Determination of Manganese, Copper, Cadmium and Lead by FAAS after Solid-Phase Extraction of Their Phenylpiperazine Dithiocarbamate Complexes on Activated Carbon

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A solid-phase extraction method was developed for the pre-concentration of manganese, copper, cadmium and lead in water samples prior to their determination by flame atomic absorption spectrometry using phenylpiperazine dithiocarbamate as a new reagent. The optimum pre-concentration conditions have been investigated such as pH, volume of sample solution and the effects of some matrix elements. The obtained recovery was nearly 90 to 100, while the enrichment factor was 400 for metal spiked solutions.

Key Words: Solid-phase extraction, phenylpiperazine dithiocarbamate, manganese, copper, cadmium, lead, flame atomic absorption spectrometry, activated carbon.

Introduction

Solid phase extraction (SPE) techniques have been widely used for the pre-concentration and separation of trace metal ions in aqueous systems prior to their determination. Among the techniques available, the dithiocarbamate solid-phase extraction method is very selective because dithiocarbamate reagents do not react with many metals (alkali, earth alkali and some other metals such as Al and Cr) that are fairly abundant in environmental samples, and enrichment factors are generally high. Recently, this method has been applied prior to trace metal determination by UV-VIS[1−2], ICP-AES[3−5], AAS[6−13] and electro-analytical methods[14−16].

The mechanism for the sorption of low levels of metal ions on solid adsorbent is still under investigation, but it is known that it is particularly related to the chelating agent and adsorbent; it is also known that metal retention can be improved while in the presence of a chelating or precipitating agent.

In our previous work, some dithiocarbamate reagents were tested for the absorption of cadmium on microcrystalline naphthalene. It was found that the adsorption productivity of the metal ions on an adsorbent was directly connected with the dithiocarbamate reagent[17]. In this study, potassium phenylpiperazine dithiocarbamate (KPPzDC) as a new chelating agent (Figure 1) was tested for the solid-phase extraction

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of Mn(II), Cu(II), Cd(II) and Pb(II) on activated carbon in water samples prior to determination by flame atomic absorption spectrometry (FAAS).
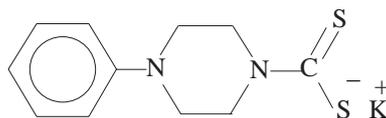
Figure 1. Structure of potassium phenylpiperazine dithiocarbamate (KPPzDC).

Experimental

Apparatus and Reagents

A UNICAM 929 model flame atomic absorption spectrophotometer with deuterium-lamp background correction was used to determine Mn(II), Cu(II), Cd(II) and Pb(II). The measuring conditions were as follows: UNICAM hollow cathode lamps, 10 cm 1-slot burner, air-acetylene flame (fuel gas flow 1.50 l/min), 0.5 nm spectral bandwidth, and 7 mm burner height. The wavelengths and the lamp currents of Mn, Cu, Cd and Pb were 279.5 nm, 324.8 nm, 228.8 nm and 217.0 nm, and 10 mA, 4 mA, 8 mA and 12 mA, respectively. pH measurements were performed with a JENWAY 3040 model digital pH-meter.

Potassium salts of phenylpiperazine dithiocarbamic acid (KPPzDC) were synthesized for this study in our laboratory as described below. Stoichiometric amounts of the amine (phenylpiperazine, 0.1 mol in 200 ml of diethyl ether), KOH (0.1 mol in 200 ml of deionized water) and 0.1 mol of CS_2 were mixed, and refluxed for 2 h at 0 °C. After the separation of phases the water phase was taken and evaporated. The residue was washed with diethyl ether and dried at 90 °C. It was then characterized by elemental analysis and infrared spectrometry. Reagent solution was prepared with 2.0 g of KPPzDC in 100 ml of deionized water. Mn(II), Cu(II), Cd(II) and Pb(II) stock solutions (1.000 mgml^{-1}) were prepared by dissolving the appropriate amount of their nitrate salts (Merck, 99.5%). Activated carbon was purchased from Aldrich Chemical Company (RO. 0.8 Pellets). It was pounded in a porcelain mortar and sieved with an 80-mesh sieve. Deionized water was produced by ELGA Maxima Ultra Pure Water Systems. All other reagents were of analytical reagent grade.

General Procedure

A 2000 ml solution containing 1-50 μg of the metals was placed in an Erlenmeyer flask, and 2 ml of KPPzDC reagent solution (2.0%) was added. After the metal complexes were formed in aqueous phase (nearly 10 min), the pH was adjusted with 20 ml of phosphate buffer solution; 0.50 g activated carbon was added as an adsorbent and the mixture was vigorously stirred for 30 min. It was then passed through a glass filter (20 μm porosity) and washed with deionized water. The metal ions were eluted with 5.0 ml of 20% nitric acid (the enrichment factor was 400) and they were collected for measurement by FAAS.

Results and Discussion

Effect of pH

A 100 ml metal solution containing 3 mgl^{-1} of Mn(II), Cu(II), Cd(II) and Pb(II) was placed in a 250 ml Erlenmeyer flask and 2.0 ml of KPPzDC reagent solution (2.0%) was added. After the metal complexes were constituted in the aqueous phase, the pH of the solution was adjusted with NaH$_2$PO$_4$-HNO$_3$-KOH solutions; 0.50 g of activated carbon was added and the mixture was vigorously stirred for 30 min and it was then passed through a glass filter. The metal concentration was measured by FAAS and the recovery amount calculated. The results are presented in Figure 2. The adsorption pH of the metal ions is one of the most important parameters and it should be between 4 and 7. The pH should not fall below 4 because of the fast decomposition of dithiocarbamate anion at low pH levels. In addition, it should not rise above 7 as metal hydroxides precipitate and their hydroxo complexes can occur at high pH levels[19]. The adsorption of the metal ions was completed between pH 5 and 9 and pH 6.0-6.5 was chosen for the subsequent studies.
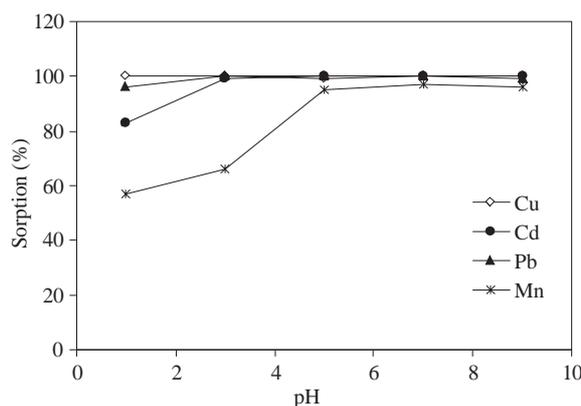
Figure 2. Effect of pH for the sorption of Cu(II), Cd(II), Pb(II) and Mn(II) on activated carbon.

Effect of Extraction Time

A 1000 ml metal solution containing 15 μgl^{-1} of Mn(II), Cu(II), Cd(II) and Pb(II) was obtained and extracted over various periods according to the procedure described previously. The adsorbent containing the metal complexes was eluted with concentrated HNO$_3$. The mixture was heated on a hot plate until dryness. It was then cooled and 5.0 ml of 20% HNO$_3$ solutions was added. The metal concentration of the solution was measured by FAAS and the recovery calculated. We found that the quantitative extraction of the metals finished at 30 min. The results are presented in Figure 3. The extraction period was 30 min.

Elution of the Metal Ions

The elution material is very important in the dithiocarbamate solid-phase extraction method. The metals on the solid phase can be eluted with isobutyl methyl ketone (IBMK) into the organic phase or with acid solutions (nitric or hydrochloric acid) into the aqueous phase. In addition, metal solutions such as Hg(II), Pd(II) or complexing agents such as potassium cyanide and EDTA can be used. Experience has shown that AAS may be handicapped by the presence of a complex organic matrix that causes severe suppression of analyte signal[18]. The use of metal solutions can create an interfering effect in metal analyses. Complexing

agents are very suitable, but because some metal dithiocarbamate complexes are more stable than cyanide or EDTA metal complexes, the elution efficiencies may be small. Thus, a nitric acid solution was selected for the elution of the metal ions. A 1000 ml solution containing 15 μgl^{-1} of Mn(II), Cu(II), Cd(II) and Pb(II) was extracted on activated carbon according to the general procedure. The adsorbent containing the metal complexes was eluted with various HNO$_3$ solutions. It was found that back extraction recovery was related to the concentration of the HNO$_3$ solutions. The results are given in Figure 4. The concentration selected was 20%.
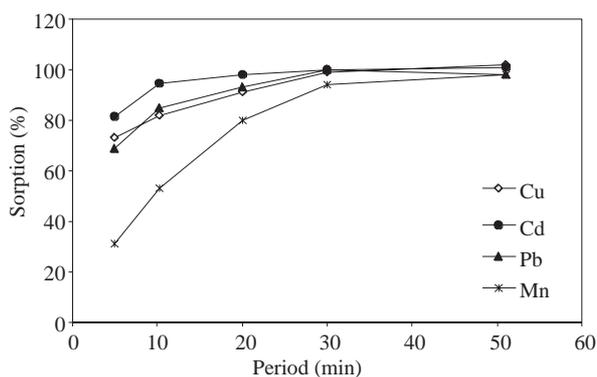
Figure 3. Effect of extraction time sorption of Cu(II), Cd(II), Pb(II) and Mn(II) on activated carbon.
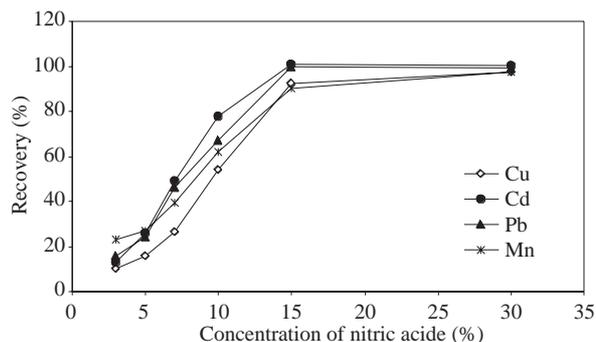
Figure 4. Effect of concentration of HNO$_3$ for the recoveriy of Cu(II), Cd(II), Pb(II) and Mn(II) on activated carbon.

Effect of Volume Aqueous Phase

The extraction of the metals was studied by varying volumes of the aqueous phase. Solutions containing 15 μg of metals were diluted from 50 to 4000 ml with deionized water and the metals were analyzed by the general procedure. The results are given in Figure 5. Quantitative extractions of the metals were attained with 2500 ml. The volume of the aqueous phase was selected to be 2000 ml.
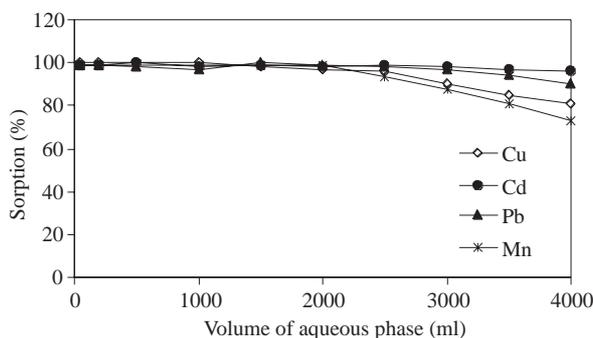
Figure 5. Effect of volume aqueous phase for the sorption of Cu(II), Cd(II), Pb(II) and Mn(II) on activated carbon.

Effect of the Diverse Salts

The effect of diverse salts on the determination of the metals was investigated with a sample solution containing 3 μgml^{-1} of metal and different metal salts. The determination of metal content was carried out by the general procedure. The tolerance limits (error $\leq 5\%$) are given in Table 1. Many of the salts can be tolerated up to gram levels.

Table 1. Tolerance limits* for diverse metal salts in 3 μgml^{-1} of Mn(II), Cu(II), Cd(II) and Pb(II) in deionized water.

Salt (mgml^{-1})	Mn	Cu	Cd	Pb
NaNO$_3$	>200	>200	>200	>200
NaCl	170	>200	>200	165
NaI	96	180	170	150
KCN	2.1	0.1	7.3	28
Na$_2$HPO$_4$	19	40	24	66
FeCl$_3$	17	19	36	72
Hg(NO$_3$)$_2$	13	8.3	3.6	25
Mn(NO$_3$)$_2$	-	38	22	34
Cu (NO$_3$)$_2$	43	-	36	57
Cd(NO$_3$)$_2$	16	54	-	62
Pb(NO$_3$)$_2$	65	32	23	-
sodium acetate	>200	190	>200	¿200
sodium tartrate	93	170	186	175
disodium EDTA	195	189	200	193
sodium oxalate	97	>200	187	156

*Tolerance limit is the maximum amount in which there is less than 5% effect on absorbance.

Calibration Curve, Detection Limit, Determination Limit and Recovery

Calibration graphs were constructed with eight standard solutions containing 1-100 μgml^{-1} of each of metal according to the general procedure. The linearly ranges, regression equation and correlation coefficient were obtained with the method of least squares. Detection and determination limits were evaluated as the concentration corresponding to three times and 10 times the standard deviations of the blank signal, respectively. The results are given in Table 2. In order to calculate the recoveries, spiked sample solutions were analyzed according to the general procedure. The results are presented in Table 3.

Table 2. The range of linearities, correlation coefficients, regression equations, detection and determination limits.

in HNO$_3$ 20% final solution	Mn(II)	Cu(II)	Cd(II)	Pb(II)
Linear ranges (μgml^{-1})	0.1-4	0.1 -6	0.1-4	0.5-14
Regression equation	1.2231X-0.0039	0.0847X+0.0026	0.1224X+0.0017	0.0368X+0.0012
Correlation coefficient (R^2)	0.998	0.998	0.999	0.997
Detection limit (ngml^{-1})	17	15	11	56
Determination limit (ngml^{-1})	142	136	98	443

Table 3. The recoveries of Mn(II), Cu(II), Cd(II) and Pb(II) in spiked sample solutions.

Sample	Added (μgl^{-1})	Recovery* (%)			
		Mn(II)	Cu(II)	Cd(II)	Pb(II)
Deionized water	5	94.8 ± 1.6	99.2 ± 0.6	99.3 ± 0.3	97.5 ± 0.2
	10	95.4 ± 0.8	99.4 ± 0.5	98.6 ± 0.9	96.4 ± 0.9
	15	93.1 ± 0.7	98.5 ± 0.2	100.2 ± 0.6	97.3 ± 0.5
River water	5	93.4 ± 0.7	98.3 ± 0.8	99.3 ± 0.8	95.7 ± 0.5
	10	94.8 ± 0.6	97.7 ± 0.9	99.6 ± 0.3	96.5 ± 0.7
	15	92.9 ± 0.8	99.5 ± 0.1	99.9 ± 0.7	97.2 ± 0.7
Seawater	5	90.1 ± 0.6	94.9 ± 0.7	96.8 ± 0.2	93.2 ± 0.3
	10	91.3 ± 0.4	96.3 ± 0.9	97.0 ± 0.3	94.8 ± 0.6
	15	92.8 ± 0.5	97.6 ± 0.6	98.4 ± 0.1	93.9 ± 0.7

* Values after ± are the relative standard deviation (%) for n = 4.

Applications

The method was applied successfully for the determination of Mn(II), Cu(II), Cd(II) and Pb(II) in river and seawater samples. River water samples were taken from Mert Irmağı and seawater samples were taken off the coast Samsun (Black Sea). The samples were filtered and HNO$_3$ was added to ensure a pH below 2. The pH was adjusted by phosphate buffer and analyzed by the general procedure. The results are presented in Table 4.

Table 4. Determination of Mn(II), Cu(II), Cd(II) and Pb(II) in water samples.

Samples	Mn(II)	Cu(II)	Cd(II)	Pb(II)
River water (μgl^{-1})	0.58 ± 0.3	1.27 ± 1.1	-	2.45 ± 0.4
Seawater (μgl^{-1})	0.96 ± 1.4	2.11 ± 1.8	0.39 ± 1.3	1.67 ± 1.9

* Values after ± are the relative standard deviation (%) for n = 4.

The method was also applied for the determination of Mn(II), Cu(II), Cd(II) and Pb(II) in standard metal alloys. The standard (1) sample contained 0.18% C, 0.45% Si, 0.032% S, 0.029% P, 0.70% Mn, 0.03% Sn, 0.005% Co, 0.10 % Mo, 0.35% Al, 0.29% W, 0.054% Ti, 0.02% V, 0.070% As, 0.31% Cr, 0.15% Cu and 0.18% Ni; while the standard (2) sample contained 0.027% Pb, 0.10% Mg, 4.0% Al, 0.085% Fe, 0.006% Sn, 1.41% Cu, 0.018% Ni, 0.001% Mn, and 0.003% Cd. A 1.0000 g sample of the alloy was placed in a 100 ml beaker and 10 ml of HNO$_3$ and 20 ml of HCl were added. The mixture was heated on a hot plate until near dryness. Then, 5 ml of nitric acid was added and it was diluted with deionized water. It was filtered and made up to 1000 ml in a standard flask. An aliquot of the solution of alloy was taken and the amount of the

metal was determined by the proposed method. For the standard (1) and standard (2) samples, the results given in Table 5 are in good agreement with the certified values.

Table 5. Determination of Mn(II), Cu(II), Cd(II) and Pb(II) in various alloys.

Standard alloys	Found*	(mgl^{-1})	Taken (mgl^{-1})
Standard (1) 12X3500	Mn(II)	3.4 ± 0.8	3.5
Mild steel	Cu(II)	3.0 ± 1.4	3.0
Standard (2)	Cu(II)	1.42 ± 1.2	1.41
43 X Z3 F Zn / Al / Cu	Cd(II)	3.1 ± 2.0	3.0
Zinc base alloy	Pb(II)	2.6 ± 0.4	2.7

* Values after are the relative standard deviations (%) for n = 4

Conclusion

The dithiocarbamate solid phase extraction method is a very selective and useful technique for the separation and pre-concentration of trace metals. In this technique, sorption of the metal ions is particularly related to the chelating agent. The effect of dithiocarbamate reagents on the sorption of various metals has been studied previously[20]. From the extraction point of view, the efficiency of the present phenylpiperazine dithiocarbamate reagent, particularly for Mn(II), and Cd(II) is more advantageous than the traditional reagent, namely of sodium diethyldithiocarbamate.

In this study, it was found that using the PPzDC reagent for the pre-concentration of trace Mn(II), Cu(II), Cd(II) and Pb(II) in water samples prior to their determination by FAAS is beneficial due to higher recoveries. In the presence of the same diverse ions, which are fairly abundant in environmental samples, the reagent provides more quantitative results. The metals adsorbed on to activated carbon could be easily eluted with a 20% HNO_3 solution. In conclusion the present method is selective and accurate, and could be used for the determination of Mn(II), Cu(II), Cd(II) and Pb(II) in water samples, alloys and other materials.

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