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Solid Phase Extraction of Trace Amounts Cu, Fe and Pb as 5-(6-Methoxy-2-benzothiazoleazo)-8-aminoquinoline Complexes on Naphthalene Adsorbent and Flame Atomic Absorption Determination

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A simultaneous preconcentration method was developed for the determination of trace amounts of Cu, Fe and Pb by atomic absorption spectrometry. The method is based on the retention of their 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline complexes by naphthalene methyltrioctyl ammonium chloride adsorbent in a column. The adsorbed metal complexes were eluted from the column with nitric acid and Cu, Fe and Pb were determined by flame atomic absorption spectrometry. Several parameters such as pH of the sample solution, ligand concentration, volume of the sample and the amount of methyltrioctyl ammonium chloride loaded on naphthalene were evaluated. The effect of diverse ions on the preconcentration was also investigated. A preconcentration factor of up to 100 or more can easily be achieved depending on the volume of the sample taken. The calibration graphs were obtained in the range of 5-40, 10-100 and 10-200 ng mL^{-1} for Cu, Fe and Pb in the initial solution, respectively, when using 500 mL of the solution. The detection limit based on three standard deviations of the blank was 0.54, 3.1 and 4.5 ng mL-1 for Cu, Fe and Pb, respectively. The relative standard deviations of 1.1-2.4 % for Cu, 2.0-3.1 % for Fe and 1.1-2.0 % for Pb were obtained. The method was applied to the determination of Cu, Fe and Pb in river and wastewater samples.

Key Words: Solid-phase, Preconcentration, Lead, Iron, Copper, 5-(6-Methoxy-2-benzothiazoleazo)-8-aminoquinoline, Naphthalene-methyltrioctyl ammonium chloride.

INTRODUCTION

Determination of metal ions in natural samples such as waters, soils and biological fluids is very important part of environmental and public health studies. However, the direct determination of metal ions at trace level is limited due to their low level concentration and matrix interferences. Flame atomic absorption spectrometry (FAAS) which has been continuously used for the determination of trace metal ions suffers from insufficient sensitivity for direct determination of metal ions in

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environmental samples. Therefore a preconcentration or separation step is frequently necessary to improve the detection limit and sensitivity. For this purpose several separation and preconcentration procedures have been developed for trace metal ion determination involving different analytical strategies. These methods include ion exchange[1] liquid extraction[2], anodic stripping voltammetry[3], cloud point[4], coprecipitation[5] and solid-phase extractions[6-18]. Among the various methods, solid-phase extraction has received more acceptances due to its simplicity, rapidity and attainability of large preconcentration factor.

A variety of solid materials such as modified ion exchange resins[19-21], functionalized resins with chelating reagents[22], activated carbon[23], zeolites[24], cellulose[25] and immobilized microorganisms on sepiolite[26] have been used for preconcentration of trace metals. Microcrystalline naphthalene[27-29] and benzophenone[30] have also been used as solid-phase for adsorptive extraction of metal ion complexes.

In this work, a simultaneous solid-phase preconcentration method for the determination of copper, iron and lead by atomic absorption is described. The method is based on the adsorption of their 5-(6-methoxy-2-benzothiazoleazo)-8- aminoquinoline (MBTAQ) complexes on methyltrioctyl ammonium chloride supported on naphthalene used as an adsorbent in a column. The complexes adsorbed on the naphthalene adsorbent are then eluted with nitric acid solution and Cu, Fe and Pb are determined by flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

A Philips PU9100X flame atomic absorption spectrometer was used for the determination of copper, iron and lead. It was equipped with appropriate hallow cathode lamp and air-acetylene burner. The instrumental parameters were as follows: wavelength 324.8, 248.2 and 217.0 nm for Cu, Fe and Pb, respectively. The lamp currents of 3, 13 and 7.5 mA were used for Cu, Fe and Pb, respectively. Band pass was 0.5 nm for these three elements. All pH measurements were made using a Metrohm digital pH meter with a combined glass electrode. A Shimadzu rotary oil vacuum pump type SA18 was used.

Doubly distilled de-ionized water and analytical grade reagents were used for the preparation of all the solutions. The stock solution of 1000 μg mL^{-1} copper was prepared by dissolving 0.6706 g of $CuCl_2{\cdot}5H_2O$ (Merck) in water and diluted to 250 mL in a volumetric flask. This solution was standardized iodometric procedure[31]. The required concentration of copper solution was prepared by appropriate dilution of the stock solution. The stock solution of 1000 μg mL^{-1} iron was prepared by dissolving 0.8634 g of $(NH_4)_2(SO_4)_2{\cdot}FeSO_4{\cdot}12H_2O$ (Merck) in 100 mL of distilled water containing 10 mL of concentrated hydrochloric acid. This solution was standardized using dichromate procedure[31]. More dilute solutions were prepared by appropriate dilution of the stock solution. The stock solution of 1000 μg mL^{-1} lead was prepared by dissolving 0.1599 g of $Pb(NO_3)_2$ (Merck) in water and diluted to 100 mL in a volumetric flask. The required concentration of lead solution was prepared by appropriate dilution of the stock solution. A 3.0 mol L^{-1} nitric acid solution was prepared by diluting 20 mL of HNO_3 (Merck) to 100 mL in a volumetric flask. The ligand MBTAQ was prepared and purified according to reported method[18].

A 2.15×10^{-4} mol L^{-1} of 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline solution was prepared by dissolving 0.0910 g of this reagent in water and diluting to 500 mL in a volumetric flask. A formate buffer of pH 5 was prepared by addition of 0.1 M NaOH to 0.1 M formic acid and using a pH meter to adjust the pH at 5. The naphthalene adsorbent solution was prepared by dissolving 10 g of naphthalene and 1 g of methyltrioctyl ammonium chloride in 45 mL of acetone on a hot-plate stirrer at 40 ºC. This solution was transferred to 1000 mL of water while stirring the solution at room temperature. It was stirred for 1-2 h and allowed to stand for 0.5 h. The supernatant solution of naphthalene coprecipitated with methyltrioctyl ammonium chloride was drained off by decantation and washed twice with water in the same way. This adsorbent slurry was stored in a bottle for further use.

General procedure: A funnel-tipped glass tube (80 mm length and 8 mm i.d.) with a very fine bore was used as a preconcentration column. It was filled with the adsorbent slurry to a height of 7 cm after slightly pressing the adsorbent in the column with a flat glass rod. Solution (500 mL) containing 5-50, 10-50 and 10-150 ng mL^{-1} of Cu, Fe and Pb, respectively, 1.93×10^{-5} mol L^{-1} 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline and formate buffer solution (pH 5) was passed through the column at a flow rate of 8 mL min^{-1}. The column packing was then washed with a small volume of water and the naphthalene material was pushed down with a flat glass rod to eliminate the excess water attached to naphthalene. The metal ion complexes were eluted with 5 mL of HNO_3 solution (3 mol L^{-1}) and Cu, Fe and Pb were determined by FAAS. A blank solution was also run under the same analytical conditions without adding any Cu, Fe and Pb.

RESULTS AND DISCUSSION

The preliminary experiments showed that Cu, Fe and Pb complexes with 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline, could be simultaneously retained on the methyltrioctyl ammonium chloride-naphthalene adsorbent. Therefore, the retention of these complexes on a column containing methyltrioctyl ammonium chloride-naphthalene adsorbent was chosen for simultaneous preconcentration of Cu, Fe and Pb with subsequent determination by FAAS.

Effect of pH: The effect of pH of the test solution on the retention of Cu, Fe and Pb was studied. The pH values of solutions containing Cu, Fe and Pb complexes with 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline was adjusted in the range of 2-6 using appropriate buffer solutions and the general procedure was followed. The results of this study showed that maximum retention of the Cu, Fe and Pb was obtained at pH 5 (Fig. 1). Thus a formate buffer with pH 5 was selected for further work.

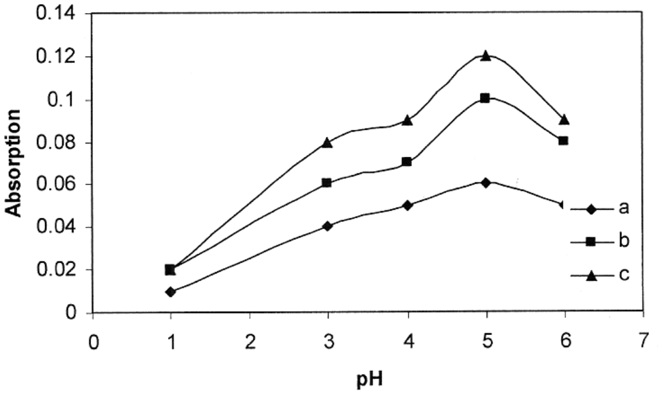

Fig. 1. Effect of pH on the absorbance of the (a) 50 ng mL^{-1} of Cu, (b) 50 ng mL^{-1} of Fe and (c) 150 ng mL^{-1} of Pb. Conditions: volume of the sample 100 mL, 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline concentration 1.93×10^{-5} mol L^{-1}

Effect of MBTAQ concentration: The effect of MBTAQ concentration on the retention of the Cu, Fe and Pb complexes was also investigated. The concentration of MBTAQ was varied in a number of 100 mL volumetric flasks containing 50, 50 and 150 ng mL^{-1} of Cu, Fe and Pb, respectively and the general procedure was followed. The results shown in Fig. 2 indicate that the concentration of MBTAQ did not affect the retention of all the copper and iron ions very much. However, the retention of lead was increased with increasing MBTAQ concentration up to 1.93×10^{-5} mol L^{-1} and remained constant at higher concentrations. This behaviour could probably be due to the difference in the formation constants of the metal ion complexes and the number of moles of the ligand required for each metal ion to form a complex. Therefore, MBTAQ concentration of 1.93×10^{-1} mol L^{-1} was selected as optimum.

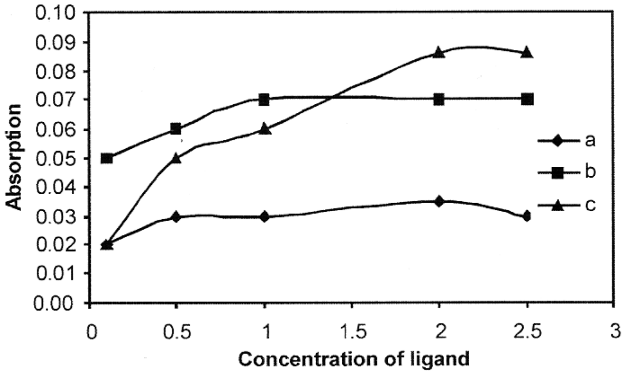

Fig. 2. Influence of 5-(6-methoxy-2-benzothiazoleazo)-8- aminoquinoline concentration on the absorbance of (a) 50 ng mL^{-1} of Cu, (b) 50 ng mL^{-1} of Fe and (c) 150 ng mL^{-1} of Pb. Conditions: Volume of the sample 100 mL, pH 5

Effect of nitric acid as the eluent: Studies were carried out to investigate the influence of different acids as eluents for the retained complexes. Nitric acid was chosen as an eluent owing to its effective elution of the adsorbed complexes. The effect of eluent concentration on the absorbance of eluted solution containing Cu, Fe and Pb was examined. The absorbance of all the three ions was increased, as the HNO_3 concentration increased up to 3.0 mol L^{-1} and it remained constant above this concentration. Therefore a nitric acid concentration of 3.0 mol L^{-1} was selected for subsequent studies. In order to choose proper volume of the eluent, the retained complexes were stripped with different volumes (3-10 mL) of 3.0 mol L^{-1} nitric acid. 10 mL would not be suitable because it gave a smaller preconcentration factor and 3 mL was not sufficient for the elution. Hence, 5 mL of 3.0 mol L^{-1} nitric acid was chosen for subsequent elution of the metal ion complexes for more convenient.

Effect of amount of methyltrioctyl ammonium chloride: The amount of methyltrioctyl ammonium chloride loaded on naphthalene was optimized and the results are shown in Fig. 3. A loading of 1 g of methyltrioctyl ammonium chloride on 10 g of naphthalene gave highest absorbance for the three ions.

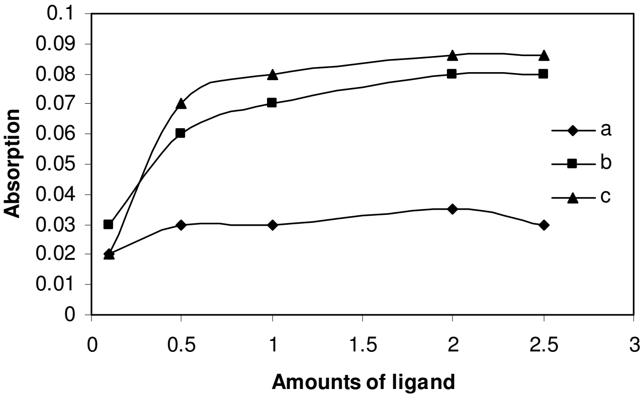

Fig. 3. Effect of the amount of methyltrioctyl ammonium bromide loaded on the column: (a) 50 ng mL^{-1} of Cu, (b) 50 ng mL^{-1} of Fe and (c) 150 ng mL^{-1} of Pb. Conditions: Volume of the sample 100 mL, pH 5 5-(6-methoxy-2-benzothiazoleazo)-8- aminoquinoline concentration 1.93×10^{-5} mol L^{-1}

Effect of sample and elution flow rate: The retention of Cu, Fe and Pb complexes with MBTAQ on naphthalene adsorbent was not affected by sample flow rates in the range of 2-8 mL min^{-1}. Thus the experiments were performed at a sample flow rate of 8 mL min^{-1} which was the maximum flow rate attainable by the pump we used. It is the same for the elution flow rate and flow rates in the range of 2-8 mL min^{-1} can be applied without any loss in recovery.

Effect of sample volume: The volume of the aqueous-phase was varied from 25 to 500 mL all containing same amounts of Cu, Fe and Pb, so that the final solutions after performing the preconcentration procedure would have the same concentrations. It was found that the absorbance was constant in all solutions after following the preconcentration procedure. However, at higher volumes the analysis time is increased. Therefore a preconcentration factor of 100 can be easily achieved when using 500 mL nitric acid concentration of 3.0 mol L^{-1} was selected for subsequent studies. In order to choose proper volume of the eluent, the retained complexes were stripped with different volumes (3-10 mL) of 3.0 mol L^{-1} nitric acid. 10 mL would not be suitable because it gave a smaller preconcentration factor and 3 mL was not sufficient for the elution. Hence, 5 mL of 3.0 mol L^{-1} nitric acid was chosen for subsequent elution of the metal ion complexes for more convenient.

Sorption capacity: The sorption capacity of the adsorbent was determined by batch process. The adsorbent slurry was filtered on a filter paper and air-dried. Adsorbent (1 g) was equilibrated with 100 mL of a solution containing 1, 1 and 5 µg mL^{-1} of Cu, Fe and Pb, respectively, for 24 h at optimum conditions. The loading capacity for each metal ion was calculated from the difference between the metal ion concentration before and after adsorption. The values were 100, 100 and 300 µg g^{-1} of adsorbent for Cu, Fe and Pb, respectively.

Kinetics of the metal sorption: The rate of loading of Cu, Fe and Pb ions on the adsorbent was determined by batch experiment. Adsorbent (1 g) was stirred with 100 mL solutions containing 50, 50 and 250 ng mL^{-1} of Cu, Fe and Pb, respectively, for different time intervals. After a predetermined time, the amount of metal ions loaded was determined using the general procedure. The variation of sorption as a function of time for the metal ions is shown in Fig. 4. The loading half time ($t_{½}$) defined as the time to reach 50 % of total loading capacity as estimated from Fig. 4 is about 7 min for Cu and Fe and 15 min for Pb. It is also observed that an equilibrium time of 15 min was required for 95-99 % sorption of Cu and Fe and 0.5 h for 90 % sorption of Pb.

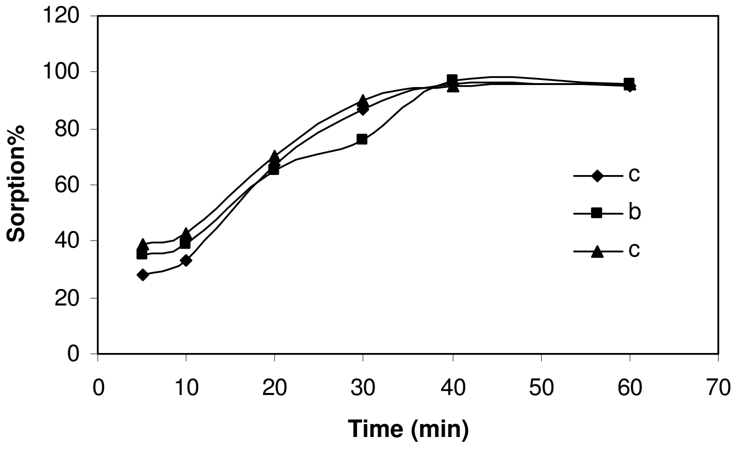

Fig. 4. Kinetics of metal ions sorption on the adsorbent: (a) 50 ng mL^{-1} of Fe, (b) 50 ng mL^{-1} of Cu and (c) 250 ng mL^{-1} of Pb

Analytical performance: The calibration graphs were obtained using the recommended procedure under the optimum conditions with a sample volume of 500 mL. Linear graphs were obtained in the range of 5-40, 10-100 and 10-200 ng mL^{-1} for Cu, Fe and Pb in the initial solution, respectively. (The concentration range in the final solution after preconcentration is in the range of 0.5-5.0, 1.0-5.0 and 1.0-15.0 µg mL^{-1} for Cu, Fe and Pb, receptively.) The equations for the lines were $A = 7.2 \times 10^{-3}$ C-3.6×10^{-4}, with r = 0.9995 for Cu, $A = 2.9 \times 10^{-3}$ C+ 3.0×10^{-4} with r = 0.9998 for Fe and $A = 1.1 \times 10^{-3}$ C+ 1.7×10^{-4} with r = 0.9991 for Pb. The detection limit based on three standard deviations of the blank was 0.54, 3.1 and 4.5 ng mL^{-1} for Cu, Fe and Pb, respectively, when using sample volume of 500 mL.

The relative standard deviations for 10 replicate measurements of 10 and 30 ng mL^{-1} of Cu was 2.4 and 1.0 %, for 10 and 30 ng mL^{-1} of Fe was 3.1 and 2.0 % and for 50 and 150 ng mL^{-1} Pb was 2.0 and 1.1 %.

Effect of foreign ions: The interference of co-existing ions on the determination of Cu, Fe and Pb was studied. Solution (100 mL) containing 50, 50 and 150 ng mL^{-1} of Cu, Fe and Pb, respectively and various amounts of foreign ions were prepared and the procedure described in the experimental section was applied. Any deviation of ± 4 % or more from the absorbance value of the standard solution was taken as interference. Table-1 shows the results. As can be seen a very good selectivity is achieved.

TABLE-1
EFFECT OF INTERFERING IONS ON THE RECOVERY OF
50, 50 AND 150 ng mL^{-1} OF Cu, Fe AND Pb

Interfering ion	Concentration of interfering (mg L^{-1})	Recovery[a] (%)		
		Fe	Cu	Pb
Cd^{2+}	1000	99 ± 1	100 ± 2	101 ± 1
NH_4^+, K^+, Mg^{2+}, Li^+, Cl^-, NO^{2-}, SCN^-, SO_4^{2-}	100	100 ± 1	101 ± 2	98 ± 1
Hg^{2+}, Zn^{2+}, Cr^{3+}, Ca^{2+}, Se^{4+}, F^-, Al^{3+}	10	100 ± 1	99 ± 2	102 ± 1

[a] $x \pm ts/\sqrt{n}$ at 95 % confidence (n = 3). [b] Masked by $NaBH_4$.

Application: The proposed method was applied to the preconcentration and determination of Cu, Fe and Pb content of tap water (Saveh, 20 February, 2007), seawater (taken from the Caspian sea, Anzali port, 11 November 2006)water samples. The water samples were collected in polyethylene bottles and kept in a refrigerator before use. The seawater sample solution (50 mL) and 500 mL for tap water were treated under the recommended procedure. Accuracy of the results was verified by analyzing the spiked water samples. The recoveries for these elements were very satisfactory (Table-2) indicating that the method can be used reliably for the analysis of water samples.

Conclusion

To our best of knowledge this is the first time naphthalene adsorbent is used for simultaneous preconcentration of three ions and their determination in the same

TABLE-2
DETERMINATION OF Cu, Fe AND Pb IN WATER SAMPLES

Sample	Copper concentration (ng mL^{-1})			Iron concentration (ng mL^{-1})			Lead concentration (ng mL^{-1})		
	Added	Found[a]	Recovery	Added	Found[a]	Recovery	Added	Found[a]	Recovery
River water (Varamin)[b,c]	0	36 ± 1	–	0	68 ± 3	–	0	255 ± 3	–
	100	135 ± 2	100	100	170 ± 4	100	500	770 ± 9	102
	200	248 ± 4	102	200	270 ± 6	100	1000	1262 ± 16	100
Seawater[d]	0	29 ± 1	–	0	61 ± 1	–	0	258 ± 3	–
	100	123 ± 2	95	100	164 ± 5	102	500	749 ± 9	99
	200	225 ± 4	98	200	256 ± 6	98	1000	1269 ± 16	101
Tap water (Saveh)[f]	0	73 ± 1	–	0	ND	–	0	13 ± 1	–
	10	82 ± 1	99	10	10 ± 1	100	50	66 ± 2	102
	20	92 ± 1	99	20	19 ± 1	95	100	116 ± 2	101

ND = not detected.
[a] $x \pm ts/\sqrt{n}$ at 95 % confidence (n = 5). [b] A preconcentration factor of 10 was applied.
[c] From a polluted area. [d] Rolling and Pipe Mills Company. [f] A preconcentration factor of 100 was applied.

sample batch. The adsorbent is economical and can easily be prepared. The proposed method for simultaneous preconcentration and separation of Cu, Fe and Pb is selective and allows the determination of trace amounts of these elements to be carried out by FAAS. The detection limits achieved are better than some of the previously reported methods using FAAS as detection method[20,21,26]. The linear range of the method is sufficient for the determination of Cu, Fe and Pb in some environmental samples and was successfully applied to the determination of Cu, Fe and Pb in tap water and seawater water samples with good recoveries.

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