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Determination of Trace Metals in Water Samples by Flame Atomic Absorption Spectrometry using Column Solid-Phase Extraction

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Novel and sensitive method exploiting solid-phase extraction (SPE) was developed for the determination of Co, Cu, Ni, Zn and Cd in water samples. Sodium diethyldithiocarbamate (Na-DDC) is impregnated with activated carbon has been used in this preconcentration technique. At pH 4.5 these trace metal ions were quantitatively sorbed and eluted with 1 M nitric acid in acetone solution at a flow rate of 1.5 mL min^{-1} The effects of sample volume, volume of eluent and recovery have been investigated. The developed method was applied to the determination of trace metal ions with satisfactory results. The reliability of the procedures has been verified by analyzing standard reference materials. Results obtained are in good agreement with the certified values and the relative standard deviations.

Key Words: Solid-phase extraction, Sodium diethyldithiocarbamate, Activated carbon, Water samples, Flame atomic absorption spectrometry.

INTRODUCTION

Now a day's determination of trace metals in environmental samples is essential, because of these metals have been used in various industries. Various techniques have been reported for the determination of trace metals in environmental samples. Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions. However, direct determination of metal ions at trace levels by FAAS is limited due to their low concentrations and matrix interferences[1]. In trace analysis, therefore, preconcentration leads to simplify trace metal determination. Several methods of preconcentration, include solvent extraction[2,3], adsorption[4,5], membrane extraction[6], coprecipitation[7-9], ion-exchange[10,11] etc,. But, solid-phase extraction (SPE) is multielement preconcentration methods because of its simplicity, rapidity and ability to attain a high concentration factor.

Activated carbon has been widely used for many purposes due to its ability[12,13], to adsorb organic compounds and organic metal complexes. Enrichment of trace metals using activated carbon has been carried out with very high preconcentration factors in different matrices[14-20]. Sodium diethyldithiocarbamate (Na-DDC) is one of a few chelating agents that permits the preconcentration of trace metals from solution[21]. The standard method for determination of trace metals in water samples involves the use of NA-DDC for complex formation, followed by extraction of the metal complex with methyl isobutyl ketone (MIBK)[22] and subsequent determined by flame atomic absorption spectrometry (FAAS).

In the present study, sodium diethyldithiocarbamate was impregnated onto activated carbon for the preconcentration of Co, Ni, Cu, Zn and Cd in water samples by AAS.

EXPERIMENTAL

Flame atomic absorption spectrometer (Perkin-Elmer Model Analytst100) was used to determine metal concentrations using an air/acetylene flame. The instrumental parameters were those recommended by the manufacturer. The wavelengths (nm) selected for the determination of the analytes were as follows: Co 240.7, Ni 232.0, Cu 324.8, Zn 213.9 and Cd 228.8 nm. The SPE was performed using 25 mL polyethylene tubes and frits. A digital pH meter (Elicho Li 129 model) was used for all pH measurements.

All reagents and solvents were standard analytical grade and used without further purification. Double distilled water has been used for the preparation of the all reagents. Na-DDC (Sigma) solution (1%, w/v) was prepared daily by dissolving Na-DDC in double distilled water. Working standard solutions of Co, Ni, Cu, Zn and Cd, were prepared by stepwise dilution of 1.0 μg L^{-1}. Stock standard solutions in 0.007 M sodium acetate buffer (pH 4.5). Sodium acetate buffer solution was prepared by adding an appropriate amount of acetic acid to sodium acetate solution until pH 4.5 was attained.

Preparation of Na-DDC impregnated activated carbon (Na-DDC-AC): Activated carbon powder (Merck) was treated with 20 % nitric acid and washed with double distilled water and dried at room temperature for 24 h. SPE tubes and frits were soaked in 1% nitric acid overnight and then washed with double distilled 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 (450 mg) was impregnated with Na-DDC by percolating 10 mL of 1 % (w/v) Na-DDC solution through the column packed with AC at a flow rate of 1.5 mL min^{-1}. The column was then washed twice with 4 mL distilled water, impregnated with Na-DDC and analysed by FAAS. The retained amount of Na-DDC on the AC column was 65 mg/g (11 % relative range).

Extraction procedure: The metal solutions (0.75 µg L^{-1} of each metal) were passed through the Na-DDC-AC column at a flow rate of 1.5 mL min^{-1}. The filtrate was collected and analyzed for unsorbed metals by FAAS. The effects of sample volume, amount of Na-DDC-AC, and working solution ionic strength on the recoveries of metal ions were investigated.

Desorption procedure: The desorption of retained metal from the column containing 450 mg Na-DDC-AC was investigated using 50 mL of various eluting agents. A standard solution for preconcentration contained 0.75 µg L^{-1} Cu(II) (pH 4.5, 50 mL). 1 M 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 Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The effect of volume of eluent on the recoveries of metal ions has also been investigated.

Determination of metals in water sample: Natural surface water and tap water were collected by grab sampling method in a polypropylene container from Kapilatheertham (10 feet depth from the beginning) and at Chandragiri Gram panchayat, 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 4.5. The sample solution was passed through a SPE column packed with 100 mg Na-DDC-AC at a flow rate of 1.5 mL min^{-1}. The sorbed metals were eluted with 1 M nitric acid in acetone solution at a flow rate of 0.9 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 double distilled 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 RSD (%), respectively. The limit of detection was measured by using 50 mL of double distilled water as a blank following the same preconcentration procedure.

RESULTS AND DISCUSSION

Efficiency of impregnated activated carbon: The efficiency of the Na-DDC-AC column for the sorption of metals was studied by using 450 mg of Na-DDC-AC in comparison with 450 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). The Na-DDC-AC can retain all the metal ions while the untreated AC cannot quantitatively retain Co, Ni, Zn and Cd. Evidently; the preconcentration of the metals with the untreated AC is not suitable for Co, Ni, Zn and Cd. Therefore, Na-DDC-AC seems to be a better sorbent in simultaneous sorption of the studied elements.

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. Organic solvents and inorganic acids have been found to meet the requirements. In present study, all metal ions have the same *d*-10 valence electrons so the adsorption on Na-DDC-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 0.75 μg L^{-1} Cu (II) (pH 4.5, 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 Na-DDC-AC was evaluated from the recovery (%) of copper. The recovery (%) in this section was calculated from the amount of metals (μg) in the starting solution (*N*s) and the amount of metals (μg) eluted from the column (*N*f). According to experimental observations, MIBK could not elute the Cu (II), while the other solvents could elute Cu (II) with recoveries (%) ranging from 8 to 98.60 %. It is clear that 1M nitric acid in acetone was the best eluent allowing 98.60% recovery and 7.89% R.S.D. Thus, this solvent mixture was chosen for the desorption of all heavy metals studied in further experiments.

The recovery of Co, Ni, Cu, Zn and Cd was investigated. A solution containing 5 metal ions (0.75 μg L^{-1} of each metal ion) was used in this experiment. 50 mL of solution was percolated through the column with a flow rate of 1.5 mL min^{-1}. The elution step was performed using a flow rate of 0.9 mL min^{-1}. The recoveries of Co, Ni, Cu, Zn and Cd using 1 M nitric acid in acetone as eluent are shown in Table-1. The results show that the recoveries higher than 97.20 % with RSD values less than 5 % could be obtained for all metal ions.

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 behaviour of the analytes was investigated by passing 10, 50 and 100 mL of solutions containing Co, Ni, Cu, Zn and Cd ion (40 μg of each metal ion) into a column (450 mg Na-DDC-AC) and comparing the percentage of metal sorption. More than 99.5 % 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 was in the range of 97.2-107.0 %.

TABLE-1
RECOVERIES OF TRACE ELEMENTS USING ELUENT

Element	Recovery[a] (%)	RSD (%)
Co	97.2	4.6
Cu	104.6	2.6
Ni	102.0	4.9
Zn	106.4	4.2
Cd	94.7	4.8

[a] Mean value, n=5.

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. 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 4.5). The amount of Na-DDC-AC 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 0.9 mL min^{-1}. The volume of the eluent was varied from 10 to 50 mL. 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 Na-DDC-AC, the volume of eluent from 10 to 50 mL did not affect the recoveries of the metals. When higher amounts of sorbent were used, the metal recoveries increased with increasing volume of eluent. In this study, 100 mg of Na-DDC-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.

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 interact with metal ions. Therefore, the interaction of the impregnated ligands with metal ions may be reduced resulting in a reduction of the recovery.

TABLE-2

CONCENTRATION AND RECOVERY OF Co, Cu, Ni, Zn AND Cd IN WATER SAMPLES

Metal	Added (μg)	Well water[1]			Gram Panchat water[2]			River water[3]		
		Found[a] (μg)	Recovery[b] (%)	RSD (%)	Found[a] (μg)	Recovery[b] (%)	RSD (%)	Found[a] (μg)	Recovery[b] (%)	RSD (%)
Co	-	ND	-	-	ND	-	-	ND	-	-
	2	1.96 ± 0.08	98.0	1.6	1.95 ± 0.26	97.9	3.2	1.95 ± 0.18	97.7	3.6
	3	2.93 ± 0.16	97.8	2.7	2.98 ± 0.08	99.4	2.8	3.13 ± 0.20	104.5	4.6
	4	4.04 ± 0.32	101.2	4.6	4.10 ± 0.12	102.6	1.6	4.02 ± 0.32	100.7	1.8
	5	4.98 ± 0.10	99.6	3.2	4.98 ± 0.06	99.6	4.2	4.93 ± 0.12	98.6	3.2
Cu	-	1.75 ± 0.16	99.0	2.3	ND	-	-	1.72 ± 0.26	98.7	2.2
	2	1.94 ± 0.14	97.2	5.6	1.97 ± 0.10	98.6	5.2	1.99 ± 0.10	99.6	1.8
	3	2.94 ± 0.08	98.0	3.2	3.20 ± 0.16	106.8	2.8	2.96 ± 0.14	98.8	3.4
	4	4.26 ± 0.10	106.5	1.8	4.09 ± 0.24	102.4	3.6	4.28 ± 0.02	107.0	4.6
	5	4.91 ± 0.06	98.2	4.3	5.04 ± 0.06	100.8	2.4	5.21 ± 0.06	104.2	3.6
Ni	-	ND	-	-	ND	-	-	ND	-	-
	2	1.97 ± 0.08	98.6	0.8	2.02 ± 0.28	101.2	3.4	1.98 ± 0.22	99.4	2.6
	3	3.01 ± 0.24	101.2	3.6	2.95 ± 0.32	98.6	3.7	2.95 ± 0.28	98.6	2.4
	4	3.91 ± 0.22	97.9	1.7	4.17 ± 0.24	104.4	2.8	3.92 ± 0.32	98.2	3.2
	5	4.93 ± 0.20	98.7	2.6	4.97 ± 0.18	99.5	1.6	5.02 ± 0.06	100.4	2.8
Zn	-	1.65 ± 0.36	98.2	3.2	ND	-	-	1.76 ± 0.18	98.8	1.6
	2	2.05 ± 0.26	102.8	1.8	1.95 ± 0.12	97.6	2.6	2.10 ± 0.22	105.2	0.9
	3	3.01 ± 0.32	100.6	2.9	2.99 ± 0.16	99.8	1.7	2.99 ± 0.24	99.8	2.4
	4	3.98 ± 0.34	99.7	4.6	4.02 ± 0.22	100.7	2.2	4.02 ± 0.18	100.6	2.6
	5	4.93 ± 0.08	98.6	2.3	4.92 ± 0.08	98.4	3.4	4.89 ± 0.16	97.9	1.8
Cd	-	ND	-	-	ND	-	-	ND	-	-
	2	1.94 ± 0.28	97.4	3.4	1.96 ± 0.18	98.2	3.4	2.04 ± 0.12	102.3	2.8
	3	2.95 ± 0.30	98.6	5.6	2.99 ± 0.06	99.7	1.6	3.10 ± 0.06	103.4	1.7
	4	4.09 ± 0.18	102.4	1.2	4.09 ± 0.22	102.4	0.7	4.20 ± 0.22	105.2	0.6
	5	4.99 ± 0.06	99.4	3.7	4.98 ± 0.02	99.6	2.9	5.03 ± 0.04	100.6	1.2

[1]well water collected at in and around Chandragiri mandalam; [2] Collected tap water from Chandragiri Gram panchayats, [3]River water collected near Renigunta industrial area; [a]Mean value± confidence interval at 98.9 %; [b]Mean value, n=5; ND= not detectable.

In the present investigation, the effect of ionic strength on the sorption of metals was tested by adding sodium nitrate in the range of 0.5-2.0 M into a model solution containing 40 μg mL^{-1} of each metal ion at pH 4.5.

Method detection limit: The method detection limits were calculated by 5 times the standard deviation (n = 25) of the blank. The values were 0.26 ng mL^{-1} for Co, 0.16 ng mL^{-1} for Cu, 0.21 ng mL^{-1} for Ni, 0.31 ng mL^{-1} for Zn and 0.24 ng mL^{-1} for Cd. These limits were based on 50 mL of blank undergoing the preconcentration. They can be improved by increasing the sample volume.

Determination of metals in water sample: The proposed method was applied for the determination of Co, Ni, Cu, Zn and Cd in well water, tap water and river water samples. The results are given in Table-2. The recoveries of the metal ions were in the order of 97.2-107.0 %. The RSD values were less than 6 %. The concentrations of the metal ions in the samples were lower than the method detection limit.

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