

Review of preconcentration and solid phase extraction for the determination of trace Lead

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ABSTRACT: Spectrometric techniques for the analysis of trace lead have developed rapidly due to the increasing need for accurate measurements at extremely low levels of this element in diverse matrices. This review covers separation and preconcentration procedures, and considers the features of the application with several spectrometric techniques. The use of an appropriate sample handling technique is a must in an analysis of trace lead in water. The efforts to use a solid phase for the recovery of analytes from a water matrix prior to their detection have a long history. The initial experimental applications of SPE resulted in widespread use of this technique in current water analysis and also adoption of SPE into standardized analytical methods. Lead is recognized worldwide as a poisonous metal. Thus, the determination of this element is often required in environmental, biological, food and geological samples. However, these analyses are difficult because such samples contain relatively low concentrations of lead, which fall below the detection limit of conventional analytical techniques such as flame atomic absorption spectrometry and inductively coupled plasma optical emission spectrometry. Several preconcentration procedures to determine lead have therefore been devised, involving separation techniques such as liquid–liquid extraction, solid phase extraction, coprecipitation and cloud point extraction. Review of preconcentration procedures for determining lead using spectroanalytical techniques. A brief overview of the history of the use of SPE in trace lead analysis of water is given in presented paper.

Keywords: *Preconcentration; Reviews; Solid-phase extraction; Trace lead; Water analysis*

INTRODUCTION

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace lead before their analysis due to their frequent low concentrations in numerous samples (especially water samples). Additionally, since high levels of non-toxic components usually accompany analytes, a clean-up step is often required. Liquid–liquid extraction is a

classical method for preconcentrating metal ions matrix removal. Solid phase extraction (SPE) is another approach that offers a number of important benefits. It reduces solvent usage and 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. After outlining the theory of this technique, guidelines are given for the develop-

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ment of SPE-based methods for preconcentration of many trace lead. Finally, examples of applications are presented.

From the analytical tools above listed, FAAS presents low costs, operational facility and high sample throughput. The determination of cadmium by flame atomic spectrometry is free of interference and this can be easily atomized in air-acetylene flame. In the resonance line 228 nm, the characteristic concentration is 0.02 mg L⁻¹. The analytical line at 326.1 nm is suitable for determining higher Cd concentrations and the characteristic concentration is about 6mg L⁻¹, so that excessive dilution can be avoided (Stevens, *et al.*, 2007). Cadmium can be determined by CV AAS where atomic Cd vapor is measured by AAS in an unheated quartz cell. LOD of 80 ng L⁻¹ was obtained which can be further improved by working at low temperature. The sensitivity can be increased collecting the atomic Cd vapor in a graphite tube pretreated with palladium at 150°C and then reatomizing at 1600°C (Rendle, *et al.*, 2000). Cold vapor generation coupled to atomic absorption spectrometry with flow injection (FI-CV AAS) was evaluated as a rapid and simple method for the determination of cadmium (Graf, *et al.*, 2007). The determination of cadmium by ETAAS was, for a long period, difficult because the cadmium is an element with high volatility (Thistlethwaite, *et al.*, 2000).

The principle of SPE is similar to that of liquid-liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves partitioning between a liquid (sample matrix) and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the analytes. After all of the samples have been passed through the sorbent, retained analytes are subsequently recovered upon elution with an appropriate solvent. The first experimental applications of SPE started fifty years ago (Taguchi, *et al.*, 1997). However, numerous studies have also shown the great potential of this technique for speciation studies (Taguchi, *et al.*, 1997).

Basic principles

An SPE method always consists of three to four successive steps, as illustrated in Fig. 1. First, the solid sorbent should be conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step is crucial, as it enables the wetting of the packing material and the solvation of the functional groups. In addition, it removes possible impurities initially contained in the sorbent or the packaging. Also, this step moves the air present in the column and fills the void volume with solvent. The nature of the conditioning solvent depends on the nature of the solid sorbent. Typically, for reversed phase sorbent (such as octadecyl-bonded silica), methanol is frequently used, followed with water or aqueous buffer whose pH and ionic strength are similar to that of the sample. Care must be taken not to allow the solid sorbent to dry between the conditioning and the sample treatment steps, otherwise the analytes will not be efficiently retained and poor recoveries will be obtained. If the sorbent dries for more than several minutes, it must be reconditioned.

The second step is the percolation of the sample through the solid sorbent. Depending on the system used, volumes can range from 1 mL to 1 L. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow-rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive eduration. During this step, the analytes are concentrated on the sorbent. Even though matrix components may also be retained

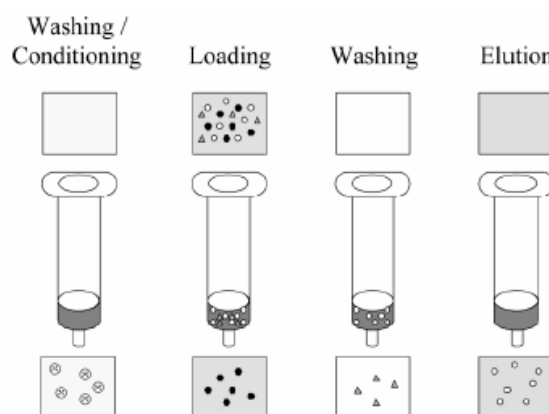


Fig. 1: SPE operation steps.

by the solid sorbent, some of them pass through, thus enabling some purification (matrix separation) of the sample. The third step (which is optional) may be the washing of the solid sorbent with an appropriate solvent, having low elution strength, to eliminate matrix components that have been retained by the solid sorbent, without displacing the analytes.

A drying step may also be advisable, especially for aqueous matrices, to remove traces of water from the solid sorbent. This will eliminate the presence of water in the final extract, which, in some cases, may hinder the subsequent concentration of the Extract the analysis. The final step consists in the elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The solvent volume should be adjusted so that quantitative recovery of the analytes is achieved with subsequent low dilution. In addition, the flow-rate should be correctly adjusted to ensure efficient elution. It is often recommended that the solvent volume be fractionated into two aliquots, and before the elution to let the solvent soak the solid sorbent.

Retention of trace Lead on the sorbent

Adsorption of trace lead on the solid sorbent is required for preconcentration (see Fig. 2). The mechanism of retention depends on the nature of the sorbent, and may include simple adsorption, chelation or ion-exchange. Also, for trace lead, ion-pair solid phase extraction may be used.

Adsorption

Trace lead are usually adsorbed on solid phases through van der Waals forces or hydrophobic interaction. Hydrophobic interaction occurs when the solid sorbent is highly non-polar (reversed phase). The most common sorbent of this type is octadecyl-bonded silica (C₁₈-silica). More recently, reversed polymeric phases have appeared, especially the styrene-divinylbenzene-copolymer that provides additional interaction when p-electrons are present in the analyte w4x. Elution is usually performed with organic solvents, such as methanol or acetonitrile. Such interactions are usually preferred with online systems, as they are not too strong and thus they can be rapidly disrupted. However, because most trace element species are ionic, they

will not be retained by such sorbents.

Chelation

Several functional group atoms are capable of chelating trace lead. The atoms most frequently used are nitrogen (e.g. N present in amines, azo groups, amides, nitriles), oxygen (e.g. O present in carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (e.g. S present in thiols, thiocarbamates, thioethers). The nature of the functional group will give an idea of the selectivity of the ligand towards trace lead. In practice, inorganic cations may be divided into 3 groups:

– *Group I- 'hard' cations*: these preferentially react via electrostatic interactions (due to a gain in entropy caused by changes in orientation of hydration water molecules); this group includes alkaline and alkaline-earth metals (Ca²⁺, Mg²⁺, Na⁺) that form rather weak outer-sphere complexes with only hard oxygen ligands.

– *Group II- 'borderline' cations*: these have an intermediate character; this group contains Fe, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Mn²⁺. They possess affinity for both hard and soft ligands.

– *Group III- 'soft' cations*: these tend to form covalent bonds. Hence, Cd²⁺ and Hg²⁺ possess strong affinity for intermediate (N) and soft (S) ligands.

For soft metals, the following order of donor atom affinity is observed: O-N-S. A reversed order is observed for hard cations. For a bidentate ligand, affinity for a soft metal increases with the overall softness of the donor atoms: (O, O)-(O, N)-(N, N)-(N, S). The order is reversed for hard metals. In general, the competition for a given ligand essentially involves Group I and Group II metals for O sites, and metals of Group II and Group III for N and S sites. The competition between metals of Group I and Group III is weak.

Chelating agents may be directly added to the sample for chelating trace lead, the chelates being further retained on an appropriate sorbent. An alternative is to introduce the functional chelating group into the sorbent. For that purpose, three different means are available: (1) the synthesis of new sorbents containing such groups (new sorbents); (2) the chemical bonding of such groups on existing sorbents (functionalized sorbents); and (3) the physical binding of the group

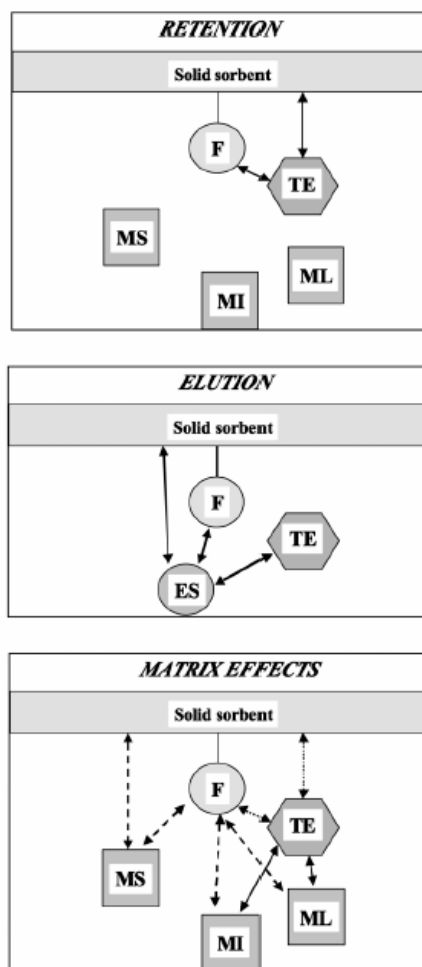


Fig. 2: Interactions occurring at the surface of the solid sorbent. F, functional group; TE, trace element; MS, matrix solvent; MI, matrix ions; ES, elution solvent

son the sorbent by impregnating the solid matrix with a solution containing the chelating ligand (impregnated, coated or loaded sorbents). The latter remains the most simple to be used in practice. Its main drawback is the possible flush of the chelating agent out of the solid sorbent during sample percolation or elution that reduces the lifetime of the impregnated sorbent. Different ligands immobilized on a variety of solid matrices have been successfully used for the preconcentration, separation and determination of trace metal ions. Chelating agents with a hydrophobic group are retained on hydrophobic sorbents (such as C_{18} -silica). Similarly, ion-exchange resins are treated with chelating agents containing an ion exchange group, such as a sulfonic acid derivative of dithizone (i.e. diphenylthiocarbazone) (DzS), 5-sulfo-8-quinolinol, 5-sulfo-salicylic acid, thiosalicylic acid, chromotropic acid,

or carboxyphenyl porphyrin (TCPP) (Saitoh, *et al.*, 2007). Binding of metal ions to the chelate functionality is dependent on several factors: (1) nature, charge and size of the metal ion; (2) nature of the donor atoms present in the ligand; (3) buffering conditions which favor certain metal extraction and binding to active donor or groups; and (4) nature of the solid support (e.g. degree of cross-linkage for a polymer). In some cases, the behavior of immobilized chelating sorbents towards metal preconcentration may be predicted using the known values of the formation constants of the metals with the investigated chelating agent (Schnatter, 2000). However, the presence of the solid sorbent may also have an effect and lead to the formation of a complex with a different stoichiometry than the one observed in a homogeneous reaction (Roma-Torres, *et al.*, 2006). In fact, several characteristics of the sorbent should be taken into account, namely the number of active groups available in the resin phase (Roma-Torres, *et al.*, 2006). The length of the spacer arm between the resin and the bound ligand (Fattahi, *et al.*, 2007) and the pore dimensions of the resin (Fattahi, *et al.*, 2007).

Lead determination

Atomic absorption spectrometry (AAS)

The determination of lead by flame atomic absorption spectrometry (FAAS) is practically free of interference and requires an air-acetylene flame (Fattahi, *et al.*, 2007). The interference caused by aluminum and iron can be overcome by the addition of ascorbic acid, citric acid and EDTA (Fattahi, *et al.*, 2007). The threshold of sensitivity of this technique is very low (LOD 0.01 mg L^{-1}) and is often unsuitable for trace analysis (Fattahi, *et al.*, 2007). In this sense, many preconcentration procedures must be performed to determine trace amounts of lead, as indicated in the tables shown here. The most important analytical lines of lead are 217.00 and 283.31 nm. The 217.00 nm line is more sensitive, notwithstanding the greater amount of background absorption effects (Fattahi, *et al.*, 2007). Electrothermal atomic absorption spectrometry (ETAAS) is a good alternative for determining trace amounts of lead in several types of samples in view of its good sensitivity (Fattahi, *et al.*, 2007). However, in some cases, previous preconcentration and separation

steps are carried out before analytical measurements by ETAAS. The use of a modifier stabilizes lead, allowing for its determination without causing matrix effects. The Pd–Mg modifier is the one most commonly used, since it produces the best results. This modifier allows for the application of pyrolysis temperatures ranging from 1200 to 1400°C, which enables the separation of most interfering elements (Fattahi, *et al.*, 2007). The stabilizing effect of this modifier also raises the atomization temperature to 2000°C, which allows a characteristic mass of about 16 pg (Fattahi, *et al.*, 2007). Ammonium phosphate is another modifier frequently used for determining lead by ETAAS, allowing for an atomization temperature of 1600°C and enabling a low characteristic mass of 12 pg (Fattahi, *et al.*, 2007).

Inductively coupled plasma optical emission spectrometry (ICP OES)

Inductively coupled plasma optical emission spectrometry is an analytical technique often employed to determine lead in various types of samples (Szabo, *et al.*, 2005). The main emission lines are: Pb II 220.353 nm, Pb I 216.999 nm and Pb I 283.306 nm, with 220.353 nm being the most sensitive. However, the low level of lead in many samples lies below the detection limit of this technique. Moreover, several types of spectral interference have been reported in the determination of lead by ICP OES. Virtually all photomultiplier-based ICP spectrometers use the Pb 220.353 nm analytical line, despite its severe background continuum and inter-element interference from Al 220.4 nm and background shift due to iron (Fe). Direct spectral overlap interference due to iron has also been found in the 216.9 and 283.9 nm analytical lines (McAllister, *et al.*, 2007). Thus, preconcentration and separation procedures have been devised to allow trace amounts of lead to be determined in complex matrices using ICP OES. Several tables shown in this paper summarize the use of separation techniques such as liquid–liquid extraction, solid phase extraction, cloud point extraction and others, as pre-steps in determining lead using ICP OES.

Lead separation and preconcentration

Separation techniques such as coprecipitation

(Rykowska, 2007), liquid–liquid extraction (Moghimi *et al.*, 2010), solid phase extraction (Su, *et al.*, 2003; Moghimi, *et al.*, 2009) and more recently, cloud point extraction (Su, *et al.*, 2003; Moghimi, *et al.*, 2009; Moghimi, *et al.*, 2014) and on-line coprecipitation using a knotted reactor (Moghimi, *et al.*, 2012; Moghimi, *et al.*, 2011; Moghimi, *et al.*, 2013) have been successfully employed to determine trace levels of lead. Each technique has its pros and cons and should be chosen according to the analytical problem.

Coprecipitation

Coprecipitation is one of the most efficient separation/enrichment techniques for trace heavy metal ions. The main requirement for this technique is that the collector should separate easily from the matrix solution. This can be done by filtering, centrifuging and washing of the precipitate. In addition, it is desirable that the collector should be a pure and readily available substance. The advantages of this technique are its simplicity and the fact that various analyte ions can be preconcentrated and separated simultaneously from the matrix. Inorganic or organic coprecipitants have been used as efficient collectors of trace elements. However, this process is slow and samples sometimes have to be kept over-night for complete coprecipitation (Rykowska, *et al.*, 2004). This technique has been widely applied in preconcentration procedures for determining lead in water samples. Inorganic coprecipitants such as manganese dioxide and aluminum, gallium, cerium(IV), erbium, iron(III), magnesium, samarium and zirconium hydroxides have been widely and successfully used for preconcentrating trace lead ions from different mediums (Rykowska, 2007). A fast procedure for separation and preconcentration using ultrasound-assisted coprecipitation with manganese dioxide has recently been proposed for determining lead in environmental samples by ICP OES (Taguchi, *et al.*, 1997). Coprecipitation parameters, including concentration of oxidizing agent-KMnO₄, concentration of MnSO₄ and exposure time to ultrasound irradiation, are discussed. The time required for coprecipitation is about 60. Another paper proposed an aluminum hydroxide coprecipitation method for the determination of trace amounts of Cu, Cd and Pb by FAAS in seawater and mineral water after a 125-

fold preconcentration (Szabo *et al.*, 2005). Table 1 lists several methods for determining lead in many samples, using coprecipitation as the separation and preconcentration technique.

Liquid-liquid extraction

Solvent extraction has been one of the most extensively studied and widely applied methods in preconcentration and separation procedures for the determination of trace elements due to its simplicity, convenience, wide scope, etc. In this technique, the metal is distributed between two immiscible liquid phases (usually an aqueous and an organic phase). Metal ion stripping from aqueous solution to organic phase takes place after a complexation reaction. For the analytical measurement, the extracted metal ion can be directly measured in organic extract or a back

extraction step is carried out in an aqueous medium, usually acid (Cui, *et al.*, 2007). Separation and preconcentration procedures using solvent extraction generally result in a high enrichment factor due to the difference between the volumes of aqueous and organic phases. Although this procedure is operated in batch mode, it is time-consuming and produces large amounts of potentially toxic organic solvents as waste. The implementation of methods in continuous mode overcomes these drawbacks. Such unit operations are, instead, carried out in flow injection (FI) and/or sequential injection (SI) systems, which, besides reducing sample and reagent consumption, allow all manipulations to be done automatically in an enclosed environment, thus minimizing the risk of sample contamination. Analytical procedures for lead separation and preconcentration by solvent extraction

Table 1: Preconcentration procedures using coprecipitation for the determination of lead.

Sample	Collector	Technique	LOD (μgL^{-1})	R.S.D. (%)	Reference
Ground water	MnO ₂	FAAS		3.3-8.3	Rykowska, 2007
Natural water	MnO ₂	FAAS			Rykowska, <i>et al.</i> , 2008
Rain water	MnO ₂	FAAS			Unger, 1979
Sea water	MnO ₂	FAAS			Mijatovic, <i>et al.</i> , 2000
Zinc and zinc ~aluminum alloys	MnO ₂	ICPOES			Rao, <i>et al.</i> , 2009
River waters	MnO ₂	ICPOES	3.2	5.0	Geim, <i>et al.</i> , 2007
Sea waters and mineral water	Aluminum hydroxide	FAAS	16	2.0-3.0	Lee, <i>et al.</i> , 2008
Sea waters	Cerium(IV) hydroxide	FAAS	7	8	Yang, <i>et al.</i> , 2009
Tap water	Erbium hydroxide	FAAS	0.24	1-9	Chang, <i>et al.</i> , 2010
Sea water	Gallium hydroxide	ICPOES	0.15		Zhang, <i>et al.</i> , 2010
Sea water	Gallium hydroxide	ICPOES	0.15		Hashemi, <i>et al.</i> , 2001
Sea water	Iron hydroxide	ETAAS			Hummers, <i>et al.</i> , 1958
Sodium tungstate	Lanthanum hydroxide	ICPOES	1.1	3.1-5.5	Raoufi, <i>et al.</i> , 1999
Dialysis concentrate	Magnesium hydroxide	ETAAS			Hagen, <i>et al.</i> , 1990
Sea water	Magnesium hydroxide	ICP-MS	2.7.10 ⁻⁴		Yamini, <i>et al.</i> , 1997
Urine, sediment	Samarium hydroxide	EAAS	24.0	5.0	Petit de Pena, <i>et al.</i> , 1995
Natural water	Zirconium hydroxide	E,AAS	4.2.10 ⁻⁴	<10	Alizadeh, <i>et al.</i> , 1999
Infant formulas and milk	Ammonium Pyrrolidine	ETAAS	0.04		Moghimi, <i>et al.</i> , 2008
Cupric sulfate	Ammonium Iron sulfate	ICPOES		4.4-5.8	Choi, <i>et al.</i> , 2003
Natural water	Bismuth dithyldithiocarbamate	ETAAS			Moghimi, 2007
Natural water	Copper dithyldithiocarbamate	FAAS	1.5	4.4	Moghimi, 2007
Natural water	Copper dithyldithiocarbamate	FAAS	3.2	2.0	Moghimi, <i>et al.</i> , 2008
Cobalt sulfate	Cerium phosphate	FAAS	55.9		Ekinci Dogan, <i>et al.</i> , 2007
Water	Lanthanum phosphate	ICPOES		1.6	Gonzalez, <i>et al.</i> , 2001
Sea water	Palladium	ETAAS		3.8	Nayebi, <i>et al.</i> , 2006
Natural water	Sodium dithyldithiocarbamate	ICPOES			Moghimi, 2006
River water	Sodium dithyldithiocarbamate	ICPOES	10.0		Roldan, <i>et al.</i> , 2005
Sea water	Sodium sulphide	ICPOES		1.9	Hatay, <i>et al.</i> , 2005

(^(*)) Pg/mL; (^(a)) ng/g

Table 2: Procedures for lead preconcentration based on solvent extraction.

Sample	Technique	Complication agents	Solvent	Enrichment factor	Reference
Table salt	FAAS	Dithizone	MIBK ^a	99	Ngeontae 2007
Waste Water	FAAS	HBDAP ^b	HNO ₃ /HCl		Tuzen, <i>et al.</i> , 2009
Estuarine water	GFAAS	APDC ^c and DDC ^d			Liu, <i>et al.</i> , 2010
Urine and CRF	ICP-MS	APDC	MIBK/HNO ₃	23.3	Wang, <i>et al.</i> , 2002
High Purity aluminum salts	ICPOES	APDC	HNO ₃ /H ₂ O ₂		Koksal, <i>et al.</i> , 2002
Natural water	FAAS	Dithizone	Xylene		Carasek, <i>et al.</i> , 2002
Natural water	FAAS	Dithizone	HNO ₃	543	Carasek, <i>et al.</i> , 2002
Aragonite	ET AAS	NaDDC	MIBK		Zendelovska, 2001
water	FAAS	APDC	MIBK		Ansari, 1999
Seawater	ICP-MS	DOC			Batterham, <i>et al.</i> , 1997
Drinking water	FAAS	CMPQ ^e			Saran, <i>et al.</i> , 1992

^(a) Methylisobutyl ketone; ^(b) NN-bis(2-hydroxy-5-bromo-benzyl)-1-2diaminopropane; ^(c) Ammonium Pyrrolidinedithiocarbamate; ^(d) Dithyldithiocarbamate; ^(e) 5-(2-Cabomethoxyphenyl)azo-8 quinolinol

and determination by atomic spectrometric techniques have been widely applied since these techniques were invented (Becerril, *et al.*, 2008).

Procedures in flow injection systems for separation and preconcentration with the application of solvent extraction to determine metals, including lead, are extensively discussed in the literature (Muresanu, *et al.*, 2008; Moghimi, 2007). Table 2 lists several analytical systems proposed for lead separation and preconcentration by solvent extraction and lead determination using atomic spectrometric techniques.

Solid phase extraction

Solid phase extraction is based on the partition between a liquid (sample matrix) and a solid phase (sorbent). Several sorbents coupled to detection systems have been used for lead preconcentration and determination. The basic approach is the contact of a liquid sample through a column, a flask, a cartridge, a tube or a disk containing an adsorbent that retains lead ions. After this first step, the retained lead is recovered upon elution with an appropriate solvent (Camel, 2003). Sorbents used in preconcentration systems for lead determination can be unloaded, loaded or chemically modified with the help of complexing reagents. Unloaded supports are potential collectors of analytes in the form of a single ion or associated with other species such as complexes.

The sorbents in this class include activated carbon (Camel, 2003), natural adsorbents (Pereira, *et al.*, 2004), Amberlite XAD resins (Tuzen, *et al.*, 2004; Tokahoglu, *et al.*, 2002), polyethylene (Fernandes, *et al.*, 2003) and others (Castillo, *et al.*, 2005). Lead can also be complexed with ligands loaded in several supports, such as polyurethane foam (Ferreira, *et al.*, 2003), activated carbon (Ensafi, *et al.*, 2003), and polymeric materials (Elci, *et al.*, 2000), which make for efficient preconcentration procedures. Many reagents have been used to load these supports and to retain lead ions by complexation. These include: 2-(2-thiazolylazo)-p-cresol (TAC) (Moghimi, 2010), 2-propylpiperidine-1-carbodithioate (Moghimi, 2010), 2-(2-benzothiazolylazo)-2-p-cresol (BTAC) (Lemos, *et al.*, 2002), pyrogallol red (Ensafi, *et al.*, 2003), 1-(2-pyridylazo)-2-naphthol (PAN) (Poursharifi, *et al.*, 2012) dithizone (Moghimi, *et al.*, 2009) and 2-(5-bromo-2-pyridylazo)-5-diethyl-aminophenol (5-Br-PADAP) (Moghimi, 2008) Supports can also be functionalized with chelating reagents, which render them powerful absorbents for lead preconcentration. Supports such as Amberlite XAD series (Moghimi, 2014) silica gel (Shojai *et al.*, 2015) and cellulose (Pyrzynska *et al.*, 2000), have been modified with reagents by several routes. Several methods have been proposed for preconcentrating lead using the solid phase batch extraction procedure.

Automation and possible on-line coupling to analysis techniques

SPE can be easily automated, and several commercially available systems have been recently reviewed (Moghim, *et al.*, 2012). Home-made systems have also been reported (Moghim, 2013). In addition, all the sample volume is further analyzed, which enables smaller sample volume to be used. However, in the case of complex samples, off-line SPE should be preferred due to its greater flexibility, and the opportunity to analyze the same extract using various techniques.

On-line coupling to liquid chromatography

On-line systems mainly use a micro-column. The sorbent is chosen not only for its efficiency in trapping analytes, but also for its compatibility with the stationary phase packed into the chromatographic column. Indeed, it is highly recommended to use the same packing in the precolumn and the chromatographic column to prevent losses in efficacy upon analysis. For the case of two different sorbents being used, the retention of the analytes in the pre column should be lower than in the analytical column to ensure band refocusing at the head of the chromatographic column. On-line systems with several detectors have been reported, such as ultraviolet (UV) detector or inductively coupled plasma mass spectrometer (ICP-MS), with detection limits in the 0.05–50 mg.l⁻¹ range. Detection limits as low as 0.5 g.l⁻¹ could even be achieved by detection at the maximum absorption wavelength using a photodiode array UV detector (Moghim, *et al.*, 2014).

(Olsen, *et al.*, 1983) and (Fang, *et al.*, 1984) were the first to describe an on-line flow injection (FI) sorbent extraction preconcentration system for flame AAS (F-AAS) using microcolumns packed with a cation-exchanger. Later, they also proposed a system for on-line flow injection sorbent extraction preconcentration with electrothermal vaporization AAS (ET-AAS) using lead as a model trace element (Fang, *et al.*, 1990). Since then, numerous papers reported FI with on-line preconcentration followed by AAS, as exemplified by determination of Pb (Fang, *et al.*, 1990). Selected applications are reported in Table 3. The sorbent should provide for rapid sorption and desorption of the analytes to be used in FI systems (Ruzicka, *et al.*, 1989). In addition, it should be provided for a high selectivity. In practice, C₁₈-silica is very frequently used as

organic solvents (such as methanol) can be used as eluting solvents leading to a high sensitivity in flame AAS. Complexing reagents are, therefore, added for efficient retention of trace metals. Their choice is based on their fast reaction with metals, such as diethyldithiocarbamate (DDTC) and ammonium pyrrolidinedithiocarbamate (APDC). In addition, both reagents are water soluble and do not adsorb on C₁₈-silica so that it does not overload with the reagent itself. However, these reagents lack selectivity, so that other reagents have been used for particular applications, like 1-10-phenanthroline (Moghim, *et al.*, 2012), 0,0-diethyl-dithiophosphate (DDTP) (Moghim, *et al.*, 2013). The micro column can be inserted into the tip of the PTFE capillary in the autosampler arm of a graphite furnace atomic absorption spectrometer (Tajodini, *et al.*, 2010). Even though C₁₈-silica has been the most frequently used sorbent for FI preconcentration, other sorbents were found satisfactory for some applications as shown in Table 3, such as functionalized activated carbon (Muresanu, *et al.*, 2008), polyurethane foam (PUF) (Moghim, *et al.*, 2012), or PTFE turnings (Zhang, *et al.*, 2010). A particular knotted reactor (KR) has been recently developed, which consists of a long tube properly knotted usually made of PTFE.

On-line coupling to ICP-AES or ICP-MS

The first report of FI on-line preconcentration coupled to ICP-atomic emission spectrometry (AES) appeared nearly twenty years ago (Seki, *et al.*, 2000). Since then, several studies have used this coupling with different sorbents such as ZrO₂ or functionalized silica gel for example (Muresanu, *et al.*, 2008).

On-line coupling to spectrophotometry

Spectrophotometry offers the advantage of requiring inexpensive and very common instrumentation. In addition, by choosing a non-selective chromogenic reagent, multi-metal determinations may be possible (Li, *et al.*, 2002). Its coupling to FI analysis is well suited for monitoring purposes and a few studies present such systems as indicated in Table 3 (Lemos, *et al.*, 2002). Solid-phase spectrophotometry (SPS) has also been reported with FI systems due to its simplicity and low detection limits. The solid sorbent is packed in ei-

Table 3: Applications of SPE to FI on-line preconcentration systems.

Matrix	Sorbent	Eluent	Analysis method	Recovery (%)	Preconcentration factor	LOD (ng/l)	Ref.
Certified biological, Vegetable samples	polyurethane foam	IBMK	F-AAS	99.2– 101	60–189	3000	Moghimi, <i>et al.</i> , 2012
Standard solutions	C ₁₈ -silica	EtOH	F-AAS	--	4–1000	300–3000	Moghimi, <i>et al.</i> , 2014
Standard solutions	C ₁₈ -silica	MeOH	F-AAS	--	14–60	4000-10000	Mureseanu, <i>et al.</i> , 2008
Tap, river and coastal waters, Marine sediment, fish and mussel tissues	PTFE turnings	IBMK	F-AAS	95–102	330	800	Moghimi, <i>et al.</i> , 2014
Standard solutions	PUF	EtOH	F-AAS	--	4–1000	300–3000	Lemos <i>et al.</i> , 2002
River, ground waters	Lewatit TP807'84 PAPHa	HCl	Spectrophotometry	80–120	50	2000-5500	Zhang <i>et al.</i> , 2010

TAN: 1-(2-Thiazolylazo)-2-naphthol; Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol; DDTP: O,O-diethyldithiophosphate ng.L⁻¹

ther commercially available or customized flow cells. On-line FI sorbent extraction procedures have several advantages over the corresponding off-line methods: higher sample throughput (increased by 1 to 2 orders of magnitude), lower consumption of sample and reagent (also reduced by 1 to 2 orders of magnitude), better precision (with relative standard deviations approx. 1–2%), lower risk of loss or contamination and easy automation.

CONCLUSIONS

Considering the poisonous nature of lead and the low concentration of this element in samples, preconcentration procedures have been devised involving separation techniques such as liquid–liquid extraction, solid phase extraction, coprecipitation and cloud point extraction. Nevertheless, each technique has its pros and cons and should therefore be chosen according to the analytical problem. Most of the proposed methods were established using solid phase extraction. In recent years, on-line systems have been preferred.

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