



New sorbents for solid phase extraction of trace analyte enrichment

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ABSTRACT

Sample pretreatment methods, such as separation / preconcentration prior to the determination of metal ions have developed rapidly due to the increasing need for accurate and precise measurements at extremely low levels of ions in diverse matrices. The development of new sorbents and their application in preconcentration methods for determination of trace analytes is subject of great interest. This review summarizes and discusses several analytical methods involving the preparation and use of new solid phase extractant. A literature survey of the last ten years offering a critical review of these new sorbents available for use in trace analyte enrichment is provided.

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Introduction

The determination of trace concentrations of analytes in different samples is a subject of great interest. This determination can be made by using diverse analytical techniques. However, the direct determination of extremely low concentrations of required elements by most analytical techniques is often difficult. The limitations can be associated to matrix interference or insufficient sensitivity of these techniques. For this reason, a preliminary separation and preconcentration of trace analytes from matrix are frequently required. Preconcentration is a process in which the ratio of the quantity of a desired trace element to that of the original matrix is increased. Preconcentration improves the analytical detection limits, increases the sensitivity by several orders of magnitude, enhances the accuracy of results and facilitate the calibration. In general, it can be referred to as the enrichment process which involves separating the minor component (analyte) from complex matrix or extraction of particular analyte from one phase to other in which latter one is of less volume than first one. Separation and preconcentration techniques are of great importance owing to the limited sensitivity of modern instrumental methods for trace analysis. Pre-treatment of an aqueous sample by different sorption technique not only increases the ion concentration to a detectable level but also eliminates matrix effects. The use of chelating sorbents can provide a concentration factor up to several hundred folds, better separation of interferent ions and high efficiency. The general trend of modern analytical chemistry is towards the elaboration of simple, ecologically safe, sensitive, and selective methods for the determination of trace components combining previous concentration methods and further determination by physical or physico-chemical methods. Metal quantification at low concentration levels comprises one of the most considered targets in analytical chemistry. Sample pretreatment methods, such as separation and/or preconcentration prior to the determination of metal ions have developed rapidly due to the increasing need for accurate and precise measurements at extremely low levels of ions in diverse matrices.

Preconcentration improves the reliability of the analytical results since it decreases the matrix effects. Sample preparation processes including separation and preconcentration have a direct impact on accuracy, precision and detection limits for many analytical methods [1-7].

Liquid-liquid extraction [8-15], coprecipitation [16-22], ion-exchange resins [23-31], electrothermal deposition [32-33] and solid-phase extraction used techniques for preconcentration and separation of trace elements [34-53]. Preconcentration is a process in which the ratio of the desired trace element to that of the original matrix is enhanced. Preconcentration improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results and facilitates easy calibration. In general, it can be referred to as the enrichment process consisting of either removing the major component from minor ones or transfer of analyte from a large volume of one phase into a second phase of lesser volume. Enrichment is attained by the use of various preconcentration techniques based on physical, physio-chemical and chemical principle. The techniques generally employed in analytical chemistry are liquid-liquid extraction, electrochemical method, ion-exchange, co-precipitation and solid phase extraction. Electrochemical deposition used for the preconcentration of different pollutants by applying the laws of electrolysis in which cationic species are deposited on the electrode surface. The only disadvantage of this method is that limitation related to pH control. This control is necessary because in the acid medium, hydrogen ions are reduced to hydrogen gas on the work electrode surface. The hydrogen gas generation occurs when more negative potentials are applied. The reduction of electrode lifetimes is also observed at higher acidity conditions. In coprecipitation or precipitation is characterized by the formation of insoluble compounds. The coprecipitation is adopted when direct precipitation can not separate the desired metallic species due to its low concentration in solution. The coprecipitation phenomenon can be associated with metal adsorption on the precipitate surface or due to metal incorporation onto the precipitate structures. The coprecipitation occurs by the

formation of an insoluble compound containing some metallic species. Thus, there is a natural limitation according to this phenomenon, because the metal used for this purpose cannot be determined. The separation and preconcentration of metal ions and organic pollutants, after the formation of sparingly water-soluble complex, based on cloud point extraction have been largely employed in analytical chemistry. Current research in this field has focused on the development of new surfactant phase separations that surpassed the limitations associated with non-ionic surfactants. The search for alternatives to traditional organic solvents in liquid-liquid extraction has fostered the use of more environmentally friendly liquids. Cloud point extraction that is the temperature-induced phase separation of nonionic surfactants, continues as one of the leading techniques for the preconcentration of metal ions [54-56]. But application of cloud point extraction to the extraction of organic pollutants is less straightforward because of the coelution problems originated by non-ionic surfactants which are commercially available as a mixture of homologues and isomers.

But according to Hitherto, liquid-liquid extraction is among the most often used method for the various preconcentration or separation techniques in view of its simplicity, rapidity, ready adaptability and easier recovery of analyte. There are, however physical difficulties associated with the use of solvent extraction for enrichment of large number of samples and /or requires vigorous agitation to ensure complete partition of the analyte between two immiscible phases, and this can be achieved only by the application of significant human or mechanical effort. In addition, there are increasing environmental and cost pressures to replace, or at the very least reduce, the volume of solvents employed in analytical procedures. Current trends in preconcentration focus on the development of faster, safer and more environment friendly extraction techniques. Solid phase extraction continues to be the leading technique for the extraction of pollutants in aquatic systems; recent developments in this field are mainly related to the use of new sorbents. Solid phase extraction (SPE) has emerged as a powerful tool for separation/ enrichment of inorganics, organics and biomolecules. The basic principle of SPE is transfer of analytes from aqueous phase to active sites of adjacent solid phase. Recently, solid-phase extraction technique for preconcentration of heavy metal ions has become very popular, compared with traditional solvent extraction techniques and has almost replaced liquid-liquid extraction techniques because of several advantages [57-58].

- (1) The fast, simple and direct sample application in very small size (micro liter volume) without any sample loss.
- (2) Higher preconcentration factor.
- (3) The ability of combination with different modern analytical techniques.
- (4) Time and cost saving.
- (5) There is no use of organic solvents which are flammable, toxic and even some of them carcinogenic.
- (6) Absence of emulsion.
- (7) Rapid phase separation.
- (8) Stability and re-usability of solid phase.
- (9) Isolate analytes from large volumes of sample with minimal or zero evaporation losses.

The choice of solid-phase extractant is a decisive factor that affects the analytical sensitivity and selectivity [59]. The main requirement with respect to substances to be used as solid-phase extractants are as follows:

- (1) Possibility of extracting a large number of elements over a wide pH range.
- (2) High surface area and high purity.
- (3) Good sorption properties including porosity, durability and uniform pore distribution.
- (4) Selectivity for specific analytes.
- (5) Fast quantitative sorption and elution.
- (6) Regenerability and accessibility.

Numerous substances have been used solid-phase extractants such as ion-exchange resins [60-62], chelating resins [63-67], [68-93] and alumina [94], activated carbon [95-102], zeolite [103-105], chitosan [106-108] and polyurethane foam [109-114].

In this review, the chelating resins, modified silica, ion exchange resins, carbon nanotubes, ion-imprinted polymers, biosorbents, nanoparticles, fullerenes and other solid materials that are used for the separation and/ or preconcentration of analytes are considered.

Inorganic Resins

Inorganic resins such as silica gel, celetek clay, montmorillonite and alumina have recently used for the enrichment of metal ions. Chelating agents immobilized on silica gel have various types of functional groups that form complexes with analytes. Although silica gel immobilized with different chelating agents is accepted as an inorganic resin in this review. Some examples are given in Table 1.

Chelating/ organic resins

Sorption with chelating resins is mostly due to the complexation of trace analytes with functional groups. Much attention has been drawn to the synthesis of chelating resins and to investigate of their sorption behavior for the selective and quantitative separation of specific analytes from various sources. Adsorption ability and adsorption selectivity of chelating resins are superior to those of ion exchangers in the trace or ultra-concentration ranges. Currently, many chelating sorbents have been synthesized for the preconcentration of trace analytes. The majority of the sorbents contain heterocyclic groups such as imidazole, pyrazole, thiazole and pyridine. Many chelating resins obtained by immobilization on solid support have been practically applied in the separation of trace analytes from various sources. Table 2.

Fullerenes

Buckminsterfullerenes, third allotropic form of carbon, are closed-cage carbon molecules containing pentagonal and hexagonal rings arranged in such a way that they have the formula $C_{20}m$, with m being an integer number. Fullerenes comprise a wide range of isomers and homologous series, from the most studied C_{60} or C_{70} , to the so-called higher fullerenes, C_{240} , C_{540} , and C_{720} . The analytical potential of C_{60} as an effective sorbent material for preconcentration of metals was recently demonstrated. Subsequent experiments with C_{60} and C_{70} fullerenes showed that both sorbents have a high analytical potential for metal preconcentration probably because of their large molecular surface area and volume. Higher sensitivity and selectivity are obtained with neutral chelates than by formation of ion pairs. Fullerenes with chemically modified surfaces combine the advantages of high enrichment factors offered by the large surface area and the selectivity associated with impregnated chemical groups. For example, C_{60} can be covalently bonded to classical chelating reagents, leading to stable fullerene derivatives that join the advantages of both compounds. Table 3.

Table 1. Silica gel for the preconcentration of analytes

Sorbent	Reagent	Analyte	Sample	Technique	Ref
Silica gel	Morin	Ag, Au, Pd, Pt, Rh	Spiked water	FAAS	115
Silica gel	DDE, DDS, o-HB	Zn, Mn, Cr	Drinking water	FAAS	116
Silica gel	Purpald	Cd, Hg, Pb	Pharmaceutical and vitamins	FAAS	117
Silica gel	Xylenol orange	Hg	Surface and tap water	FAAS	118
Silica gel	Hydroxamic acid	Cu, Zn, Cd	Natural water	FAAS	119
Silica gel	N-(3-propyl)-O-phenylenediamine	Cd, Zn, Fe, Cu, Pb	Natural aqueous systems	FAAS	120
Silica gel	LIX 622	Cu	Synthetic water	FAAS	121
Silica gel	Di(n-propyl)thiuram disulfide	Ag	Photographic waste and lake water	FAAS	122
Silica gel	Poly(propyleneimine) dendrimer	Pt	Ni alloy, anode slime	FI-FAAS	123
Silica gel	N-propylsalicylaldimine	Fe, Co, Ni, Zn	River water	CV-FAAS	124
Silica gel	TOA	Cr, Cu, Mn, Ni, Zn	Waste water	FAAS	125
Silica gel	γ -mercaptopropyl groups	Pb, Cd, Zn	Natural water	XRF	126
Silica gel	Salicyldoxime	Cd, Ni, Co, Cu, Zn	Environmental water	---	127
Silica gel	N-propylsalicylaldimine	Cd, Cr, Cu, Mn, Pb	Aquatic environments	AAS	128
Silica Gel	1-nitroso-2-naphthol	Co	Flow analytical systems	Spectrophotometry	129
Silica Gel	dibenzo-18-crown-6	Co, Zn, Cu, Ni,	Alloys and water	AAS	130
Silica gel	Thiosemicarbazide	Pb	Environmental samples	FAAS	131
Celtek clay	benzaldehyde	Cu, Cd, Pb, Cr, Ni	Natural waters, wheat, human hair	FAAS	132
Bentonite	Trioctylamine	Cd, Fe, Sb	Waste water	FAAS	133
Montmorillonite	Trioctylamine	Fe, Cd, Zn, Ni, Mn	Tap and river water	FAAS	134
Alumina Bis(2-hydroxyphenylamino)glyoxime		Hg	Natural tap water	CVAAS	135

Table 2. Organic sorbents for the preconcentration of analytes.

Sorbent	Analytes	Sample	Technique	Reference
POLYORGS 4	Au, Pd, Pt, Rh, Ir	Pt-containing ore, Cu-Ni sulfide ore, Cu alloy	ETAAS and ICP-OES	136
Iminodiacetate resin	V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, U	Sea water, certified reference materials	ICP-MS	137
Iminodiacetate	Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Pb	Tap and rain water	XRF	138
Epoxy-tetraethylene pentamine chelating resin	Au, Pt, Pd	Wastewater	ICP-OES	139
Chelex-100 resin	REEs	Coastal sea water	ICP-MS	140
Epoxy-polyamide	Rh, Ru, Ir	Metal smelter, alloys	ICP-OES	141
Sepharose beads	Cd, Pb, Ni	Sea lettuce, river sediment, natural water	ETAAS	142
Metalfix Chelamine	Au, Ir, Pd, Pt, Rh, Ru	Anodic sludge	ICP-OES	143
Amberlite XAD-2 Anchored with pyrocatechol	Cd, Co, Cu, Ni,	Food samples (spinach, black, tea and rice flour)	FAAS	144
SPHERON Thiol 1000	Au, Ag	Water samples	ETAAS	145

Table 3. Methods for metal separation and preconcentration using fullerenes.

Analyte	Detection Technique	Sample	Ref
Cd	FAAS	Fish liver,	146
Cd	FAAS	Oyster tissues,	147
		Bovine liver, pig kidney	
Cd	TS-FF-AAS	Water, pig, kidney, rye grass	148
Pb			
Co	ETAAS	Wheat Flour	149
Cu	FAAS	Pesticides	150
MeHg ⁺	GC/MS	Water, sediments	160

Table 4. Methods for metal separation and preconcentration using carbon nanotubes.

Sample	Detection technique	Sample	Ref
Cu(II)	FAAS	Water	161
Cd(II)	ICP-OES	Biological material and natural water	162
Mn(II)			
Ni(II)			
Cd(II)	FAAS	Biological material, water	163
Co(II)			
La(III)	ICP-OES	Biological material, water	164
Sm(III)			
Eu(III)			
Gd(III)			
Tb(III)			
Ho(III)			
Yb(III)			

Table 5. Preconcentration of metal ions by nanoparticles.

Nanoparticles	Analytical method	Analyte	Sample	Reference
TiO ₂	ICP-AES	Cu(II) Cr(III) Mn(II) Ni(II)	Environmental water samples	165
TiO ₂	FAAS	Zn(II) Cd(II)	Environmental water samples	166
TiO ₂	GFAAS	Se(IV) Se(VI)	Sediment, water samples	167
TiO ₂	ICP-AES	Sm(III) Ho(III) Nd(III) Tm(III)	Stream sediments	168
TiO ₂	ICP-AES	Au(III) Pd(II) Ag(I)	Geological samples	169
TiO ₂	ICP-AES	La(III) Yb(III) Y(III) Eu(III) Dy(III)	Stream sediments	170
TiO ₂ -PAN	ICP-AES	Cu(II) Co(II) Cr(III) Y(III) Bi(III) Yb(III)	Environmental samples	179

Carbon nanotubes

Since its discovery in 1991, carbon nanotubes (CNTs) have attracted great attention because of their unique properties. CNTs can be visualized as a sheet of graphite that has been rolled into a tube, and are divided into single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) according to the carbon atom layers in the wall of the nanotubes. With the great progress in the methods of preparing CNTs, large efforts have been devoted to their fields of application. Their perceived novel mechanical and electronic properties, large specific surface area and high thermal stability indicate their tremendous potential for engineering applications, such as hydrogen storage, field emission, quantum nanowires, catalyst supports, chemical sensors and packing material for gas chromatography. The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface have a strong interaction with other molecules or atoms, which make CNTs a promising adsorbent material substituted for activated carbon in many ways.

CNTs possess a high electrical conductivity, chemical stability, mechanical strength, large specific surface area, and high thermal stability, indicating potential for various applications and one of the applications of the CNTs is as adsorbent material: the hexagonal arrays of carbon atoms in graphite sheets of CNTs surface have a strong interaction with other molecules or atoms, revealing a great analytical potential as a solid-phase extraction adsorbent. Additionally, CNTs' surfaces can be modified by introducing various organic functional groups, thus providing a strongly physisorbing surface area, adjustable surface charge, and a source of protons for chemical ionization. It has been demonstrated that the surfaces of CNTs can be easily modified in numerous ways, either by covalent or noncovalent functionalization. All the facts mentioned before reveal that carbon nanotubes, and specially multiwalled carbon nanotubes, have great analytical potential as an effective solid-phase extraction adsorbent for chelates or ion pairs of metal ions, organic compounds, and organometallic compounds. Table 4.

Nanoparticles

The field of nanometer-sized materials has gained the attention of scientists and engineers in recent years due to their special properties. Nanoparticles are clusters of atoms or molecules of metal oxide, ranging in size from 1 nm to almost 100 nm. One of their most interesting properties is that a high percentage of the atoms of the nanoparticles is on the surface. The unsaturated surface atoms can bind with other atoms that possess strong chemical activity. Consequently, nanometer material can adsorb selective metal ions and has a very high adsorption capacity. Nanometer-sized metal oxides, such as Al₂O₃, TiO₂, ZrO₂, CeO₂, and SiO₂ exhibit intrinsic surface reactivity and high surface areas and can strongly chemisorb several substances. In recent years, these materials have been proposed and applied in the preconcentration of trace metals due their high surface area, high adsorption capacity, and high chemical activity. Moreover, the preparation of these adsorbents is very simple and low cost when compared with other commercially available solid-phase materials. Additionally, the coating of complexing reagents onto nanometer-sized oxides increases the number of binding sites able to interact with metal ions and changes the binding sites in order to enhance the uptake of metal ions. The modification of nanometer-sized adsorption materials with an organic could also increase their selectivity.

This modification generally is made by two different means: (1) the chemical bonding of the chelating ligand on nanometer oxide; and (2) the physical binding of the chelating ligand on the sorbent by impregnating the solid matrix with a solution containing specific molecules. Table 5

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