and determination of trace elements by flow injection inductively coupled plasma-mass spectrometry (ICP-MS), Analyst 131 (2006) 1232–1240.

[9] D. Kara, A. Fisher, S.J. Hill, Preconcentration and determination of trace elements with 2,6-diacetylpyridine functionalized Amberlite XAD-4 by flow injection and atomic spectroscopy, Analyst 130 (2005) 1518–1523.

[10] V.N. Bulut, A. Gundogdu, C. Duran, H.B. Senturk, M. Soylak, L. Elci, M. Tufekci, A multi-element solid-phase extraction method for trace metals determination in environmental samples on Amberlite XAD-2000, J. Hazard. Mater. 146 (1–2) (2007) 155–163.

[11] M.C. Yebra, J. Salgado, L. Puig, A. Moreno-Cid, Field preconcentration of cadmium from seawater by using a minicolumn packed with Amberlite XAD-4/4-(2-pyridylazo) resorcinol and its flow-injection-flame atomic absorption spectrometric determination at the ng L^{-1} level, Anal. Bioanal. Chem. 374 (2002) 530–534.

[12] M.C. Yebra, N. Carro, M.F. Enríquez, A. Moreno-Cid, A. García, Field sample preconcentration of copper in sea water using chelating minicolumns subsequently incorporated on a flow-injection–flame atomic absorption spectrometry system, Analyst 126 (2001) 933–937.

[13] K. Kiran, K. Suresh Kumar, K. Suvardhan, K. Janardhanam, P. Chiranjeevi, Preconcentration and solid phase extraction method for the determination of Co, Cu, Ni, Zn and Cd in environmental and biological samples using activated carbon by FAAS, J. Hazard. Mater. 147 (1–2) (2007) 15–20.

[14] M. Alan, A.S. Fisher, D. Kara, Preconcentration of heavy metals and matrix elimination using silica gel chemically modified with 2,3-dihydroxybenzaldehyde, Sep. Sci. Technol. 42 (4) (2007) 879–895.

[15] S. Feng, Z. Guo, J. Fan, X. Chen, J. Sun, Kinetic spectrophotometric determination of total iron in natural water by flow injection analysis using on-line preconcentration, Microchim. Acta 149 (2005) 61–65.

[16] N. Ramos-Martos, P. Cañada-Rudner, A. García de Torres, J.M. Cano-Pavón, Development of an FI-ICP method for on-line preconcentration and determination of platinum, Microchim. Acta 148 (2004) 35–42.

[17] Y. Rodriguez, J.F. Tyson, Determination of antimony by atomic absorption spectrometry with flow injection hydride generation by a tetrahydroborate-form anion-exchanger, J. Anal. Atom. Spectrom. 21 (2006) 757–762.

[18] D. Kara, Separation and removal of mercury(II) from water samples using (acetylacetone)-2-thiol-phenyleneimine immobilized on anion-exchange resin prior to determination by cold vapor inductively coupled plasma atomic emission spectroscopy, Anal. Lett. 38 (2005) 2217–2230.

[19] A.O. Martins, E. Luiz da Silva, M.C.M. Laranjeira, V.T. de Favere, Application of chitosan functionalized with 8-hydroxyquinoline: determination of lead by flow injection flame atomic absorption spectrometry, Microchim. Acta 150 (2005) 27–33.

[20] M.H. Mashhadizadeh, M. Pesteh, M. Talakesh, I. Sheikhshoaie, M.M. Ardakani, M.A. Karimi, Solid phase extraction of copper (II) by sorption on octadecyl silica membrane disk modified with a new Schiff base and determination with atomic absorption spectrometry, Spectrochim. Acta Part B 63 (2008) 885–888.

[21] T. Shamspur, A. Mostafavi, I. Sheikhshoaie, Determination of copper in water and plant samples by flame atomic absorption spectrometry after preconcentration on octadecyl silica membrane disks modified with a recently synthesized Schiff base, J. AOAC Int. 91 (4) (2008) 865–870.

[22] F. Shemirani, A.A. Mirroshandel, M. Salavati-Niasari, R.R. Kozani, Silica gel coated with Schiff's base: synthesis and application as an adsorbent for cadmium, copper, zinc, and nickel determination after preconcentration by flame atomic absorption spectrometry, J. Anal. Chem. 59 (3) (2004) 228–233.

[23] A.M. Donia, A.A. Atia, K.Z. Elwakeel, Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde, J. Hazard. Mater. 151 (2–3) (2008) 372–379.

[24] M.B. Gholivand, F. Ahmadi, E. Rafiee, Solid phase extraction and determination of ultra trace amounts of copper using activated carbon modified by N,N′-bis(salicylidene)-1,2-phenylenediamine, Sep. Sci. Technol. 42 (4) (2007) 897–910.

[25] J.L. Burguera, Flow Injection Atomic Spectroscopy, Marcel Dekker, New York, 1989.

[26] Z.L. Fang, Flow Injection Atomic Absorption Spectrometry, Wiley, Chichester, 1995.

[27] Z.L. Fang, Flow Injection Separation and Preconcentration, VCH Publishers, Weinheim, Germany, 1993.

[28] C. Boukhalfa, A. Mennour, L. Reinert, L. Duclaux, Removal of copper from aqueous solutions by coprecipitation with hydrated iron oxide, Asian J. Chem. 19 (6) (2007) 4267–4276.

[29] E. Morgan, Chemometrics: Experimental Design, John Wiley & Sons, London, 1991, 19.