Celtek clay as sorbent for separation–preconcentration of metal ions from environmental samples

Mustafa Tuzen [a], Esra Melek [a], Mustafa Soylak [b],*

[a] *Gaziosmanpasa University, Faculty of Science and Arts, Chemistry Department, 60250 Tokat, Turkey*
[b] *Erciyes University, Faculty of Science and Arts, Chemistry Department, 38039 Kayseri, Turkey*

Abstract

The sorption conditions including pH of the aqueous solution, sample volume, etc., on Celtek clay of copper(II), cadmium(II), lead(II), chromium(III), nickel(II) and cobalt(II) ions from environmental samples has been studied. The effects of electrolytes as matrix on the preconcentration were also investigated with the recoveries >95%. The 3 sigma detection limits for copper, cadmium, lead, chromium, nickel and cobalt ions were found to be 0.25, 0.32, 0.73, 0.45, 0.50 and 0.41 μg/l, respectively. The relative standard deviation was <10% for the determination of analytes. The procedure was validated by analysis of a NRCC-SLRS 4 Riverine Water, SRM 1573a Tomato leaves and IAEA 336 Lichen standard reference materials. The developed method was successively utilized for the determination of Cu(II), Cd(II), Pb(II), Cr(III), Ni(II) and Co(II) in various samples including natural waters, wheat and human hair by flame atomic absorption spectrometry (FAAS) with satisfactorily results (recoveries > 95% and R.S.D.'s < 10%).
© 2005 Elsevier B.V. All rights reserved.

Keywords: Celtek clay; Preconcentration; Solid-phase extraction; Flame atomic absorption spectrometry

1. Introduction

Heavy metals are considered to be one of the main sources of pollution in the environment, since they have a significant effect on its ecological quality [1,2]. One of the major problems in ecology is related to the path of toxic metals contained in all matrices involved in foods and food chain [3,4]. Trace heavy metals, such as zinc, copper and cobalt are essential for most biological systems including humans at appropriate levels; while others, such as cadmium and lead are highly toxic to plants, animals and human [4,5]. The accumulation of toxic and persistence substances in the environment continuously increases owing to the anthropic activities [4,6]. Because of these impotencies of heavy metal ions, their accurate and sensitive determination is very important for analytical and environmental chemists. Flame atomic absorption spectrometry (FAAS) is one of the main instruments at this area due to its lower costs and its easy usage. However, direct instrumental analysis of high salt content samples for their heavy metal contents is difficult because of influences of matrices by flame atomic absorption spectrometer. In addition, heavy metals generally have low concentrations, which are near or below the limit of detection of flame atomic absorption spectrometer [7–9]. Preconcentration–separation can solve these problems and leads to simplified heavy metal determination [9,10]. Cloud point extraction [11,12], solvent extraction [13,14], electroanalytical techniques [15,16], membrane filtration [17,18], ion exchange [19,20] are used for the preconcentration and separation of metal ions prior to their instrumental determinations. Also solid-phase extraction (SPE) is an attractive enrichment–separation technique for heavy metal ions. SPE reduces solvent use, solvent exposure, disposal costs and extraction time for sample preparation. Various solid-phase extractors including activated carbon and multiwalled carbon nanotubes [21–23], silica gel and sol–gel [24–26], synthetic polymeric resins [27–29] and natural materials [30–32] have been used for preconcentration of heavy metals from various samples including natural waters and food samples.

Clay is a natural, earthy, fine-grained material composed largely of a group of crystalline minerals. Clays have been used for thousands of years and they still keep their position

---

* Corresponding author. Fax: +90 352 4378802.
E-mail address: soylak@erciyes.edu.tr (M. Soylak).

among the most important industrial material [33–36]. Clays have been also used for chemical studies for various purposes including adsorption of various organic and inorganic substances [36–38]. One of the important are for the usage of clays is preconcentration–separation of metal ions. Solid-phase extraction conditions for copper(II), cadmium(II), silver(I), nickel(II) and lead(II) ions on modified clays have been investigated by Krikorian and Martin [9]. Without adjusting the pH, better than 90% of analytes could be removed on clay. Akcay and Kurtulmus [39] have been investigated adsorption conditions for uranium on Turgutlu and Kula clays. Dias et al. [40] have been used 2-mercaptobenzothiazole loaded on clays for solid-phase extraction of Hg(II), Pb(II), Zn(II), Cd(II), Cu(II) and Mn(II) from an aqueous solution. Mohamed et al. [41] have been used Aswan clay from Egypt for speciation and preconcentration of Cr(III) and Cr(VI) from synthetic solution and tannery wastewater.

Celtek clay is a clay mineral was chosen as adsorbent material. The clay is collected from Celtek town of Amasya-Turkey. This material is commonly used as industrial raw material for the construction of ceramic and brick in the middle Anotalia-Turkey. According to our literature survey, Celtek clay was not been used as adsorbent for traces metal ions from various samples.

In the presented work, the adsorption conditions for copper(II), cadmium(II), lead(II), chromium(III), nickel(II) and cobalt(II) ions on Celtek clay have been investigated. On the optimal conditions, the analyte ions in the various environmental samples have been determined.

2. Experimental

2.1. Instrument

A Perkin-Elmer AAnalyst 700 atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp and an air–acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer.

A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi and maximum temperature 300 °C) was used. Digestion conditions for microwave system for SRM 1573a Tomato leaves and IAEA 336 Lichen, wheat and human hair samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W and 8 min for 550 W; vent: 8 min [42,43].

2.2. Reagents and solution

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionized water (Milli-Q Millipore 18.2 MΩ/cm resistivity) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO$_3$ (1 + 9) and were rinsed with distilled water

Table 1
Analytical characteristics of the calibration curves of the analytes

Analyte	Correlation coefficient	Linear range (mg/l)	Regression equation
Copper	0.9999	0.25–5.0	$A = 0.0539C + 0.0010$
Cadmium	0.9997	0.02–2.0	$A = 0.1415C + 0.0014$
Lead	0.9997	0.5–10.0	$A = 0.0085C - 0.0007$
Chromium	0.9998	0.5–10.0	$A = 0.0247C + 0.0010$
Nickel	0.9998	0.25–5.0	$A = 0.0320C + 0.0003$
Cobalt	0.9996	0.25–5.0	$A = 0.0356C + 0.0006$

A, absorbance; C, concentration of analyte.

prior to use. The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg/l of the given element supplied by Sigma and Aldrich. Stock solutions of diverse elements were prepared from high purity compounds.

The calibration curves for analyte ions were drawn after setting various parameters of FAAS including wavelength, slit width and lamp current at an optimum level. The optimum concentration ranges and regression equations for analytes are given in Table 1. The statistical calculations are based on the average of triplicate readings for a standard solution the analyte ions. The precision of the method was investigated by using the model solutions containing the spiked elements on the optimal conditions of the method (Table 1). The calibration standards were not submitted to the preconcentration procedure.

Acetate buffer solutions (CH$_3$COO$^-$/CH$_3$COOH) were prepared by mixing of appropriate volumes of 0.1 M acetic acid and 0.1 M sodium acetate solutions for pH 4 and 6. For pH 7, a 250 ml of borate buffer was prepared by use of 2.5 ml of 1 M HCl and 0.445 g NaBO$_2$. Ammonium buffer solutions (NH$_4^+$/NH$_3$) were prepared by mixing of appropriate amounts of 0.1 M ammonia and 0.1 M ammonium chloride solutions for pH 8–10. Standard reference materials (NRCC-SLRS 4 Riverine Water, SRM 1573a Tomato leaves and IAEA 336 Lichen) were used in the experiment.

Celtek clay was collected from Celtek town of Amasya-Turkey. The specific surface area of Celtek clay was found to be 69 m^2/g by BET method. Celtek clay was first dried and sieved form 200-mesh, then washed with distilled water several times to remove any dust and other water-soluble impurities. The washed Celtek clay was dried in electric oven at 105 °C for 24 h and then placed in desiccators before adsorption experiments.

2.3. Test procedure

A sample volume of 50 ml, containing 10 μg of copper(II), 5 μg of cadmium(II), 20 μg of lead(II), 20 μg of chromium(III), 10 μg of nickel(II) and 10 μg of cobalt(II) ions, was transferred into a beaker; 10 ml of buffer solution was added. After a fast shaking, 100 mg of Celtek clay was added and the mixture was shaken again for 30 min. The system was then filtered under vacuum through blue band filter paper. Then, the filter and constituents were washed with distilled water. In order to elute the adsorbed analytes on Celtek clay, 6–8 ml of 1 mol/l HCl was used. The final volume was completed to 10.0 ml with 1 mol/l HCl. Analyte contents of the final solution were determined by

flame atomic absorption spectrometry. The same procedure was applied to the blank solution. In order to use the Celtek clay for next experiment, the Celtek clay was washed with excess of 1 mol/l HCl and distilled water, sequentially.

2.4. Analysis of the real samples

SRM 1573a Tomato leaves and IAEA 336 Lichen standard reference materials (250 mg) were digested with 6 ml of HNO_3 (65%), 2 ml of H_2O_2 (30%) in closed microwave digestion system and diluted to 50.0 ml with deionized water. A blank digest was carried out in the same way. Then, the preconcentration procedure given above was applied to the final solutions.

For the microwave digestion of wheat and human hair samples, 1.0 g of sample from Tokat was digested with 6 ml of concentrated HNO_3 and 2 ml of H_2O_2 (30%) in microwave system. After digestion the samples, the volume of the digested sample was made up to 50.0 ml with distilled water. The blank solutions were prepared in the same way as the real sample, but omitting the sample. The preconcentration procedure given above was applied to the samples.

Natural waters including NRCC-SLRS 4 Riverine water, tap, river, sea and spring waters from Tokat region of Turkey analyzed were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the water samples was adjusted to 8.0 with buffer solution. The preconcentration procedure given above was applied to the samples. The levels of analyte ions in the samples were determined by flame atomic absorption spectrometry.

3. Results and discussion

3.1. Influences of pH

Since the pH of the aqueous solutions is an important analytical factor on the solid-phase extraction studies of heavy metal ions [8,24,29], the influences of pH on the recoveries of analyte ions on Celtek clay were examined in the pH range of 4–10 by using buffer solutions given in Section 2.2. The results are
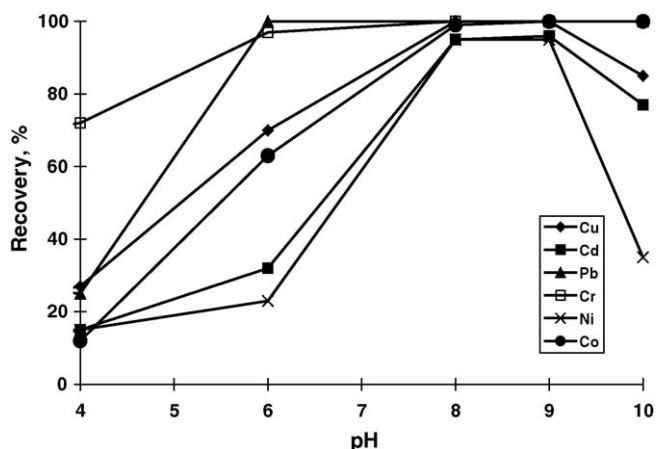
depicted in Fig. 1. Chromium(III) and lead(II) ions were quantitatively recovered in the pH range of 6–10 on Celtek clay, while cobalt could be recovered at pH range 8–10. Quantitative recovery values for the other analyte ions were obtained in the pH range of 8–9. In all subsequent works, the pH was kept as 8.0 by using ammonium buffer solution.

3.2. Desorption studies

The desorption of adsorbed analyte ions on the Celtek clay were also studied by using HCl and HNO_3 at various concentrations. Analyte ions were not desorbed from Celtek clay with HNO_3. Subsequent elution with 1 M HCl readily strips the sorbed metal ions from Celtek clay.

3.3. Effect of stirring time

The influences of the stirring time for the adsorption of analyte ions on Celtek clay were examined. Copper(II), cadmium(II), lead(II), chromium(III), nickel(II) and cobalt(II) ions were quantitatively recovered after 25 min of stirring time. The recoveries were not quantitative below 25 min. In all subsequent works, 30 min was selected as stirring time.

3.4. Effect of sample volume

To obtain high preconcentration factor, the effect of the sample volume on the recoveries of analyte ions on Celtek clay was also investigated in the range of 20–500 ml. The results are recorded in Fig. 2. The recovery values of analytes were very efficient (>95%) in the sample volume range of 20–250 ml. For more than 250 ml of the sample volume, the recoveries of analytes were decreased.

3.5. Effect of divers ions

Because of the determination of the levels of traces metal ions of the highly saline samples were aimed, the influences of possible matrix ions in the environmental samples and some transition metals were also examined. The effect of foreign ions coexisting
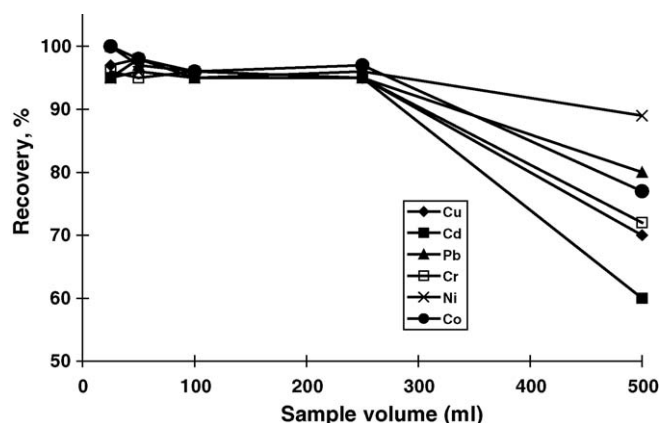
Fig. 1. The effects of pH on the recoveries of analyte metal ions on Celtek clay (N = 3).

Fig. 2. Effects of sample volume on the adsorption of metal ions on Celtek clay (N = 3).

Table 2
Tolerable limits of some divers ions on the recoveries of metal ions on Celtek clay (sample volume 50 ml, pH 8 and $N = 4$)

Ion	Added as	Concentration (mg/l)	Cu	Cd	Pb	Cr	Ni	Co
Na^+	NaCl	20000	97 ± 3	95 ± 2	100 ± 1	95 ± 3	98 ± 2	95 ± 1
K^+	KCl	5000	100 ± 2	95 ± 4	100 ± 1	95 ± 2	95 ± 3	95 ± 2
Ca^{2+}	$CaCl_2$	3000	95 ± 3	95 ± 2	100 ± 2	96 ± 3	95 ± 2	96 ± 3
Mg^{2+}	$MgCl_2$	3000	96 ± 3	95 ± 3	100 ± 1	97 ± 2	95 ± 2	95 ± 3
Cl^-	NaCl	25000	96 ± 2	95 ± 2	100 ± 2	95 ± 3	98 ± 3	97 ± 1
F^-	NaF	2000	97 ± 3	96 ± 3	100 ± 1	98 ± 3	95 ± 2	96 ± 2
NO_3^-	KNO_3	3000	98 ± 2	95 ± 2	99 ± 3	96 ± 2	95 ± 3	95 ± 2
SO_4^{2-}	Na_2SO_4	2000	97 ± 3	96 ± 3	95 ± 2	95 ± 3	95 ± 2	95 ± 1
PO_4^{3-}	Na_3PO_4	1000	95 ± 2	95 ± 3	95 ± 1	95 ± 3	97 ± 3	95 ± 2
Al^{3+}	$Al_2(SO_4)_3$	25	95 ± 2	95 ± 3	97 ± 1	95 ± 3	95 ± 2	95 ± 3
Ag^+	$AgNO_3$	10	95 ± 3	95 ± 2	100 ± 2	95 ± 3	95 ± 3	95 ± 3
Mn^{2+}	$MnCl_2$	25	97 ± 2	95 ± 4	100 ± 1	95 ± 3	95 ± 2	95 ± 2
Zn^{2+}	$ZnSO_4$	10	95 ± 3	95 ± 3	96 ± 1	95 ± 3	95 ± 2	95 ± 3

in natural samples on the determination of the analyte ions on Celtek clay was investigated. A 50 ml portion of sample solution containing analytes and a given amounts of foreign ions were concentrated. The experimental results are shown in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the preconcentration and determination of analytes. The ions normally present in water do not interfere under the experimental conditions used. Some of the transition metals (Table 2) at milligram per liter levels were not interfered on the recoveries of the analyte ions. This results show that the proposed preconcentration/separation

method could be applied to the highly saline samples and the samples that contains some transition metals at milligram per liter levels.

3.6. Adsorption capacity

In order to study the adsorption capacity of Celtek clay, 0.1 g clay was added 50 ml of solution containing 1.0 mg of metal ion at pH 8.0. After shaking for 30 min, the mixture was filtered. Ten milliliters of the supernatant solution was diluted to 100 ml and determined by flame atomic absorption spectrometry. This

Table 3
Analysis of two waters spiked analyte ions (sample volume 50 ml and $N = 4$)

Element	Added (µg)	River water		Sea water	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Cu	0	ND	–	ND	–
	5	4.8 ± 0.4	96	4.8 ± 0.5	96
	10	9.9 ± 0.3	99	9.5 ± 0.4	95
	20	19.6 ± 0.5	98	19.2 ± 0.6	96
Cd	0	ND	–	ND	–
	2.5	2.4 ± 0.3	96	2.5 ± 0.2	100
	5	4.8 ± 0.3	96	4.9 ± 0.5	98
	10	10.1 ± 0.5	101	9.7 ± 0.4	97
Pb	0	ND	–	ND	–
	10	9.7 ± 0.2	97	9.5 ± 0.4	95
	20	19.6 ± 0.4	98	19.2 ± 0.5	96
	40	40.8 ± 0.5	102	39.6 ± 0.7	99
Cr	0	ND	–	ND	–
	10	9.9 ± 0.4	99	9.7 ± 0.4	97
	20	19.6 ± 0.6	98	20.2 ± 0.5	101
	40	40.8 ± 0.7	102	39.6 ± 0.4	99
Ni	0	ND	–	ND	–
	5	4.8 ± 0.3	96	4.9 ± 0.4	98
	10	9.8 ± 0.5	98	9.7 ± 0.5	97
	20	20.2 ± 0.6	101	19.6 ± 0.6	98
Co	0	ND	–	ND	–
	5	5.1 ± 0.3	102	4.8 ± 0.4	96
	10	10.3 ± 0.5	103	9.8 ± 0.5	98
	20	19.6 ± 0.6	98	19.2 ± 0.6	96

ND, not detected.

Table 4
The results for reference standard materials after application of presented procedure ($N = 4$)

Element	NRCC-SLRS 4 Riverine Water (µg/l)		SRM 1573a Tomato leaves (µg/g)		IAEA 336 Lichen (µg/g)	
	Certified value	Our value	Certified value	Our value	Certified value	Our value
Cu	1.81	1.79 ± 0.08	4.7	4.65 ± 0.30	3.55	3.50 ± 0.14
Cd	0.012	BDL	1.52	1.57 ± 0.10	0.117	0.114 ± 0.01
Pb	0.086	BDL	–	BDL	(5)[a]	4.90 ± 0.24
Cr	0.33	BDL	1.99	1.89 ± 0.12	(1.03)[a]	0.99 ± 0.08
Ni	0.67	BDL	1.59	1.52 ± 0.11	–	BDL
Co	0.033	BDL	0.57	0.54 ± 0.04	0.287	0.279 ± 0.02

BDL, below the detection limit.
[a] The values in the parentheses are not certified.

procedure was repeated for each analyte ions separately. The capacity of sorbent for analytes were found as—Cu: 0.12, Cd: 0.04, Pb: 0.05, Cr: 0.19, Ni: 0.03 and Co: 0.06 mmol/g. A mixed mode mechanism of the inaction between metal ions and the clay attributed which was included ion exchange, physical and chemical inactions. The stability of Celtek clay was excellent. On storing for six mounts its properties and sorption capacity do not change significantly.

3.7. Figure of merits

The relative standard deviations for flame atomic absorption spectrometric determinations for analytes are between 1.0 and 9.0%. The detection limits, defined as the concentration equivalent to three times the standard deviation ($N = 13$) of the reagent blank were found as—Cu: 0.25, Cd: 0.32, Pb: 0.73, Cr: 0.45, Ni: 0.50 and Co: 0.41 µg/l.

To estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked in river water and sea water. The resulting solutions were submitted to the presented procedure given in Section 2. The results are given in Table 3. Good agreement was obtained between the added and found analyte content. The recovery values for the analyte ions were in the range of 95–102%.

3.8. Application

The first application of proposed method was performed to three standard reference materials (NRCC-SLRS 4 River-

Table 5
The application of presented method in natural water samples for contents of analyte ions ($N = 4$)

Element	Concentration (µg/l)			
	Tap water	River water	Sea water	Spring water
Cu	3.12 ± 0.16[a]	5.66 ± 0.28	2.43 ± 0.11	4.15 ± 0.17
Cd	BDL	BDL	BDL	3.26 ± 0.20
Pb	6.68 ± 0.43	7.16 ± 0.52	11.9 ± 0.9	4.12 ± 0.31
Cr	BDL	3.12 ± 0.18	0.82 ± 0.05	2.60 ± 0.19
Ni	4.54 ± 0.21	2.72 ± 0.10	5.45 ± 0.34	3.51 ± 0.25
Co	3.29 ± 0.25	3.58 ± 0.22	BDL	BDL

BDL, below the detection limit.
[a] $(x \pm \text{t.s.})/\sqrt{N}$, $p = 0.95$.

Table 6
Levels of analytes in a wheat and human hair samples after application presented procedure ($N = 4$)

Element	Concentration (µg/g)	
	Wheat	Human hair
Cu	2.60 ± 0.15[a]	3.68 ± 0.22
Cd	BDL	BDL
Pb	BDL	2.57 ± 0.19
Cr	1.23 ± 0.10	1.40 ± 0.10
Ni	1.85 ± 0.14	2.75 ± 0.15
Co	BDL	BDL

BDL, below the detection limit.
[a] $(x \pm \text{t.s.})/\sqrt{N}$, $p = 0.95$.

ine Water, SRM 1573a Tomato leaves and IAEA 336 Lichen). Tomato leaves and lichen SRM's were digested by using closed microwave digestion system. Then, the method given in Section 2.3 was applied. The results are given in Table 4. There is generally a good harmony between our results and certified values.

The procedure was also applied to the four different natural water samples given in Table 5 from Tokat region of Turkey. Microwave digested wheat and human hair samples were also analyzed by the proposed method. The results for wheat and human hair are given in Table 6.

4. Conclusion

The Celtek clay was successfully applied for the adsorption of Cu(II), Cd(II), Pb(II), Cr(III), Ni(II) and Co(II) with satisfactory results. The Celtek clay can be used at least 100 times for the experiments. The proposed methodology is very simple, cheap, efficient, precise and accurate since results obtained with the analysis of the certified samples presented agreement with the certified results. The method could be applied for the preconcentration of analyte ions from other matrices.

University and the Unit of the Scientific Research Projects of Erciyes University.

References

[1] M. Tuzen, Determination of heavy metals in soil, mushroom and plant samples by atomic absorption spectrometry, Microchem. J. 74 (2003) 289–297.

[2] J.K. Kiptoo, J.C. Ngila, W.R.L. Masamba, G.M. Sawula, Comparative studies of the speciation patterns of nickel and chromium in surface-, ground- and wastewater systems in Botswana, S. Afr. J. Chem. 58 (2005) 120–126.

[3] C. Locatelli, Heavy metals in matrices of food interest: sequential voltammetric determination at trace and ultratrace level of copper, lead, cadmium, zinc, arsenic, selenium, manganese and iron in meals, Electroanalysis 16 (2004) 1478–1486.

[4] Y. Cui, Y.G. Zhu, R. Zhai, Y. Huang, Y. Qiu, J. Liang, Exposure to metal mixtures and human health impacts in a contaminated area in Nanning, China, Environ. Int. 31 (2005) 784–790.

[5] S. Baslar, Y. Dogan, N. Yenil, S. Karagoz, H. Bag, Trace element biomonitoring by leaves of *Populus nigra* L. from Western Anatolia, Turkey, J. Environ. Biol. 26 (2005) 665–668.

[6] S. Melaku, T. Wondimu, R. Dams, L. Moens, Simultaneous determination of trace elements in Tinishu Akaki River water sample, Ethiopia by ICP-MS, Can. J. Anal. Sci. Spectrosc. 49 (2004) 374–384.

[7] F.O. Omarilis, Desarrollo de un analizador automático para la determinación del ion plomo en muestras medioambientales, Ph.D. Thesis, Universitat Autonomia de Barcelona, Barcelona, 2003.

[8] M. Imamoglu, A.O. Aydin, Column solid phase extraction of gold, palladium and copper at trace levels on modified silica gel for their atomic absorption spectrometric determination, Fresenius Environ. Bull. 14 (2005) 940–946.

[9] N. Krikorian, D.F. Martin, Extraction of selected heavy metals using modified clays, J. Environ. Sci. Health A 40 (2005) 601–608.

[10] L. Ming, C. Huanwen, Z. Jian, Z. Xiangyu, Y. Aimin, J.Q. Han, Several advances of flow injection analysis techniques, Anal. Instrum. 3 (2003) 1–5.

[11] Z. Fan, Speciation analysis of antimony(III) and antimony(V) by flame atomic absorption spectrometry after separation–preconcentration with cloud point extraction, Microchim. Acta 152 (2005) 29–33.

[12] M.A.M. da Silva, V.L.A. Frescura, F.J.N. Aguilera, A.J. Curtius, Determination of Ag and Au in geological samples by flame atomic absorption spectrometry after cloud point extraction, J. Anal. At. Spectrom. 13 (1998) 1369–1373.

[13] V. Pavski, A. Corsini, Multielement preconcentration of trace metals from natural waters by solvent extraction with an alkylated oxine derivative, Talanta 36 (1989) 367–372.

[14] S. Igarashi, N. Ide, Y. Takagai, High-performance liquid chromatographic-spectro-photometric determination of copper(II) and palladium(II) with 5,10,15,20-tetrakis(4N-pyridyl) porphine following homogeneous liquid–liquid extraction in the water–acetic acid–chloroform ternary solvent system, Anal. Chim. Acta 424 (2000) 263–269.

[15] S.M. Skogvold, O. Mikkelsen, K.H. Schrøder, Electrochemical properties and application of mixed silver–bismuth electrodes, Electroanalysis 17 (2005) 1938–1944.

[16] N.B. Li, J.P. Duan, G.N. Chen, Differential pulse anodic stripping voltammetric determination of Pb with heparin modified electrode, Chin. J. Chem. 22 (2004) 553–557.

[17] A.U. Karatepe, M. Soylak, L. Elci, Separation/preconcentration of Cu(II), Fe(III), Pb(II), Co(II) and Cr(III) in aqueous samples on cellulose nitrate membrane filter and their determination by atomic absorption spectrometry, Anal. Lett. 35 (2002) 1561–1574.

[18] M. Soylak, I. Narin, U. Divrikli, S. Saracoglu, L. Elci, M. Dogan, Preconcentration–separation of heavy metal ions in environmental samples by membrane filtration–atomic absorption spectrometry combination, Anal. Lett. 37 (2004) 767–780.

[19] S. Nabi, A. Alim, A. Islam, M. Amjad, Column chromatographic separation of metal ions on 1-(2-pyridylazo)-2-napthol modified Amberlite IR-120 resin, J. Sep. Sci. 28 (2005) 2463–2467.

[20] B. Yao, S.K. Xu, Z.L. Fang, Determination of cadmium at ultra-trace level by FI cold vapor generation AAS with on-line ion exchange preconcentration, Chem. J. Chin. Univ.-Chin. 22 (2001) 1301–1304.

[21] M.S. Tehrani, F. Rastegar, A. Parchehbaf, Z. Rezvani, Determination of copper by flame atomic absorption spectrometry after preconcentration with activated carbon impregnated with a new schiff base, Chin. J. Chem. 23 (2005) 1437–1442.

[22] M.A. Taher, A. Mostafavi, D. Afzali, F.S. Mahani, A.R. Mohadesi, Modified natrolite as a new sorbent for separation and preconcentration of trace amounts of cadmium ions, Chem. Anal. 50 (2005) 841–850.

[23] P. Liang, Q. Ding, F. Song, Application of multiwalled carbon nanotubes as solid phase extraction sorbent for preconcentration of trace copper in water samples, J. Sep. Sci. 28 (2005) 2339–2343.

[24] C.R.T. Tarley, E.C. Figueiredo, G.D. Matos, Thermospray flame furnace-AAS determination of copper after on-line sorbent preconcentration using a system optimized by experimental designs, Anal. Sci. 21 (2005) 1337–1342.

[25] T. Madrakian, A. Afkhami, M.A. Zolfigol, M. Solgi, Separation, preconcentration and determination of silver ion from water samples using silica gel modified with 2,4,6-trimorpholino-1,3,5-triazin, J. Hazard. Mater. 128 (2006) 67–72.

[26] B. Saad, C.C. Chong, A.S.M. Ali, M.F. Bari, I.A. Rahman, N. Mohamad, M.I. Saleh, Selective removal of heavy metal ions using sol–gel immobilized and SPE-coated thiacrown ethers, Anal. Chim. Acta 555 (2006) 146–156.

[27] M.A. Taher, E. Rezaeipour, D. Afzali, S.Z.M. Mobarakeh, Flame atomic absorption spectrometric determination of trace amounts of thallium in natural waters and standard pepperbush after solid-phase extraction on to amberlite XAD-2 resin modified with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, Asian J. Chem. 17 (2005) 1463–1468.

[28] E. Kenduzler, A.R. Turker, Optimization of a new resin, Amberlyst 36, as a solid-phase extractor and determination of copper(II) in drinking water and tea samples by flame atomic absorption spectrometry. A new simple and reliable method has been developed to separate and preconcentrate, J. Sep. Sci. 28 (2005) 2344–2349.

[29] S. Baytak, A.R. Turker, Determination of lead and nickel in environmental samples by flame atomic absorption spectrometry after column solid-phase extraction on Ambersorb-572 with EDTA, J. Hazard. Mater., in press.

[30] Y. Liu, P. Liang, L. Guo, Nanometer titanium dioxide immobilized on silica gel as sorbent for preconcentration of metal ions prior to their determination by inductively coupled plasma atomic emission spectrometry, Talanta 68 (2005) 25–30.

[31] P. Hashemi, Z. Rahmani, A novel homocystine–agarose adsorbent for separation and preconcentration of nickel in table salt and baking soda using factorial design optimization of the experimental conditions, Talanta, in press.

[32] H. Akhlaghi, P. Hashemi, J. Boroum, H. Ghafurian, Comparison of three agarose based chelating adsorbents and their application to the preconcentration of some metal ions in water, Asian J. Chem. 16 (2004) 1367–1373.

[33] G. Ataman, Chemical composition of clay-minerals and shales of Anatolian tertiary sediments—global interpretation, Chem. Geol. 26 (1979) 311–320.

[34] B. Baran, T. Erturk, Y. Sarikaya, T. Alemdaroglu, Workability test method for metals applied to examine a workability measure (plastic limit) for clays, Appl. Clay Sci. 20 (2001) 53–63.

[35] M. Ozer, F. Arslan, G. Onal, Sedimentation of clays prior to ceramic production, Key Eng. Mater. 264 (2004) 1439–1442.

[36] A. Sari, M. Soylak, Adsorption isotherms and thermodynamic parameters of stearic acid onto Celtek clay at 298, 308 and 318 K, J. Sci. Ind. Res., submitted for publication.

[37] A. Kaya, H.Y. Fang, Experimental evidence of reduction in attractive and repulsive forces between clay particles permeated with organic liquids, Can. Geotech. J. 42 (2005) 632–640.

[38] A.E. Osmanlioglu, Immobilization of radioactive waste by cementation with purified kaolin clay, Waste Manage. 22 (2002) 481–483.

[39] H. Akcay, F. Kurtulmus, Study of uranium sorption and desorption on some Turkish clays, J. Radioanal. Nucl. Chem.-Lett. 200 (1995) 529–544.

[40] N.L. Dias, W.L. Polito, Y. Gushikem, Sorption and preconcentration of some heavy-metals by 2-mercapto-benzothiazole clay, Talanta 42 (1995) 1031–1036.

[41] O.A. Mohamed, S.A. Sayed, H.S. Mohamady, N.H. El-Sayed, Aswan clay as sorbent for removal of Cr(III) and Cr(VI) from synthetic solution and tannery wastewater, J. Soc. Leather Technol. Chem. 89 (2005) 204–209.

[42] M. Tuzen, M. Soylak, L. Elci, Multi-element pre-concentration of heavy metal ions by solid phase extraction on Chromosorb 108, Anal. Chim. Acta 548 (2005) 101–108.

[43] M. Soylak, H. Colak, M. Tuzen, O. Turkoglu, L. Elci, Comparison of digestion procedures for commercial powdered soup samples for the determination of their trace metal contents by AAS, J. Food Drug Anal., in press.