Uses of Activated Carbon Columns for Solid Phase Extraction Studies Prior to Determinations of Traces Heavy Metal Ions by Flame Atomic Absorption Spectrometry

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Column solid phase extractions of trace heavy metal ions from various matrices including natural water, urine, etc. have been widely used by using activated carbon. The separation/pre-concentration methods developed for the atomic absorption spectrometric determination of trace heavy metals in our laboratory based on activated carbon column are reviewed in the present study.

Key Words: Activated carbon, Solid phase extraction, Preconcentration, Flame atomic absorption spectrometry.

INTRODUCTION

To overcome matrix effects and increase sensitivity for the determination of trace metals in various samples including urine, salts, dialysis concentrates, highly saline water samples, etc., preliminary preconcentration and/or selective separation step is necessary. Among the many preconcentration methods used in the analytical procedures, membrane filtration, liquid-liquid extraction, cloud point extraction and sorption on solid sorbents and exchangers are most useful for combination with flame atomic absorption spectrometry[1–10].

Column techniques based on solid phase extraction of the heavy metals are popular. Activated carbon has been used for separation and preconcentration of trace metal ions. Generally, activated carbon filters were used for this purpose. The use of activated carbon on the columns is limited.

In order to use activated carbon on the chromatographic column procedures for preconcentration and separation of trace heavy metal ions from the several matrices, firstly metal-chelates are introduced with a chelating agent in an aqueous solution. These metal-chelates are sorbed on activated carbon, then are desorbed from activated carbon with a suitable eluting agent to a few mL volume. The concentrations of the trace heavy metal ions in the eluent are detennined by using instrumental methods such as AAS, ICP-OES, ICP-MS, spectrophotometry etc.

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This paper describes a review of the studies performed in our laboratory by using activated carbon columns for the preconcentration and separation of heavy metal ions at trace levels.

Optimal conditions for column preconcentration by using activated carbon

Activated carbon was used after purification with HCl. Glass columns are preferably used for the enrichment of trace metal ions. Columns have various lengths and diameters. The diameter of the column is important for the quantitative recoveries. When column diameter is greater than 1.0 cm, because of the decrease in the bed height at constant amount of activated carbon, the recoveries of metal ions are not quantitative. Also when the diameter is smaller than 0.5 cm, the flow rate of the solution is decreased. The same results are also obtained with polyethylene columns.

Preconcentration columns are 10 cm long and 1.0 cm in diameter. The column that has a sintered glass disc over its stopcock is filled with activated carbon by aspirating a water slurry of purified activated carbon into the column. The column is conditioned with 10–15 mL of a blank solution used for preconcentration studies.

Adsorptions of metal ions on activated carbon column were studied at different pH values, with the other parameters kept constant. The pH of the model solution was adjusted to pH 2 with phosphate buffer, pH 2–6 with CH_3COO^-/CH_3COOH buffers, pH 7 with 0.01 M borate buffer, and pH 8–10 with NH_3/NH_4^+ buffers.

The influences of the concentration of ligands on the recovery of the metal ions were also investigated. The concentrations of the ligands were varied from 0.05×10^{-3} to 2.0×10^{-3} mol/L. The recoveries increased with increasing ligand concentrations and reached a maximum at 0.5×10^{-3} mol/L.

Quantitative recoveries were obtained for various ligands in the range of 300–700 mg of activated carbon. Generally, 500 mg of activated carbon was used in the preconcentration studies. We also examined how many times an activated carbon can be used; 500 mg of activated carbon can be used 40 times.

The influence of the flow rate on the sorption of the investigated metals was studied in the range of 1–20 mL/min. The sample volumes passed through activated carbon columns were generally 50 mL. Quantitative recoveries for metal ions can be attained at the flow rate < 10 mL/min.

Desorption of metal ions from activated carbon column was efficiently performed by using 10 mL of different eluents (*e.g.*, 1 M HCl in acetone, 1 M HNO_3 in acetone, 1 M HNO_3 in ethanol and 1 M HCl in ethanol).

An important factor for effective enrichment is the volume of the eluent. Because a high enrichment factor could be obtained due to the small final eluent volume, effects of the eluent volume on the recoveries were also investigated. Quantitative recoveries were obtained from 2 mL to 15 mL of eluting agent.

The effect of the volume of the sample solution on the sorption of the metal-chelates was studied by passing 100–2000 mL volume through activated carbon column at a 25 mL/min flow rate. The adsorption of the metal ions with 0.5 g activated carbon was not affected by sample volume below 1000 mL. Above 1000 mL, the percentage sorption of metal ions was decreased.

The effects of matrix ions of samples on the recovery of trace heavy metals were investigated. The recoveries were not affected by large amounts of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} because the matrix ions are not complexed with complexing agents. Thus they are not retained on activated carbon column, prior to elution of metal ions from activated carbon column. They can be easily washed out through the column.

The detection limits for metal ions based on three times the standard deviations of the blank were generally in the range of 0.1 µg/L–100 µg/L (N = 21) respectively. The relative standard deviations for metal ions were 2% (N = 10) at 5 µg/100 mL of each element respectively.

Various methods have been employed for the preconcentration of various metal ions in hot springs, river and drinking water samples, salt samples, etc. The results have been calculated on the assumption of 100% recovery of metal ions. Some applications of the column procedures using activated carbon are listed in Table-1.

TABLE-1
DETERMINATIONS OF TRACE HEAVY METAL IONS PRESENT
IN DIFFERENT MATRICES

Elements	Reagent	Matrix	Medium (pH)	Eluting agent	Ref.
Cu	HMDC, NN	Natural waters	6	2 M HCl in Acetone	12
Cu, Ni, Pb, Fe, Cd, Zn, Co	APDC	Table salts	6	1 M HNO$_3$	13
Cu, Pb, Ni, Cd	PAN	Drinking waters	4	2 M HCl in acetone	14
Cu	HMDC	Metallic aluminium	6	2 M HCl in acetone	15
Cu, Pb, Ni, Cd	PAN	Sewage waters	4	2 M HCl in acetone	16
Cu, Pb, Ni, Cd	PAN	Urine	4	2 M HCl in acetone	17
Ni, Pb, Cd, Cu, Mn, Fe	ADPC	Table salts	6	1 M HNO$_3$ in acetone	18
Ag, Au, Pd	DDTP	Potassium salts	0.1 M HCl	1 M NH$_3$ in acetone	19
Cu, Mn, Co, Cd, Pb, Ni, Cr	PV	Waters	6	1 M HNO$_3$ in acetone	20
Cu, Mn, Co, Cd, Pb, Ni, Cr	PV	Table salts	6	1 M HNO$_3$ in acetone	21
Ag, Au, Pd	DDTP	Al and Mn salts	0.1 M HCl	1 M NH$_3$ in acetone	22
Cu, Mn, Co, Cd, Pb, Ni, Cr	PV	Mineral water	6	1 M HNO$_3$ in acetone	23

APDC: Ammonium pyrolidine dithiocarbamate   PAN: 1-(2-Pyridylazo)-2-naphthol
HMDC: Hexamethylene dithiocarbamate   NN: I-Nitroso-2-naphthol,
       hexamethylene-ammonium salt
DDTP: Dithiophosphoric acid O,O-diethyl ester   PV: Pyrocatechol violet

Conclusion

Metal chelate complexes can be concentrated from aqueous solutions over a wide concentration range using short columns filled with activated carbon, without serious interference from excesses of many ions. Only 300–500 mg of activated carbon is sufficient and can be repeatedly used. Various methods have been applied to determine some trace heavy metals in various matrices with satisfactory results.

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