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A review on solid phase microextraction—High performance liquid chromatography as a novel tool for the analysis of toxic metal ions

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Abstract

This paper reviews the practical applications of solid phase microextraction-High performance liquid chromatography in the analysis of toxic metal species as these are important contaminants and are carcinogenic. Their determination in formulations, in feed and food, and in complex environmental matrices (e.g., waste water and industrial effluents) often requires analytical methods capable of high efficiency, unique selectivity, and high sensitivity. Solid phase microextraction (SPME) requires low solvent consumption and is quick in use. SPME is used for extraction and online desorption of analytes with the mobile phase of HPLC and subsequent detection by UV, ICP-MS or ESI-MS as detectors. Different SPME–HPLC methods are summarized in this article to demonstrate the usefulness of this technique for metallic species of As, Cr, Pb, Hg and Se.

Keywords: Solid phase microextraction; High performance liquid chromatography; Metal ions

1. Introduction

Some of the metals found predominantly as particulate matter in polluted atmosphere are known to be hazardous to human health [1]. Except beryllium all toxic metals are so called heavy metals. Lead is toxic metal of greatest concern in the urban atmosphere because it comes closest to being present at toxic levels. Mercury is the second most toxic metal. Other toxic metals include Be, Cr, V, Ni, Cu, As and Se, etc.

The term 'speciation' means distribution of an element amongst defined chemical species in a system [2]. Speciation of trace elements provides more specific information about real status and impact of given elements in a system. The effects of toxicity of an element depend upon the particular form in which the element is present in the system. Therefore, speciation of toxic species present in the sample is very much needed. It has been observed that a particular oxidation state/form of an element may be hazardous whereas other forms may be useful, e.g., Cr(III) is present in the sea food in ppm levels and is essential element whereas Cr(VI) is far more toxic and carcinogenic. In contrast to chromium, more reduced species of As are more toxic, e.g., arsine (AsH_3)>arsenite (As(III))>arsenate(As(V)). Hg(II) ion is toxic to the mammalian kidney and corrosive at the sites of mucosal absorption whereas CH_3Hg^+ crosses the placenta and blood brain barrier, acting as teratogen and central nervous system toxin. Hg, Ge and Sn metals undergo biomethylation. Biomethylation generally increases the toxicity of the metals but methylation of As and Se contributes to their detoxification. Metals such as As, Sn, Hg and Pb are of major interest in the speciation analysis.

Traditional methods of sample preparation are typically time consuming, employ multistep procedures having high risk for loss of analytes and use of extensive amounts of organic solvents. A special attention is focused on the techniques which are characterized by a considerable reduction or complete elimination of organic solvents. Such techniques protect the environment against additional quantities of sol-

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vents and reduce the cost of analysis. The solvent free techniques such as gas phase extraction, membrane extraction and SPE have their limited use to volatile and relatively volatile organic compounds, volatile nonpolar compounds and relatively low volatile compounds [3], respectively. SPME is relatively a new technique in which sampling, isolation and enrichment of analytes and analyte introduction to a measuring apparatus can be done in one step. It was developed by Pawliszyn and co-workers [4–6] in 1990. It has been routinely used in combination with GC, GC–MS, HPLC and LC–MS.

SPME–HPLC has limited application due to the optimization of desorption conditions and limited number of commercially available fibers. But in the last 5 years, interest towards the technique has been increased and a number of applications have been developed. Recently the approach to in tube SPME has also been developed in which the open tubular fused silica capillary column is used as SPME device instead of using the SPME fiber. This review focuses primarily on SPME–HPLC methods for the analysis of metallic and organometallic species. A brief overview of SPME principles are given together with the advantages of using HPLC-SPME as a special analytical technique.

2. SPME

2.1. Introduction

SPME is a technique whereby an analyte is sorbed onto the surface of the coated silica fiber. This is followed by desorption of the analytes into a suitable instrument such as GC or HPLC for the separation which is attached with suitable detector for quantification. Sorption of analyte onto a suitably coated silica fiber or stationary phase is the most important stage. SPME is performed with GC in most of the applications. In case of SPME-GC, the analytes are thermally desorbed into the injector of the chromatograph. It is however, generally limited to volatile and thermally stable compounds. Some of the applications involve the derivatization in the sample matrix, in the injection port and on the fiber derivatization after and/or during SPME to overcome the problem of its limited use. More recently, SPME is applied to nonvolatile and thermally unstable compounds by interfacing with HPLC. In SPME-GC, the fiber is introduced into the injector port and analytes are thermally desorbed from the coating. But in SPME–HPLC, desorption is carried out in an appropriate interface. It consists of six port injector with a special fiber desorption chamber, installed in place of sample loop. Desorption is carried out by the use of organic solvent or mobile phase because the thermal desorption at high temperature leads to degradation of the polymer and incomplete desorption of many nonvolatile compounds from the fiber.

2.2. Design of SPME

There are two different techniques for the SPME method; fiber SPME and in-tube SPME.

Fiber SPME is a modified syringe like instrument which consists of fiber holder and fiber assembly with built-in fiber inside the needle. The fused silica fiber is coated with a relatively thin film of several polymeric phases. Due to its small physical diameter, cylindrical geometry and stability at higher temperatures, it can be incorporated into a syringe like holder. The SPME holder provides protection to fiber and allows piercing of rubber septum of the GC injector. The fused silica fiber is retracted within the needle of the SPME holder when it is not in use. During operation, the silica fiber is exposed to the sample in its matrix.

In-tube solid-phase microextraction (SPME) [7] is an automated version of SPME that can be easily coupled to a conventional HPLC autosampler for on-line sample preparation, separation and quantitation. It has been termed “in-tube” SPME because the extraction phase is coated inside a section of fused-silica tubing rather than coated on the surface of a fused-silica rod as in the conventional syringe-like SPME device. The new in-tube SPME technique has been demonstrated as a very efficient extraction method for the analysis of polar and thermally labile analytes.

2.3. Working of SPME

The fiber should be cleaned before analyzing any sample as the contaminants are responsible for the background in chromatogram. It is done in desorption chamber of HPLC by running solvent. During the process, the fiber is lowered into the vial which is sealed with a septum type cap. The fiber is extended into the sample through needle. It results in the adsorption of analyte on the fiber. After sampling, the fiber is retraced within its holder for protection. The analytes are desorbed from the fiber using the mobile phase, i.e., solvent desorption. This requires a special interface which consists of six port injection valve and a desorption chamber. Desorption chamber is placed in the position of injection loop. When sample is extracted, the fiber is inserted into the desorption chamber at the ‘load’ position. After changing the injector to ‘inject’ position, the mobile phase comes in contact with the fiber. Desorption of analytes occur and mobile phase delivers them to the HPLC column where they get separated and detected by suitable detector.

3. Ways to improve extraction

There are some factors which are used to improve the SPME extraction:

3.1. Selection of extraction mode

There are two types of extraction modes [3,8] in fiber SPME; Head space SPME and direct immersion SPME. HS is used when GC is employed for final analysis. It involves the exposure of fiber in the vapour phase above the gaseous, liquid or solid sample. In this the fiber is not in contact with

the sample. The analytes need to be transported through a layer of air before they can reach the coating. In DI-SPME the coated fiber is inserted into liquid sample and the analytes are transported directly to extraction phase. For volatile compounds, fiber HS-SPME is preferred over the DI-SPME as the former has longer lifetime. The fiber coating can be damaged by high molecular weight species and other non-volatile contaminants present in the liquid sample matrix in case of DI-SPME as the fiber is directly immersed into it. It is also found that HS is more selective than DI [9].

3.2. Selection of the fiber

The technique has found limited use in high performance liquid chromatographic applications because of the unavailability of fibers that are stable and durable in strong organic solvents. Proper fiber selection is important for the efficient extraction of the analyte from the sample. It is based on the nature of the analyte. There are seven different types of fibers available with Supelco, namely polydimethylsiloxane (PDMS) [11], polydimethylsiloxane/divinylbenzene (PDMS/DVB) [10,12], stableflex polydimethylsiloxane/divinylbenzene (PDMS/DVB), polyacrylate(PA) [13–16], carboxen/polydimethyl-siloxane(CAR/PDMS), carbowax/divinylbenzene (CW/TPR) [17–20], stableflex divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS). But the modifications of fibers and preparation of new fibers increases the interest towards SPME–HPLC methods.

The modifications in the fiber have been reported by using crown ether as a reagent for the selective extraction of metal ions. It involves the preparation of hydrophobic polypropylene microporous hollow fiber (MPH). A piece of hollow fiber membrane (1.5 cm) was threaded onto the fused silica rod (o.d. 110 μm) which was glued on to one end of a piece of stainless steel tubing using epoxy glue. After few hours, the fiber was dipped into the mixture of hexane, dichloromethane and methanol (4/4/1, v/v/v) for hours to remove the residues of undried glue and other impurities. Some crown ethers have shown excellent ability to selectively extract metal ions from the aqueous solutions into an organic medium. Polymerization of macrocyclic ligands or their immobilization on support materials like silica gel is an important development in the applications of the crown ethers.

Some methods for the modifications of the fiber are reported using sol gel process [21–23], these fibers are stable in strong organic solvents (xylene and methylene chloride) as well as acidic and basic solutions. The method of preparation involves four steps. In the first step, the fused silica fiber is pretreated by burning the tip to remove the polyimide coating so that the maximum number of silanol groups, washed with methanol and then air-dried. The sol–gel solutions were prepared and stirred for 4 h at room temperature. The fiber was coated by exposing to the sol–gel solution for 20 min and end capped. The fiber was conditioned by placing it in GC injector port at temperature of 130 °C. Before use fiber was conditioned in the mobile phase for 30 min and dried at room temperature. The hydrolytic stability of these sol–gel prepared SPME fibers towards organic solvents and high and low pH solutions can be attributed to the fact that the coating is chemically bonded to the surface of the fused silica substrate. A thermal stability shows that PDMS fiber could be used upto 320 °C whereas commercial PDMS fibers began to bleed at lower temperatures (200 °C). The high degree of porosity of sol–gel fiber resulted in higher sensitivity and faster extraction times relative to commercial fibers.

3.3. Optimization of extraction

The extraction time can be improved by.

3.3.1. Internal cooling[25–28]

Analyte equilibrium concentration in the HS can be increased by heating the sample and by cooling the fiber. It is applied to the analysis of very volatile components in heavily contaminated liquid and solid samples.

3.3.2. Sample agitation

Agitation speeds up the transfer of analytes from matrix to coating of the fiber [29]. It is done by magnetic stirring, sonication and intrusive stirring [29–31]. Another way to speed up the extraction is fiber vibration [32] and rotation [33] which increases precision also.

3.3.3. Salting out effect [30,34–43]

Addition of an analyte improves the extraction time by increasing the ionic strength and reducing analyte solubility. The electrolyte generally used for this purpose are NaCl, $NaHCO_3$, K_2SO_4 and $(NH_4)_2SO_4$. The salting out effect makes HS-SPME more effective.

3.3.4. pH of the solution [30,40,42–46]

The ionisable compounds can be converted to a nonionic form and are extracted by nonpolar and weakly polar stationary phases.

3.3.5. Derivatization [47]

It is based on analyte conversion to another compound by reacting with a specially selected reagent. An analyte derivative should be characterized by better and/or selective SPME extraction. There are two derivatization approaches; in matrix derivatization and on fiber derivatization [46]. In matrix derivatization is based upon the addition of a derivatization reagent to a container with a sample and extraction of a derivative from HS. Its applications include determination of lead ions in water by converting them to tetraethyllead in reaction with sodiumtetraborate and extracting it from HS. On fiber derivatization is conducted directly on SPME fiber. The fiber is immersed in reagent solution and then in a sample. The analyte is extracted and converted to a derivative in the coating.

Table 1
Application of SPME–HPLC for the analysis of metallic and organometallic species

S. no	Analyte	Fiber used	Desorption features	Column used	Detection/technique used	Detection limit	Reference
1	Diphenylmercury (5 mg/l), trimethylphenyltin (25 mg/l), triphenylarsine (0.5 mg/l)	100 cm fused silica optical fiber (*n*-octyltrimethylethoxysilane coated), o.d. 300 μm (sol gel fiber)	Mobile phase-acetonitrile:water, 80:20% (v/v), static desorption (5 min), flow rate 1 ml/min	250 mm × 4.6 mm i.d. C_{18} column	UV (254 nm)/SPME–HPLC–UV	647, 412 and 80 μg/l	[21]
2	AsB	Platinum wire with poly(3-dodecylthiophene) coating (2 cm × 0.2 mm)	30 mM $(NH_4)CO_3$, isocratic, flow rate 1 ml/min	PRP-X 100 anion exchange	ICP-MS/SPME–HPLC-ICP-MS		[48]
3	AsB	Platinum wire with poly(3-alkylthiophene) coating,(2 cm × 0.2 mm	Mobile phase- 30 mM $(NH_4)CO_3$, isocratic, flow rate 1 ml/min	PRP-X 100 anion exchange PRP-X 100 anion exchange	ICP-MS/SPME–HPLC-ICP-MS		[49]
4	Cr(III) and Cr(VI)	Carbowax/templated resin	EDTA as complexing agent		UV		[50]
5	Trimethyllead, triethyllead	(In tube SPME)	Mobile phase- 0.1% trifluoroacetic acid + 12% methanol, flow rate −450 μl/min	C_{18} column guard column	ES-MS/SPME–HPLC–ES-MS	11.3 and 12.6 ng/ml	[51,52]
6	Hg(II) ions	Polypropylene microporous hollow fiber (i.d. 200 μm, wall thickness 30 μm)	In the mobile phase hexane-dichloromethane-methanol (4:4:1,v/v/v), isocratic, flow rate 1 ml/min	5 μM Spherisorb silica column (4.6 mm × 250 mm)	UV (254 nm, 275 nm)/SPME–RP-HPLC–ICP-MS	500 ppb	[53]

3.4. Optimization of desorption analyte

Dynamic desorption involves the removal of analytes by a moving stream of mobile phase and static desorption involves the soaking of fiber in the mobile phase for a specified time for desorption of strongly absorbed analytes. The rapid and complete desorption of analytes using minimal quantity of solvent is important for optimizing SPME–HPLC. Some of the SPME–HPLC methods are summarized for different toxic metals in Table 1.

4. Applications of SPME–HPLC to the metal species

Applications of SPME–HPLC are summarized below.

4.1. Arsenic

Arsenic is the most significant water pollutant metalloid. It occurs in the earth's crust at an average level of 2–5 ppm. It is introduced into the environment by anthropological factors such as combustion of fossil fuels, particularly coal, mine tailings, as a byproduct of copper, gold and lead refining and by use of pesticides particularly lead arsenate $Pb_3(AsO_4)_2$, sodium arsenate Na_3AsO_3, and Paris green $Cu_3(AsO_3)_2$. The natural sources include crustal weathering and volcanic activity.

Arsenic is present as oxyanion in the aqueous solution. The different species of arsenic are arsenic(V) and the inorganic ion; (AsO_4),$^{3-}$ $HAsO_4$,$^{2-}$ in aquatic systems and arsenic(III) and arsenite anion $(As_3)^{3-}$. Arsenic may be converted into more labile and toxic methyl derivatives by bacteria, according to following reactions

$$H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$$

$$H_3AsO_3 \xrightarrow{\text{methylcobalamin}} \underset{\text{methylarsinic acid}}{CH_3AsO(OH)_2}$$

$$CH_3AsO(OH)_2 \xrightarrow{\text{methylcobalamin}} \underset{\text{dimethylarsinic acid}}{(CH_3)_2AsO(OH)}$$

$$(CH_3)_2AsO(OH) + 4H^+ + 4e^- \rightarrow (CH_3)_2AsH + H_2O$$

Methylation reduces the toxicity of metal but DMA is still a mutagenic compound. Other derivative forms of arsenic are arsenobetaine (AB), arsenocholine (AC), arsenosugars, etc.

Yates et al. [48] reported the preconcentration of neutral species by electrochemical control of solid phase microextraction. Fig. 1 shows the construction of porous hollow polymer device. The polymer films were used as solid phase micro-extraction (SPME) elements for the direct and specific extraction of trace levels of AsB. Hydrophobic interactions between neutral arsenic species and an undoped polythiophene are responsible for the diffusion-controlled preconcentration. After absorption into the polymer matrix, the chemical properties of this conductive polymer were changed by applying an external potential. This potential provides a

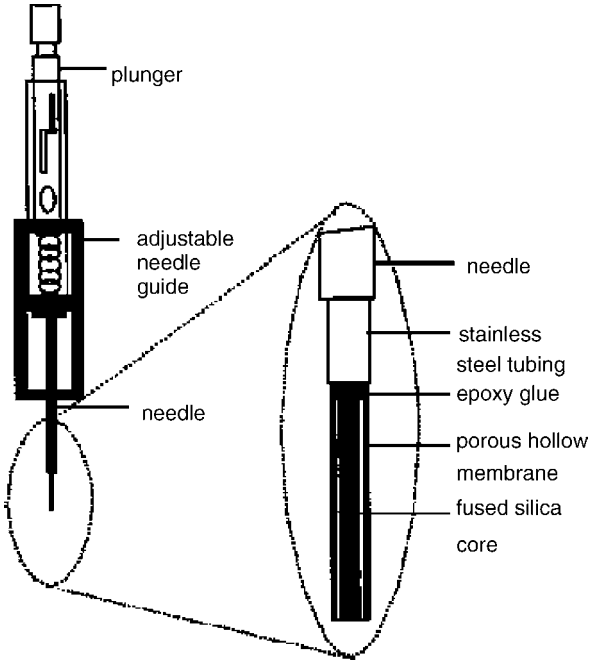

Fig. 1. Porous hollow-fiber SPME device. (Reproduced with the permission from reference [48].)

sufficient driving force for desorption of the analyte from the extraction phase into an aqueous solution for subsequent analysis. The applied positive potential oxidizes the polymer to its charged hydrophilic state, which releases the neutral analyte. The concentration and speciation of the analyte from the sample matrix was analyzed by HPLC coupled to an ICP-MS.

Tamer et al. [49] applied electrochemically aided control of solid phase micro-extraction (EASPME) for the determination of the neutral species such as arsenobetaine (AsB) by using electro-synthesized organic conducting polymer (OCP) films. Extensive usage of organic solvents during the extraction step, the complexity of each individual matrix, and limited availability of an analyte in a confined finite volume stimulated the use of SPME techniques. The separation and detection of the arsenic (As) species was attained using an HPLC-ICP-MS interfaced system. This method is selective towards neutral AsB in the presence of other anionic As-species due to the change in hydrophobic nature of the film during the doping/undoping processes. Comparison of performance of poly(3-octylthiophene), poly(3-dodecylthiophene), and poly(3-hexadecylthiophene) films is reported. The best results were obtained by using poly(3-octylthiophene) film. The detection limit and linear dynamic range using this method are 14 ng mL^{-1} and 70–1200 ng mL^{-1}, respectively. The method was tested for the determination of AsB in artificial environmental soil samples. Fig. 2 shows the chromatogram for AsB.

Gbatu et al. [24] extended the potential of SPME by developing the fibers that are stable in strong organic solvents (xylene and methylene chloride) as well as acidic and basic solutions (pH 0.3 and 13) using the sol–gel technology. This study describes the preparation of fibers. The hydrolytic stability of these sol–gel prepared SPME fibers towards organic solvents and high and low pH solutions can be attributed to the fact that the coating is chemically bonded to the surface of the fused silica substrate. These fibers were subsequently used to extract organo-arsenic, organo-mercury and organo-tin compounds from aqueous solutions followed by separation using HPLC with UV absorbance detection. The detection limits were comparable and/or slightly better than those obtained using commercial SPME fibers. The thinner coatings (resulting in faster extraction time) and the hydrolytic stability of the sol–gel fibers, towards strong organic solvents and high and low pH solutions make them superior over commercially available fibers.

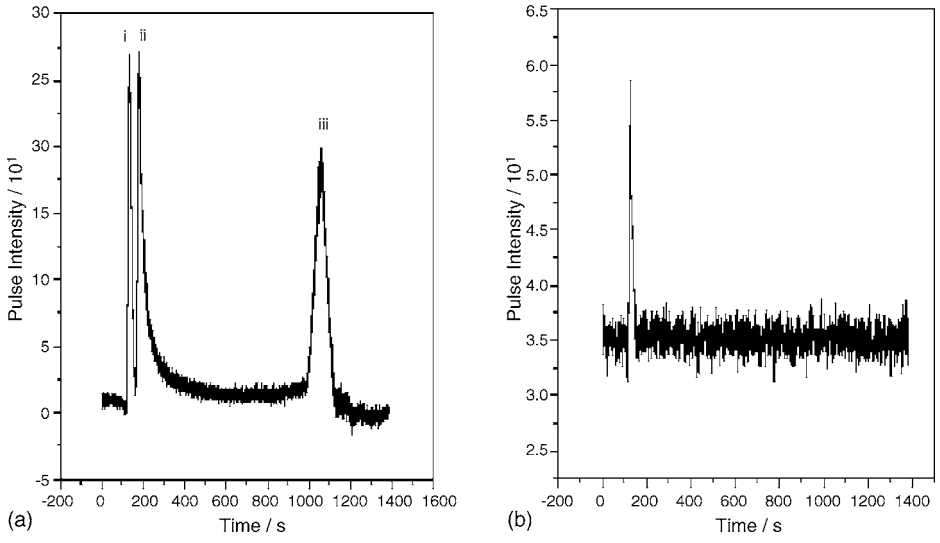

Fig. 2. Direct injection of AsB(i), AsO^{2-}(ii) and AsO_4^{3-}(iii), 100 ng mL^{-1} each without speciation (a), and after extraction/release using POT/SPME (b). (Reproduced with the permission from reference [49].)

4.2. Chromium

It is of crucial importance because of its use in stainless steel industries, metal plating, wear resistant and cutting tool alloys, chromium chemicals including chromates, sodium dichromate is the principal chemical used in industries for preserving wood in dying and tanning leather and as anticorrosive for domestic cooking systems and oil drilling mud.

It is distributed throughout the earth's crust as Cr(III) and Cr(VI) oxidation states. Cr(VI) is a highly carcinogenic and mutagenic form of the metal and can exist as chromate CrO_4 or dichromate Cr_2O_7. Its toxic and carcinogenic nature has lead to need for the monitoring of metal. WHO guidelines set a limit of 0.05 mg/l for the metal in drinking water.

Boyd-Boland et al. [50] has reviewed the application of SPME–HPLC for the speciation of Cr(III) and Cr(VI) based on the simultaneous extraction of EDTA complex of Cr(III) and direct extraction of Cr(VI). Different results were obtained by using different fibers. But the results with carbowax/templated resin (CWAX/TR) were found to be best. Different species of Cr were detected by UV detector.

4.3. Lead

It is widely distributed as metallic lead, inorganic compounds and organometallic compounds. It occurs in +2 oxidation state. It arises from a number of industrial; and mining sources, leaded gasoline, storage batteries, chemical pigments, plumbing and coal. In addition to pollutant sources, lead bearing, limestone and galena (PbS) contribute lead to natural waters in some locations.

Acute poisoning in humans causes severe disinfections in the kidneys, reproductive systems, liver brain and central nervous system. Environmental exposure is thought to have caused mental retardation in many children. Mild lead poisoning causes anaemia. The victim may have headaches and sore muscles, and may feel generally fatigued and irritable. Because of its toxicity, widespread use in industries, in gasoline, US Environmental protection agency specifies a method for the determination of lead in atmospheric particulate matter. WHO guidelines for drinking water quality stipulate allowable concentration of 0.01 mg/l.

Mester et al. [51] developed the more recent techniques by using in-tube solid phase microextraction for the determination of trimethyllead and triethyllead. The system consisted of in tube SPME coupled directly to an electrospray mass spectrometer. A schematic diagram in-tube SPME system connected to the mass spectrometer is shown in Fig. 3. The thermal stability of the non-ionic species is sometimes very low. So, with the use of ES-MS, ionic organolead compounds can be measured directly from the aqueous sample. It is significant to use ES-MS as it permits the simultaneous monitoring of both elemental and molecular forms of lead by applying different fragmentation voltages for the elemental and molecular ions.

Mester et al. [52] speciated trimethyllead and triethyllead by in-tube solid-phase microextraction high-performance liquid chromatography electrospray ionization mass spectrometry. In-tube solid-phase microextraction and HPLC are coupled to a quadrupole mass spectrometer using an electrospray as an ionization interface. The optimization of instrumental parameters is described, including the evalua-

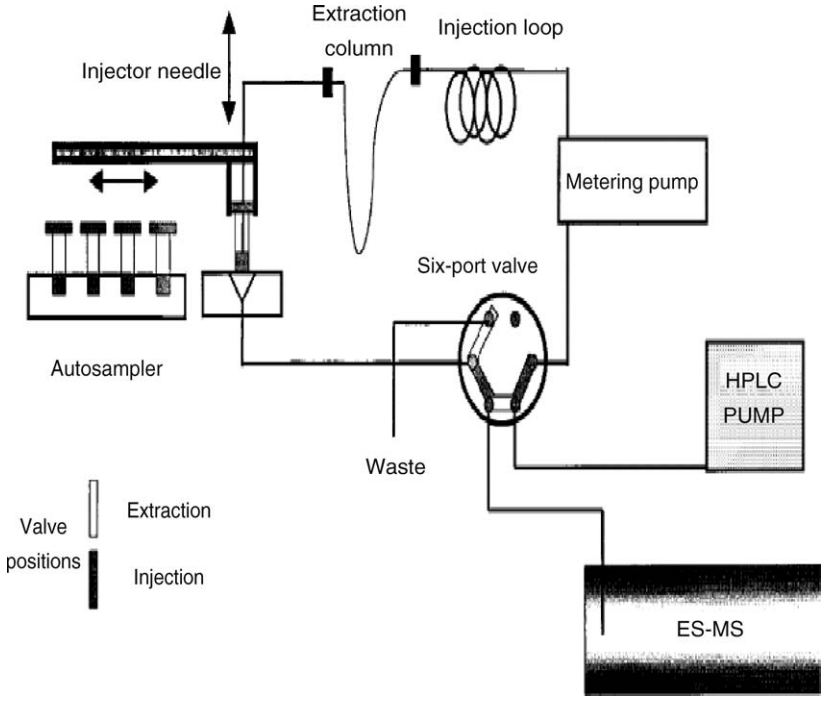

Fig. 3. Schematic of the in-tube solid phase microextraction system connected to the mass spectrometer. (Reproduced with the permission from reference [51].)

tion of three commercial GC capillaries for the in-tube SPME experiments. Elemental lead-208 (Pb^+) and molecular forms of TML and TEL (*m*/*z*) were monitored simultaneously to provide complete speciation information results from the in-tube SPME–HPLC-ESMS experiment indicated that complete separation and detection of TML and TEL can be achieved in less than 5 min. Precision is greater than 5% and estimated limits of detection are 11.3 and 12.6 ng/ml, respectively, for TML and TEL at a solution flow rate of 450 ml/min.

4.4. Mercury

Because of its toxicity, mobilization as methylated forms by anaerobic bacteria and other pollution factors, mercury generates a good deal of concern as a heavy metal pollutant. It is found as a trace component of many minerals, with continental rocks containing an average of around 80 ppb or slightly less of this element. It enters the environment from a large number of miscellaneous sources including discarded laboratory chemicals, batteries, broken thermometers, amalgam tooth filling, and formerly lawn fungicides and pharmaceutical products. Significant quantities of Hg(I) and Hg(II) are used annually. Organic mercury compounds used to be widely applied as pesticide, particularly fungicides.

High concentration of mercury found in water and in fish tissues result from the formation of monomethylmercury ion, CH_3Hg^+ and volatile dimethylmercury $(CH_3)_2Hg$ by anaerobic bacteria in sediments. WHO guidelines for drinking water quality stipulate allowable concentration of 0.001 mg/l for mercury (II).

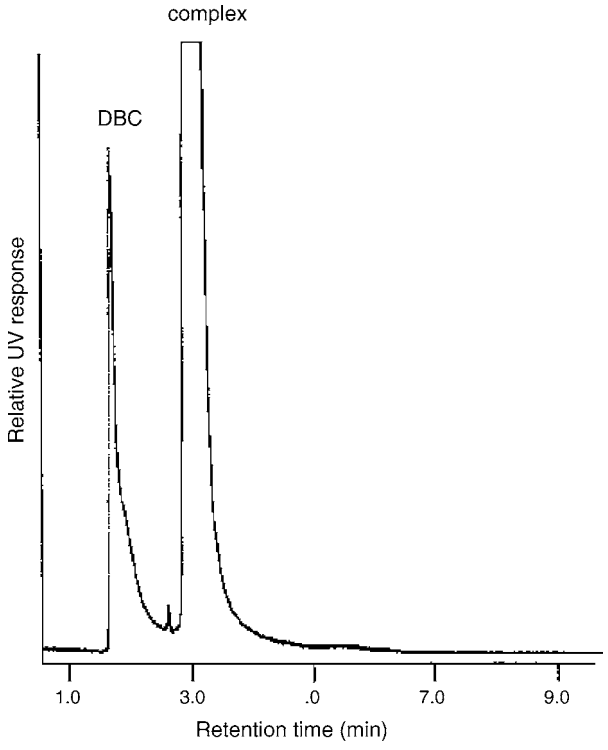

Fig. 4. Chromatogram for the complex of DBC with mercury ion (Cl^- as counter ion) using syringe injection. (Reproduced with the permission from reference [53].)

As described previously Gbatu et al. [24] prepared sol gel fibers for the determination of organo-mercury compounds. The results obtained are better than the other fibers which are commercially available.

Jia et al. [53] developed a new solid phase microextraction (SPME) method for the analysis of metal ions in aqueous samples. In this case solid phase microextraction is combined with HPLC for the determination of metal ions using crown ether as selective extracting reagent. Fibers doped with crown ether were used to extract Hg ions from aqueous solution through the formation of a stable complex. The complex is then desorbed from the fiber using HPLC for separation and UV detection. A chromatogram for the complex of DBC with mercury ion is shown in Fig. 4. Speciation also should be possible using highly selective crown ethers for extracting specific species of some elements.

5. Conclusions

In this review describes the hyphenation of SPME with HPLC has been explained for the analysis of some toxic metal ions. This widens the application of SPME considerably. From the papers, we conclude that organic conducting polymer films of 3-alkylpolythiophenes and newly developed sol–gel crown ether fibers were used as SPME element. The use of crown ether as reagent is a potentially promising method for the analysis of trace metal ions in aqueous samples. Modifications of construction of SPME and new polymeric fiber coatings increase the application ranges and improve the selectivity and the accuracy of analysis. The technique SPME–HPLC has limited application due to the optimization of desorption conditions and limited number of commercially available fibers. But in the last five years, interest towards the technique has been increased and a number of applications have been developed. Recently the approach to in tube SPME has also been developed in which the open tubular fused silica capillary column is used as SPME device instead of using the SPME fiber. SPME–HPLC is a very attractive and promising method for the toxic metal analysis. Thus, SPME can be considered as an extraction technique for the future.

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