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Multi-element preconcentration of heavy metal ions from aqueous solution by APDC impregnated activated carbon

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Abstract

Ammonium pyrrolidinedithiocarbamate impregnated activated carbon (APDC-AC) has been used for the preconcentration of Cd(II), Cu(II), Ni(II), and Zn(II) from aqueous solution by column solid phase extraction (SPE) technique. Trace metal ions in aqueous solution were quantitatively sorbed onto APDC-AC packed in a SPE column at pH 5.0 with a flow rate of 1.0 mL min^{-1}. The sorbed metals were eluted with 1 M nitric acid in acetone solution at a flow rate of 0.6 mL min^{-1} and analyzed by flame atomic absorption spectrometry. The effects of sample volume, amount of APDC-AC, volume of eluent and ionic strength of working solution on metal ion recovery have been investigated. The present methodology gave recoveries from 90 to 106% and R.S.D. from 0.6 to 5.5%.

Keywords: Preconcentration; Pyrrolidinedithiocarbamate; Activated carbon; Trace metal

1. Introduction

Various techniques have been applied for the determination of trace heavy metals in aqueous samples. Direct instrumental analysis of these samples is difficult because of complex formation and significant matrices, which invariably influence normal instrumental analysis [1]. In addition, some metals have low concentrations, which are near or below the limit of detection of the instrument. Preconcentration can solve the above two problems and leads to simplified heavy metal determination. There are many methods of preconcentration, including coprecipitation, solvent extraction, electrodeposition, membrane extraction, and solid phase extraction. In this work, solid phase extraction (SPE) was used to preconcentrate Cd, Cu, Ni, and Zn from aqueous solution.

Solid phase extraction offers a number of important benefits. It reduces solvent use, solvent exposure, disposal costs and extraction time for sample preparation. Consequently, in recent years SPE has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples.

Activated carbon has been widely used for many purposes both in the laboratory and industrial settings, due to its ability to adsorb organic compounds and organic metal complexes. Since its introduction in analytical chemistry, enrichment of trace metals using activated carbon has been carried out with very high preconcentration factors in different matrices [2].

There are general approaches to metal preconcentration using activated carbon from aqueous solutions by simply adjusting the pH to an adequate value and by using chelating agent [3]. The use of commercial and fabricated activated carbon from different natural sources for sorption and determination of metals has been recently reported [4–10]. However, activated carbon alone does not adsorb metal ions quantitatively at trace levels. Some authors reported the adsorption of metallic complexes onto activated carbon after complexation with chelating agents; for example, pyrocatechol violet for Cu, Mn, Co, Cd, Pb, Ni, and Cr [11], 8-hydroxyquinoline for Cd [12], *O*,*O*-diethyl-dithiophosphate for Pb [13], pyridyl azo resorcinol for Cu, Co, Cd, Cr, Ni, Pb, and V [14] and thiourea and bromide ion for Bi [15]. The disadvantage of

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these procedures is that it requires a series of complexation steps. For this reason, the use of chelating activated carbon has been recently proposed, such as activated carbon modified with chitosan for Cr(VI) removal [16], 1-(2-thiazolylazo)-2-naphthol for Hg(II) recovery [17], and diarylazobisphenol for U(VI) extraction [18]. The above mentioned chelating activated carbons have been used for single element recovery. To our knowledge, there is no chelating activated carbon reported for multi-element preconcentration of heavy metals.

Ammonium pyrrolidinedithiocarbamate (APDC) is one of a few chelating agents that permits the preconcentration of trace metals from solution [19]. The standard method for determination of trace metals in aqueous samples involves the use of APDC for complex formation, followed by extraction of the metal complex with methyl isobutyl ketone (MIBK) [20] and subsequent determination by flame atomic absorption spectrometry (FAAS). The disadvantages of this technique are that it requires a large amount of solvent and takes significant time to complete. APDC was also added to Sb(III), Pb(II), Cu(II), Cd(II) solutions in order to form complexes which were subsequently adsorbed on C_{18}-silica gel [3]. In addition, APDC was used to form complexes with Ni, Cd, Cu, Co, and Pb followed by adsorption on cellulose nitrate membrane [21] and to form complexes with Cu [22] and Pb [23] before being separated by activated carbon.

In this work, we combined the advantages of activated carbon and APDC for the simultaneous preconcentration of Cd, Cu, Ni, and Zn in aqueous solution, and subsequent atomic absorption spectroscopic determination. The selected method was applied for determination of the metals in water samples.

2. Experimental

2.1. Apparatus

A UV–vis Spectrophotometer (Hewllet Packard Model HP8453) was used for the determination of the APDC concentration at 277 nm. A flame atomic absorption spectrometer (Perkin-Elmer Model AAnalytst100) was used to determine metal concentrations using an air/acetylene flame. The analytical wavelength of Cd, Cu, Ni and Zn are 228.8, 324.8, 232.0 and 213.9 nm, respectively. The SPE was performed using a Visiprep^{TM} Vacuum Manifold and 6 mL polyethylene tubes and frits (Supelco). A digital pH meter (Hanna instruments Model pH 211) was used for all pH measurements.

2.2. Materials and reagents

All reagents and solvents were standard analytical grade and used without further purification. De-ionized water was obtained from cation and anion exchange resin columns. The conductivity of the de-ionized water was less than 18 μS cm^{-1}. APDC (Sigma) solution (1%, w/v) was prepared daily by dissolving APDC in de-ionized water. Working standard solutions of Cd, Cu, Ni, and Zn were prepared by stepwise dilution of 1000 mg L^{-1} stock standard solutions (BDH Laboratory Supplies) in 0.008 M ammonium acetate buffer (pH 5). Ammonium acetate buffer solution was prepared by adding an appropriate amount of acetic acid (Fisher Scientific) to ammonium acetate (Carlo Erba Reagenti) solution until pH 5 was attained.

2.3. Preparation of APDC impregnated activated carbon (APDC-AC)

Activated carbon powder (Merck) was treated with 20% nitric acid, washed with de-ionized water and oven-dried at 110 °C. SPE tubes and frits were soaked in 1% nitric acid overnight and then washed with water. The cleaned frit was placed on the bottom of the SPE tube. The column was then filled with washed activated carbon (AC) and ready for the SPE experiments. The AC (500 mg) was impregnated with APDC by percolating 10 mL of 1% (w/v) APDC solution through the column packed with AC at a flow rate of 1 mL min^{-1}. The filtrate was collected and analyzed for unadsorbed APDC with the UV–vis spectrophotometer at 277 nm. The column was then washed twice with 5 mL water and the filtrates were analyzed for APDC that was released. The retained amount of APDC on the AC column was 69 mg/g (12% relative range).

2.4. Extraction procedure

The metal solutions (0.8 mg L^{-1} of each metal) were passed through the APDC-AC column at a flow rate of 1 mL min^{-1}. The filtrate was collected and analyzed for unsorbed metals by FAAS. The effects of sample volume, amount of APDC-AC, and working solution ionic strength on the recoveries of metal ions were investigated.

2.5. Desorption procedure

The desorption of retained metal from the column containing 500 mg APDC-AC was investigated using 50 mL of various eluting agents. A standard solution for preconcentration contained 0.8 mg L^{-1} Cu(II) (pH 5, 50 mL). One molar of nitric acid, 5 M nitric acid, acetone, 1 M nitric acid in acetone and MIBK were used as eluents. Afterwards, the best eluent was chosen and used in the preconcentration of Cd(II), Cu(II), Ni(II), and Zn(II). The effect of volume of eluent on the recoveries of metal ions has also been investigated.

2.6. Determination of metals in water sample

Natural surface water and tap water were collected by grab sampling method in a polypropylene container from Chulalongkorn pond (10 cm depth from the surface) and at the Faculty of Science, Chulalongkorn University, Bangkok in October 2004, respectively. The samples were immediately filtered through 0.45 μm cellulose nitrate membranes (Millipore) before analysis. For the preconcentration, 2 mL of 0.2 M acetate buffer was added into 50 mL of the sample to attain pH 5. The sample solution was passed through a SPE column packed with 100 mg APDC-AC at a flow rate of 1 mL min^{-1}. The sorbed metals were eluted with 1 M nitric acid in acetone solution at a flow rate of 0.6 mL min^{-1}. The eluant was then rapidly evaporated with a heating gun to 1 mL, transferred to a 5 mL volumetric flask, and diluted with de-ionized water. Finally, the metals were determined by FAAS. The accuracy of the method was examined by adding 2 and 5 μg of each metal ion into water samples. The spiked water samples were analyzed by the procedure mentioned earlier. The accuracy and precision are reported in terms of recovery (%) of metals and R.S.D. (%), respectively. The limit of detection was measured by using 50 mL of de-ionized water as a blank following the same preconcentration procedure.

3. Results and discussion

3.1. *Efficiency of impregnated activated carbon*

The efficiency of the APDC-AC column for the sorption of metals was studied by using 500 mg of APDC-AC in comparison with 500 mg of AC for preconcentration of metals in a model solution. Starting with 40 μg of each metal in 50 mL of solution, the quantity of unretained metals in the filtrate was determined by FAAS. The percentage sorption of the metals retained on the sorbents was calculated from the difference between the starting amount of each metal (mg) (N_s) and the amount of metal (mg) left in the filtrate (N_f) according to Eq. (1):

$$\text{sorption}\,(\%) = \frac{N_s - N_f}{N_s} \times 100 \quad (1)$$

The results are shown in Table 1. The APDC-AC can retain all the metal ions while the untreated AC cannot quantitatively retain Cd, Ni and Zn. Evidently, the preconcentration of the metals with the untreated AC is not suitable for Cd, Ni and Zn. Therefore, APDC-AC seems to be a better sorbent in simultaneous sorption of the studied elements.

3.2. *Desorption of metals*

An appropriate eluent for metal desorption was selected by taking into account the following considerations: (i) the eluent should desorb the metals or chelate complexes, (ii) the eluent should not destroy the sorbent and (iii) the eluent should be suitable for the subsequent determination technique [23]. Organic solvents and inorganic acids have been found to meet the requirements.

Table 1
Percentage of metal sorption of untreated (AC) and impregnated activated carbon (APDC-AC)

Element	Sorption[a] (%)	
	AC	APDC-AC
Cd	14.8 ± 1.3	>99.4
Cu	>99.7	>99.7
Ni	29.1 ± 0.6	>99.9
Zn	12.2 ± 2.7	>99.8

[a] Mean value ± confidence interval at 95%, $n = 3$.

In our study, all metal ions have the same d-10 valence electrons so the adsorption on APDC-AC and desorption mechanisms are possibly similar. Cu(II) ion was chosen as a representative ion for the desorption study. In this experiment, the standard solution for preconcentration was 0.8 mg L^{-1} Cu(II) (pH 5, 50 mL). The eluents chosen were MIBK, 1 M nitric acid, 5 M nitric acid, acetone and 1 M nitric acid in acetone. The effectiveness of metal desorption from APDC-AC was evaluated from the recovery (%) of copper. The recovery (%) in this section was calculated from the amount of metals (mg) in the starting solution (N_s) and the amount of metals (mg) eluted from the column (N_f) according to Eq. (2). The results are summarized in Table 2:

$$\text{recovery}\,(\%) = \frac{N_f}{N_s} \times 100 \quad (2)$$

Table 2
Recovery of Cu with various eluents

Eluent	Recovery[a] (%)	R.S.D. (%)
MIBK	–	–
Acetone	20.2	–
1 M nitric acid	10.8	10.8
5 M nitric acid	7.5	7.3
1 M nitric acid in acetone	97.1	7.9

[a] Mean value, $n = 3$.

According to Table 2, MIBK could not elute the Cu(II), while the other solvents could elute Cu(II) with recoveries (%) ranging from 7 to 97%. It is clear that 1 M nitric acid in acetone was the best eluent allowing 97% recovery and 7.94% R.S.D. Thus, this solvent mixture was chosen for the desorption of all heavy metals studied in further experiments.

The recovery of Cd, Cu, Ni and Zn was investigated. A solution containing four metal ions (0.8 mg L^{-1} of each metal ion) was used in this experiment. Fifty milliliters of solution was percolated through the column with a flow rate of 1 mL min^{-1}. The elution step was performed using a flow rate of 0.6 mL min^{-1}. The recoveries of Cd, Cu, Ni and Zn using 1 M nitric acid in acetone as eluent are shown in Table 3. The results show that the recoveries higher than 96% with R.S.D. values less than 5% could be obtained for all metal ions.

Table 3
Recoveries of Cd, Cu, Ni, and Zn using 1 M nitric acid in acetone as eluent

Element	Recovery[a] (%)	R.S.D. (%)
Cd	96.9	4.5
Cu	101.7	2.4
Ni	99.5	4.7
Zn	104.8	4.5

[a] Mean value, $n = 3$.

3.3. Effect of the sample volume on the metal sorption

For the analysis of a real sample using preconcentration, the sample volume is one of the most important parameters for obtaining high preconcentration factors. In this study, the effect of sample volume on the sorption behavior of the analytes was investigated by passing 10, 50 and 100 mL of solutions containing Cu, Cd, Ni and Zn ion (40 μg of each metal ion) into a column (500 mg APDC-AC) and comparing the percentage of metal sorption.

More than 99% of each metal was retained on the column. The sorption of the metal ions was not affected by sample volume between 10 and 100 mL. Thus, a sample volume in this range could be used in our procedures. The recovery of metals using 1 M nitric acid in acetone were in the range of 95–106%.

3.4. Effect of the amount of activated carbon and eluent volume

In the adsorption step, an appropriate amount of activated carbon should be used in order to obtain quantitative retention of metals. On the other hand, an excess amount of the sorbent also prevents the quantitative elution of the retained metals by a small volume of eluent [11]. For this reason, the effect of the amount of activated carbon and the eluent volume were examined. The solutions used in this experiment contained 20 μg of each metal ion (50 mL, pH 5). The amount of APDC-AC was varied in the range of 100–700 mg. The sorbed metals were then eluted by 1 M nitric acid in acetone with a flow rate of 0.6 mL min^{-1}. The volume of the eluent was varied from 10 to 50 mL. The results are shown in Fig. 1.

In this study, metal ions could be quantitatively retained on the columns containing the studied amounts of sorbent. In the case of 100 mg of APDC-AC, the volume of eluent from 10 to 50 mL did not affect the recoveries of the metals. When higher amounts of sorbent was used, the metal recoveries increased with increasing volume of eluent. In this study, 100 mg of APDC-AC and 10 mL of eluent are ideal for the preconcentration of metal at a concentration of 20 μg or less in the solution having volumes up to 100 mL.

3.5. Effect of ionic strength

Common cations such as sodium, calcium, and magnesium are always found in water samples and have the capability to compete with many metal ions to complex with ligands, and common anions such as nitrate and chloride have the ability to bind with metal ions. Therefore, in their presence the efficiency of the impregnated ligand to bind metal ions may be reduced resulting in a reduction of the recovery. From the literature, Goswami and Singh [24] also mentioned

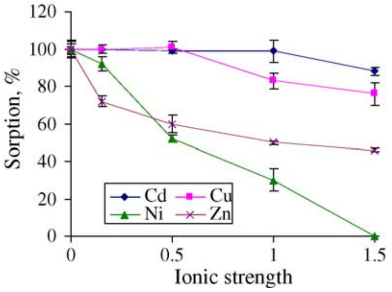

Fig. 2. Effect of ionic strength on metal sorption ($n = 2$).

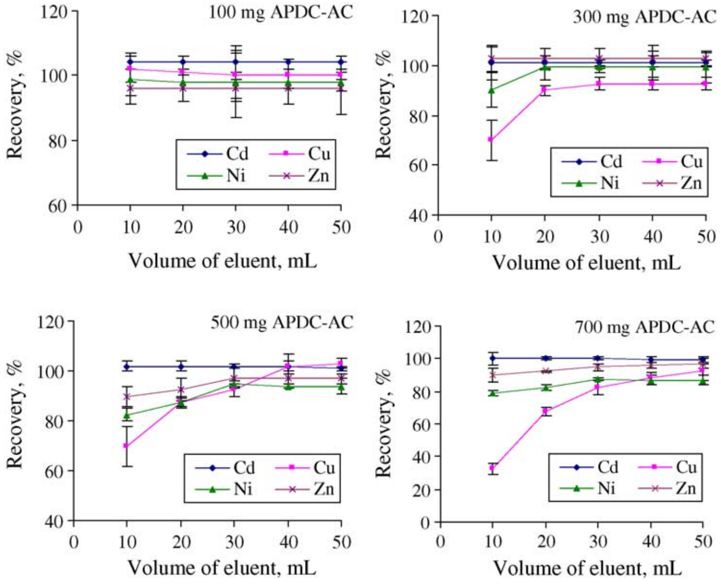

Fig. 1. Effect of the volume of eluent for 100–700 mg of APDC-AC ($n = 2$) (20 μg of each metal).

Table 4
Concentration and recoovery of Cd, Cu, Ni, and Zn in water samples (50 mL)

Sample	Element	Added (μg)	Found[a] (μg)	Recovery[b] (%)	R.S.D. (%)
Tap water	Cd	–	ND	–	–
		2	1.80 ± 0.12	90.0	2.8
		5	4.76 ± 0.37	95.2	3.2
	Cu	–	ND	–	–
		2	1.96 ± 0.25	98.0	5.1
		5	5.17 ± 0.50	103.4	3.9
	Ni	–	ND	–	–
		2	1.87 ± 0.20	93.5	5.3
		5	4.94 ± 0.20	98.8	1.6
	Zn	–	ND	–	–
		2	2.02 ± 0.25	101.0	5.0
		5	4.99 ± 0.30	99.8	2.4
Chulalongkorn pond water	Cd	–	ND	–	–
		2	1.83 ± 0.15	91.5	3.3
		5	4.51 ± 0.07	90.2	0.7
	Cu	–	ND	–	–
		2	2.12 ± 0.15	106.0	2.8
		5	4.58 ± 0.22	91.6	2.0
	Ni	–	ND	–	–
		2	2.03 ± 0.12	101.5	2.5
		5	5.04 ± 0.25	100.8	2.0
	Zn	–	ND	–	–
		2	2.04 ± 0.15	102.0	2.9
		5	5.08 ± 0.07	101.6	0.6

[a] Mean value ± confidence interval at 95%.

[b] Mean value, $n = 3$; ND = not detectable.

that sodium nitrate at concentrations higher than 0.08 M had an effect on the sorption efficiency of Zn and Cd ions in model solutions on modified silica gel. The total amount of ions can be represented by the ionic strength.

In this study, the effect of ionic strength on the sorption of metals was tested by adding sodium nitrate in the range of 0–1.5 M into a model solution containing 0.4 mg L^{-1} of each metal ion at pH 5. The results are shown in Fig. 2. In the presence of sodium and nitrate ions, the sorption (%) of Zn decreased sharply. When the amount of sodium nitrate was higher than 0.1 M, Ni could be sorbed less than 90%. The sorption (%) of Cu and Cd diminished from 100% when the concentration of sodium nitrate was higher than 0.5 and 1.0 M, respectively. The results attributed the effect of ionic strength on the sorption of the metal ions.

3.6. Method detection limit

The method detection limits were calculated by three times the standard deviation ($n = 15$) of the blank. The values were 20 ng L^{-1} for Cd, 19 ng L^{-1} for Cu, 23 ng L^{-1} for Ni, and 28 ng L^{-1} for Zn. These limits were based on 50 mL of blank undergoing the preconcentration. They can be improved by increasing the sample volume.

3.7. Determination of metals in water sample

The proposed method was applied for the determination of Cd, Cu, Ni, and Zn in tap water and natural water samples. The results are given in Table 4. The recoveries of the metal ions were in the order of 90–106%. The R.S.D. values were less than 6%. The concentrations of the metal ions in the samples were lower than the method detection limit.

4. Conclusion

A simultaneous preconcentration of Cd(II), Cu(II), Ni(II), and Zn(II) from aqueous solution on an activated carbon impregnated with ammonium pyrrolidinedithiocarbamate column was successfully developed. The conditions for preconcentration of metal ions were selected using model solutions. The accuracy and precision of the proposed SPE method was reported in term of recovery (%) ranging from 90 to 106%, and R.S.D. (%) ranging from 0.6 to 5.5%. The proposed method can be applicable for the determination of trace metal ions in a variety of water samples with low detection limit, high accuracy and high precision.

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