Review Article

Solid Phase Extraction Technique in Analytical Chemistry

(A New Preconcentration and Separation Method for The Determination of Trace Heavy Metal Ions in Natural Samples)

Mehmet Doğan

Hacettepe University Department of Chemistry, Ankara, Turkey

Abstract

Solid phase extraction technique is found a wide application in analytical chemistry as a preconcentration and separation of trace metal ions in complex matrixes in recent years. The method is efficiently, very simple and needs simple equipments, not more chemicals. Their enrichment factor is very high by the determination of heavy metal impurities in water. Therefore it is a useful and cheap technique especially for the laboratories; they have not enough good sensitive analytical instruments like GFAAS, ICP- MS or TXRF.

Key Words: Solid phase extraction technique, trace heavy metal ions, preconcentration, separation, enrichment.

INTRODUCTION

The direct determination of trace metal ions in biological materials such as hair, blood, urine etc and in natural water samples such as drinking water, spring water, sea water and dust waster and also in geological samples is difficult due to various factors, particularly their low concentrations and matrix effects. The concentration of many metal ions in natural samples is lower than the limit of detections of many analytical techniques. Many instrumental techniques are not sensitive enough to be used for direct determination of most trace elements in complex matrixes. Also, natural matrix generally causes the distributions of the analytical signals of elements. Preconcentration and separation can solve these problems.

There are many methods of preconcentration and separation such as liquid-liquid extraction [1,2], ion exchange techniques [3,4] coprecipitation [5,6], membrane filter techniques [7,8], sorption on the various adsorbents such as activated carbon [9-11], Amberlite XAD resins [12-15] and others sorbents [16-18], electrochemical deposition and also cloud point extraction [19-21].

The preconcentration and separation methods based on the sorption are considered to be superior to the liquid-liquid extraction as regards simplicity, rapidity and ability to attain a high preconcentration factor. Preconcentration methods based on adsorption of complexed metals on columns filled with activated carbon have found widespread application for this purpose.

* Correspondence to: Mehmet Doğan

Hacettepe University, Faculty of Science, Department of Chemistry, 06800, Beytepe-Ankara

Tel: +90312 297 6885 Fax: +90312 299 2163
E-mail: dogan@hacettepe.edu.tr

Activated carbon was used for the purification of drinking water for the adsorbing of aromatic and other organic materials which cause bed smelling and taste in water for many years. First of all, Jackwerth and coworker have used it for the adsorbing of metal ions in their complex form [22]. After sort time first application we have started to use the activated carbon as adsorbing media for the trace heavy metal ions from aqua solution [9,23,24].

A large number of trace elements which were enriched from various matrices and adsorbed onto activated carbon can be determined by atomic absorption spectroscopic (AAS) or spectrophoto-metric after dissolving them with an acid like HNO_3. Traces deposited on activated carbon can also be determined directly using the dc arc or other a solid sample technique such as x-Ray fluorescence, spark emission and neutron activated analysis techniques.

The activated carbon must be purified before their use and also it can be use only one time. In the last two decades, for same purpose Amberlite XAD resins and others sorbents were found application area instead of activated carbon. In particular, Amberlite XAD resins have widespread application in this field, because they have good physical and chemical properties such as porosity, high surface area, durability, nonpolar structure and purity. The adsorbents mainly packed in a mini column and for the separation of heavy metal ions from a several matrices, firstly metal-chelates are occurred with a chelating agent in an aqueous solution. These metal-chelates are sorbed on the resin during the filtration of solution. Then adsorbed metal-chelates can be desorbed from the resin with a suitable eluting agent to a few ml volumes. The concentration of metal ion in the eluent is determined by using instrumental methods such as FAAS or ICP OES.

This preconcentration and separation technique called in first years as mini column chromatography, because of their similarity to ion exchanges chromatography. Then it is called as solid-liquid extraction. Nowadays it classifies as "solid phase extraction" [25-27].

Over twenty years, our working group has been focused on the preconcentration and speciation of metal ions in various matrixes and on the Amberlite XAD resins, activated carbon and other adsorbents as metal complexes [28-86].

MATERIALS AND METHODS

An analytical procedure for the determination of heavy metal ions is based on following steps: 1- Sampling and sample storage, 2- Sample preparation, 3- Isolation of analyte,4- Qualification and quantification, 5- Data evaluation, 6- Making decision

Sampling and Sample Preparation

For this separation technique the sample must be present in aqueous solution form. The solid sample like metals, alloys, minerals and others geological samples, salary, salts biological tissue must be solved or digested in suitable acid or acidic mixture. After the dissolving of sample, mixtures are evaporated to dryness, heated in a sand band or on a hot plate, (if is necessary evaporated of acid excess). The residue dissolved with addition acid and water again and if is necessary it will be filtered and diluted to determined volume with distilled water.

The aqueous sample like sea water or drinking water after their filtration through Whatman no.42 filter paper, and adjusting pH and addition suitable chelating agent filtered through mini column filled adsorbing resin or activated carbon. This separation

and preconcentraion technique is specially good and suitable technique for the separation and preconcentraion of heavy metal ion impurities in water samples.

To Distinguish Chemical Forms of Analyte

The oxidation step of metal ions must be suitable for their efficiently complexing with chelating agents and their optimum adsorption onto solid phase like activated carbon or XAD resins.

After adjusting suitable pH with suitable buffer and addition a suitable chelating agent filtered trough mini column filled adsorbing resin or activated carbon.

Isolation of Analyte from Matrix

After dissolving solid samples or if it is necessary after adjusting the oxidation state, the clear liquid sample is ready to process. Suitable pH is adjusted according to matrix and metals which will separate and then appropriate chelating agent is added to solution. It should be take into account that at this pH and with this chelating agent, all ions which consist of matrix don't make complex and attach to the surface of adsorbent but all impurity metal ions will absorbed. The solution was buffered in order to fix the pH. But the buffer is not unavoidable.

Firstly, trace metals are converted into metal chelate or inorganic complex in aqueous solution. Then, metal complexes are adsorbed on the Amberlite XAD resin.

When all the impurity heavy metal ions get suitable complex forms, the complete mixture is passed through the column which was loaded with resin and activated carbon. If the flow rate of filtration is slow or the amount of filtered solution is high, the flow rate can be increased with the aim of water tromp or vacuum pump .Due to the residue solution contents primarily alkali and earth alkali metal ions

and undesired matrix constituents, it is throw away. The desired metal ions are absorbed on adsorbent of filter as their complex forms.

Since 1992 the various types of both activated carbon and Amberlite XAD resins which are exist in market were used as adsorbent for preconcentration of trace heavy metal ions in various mediums by us. The spectroscopic determination of trace elements were made by separating them from matrix and then preconcentrating in all type of sample (aqueous sample like sea water, drinking water, tap-, spring-, minerals-, rivers, paste- and sea water, and also haemodialysis solution, urine, saline solutions) previously in water samples (aqueous sample like sea water, drinking water, tap-, spring-, minerals-, rivers, paste- and sea water, and also haemodialysis solution, urine, saline solutions) by us.

Preconcentration parameters

The following parameters are important for the quantitative recoveries of the trace heavy metal ions on Amberlite XAD Resins. Column preparation and dimension, resin mass, pH, ligand type and amount, sample volume, eluent type and volume, flow rate, matrix effects. (Speciation of Analyte Form).

Preparation of Column

In this technique, a glass column 100 mm long and 10 mm i.d. and the resin bed height almost 1.5 cm for 500 mg resin were used in our studies. To eliminate inorganic and organic contaminants of commercial resins, the resins are washed by using of appropriate solutions.

The resin loaded in column is conditioned with 10-15 ml of the blank solution before the loading of sample. Diameter of the column is important for quantitative recoveries. Columns have various lengths and diameters. In our application recoveries of metal ions is not quantitative, because of decrease in the bed height at constant amounts of

the resin, when column diameter is wider than 10 mm, and also when diameter is smaller than 5 mm at constant amounts of the resin, the flow rate of sample solution decreases. The quantitative recoveries are obtained in the general range of 300-500 mg resin or 50- 100 mg activated carbon for the column this dimension.

There are a lot of Amberlite XAD available The Structures of Amberlite XAD resin series I: Polystyrene - divinyl benzene (PS-DVB), XAD resin series II: Polyacrylic acid ester (PAA-E), also Polyacrylic acid ester (PAA-E) In our studies we are generally used Amberlite XAD 2, 4, 7, 16, 1180. The complexing gent can also bond to resin structure.
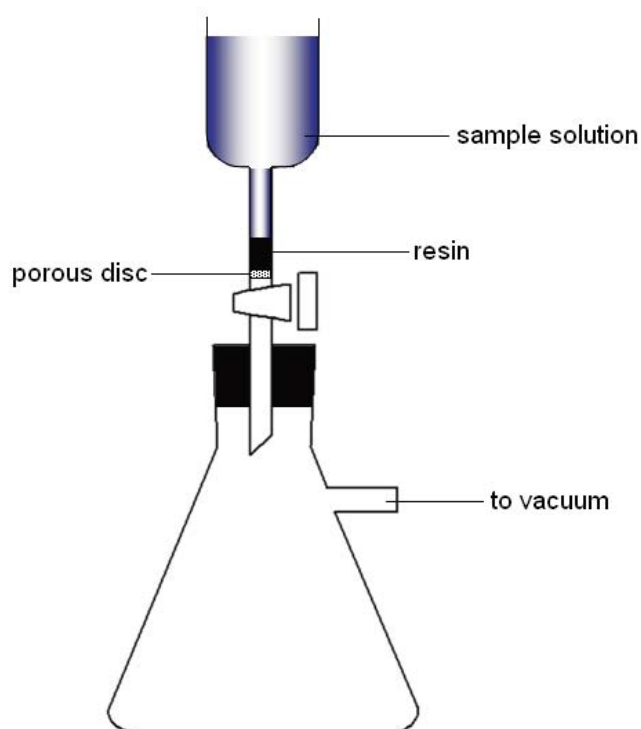

Figure 1. The schematic diagram of the technique.

Effect of pH

pH of sample solution is one of most important parameters for the quantitative retention of heavy metal ions on resin. Sample pH value depends on structure of chelating agent, nature of sorbent,

chemical form of analyte ions. Generally, buffer solutions are used to adjust working pH. Type of buffer is an effective factor on recoveries in presence of buffer including complexing ligands.

Ligand Type

Ligand type depends on mostly analyte and matrix for selective preconcentration, also resin structure. The interaction between neutral metal-chelates and some hydrophobic groups of the resin is responsible for adsorption. Therefore, generally chelating ligands such as DDTC, APDC, TAR, PAN, Oxine are preferred for the resins based polystyrene divinyl benzene. For retention of ionic species, polyacrylicacid ester polymers are preferred because of their a little ion exchange capacity and dipol moment. PS-DVB and PAA-E resins, due to their dual characters, have been used for preconcentration of ion-pair complexes and neutral species.

Ligand Amount

The concentration of ligand on the recovery of the metal ions is effective. An adsorption competition between free ligand (chelating ligands) and metal complex on the resin is possible, so amount of ligand must be definitly optimized.

Sample Volume

To obtain the high preconcentration factor, the maximum sample volume is necessary.-Sample volumes depend on chemical forms of both adsorbent and trace element, as well as on mass of adsorbent and analyte concentration. The analytes start to elute from adsorbent resulting in non-quantitative recoveries, if the sample volume is over the maximum volume for optimized adsorbent mass that a quantitative retention is obtained. So, the volume must be determined experimentally. The sample flow-rate is optimized to ensure quantitative retention. In our working, the sample flow-rate for quantitative sorption of metal complex changes in a range of 5-25 ml/min.

Eluent Type and Volume

For the XAD resin preconcentration can be use according to sample and type of resin following types of eluent: a)Pure Acetone, b)HCl, HNO_3 acid solutions at various concentrations, c)HCl, HNO_3 acid solutions in acetone,c)Ethanolic solutions of HCl and HNO3. The volume of eluent is an important factor for quantitative recovery and high preconcentration factor. Due to this, the small volume is preferred. Quantitative recoveries of metal ions from XAD columns can be obtained with 2 ml to 10 ml of eluting solution.

Eluent Flow Rate

As a rule, at the high flow-rate, the larger solvent volume is necessary for quantitative elution. A eluent flow-rate should be high to avoid excessive duration, and low to ensure quantitative recovery. So it is optimized. Typical eluent flow-rates are in a range of 1.0 to 10 ml/min in our workings.

Matrix effect

One of most important targets of preconcentration/ separation procedures is elimination of strongly interferric matrix constituents in the sample. The reliability of the method have to be examined in presence of possible matrix effects. In the chelate extraction, alkaline and alkaline earth ions and some anions in large amounts are effectively eliminated. This is an advantage for preconcentration of heavy metal ions at trace level from the saline samples.

SOME RESULTS

Solid phase extraction technique is found a wide application in analytical chemistry as a preconcentration and separation of trace metal ions in complex matrixes in resent years. The preconcentration and separation methods based on the sorption are considered to be superior to the liquid-liquid extraction as regards simplicity, rapidity and ability to attain a high concentration factor. A large number of trace elements enriched from various matrices and adsorbed onto activated carbon can be determined by atomic absorption spectroscopic (AAS) or spectrophotometric after dissolving trace elements with an acid like HNO_3 or with a suitable elution mixture. Some of our applications are given in Table 1.

Preconcentration methods based on adsorption of complexed metals on columns filled with activated carbon have found widespread application for this purpose. The enrichment factors of 100-500 were achieved by us. With this preconcentration technique a wide spread of elements like Cu, Ni,, Zn, Mn, Co, Cd, Pb could be determined from various mediums with cheap, simple instruments like AAS ve spectrophotometry in range.

CONCLUSION

In the past two decades, the use of SPE procedures has been growing for preconcentration and speciation of trace elements. Because; SPE has high preconcentration factor and very low limits of detection. There are many alternatives for selectivity, such as resin and ligand types, pH, masking and sometimes eluent type. Also automation in SPE is easy. The simplest and most effective procedure in SPE is the adding of the chelating reagent directly to the sample (Adsorption Mode). Examples given in this review show the high potential of PS- DVB and PAA-E resins for preconcentration and speciation of trace elements in SPE. Because, these resins have a possibility to extract a large number of trace elements over a wide pH range, fast and quantitative sorption and elution, a high capacity and fast and easy regenerability.

Table 1. List of some Applications of solid-phase extraction.

Adsorbent	Elements	Reagents	Matrix	Medium	Eluting Agent	Ref
Amberlite XAD-4	Cu, Pb, Fe, Cd, Co, Ni	APDC, Oxine	Dialysis Solutions, Natural Waters	pH=6	1 M HNO$_3$ in Acetone	23, 24, 34
Amberlite XAD-16	Co	TAR	Natural Waters	pH=6	1 M HNO$_3$ in Acetone	33
Amberlite XAD-8	Mo	SCN	Steel, Spring Waters, Geological	Acidic	Acetone	38, 41
Amberlite XAD-7	Au, Pd	SCN	Nickel and Manganese Salts	Acidic	Acetone	35, 41
Amberlite XAD-7	Au, Pd	Br	Anodic Slime	Acidic	Acetone	29
Amberlite XAD-1180	Cu, Cd, Pb, Bi, Fe, Mn, Co	I+SCN	Metallic Zinc	Acidic	Acetone	41
Amberlite XAD-16	Cu, Fe, Ni, Cd, Co, Zn	Na-DDTC	Sea Water, Urine	pH=4	1 M HNO$_3$ in Acetone	35, 23
Amberlite XAD-1180	W	SCN	Geological	Acidic	Acetone	31
Amberlite XAD-7	W	SCN	Spring Waters	Acidic	Acetone	30
Amberlite XAD-16	Fe, Ni, Cu	TAR	Fertilizers	pH=6	1 M HNO$_3$ in Acetone	30
Activated Carbon	Cu, Pb, Ni, Cd	PAN	Drinking Waters	pH=4	2 M HNO$_3$ in Acetone	37
Activated Carbon	Cu	HMDC, NN	Natural Waters	pH=6	2 M HNO$_3$ in Acetone	34, 30
Activated Carbon	Cu	HMDC	Metallic Aluminum	pH=6	2 M HNO$_3$ in Acetone	37, 41

APDC : Ammonium pyrolidine dithiocarbamate, **Oxine**: 8-hydroxiquinoline, **TAR**: 4-(2-Thiazolylazo) resorcinol, **Na-DDTC**: sodium diethyldithiocarbamate. **PAN**: 1-(2-pyridylazo) 2-naphtol, **HMDC**: hexamethylene dithiocarbamate hexamethylene-ammonium salt, **NN**: 1-nitroso-2-naphthol, **I+SCN**: iodide + thiocyanate, **Br**: Bromide, **SCN**: thiocyanate.

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Table 2. Concentration of Copper in water samples volume 500 mL, Eluent Volume 5 mL Ligand HMDC.

| Water | Source | Conc. of cupper (μg/L)* | |
		Activated Carbon	XAD-4 Column
Drinking	Talas	9.5±0.3	19.1±0.4
	Kocasinan	1.5±0.1	1.4± 0.2
	Melikgazi	3.3±0.2	3.3±0.1
	Univ.Tap	1.2±0.1	1.4±0.1
Hot spring	Sorgun	11.8±0.1	12.0±0.3
	Kozaklı	16.8±0.3	16.9±0.4
	Cavlak	6.3±0.1	6.7+0.1
River	Sarımsaklı	12.4±0.4	11.5±1.2
	Karasu	47.7±1.3	44.9±2.1

±ts√N, N: 7 RSD: 0.95

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