# Preparation of Soil and Sediment Samples for Determination of Organometallic Compounds

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## Abstract

Organometallic compounds are widely used in almost all sectors of industry. As a result of emissions from natural and anthropogenic sources they are released to the environment, where they undergo a variety of conversions and interactions. Some organometallic compounds exhibit high toxicity. Organometallic compounds of mercury, tin, lead, selenium and arsenic are among the most common and hazardous compounds.

Based on literature dealing with the occurrence and methods of determination of selected organometallic compounds of mercury, tin, lead, selenium and arsenic, we describe their sources, uses and the mechanism of toxicity. Fundamental problems associated with speciation analysis are discussed and the basic steps of analytical procedure used for the determination of organometallic compounds of Hg, Sn, Pb, Se, and As in soil and bottom sediments, including sample collection, preservation, storage, extraction, separation and determination, are characterized.

**Keywords:** organometallic compounds, speciation analysis, collection, preparation and storage of solid samples, extraction and enrichment of analytes, chromatographic methods, capillary electrophoresis, detectors

## Introduction

Biochemical and toxicological studies have demonstrated that the toxicity of elements does not depend solely on their content in the environment, but also on the type and quantity of different physicochemical forms in which they are introduced to the environment and exist in it. In order to obtain additional information about the toxicity of elements, it is necessary to identify and determine quantitatively individual species in a given ecosystem. This discovery has resulted in the rapid growth of speciation analysis [1].

The term *speciation analysis* first appeared in the literature in 1954 and was at the time associated with a complex biogeochemical cycle of trace elements in sea water. In the 1960s, numerous papers dealt with speciation of metals in water, but research on metal speciation in solid samples was rare. The interest in metal speciation in solid matrices did not pick up until the 1970s and at present the term *speciation analysis* also includes the analysis of organic compounds. There are diverse definitions of speciation and a number of contradictions in the literature. According to the IUPAC recommendations from 2000, the term "speciation" is defined as identification and quantitative determination of all the chemical species and their physical forms in which a given element occurs in a specific part of the environment based on the samples collected using the principles of Good Laboratory Practice, whereas the term speciation analysis pertains solely to the analysis of specific chemical forms [2].

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In environmental investigations, where one of the main objectives is the determination of potential hazards to humans from the environment, "organometallic speciation" is among the topics of interest, because organic derivatives of metals are often much more toxic than their inorganic forms [3].

Organometallic compounds are defined as a group of compounds containing in their molecules at least one metal atom bonded to the atom of carbon being a part of an organic functional group [4]. They have different physicochemical properties, which depend both on the kind of metal and the organic groups bonded to it. Many organometallic compounds are solid, others are liquid and some exhibit a substantial volatility and occur as gases [5].

The degree of difficulty of speciation analysis increases with an increase in lability of the species being determined: from thermodynamically and kinetically stable typical organometallic compounds (e.g. dimethylmercury) all the way up to labile forms of elements (e.g. hydrolyzed metal ions) [6]. Speciation analysis of heavy metals poses problems due to a variety of forms of mercury [6-8], lead [6, 9], tin [10, 11], selenium [12, 13] or arsenic [14, 15] occurring in nature (Table 1), and the solution to each problem requires the development of an individual procedure using known analytical techniques.

This review deals with speciation analysis of mercury, lead, tin, selenium and arsenic in two types of environmental samples – soil and bottom sediments.

## Speciation Analysis of Selected Organometallic Compounds

The term *speciation analysis* was originally associated with the analytical methods used to determine the quantity and form of occurrence of a given element in the sample examined. Such information has proven to be essential for the development of a number of disciplines (medicine, environmental science, geology), because it allowed us to evaluate toxicity and to understand bioavailability and biogeochemical cycles of a given element in the environment [5].

Analytical procedures used in speciation analysis are different than the procedures used for the determination of total content of elements. Speciation analysis makes use of mostly trace analysis, which poses many problems at the sample collection and preparation steps and imposes on the analyst the need for strict adherence to the analytical procedures used [5]. Only a few analytical procedures allow examination of samples in their original state, without prior preparation. As a rule, several time-consuming steps, such as extraction, enrichment or derivatization, which enable indirect determination of the analytes in a sample, are required [16]. Preparation of samples for analysis is especially important in speciation analysis due to the ease of destruction of some species of the elements being determined.

The majority of operations and processes used to prepare samples of sediments and soils for the speciation analysis of organometallic compounds of Hg, Pb, Sn, As, and Se are similar, which is depicted schematically in Fig. 1.

## Preparation of Samples of Soils and Bottom Sediments for Speciation Analysis

Preliminary steps of speciation analysis, prior to final determination, are particularly difficult because every activity is a potential interference which can disturb a complex

Table 1. Selected organometallic compounds of Hg, Pb, Sn, Se, and As occurring in the environment.

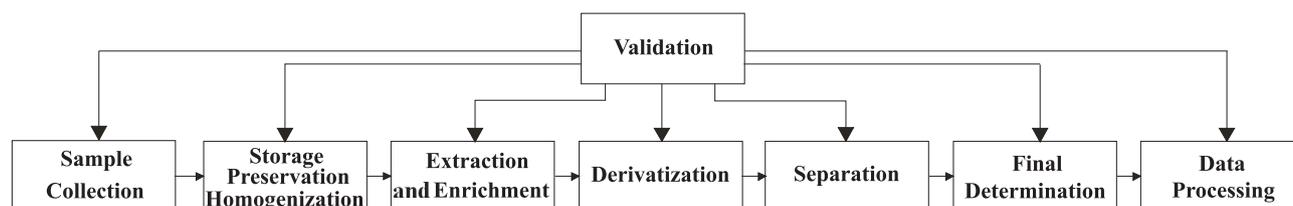| Mercury | Lead | Tin | Selenium | Arsenic |
|---------|------|-----|----------|---------|
| $Me_2Hg$, $Et_2Hg$, $Pr_2Hg$ | $Me_4Pb$, $Me_3EtPb$, $Me_2Et_2Pb$, $MeEt_3Pb$, $Et_4Pb$ | $BuMe_3Sn$, $Bu_2Me_2Sn$, $Bu_3MeSn$, $Bu_4Sn$ | $Me_2Se_2$, $Me_2Se$, $Et_2Se$, $Et_2Se_2$, $SeC(NH_2)_2$ | $MeAsO(OH)_2$, $Me_2AsOOH$, $Me_3AsO$ |
| $MeHg^+$, $EtHg^+$, $PhHg^+$ | $Me_2Pb^{2+}$, $Et_2Pb^{2+}$, $Me_3Pb^+$, $Et_3Pb^+$ | $BuSn^{3+}$, $Bu_2Sn^{2+}$, $Bu_3Sn^+$, $PhSn^{3+}$, $Ph_2Sn^{2+}$, $Ph_3Sn^{2+}$, $Ph_3Sn^+$, $Et_3Sn^+$, $MeSn^{3+}$, $Me_2Sn^{2+}$, $Me_3Sn^+$ | $Me_3Se^+$ | $Me_3AsCH_2COOH^+$, $Me_4As^+$ |



Fig. 1. Operations and processes used during preparation of samples of sediments and soils for the determination of organometallic compounds.

system of physicochemical equilibria of a given analyte in a sample. On the other hand, usually none of the steps can be avoided, since environmental analysis typically deals with the ultratrace contents of elements in samples having a very complex matrix and even very sensitive analytical techniques that require enrichment of chemical species present in samples prior to the final determination [6].

### Collection of Representative Samples

Collection of representative samples of soils and sediments for analysis, and particularly speciation analysis, being the key step of the analytical procedure, must be carried out in the way ensuring minimum losses of the elements being determined or their different forms and maximum protection from introducing contaminants, as well as protecting the collected samples from the factors disturbing the equilibria taking place in the analyzed macrosystem. This is especially important in speciation analysis, because the total content of a given element may remain constant while the ratio of different physical and chemical species initially present in the sample may change [5].

Solid materials are characterized by heterogeneity and the complexity of interactions with their surroundings (water, air), which requires proper selection of a sample collection method to minimize conversions of different species of the organometallic compounds being determined. Subsurface, nonoxidized layers of soils and sediments are isolated under oxidizing conditions of water or air, which makes it important to protect them during the entire process of sample collection. This also results in the complication of subsequent extraction and determination of different species in various solid fractions, as exposure to air can result in a rapid change in distribution of the analyte in a sample [17].

In order to ensure representativeness of the sample, parameters such as number of samples, sampling time ensuring preservation of the equilibria characteristic of a given environment, sampling depth and meteorological conditions prevailing during sample collection, should be decided upon prior to the sampling. If there is a chance of migration of a toxic substance to deeper layers of soil, two samples from different depths should be collected [16]. In speciation analysis, particular attention should be paid to the proper selection of material of a container used to collect and store a sample. Sample containers should be used solely to collect samples of the same type and properly cleaned after each use following appropriate procedures.

Speciation of organometallic compounds is usually investigated in the surface layers of soils (to a depth of 5-10 cm) and sediments, because they provide most information about the degree of atmospheric pollution and bioavailability and conversions taking place in the surrounding water [17].

Samples of soil to be analyzed for the content of organometallic compounds are usually collected from the topsoil layer using a scoop.

Collecting samples of bottom sediments using a variety of samplers is a more difficult task than collecting soil samples. In the former case, samplers and probes are generally heavy and require the use of lifts. A variety of sediment samplers, including grab samplers (in which case samples of partly disturbed structure are obtained) and core samplers are used depending on the objective of investigations. As a rule, such samplers and sampling techniques are employed that result in a possibly undisturbed structure of the surface layer of a sediment.

The above condition is met by the Niemistö core sampler, which is used to collect soft sediments. A cryogenic sampler is also utilized for the collection of sediment samples. It allows freezing of a sample right after its collection, which prevents losses of the most volatile analytes [16].

### Storage, Preservation and Homogenization of Samples

During the period between sample collection and final determination samples can change their properties due to chemical, physical or biological processes taking place in them. These adverse phenomena can be minimized through proper storage and the selection of an appropriate method of sample preservation prior to subsequent steps of the analytical procedure.

There are no definite rules for the preservation of solid samples of environmental materials prior to speciation analysis. Since sample storage can affect the distribution of species, it is recommended that the analysis be carried out immediately after sample collection. However, in most cases some form of sample storage and preparation that can influence speciation is required. The following operations are used most often [17]:

– Air drying (for up to two weeks) and desiccator drying (one week) – both operations carried out at room temperature;
– drying at elevated temperature (oven, 100 °C, 4 h) or using an IR lamp (1.5 h);
– lyophilization.

Air drying and drying at elevated temperature should be eliminated. The removal of moisture in a desiccator and through lyophilization preserves organometallic compounds for about one year [6]. The drying and storage method must, however, be selected individually, depending upon the objective of the analysis and its scope as well as the planned method of dissolving the sample. For example, lyophilization or freeze-drying, the process involving the removal of water (and some volatile organometallic compounds, which can be a source of errors) from sample bypassing the liquid state, can significantly change the sample structure. When carried out under optimum conditions, it yields a porous structure, amenable to dissolution [6]. An important step in the preparation of solid samples following their drying or freezing is homogenization using special mills or comminutors. The samples to be analyzed for their content of volatile compounds should be extracted immediately after collection [5]. The technique

which can be successfully used for direct extraction of volatile organometallic compounds is solid-phase micro-extraction [18]. Samples of soils and sediments are usually stored in polyethylene or PTFE containers.

## Isolation and Enrichment of Analytes from Solid Samples

Solid samples are an example of environmental samples in which analytes cannot be determined directly by the majority of methods employed in environmental analysis. Liquid, gas, and solid-phase extractions are used to make these samples amenable to the common methods of final determination [19]. Due to the fact that organometallic compounds are usually present in samples at very low concentration levels, the main objective of the extraction step is analyte enrichment.

The determination of organic forms of metals still presents a challenge for analytical chemists, because these species are often labile and, in addition, their concentrations in various matrices are very low: in the order of 1 µg/L (e.g. alkyl species of lead or tin) or even 1 ng/L (e.g. estuarine water), and in the order of 1 ng/g in samples of sediments, soils and biological tissues, while at the same time the inorganic metal species can be present in a sample at a thousand-fold higher concentration. For this reason, sensitive and selective atomic absorption spectroscopic techniques are useful in the area of speciation analysis, primarily in combination with chromatographic techniques. The complexity of such a system has a direct effect on the time of analysis; however, the most tedious and time-consuming step in the entire procedure is sample preparation aimed at quantitative isolation of chemical species of the analytes from the matrix to a specific solvent in order to facilitate their introduction into a chromatographic column. This requires extraction and derivatization of the analytes, which increases the number of operations and, therefore, the probability of analyte losses, and calls for experience and high qualifications of the analyst [20].

A number of extraction techniques for the analytes from such environmental samples as soils and sediments have been proposed. The techniques can be classified according to various criteria, for example:
– polarity of the solvent used,
– sample acidity used to improve analyte recovery,
– use of chelating agents.

Traditional liquid-solid extraction has significant shortcomings, of which the most important is the need for large volumes of organic solvents. Other types of extraction are based on techniques improving the effectiveness and speed of isolation of the analytes from the matrix. These include microwave- or ultrasound-assisted liquid extraction, supercritical fluid extraction and extractions carried out at elevated temperature and/or pressure as well as solid-phase microextraction, which offer new methods of chemical treatment of different species and

have an advantage over classical liquid-liquid extraction of a substantial reduction in time and the possibility of on-line analysis [19].

The new generation of sample preparation techniques finds use in extraction methods applied in the analysis of organometallic compounds occurring at a level below 1 pg. However, the disadvantages of rapid extraction techniques, such as the possibility of losses of the chemical species being determined due to their chemical instability during the extraction step resulting from the use high pressure and/or temperature (e.g. in supercritical fluid extraction, accelerated solvent extraction or microwave-assisted extraction), should also be pointed out [20].

Extractive methods of isolation can be used in speciation analysis to isolate various element species from solid materials such as soils, marine sediments, and sediments from water reservoirs and running water. The extracting agents are selected individually for each material and type of analyte (organic solvents, such as hexane, cyclohexane, chloroform, methylene chloride, methanol, acetone, dimethylformamide, solutions of acids and bases – separately or in mixtures, sometimes with an addition of complexing agents used in the case of organometallic compounds) [6].

Recent liquid-solid extraction techniques fall into one of three categories:
– "classic" techniques,
– techniques, in which additional factors (ultrasounds, microwave radiation, elevated temperature and pressure) are used to assist the extraction process,
– techniques making use of supercritical fluids [19].

Gas- and solid-phase extractions are used for volatile organometallic compounds. A number of variants of this type of extraction technique have been developed thus far.

The information on extraction of organometallic compounds from solid matrices (bottom sediments, soils) is compiled in Table 2.

## Derivatization

Derivatization is used in the majority of procedures for the determination of organometallic compounds. Individual species of the elements of interest are converted into derivatives to facilitate further analysis. Derivatization is one of the most effective ways of improving detection limits in gas and liquid chromatography and in capillary electrophoresis.

The techniques of determination of total elemental content are well known and documented [42-51]. However, identification of various species is a challenge in analytical and biomedical studies. Chromatographic techniques constitute a powerful tool for the separation of various chemical species of elements, but compounds of mercury, lead, tin, arsenic and selenium generally occur in the environment in ionic and polar forms. Consequently, when using analytical methods based on GC, the com-

Table 2. Selected techniques used for extraction and determination of organometallic compounds in samples of soils and bottom sediments.

| Analytes | Extraction conditions | Separation (and determination) technique | Additional comments | References |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| $Me_3Pb^+$, $Et_3Pb^+$, $Me_2Pb^{2+}$, $Et_2Pb^{2+}$ | Slurry 5 g sediment with 5 mL water + 10 mL 0.2 mol/L phosphate buffer (pH 9) and extract three times with 5 mL hexane/benzene (1:1 v/v) containing 1% m/v dithizone. Back extract with three 5 mL 0.15 mol/L $HNO_3$ washes, basify to pH 9, re-extract three times with 5 mL hexane + 1 mL 5 mmol/L $NH_4TMDTC$ w $H_2O$. Combine hexane extracts, dry over anhydrous $Na_2SO_4$ and evaporate to 0.2 mL under a gentle stream of $N_2$. | HPLC | Sample matrix – sediment, extraction efficiency $Me_3Pb^+$(90%), $Et_3Pb^+$(86%), $Me_2Pb^{2+}$(72%), $Et_2Pb^{2+}$(75%) | [17] |
| $Me_3Pb^+$, $Et_3Pb^+$, $Me_2Pb^{2+}$, $Et_2Pb^{2+}$ | Slurry 5 g soil with 5 mL $H_2O$ + 10 mL 0.2 mol/L phosphate buffer (pH 9) and extract three times with 5 mL hexane + 1 mL 5 mmol/L $NH_4TMDTC$ in $H_2O$. Combine hexane extracts, dry over anhydrous $Na_2SO_4$ and evaporate to 0.2 mL under a gentle stream of $N_2$. | HPLC | Sample matrix – soil, extraction efficiency $Me_3Pb^+$(83%), $Et_3Pb^+$(83%), $Me_2Pb^{2+}$(73%), $Et_2Pb^{2+}$(74%) | [17] |
| $R_4Pb$, $Me_3Pb^+$, $Et_3Pb^+$, $Me_2Pb^{2+}$, $Et_2Pb^{2+}$ | Dried (1-2 g) or wet (5 g) sediment placed in capped glass vial, add 10 mL $H_2O$ + 6 g NaCl + 1 g KI + 2 g Na benzoate + 3 mL 0.5 mol/L NaDDTC + 2 g coarse glass beads + 3 mL benzene. Shake for 2 h and separate organic phase. | GC | Sample matrix – sediment, extraction efficiency $R_4Pb$ (no recovery data reported), $Me_3Pb^+$(111%), $Et_3Pb^+$(94%), $Me_2Pb^{2+}$(113%), $Et_2Pb^{2+}$(93%), derivatization of ionic alkyl-lead species prior to determination | [17] |
| $R_4Pb$, $Me_3Pb^+$, $Et_3Pb^+$, $Me_2Pb^{2+}$, $Et_2Pb^{2+}$ | Place 10 g sample in glass-stoppered tube, add100 mL $H_2O$ + 5 g NaCl + 5 mL 0.5 mol/L NaDDTC + 5 mL n-hexane. Shake for 30 min and separate organic phase. If recovery is low, filter (0.45 µm) after shaking but without adding n-hexane. Then extract filtrate with n-hexane. | GC | Sample matrix – sediment, soil, extraction efficiency $R_4Pb$ (55%), $Me_3Pb^+$(71-112%), $Et_3Pb^+$(68-100%), $Me_2Pb^{2+}$(54-85%), $Et_2Pb^{2+}$(54-100%), derivatization of ionic alkyllead species prior to determination | [17] |
| $R_4Pb$ | Vigorously shake 5 g wet sediment with 5 mL 0.1 mol/L EDTA + 5 mL hexane in a capped test tube for 2 h. Centrifuge for 10 min and separate hexane layer. | GC | Sample matrix – sediment, extraction effectiveness $R_4Pb$ (85%) | [17] |
| $R_4Pb$, $Me_3Pb^+$, $Et_3Pb^+$, $Me_2Pb^{2+}$, $Et_2Pb^{2+}$ | Add 15 mL 0.2 mol/L phosphate buffer (pH 9.0) to 5 g sample. Extract $R_4Pb$ with 3 mL hexane, wash twice with 2 mL $H_2O$ and dry over anhydrous $Na_2SO_4$. Extract ionic alkylleads three times with 5 mL hexane containing 10% 0.15 mol/L dithizone in THF. Reduce volume under a gentle flow of $N_2$. Extract inorganic lead three times using 5 mL IBMK, back-extract combined organic phase with $HNO_3$. | GC | Sample matrix – soil, extraction efficiency $R_4Pb$ (no recovery data reported), $Me_3Pb^+$(61%), $Et_3Pb^+$(67%), $Me_2Pb^{2+}$(52%), $Et_2Pb^{2+}$(66%), derivatization of ionic alkyllead species prior to determination | [17] |
| $R_4Pb$, $Me_3Pb^+$, $Et_3Pb^+$, $Et_2Pb^{2+}$ | Sample (0.2-1.5 g) placed in extraction vessel over 0.2 g Cu powder with clean sand to fill void volume, and 50 µL methanol modifier. Static extraction for 4 min, then 4-20 min in dynamic mode using supercritical $CO_2$ at a flow rate of 0.85 mL/min, 80°C and 45 MPa. Analytes collected in methanol. | GC | Sample matrix – sediment, extraction efficiency $R_4Pb$ (no recovery data reported), $Me_3Pb^+$(96%), $Et_3Pb^+$(106%), $Et_2Pb^{2+}$(80%), derivatization of ionic alkyllead species prior to determination | [17] |
| $Me_3Pb^+$, $Et_3Pb^+$, $Et_4Pb$ | Solid-phase microextraction (SPME)<br>Fiber – 100µm PDMS<br>Extraction time – 10min<br>Extraction mode – HS<br>Derivatizing agent – $NaBEt_4$/acetate buffer, pH 4.0 | EI MS | Detection limit – $Me_3Pb^+$- 130 ng/L, $Et_3Pb^+$- 83 ng/L, $Et_4Pb$- 90 ng/L.<br>Chromatographic column – 30 m x 0.25 mm x 0.25 µm SPB-5<br>Temperature – 70°C - isothermal) | [21] |

Table 2. continued

| Analytes | Extraction conditions | Separation (and determination) technique | Additional comments | References |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| Organotin compounds | Extract 0.2 g sample with 5 mL glacial acetic acid + 5 mL $H_2O$ (60 W, 2 min), add 5 mL pH 5 buffer + 5 mL $H_2O$ + 3.8 mL concentrated $NH_3$. Add 1 mL 2% (w/v) $NaBEt_4$ and 2 mL organic solvent (hexane, toluene, or isooctane), shake for 5 min. In case of freshwater sediments the extract was centrifuged for 3 min at 3000 rpm. | GC AED | Sample matrix – sediment, detection limit 2 ng/g | [22] |
| Organotin compounds | Extract 2 g sample with 10 mL 0.5 mol/L acetic acid in methanol containing 100 µL tripropyltin solution (70 W, 3 min), add 50 mL chloride solution and 10 mL acetate(70 W, 3 min), add 50 mL chloride solution and 10 mL acetate buffer (adjust pH to 5), add 1 mL isooctane and 100 µL sodium tetraethylborate and stir vigorously for 30 min. Desulfurize the organic layer prior to analysis using tetrabutylammonium sulfide. | GC FPD | Sample matrix – sediment | [23] |
| Organotin compounds | Add 10 mL 1 N HCl to 10 g sediment, extract twice with 40 mL acetone, back-extract with 500 mL solution of 25% NaCl + 50 mL 0.1% tropolone-benzene solution (shake for 10 min). Wash extract with 2 mL 3.3% tetrabutylammonium hydrogen sulfate + 40 mL 16% sodium sulfide to remove sulfur, dry over anhydrous $Na_2SO_4$, and reduce volume to 1 mL. Derivatize using n-propylmagnesium bromide. | GC-FPD | Sample matrix – sediment, recovery for organotin compounds was 68 – 109%, detection limit 0.005 mg/kg dry mass | [10] [24] |
| TBT | To 10 g wet sediment add tri-n-propyltin chloride having concentration of about 10 µg/kg as an internal standard, acidify with HCl to pH <1, sonicate for 45 min, then add 10% sodium acetate and 20% NaOH dissolved in high purity water until pH 5 ± 0.5. Derivatize in situ using 500µL 10% sodium tetraethylborate, stir and leave for 10 min to react, extract with 10 mL n-pentane (shake vigorously for 1 min, centrifuge at 2000 rpm for 1 min), separate phases by centrifuging (20 min, 2000 x g), collect organic layer, dry over anhydrous $Na_2SO_4$ and evaporate under a gentle stream of $N_2$. | GC FPD | Sample matrix – sediment, detection limit 1µg/kg dry mass | [25] |
| Butyltin compounds | Slurry 1 g homogenized sediment with 50 mL 0.5 mol/L HCl in methanol, extract in ultrasonic bath for 2 h (hand stir every 20 min to remove matter deposited on walls), centrifuge for 15 min at 2500rpm, decant liquid, collect 0.5 – 5 mL extract, make up volume to 150 mL and add 1.5 mL 0.77 M citrate buffer (pH 5), adjust pH to 5.0 – 6.0 using NaOH or HCl, add 0.3 mL 2% sodium tetraethylborate, leave for 5 min to react prior to analysis. | GC QF-AAS | Sample matrix – sediment, internal standard 330 ng/g Sn/L containing mono-, di- and tributyltin, and masking agent (50 mL methanol, 100 µL 0.2 mol/L EDTA, 2 mL 1 g/L $Mn(NO_3)_2$) added to natural samples | [26] |
| $BuSn^{3+}$, $Bu_2Sn^{2+}$, $Bu_3Sn^+$ | Solid-phase microextraction (SPME) Fiber – 100µm PDMS Extraction time – 60 min Extraction mode – HS Derivatizing agent – $NaBEt_4$/acetate buffer, pH 4.0 | FID | Sample matrix – sediment Detection limit- $BuSn^{3+}$-1.0 µg/L, $Bu_2Sn^{2+}$- 1.2 µg/L, $Bu_3Sn^+$- 0.9 µg/L Chromatographic column- 30 m x 0.25 mm x..0 µm SPB-1 Temperature program- 40°C (1min) - 20°C/min to 140°C (1min) - 20°C/min to 220°C (1min) | [27] |

Table 2. continued

| Analytes | Extraction conditions | Separation (and determination) technique | Additional comments | References |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| DMA, MMA | 1. Extract 0.2 g sediment with 5 mL $HNO_3$ and 10 mL HCl (20 W, 12 min)<br>2. Extract 0.1 g sediment with 15 mL $H_3PO_4$ (0.3 or 0.9 mol/L) containing arsenic compounds as internal standard (microwave assisted extraction, 10 min, 20 W or magnetic stirring, 10 min) | HPLC ICP-MS | Sample matrix – sediment, recovery<br>– for $HNO_3$/HCl extraction:<br>DMA ($99 \pm 3$)%, MMA ($102 \pm 2$)%<br>– for $H_3PO_4$ extraction<br>➤ MAE:<br>DMA 98%, MMA 99%<br>➤ Magnetic stirring:<br>DMA 96%, MMA 100% | [15] |
| MMA, DMA | 1. Place 0.1 g of soil and 15mL of extractant solution (1 mol/L $H_3PO_4$ 85%, alone and with 0.5 ascorbic acid solution or 1mol/L $H_3PO_4$ 85% with 0.1mol/L hydroxylammonium hydrochloride solution), which where previously purged in an argon stream for 15 min in an open reflux vessel and maintained at 60W for 10 min.<br>2. Filter cooled mixture, dilute to 50mL with doubly deionized water, filter the mixture through an 0.22 mm nylon membrane | LC-HG-AFS | Sample matrix- soil, detection limit:<br>MMA- 0.65 mg As/kg<br>DMA- 0.20 mg As/kg | [28] |
| DMA, MMA | Extract with $NaHCO_3$, reduce MMA and DMA using sodium tetrahydroborate to volatile hydrides, retain in cryogenic trap (in n-heptane) | HG-HCT / GC MID | Sample matrix – soil detection limit 0.2 – 0.4 µg/L, recovery of DMA and MMA 97-102% | [29] |
| MMA, DMA, AsB, AsC | Microwave assisted extraction of sample, derivatization with $NaBH_4$, AsB and AsC decomposed with $K_2S_2O_8$ solution and microwaves prior to analysis. | HPLC- HG-AAS | Sample matrix – sediment, detection limit 4 – 6 µg/L | [30] |
| DMSe, DMDSe, DESe, DEDSe | 1. Place 20 g wet sample in polystyrene bottle, 1 cm² charcoal was hung on nylon thread attached to stopper, seal stopper with PTFE foil. Heat for 2 h at 125°C, then cool to ambient temperature. After 24 h extract charcoal with 1 mL $CS_2$ for 10 min. Add 200 ng/L internal standard prior to analysis;<br>2. Place 20 g wet sample in polystyrene bottle with polystyrene stopper sealed with PTFE foil and pass a stream of $N_2$ (20 mL/min), introduced through the hole in stopper. Adsorption tube packed with charcoal (2 g) and glass wool is introduced through a second hole. Heat for 1 h to 50°C, then extract charcoal with 2 mL $CS_2$. Add 200 µL 2000 ng/L internal standard in $CS_2$ prior to analysis. | GC MS | Sample matrix – sediment, detection limit for DMSe 33 ng Se/g wet mass, for DMDSe 1.0 ng Se/g wet mass, for DESe 22 ng Se/g wet mass, for DEDSe 2.3 ng Se/g wet mass. Sensitivity for dialkyldiselenium compounds can be improved by extraction with ethyl acetate and derivatization with 1-fluoro-2.4-dinitrobenzene. | [31] |
| **DMDSe, SeC** | Slurry 0.5-5 g dry sample with 70 mL 0.5 mol/L HCl (24 h, 4°C), centrifuge (2000 rpm, 20 min), decant, filter (0.45 µm), extract with 5.5 mL $CH_2Cl_2$, analyze 10 mL of aqueous layer containing SeC using DPCSV (differential pulse cathodic stripping voltammetry); to 5 mL of organic layer, containing $(CH_3)_2Se$, add 5 mL 0.2 mol/L $LiClO4$/ EtOH/HCl and analyze using DPCSV. | Stripping analysis | Sample matrix – sediment, detection limit:<br>DMDSe 0.23 ng Se/mL,<br>SeC 3 ng Se/mL | [32] |
| MeHg+, Hgtotal | MeHg+: Slurry 0.2-0.5 g dry sample with 25% $CuSO_4$ in 6 N HCl, extract three times with 2 mL toluene, evaporate to 0.1-0.5 mL. Analyze 50 µL of enriched extract.<br>Hgtotal: Dissolve 0.1-0.2 g dry sample with mixture of concentrated $HNO_3$ and 6 N HCl (10: 1), for 6 h at 120°C. | CV AFS | Sample matrix – sediment, soil, recovery for MeHg+ 95.5% | [33] |

Table 2. continued

| Analytes | Extraction conditions | Separation (and determination) technique | Additional comments | References |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| MeHg+, Hg$_{total}$ | 1. **MeHg+**: Dissolve sample in mixture of H$_2$SO$_4$/KBr/CuSO$_4$, extract with toluene, extract twice with mixture of cysteine/trisodium citrate (in aqueous solution), add acidic copper solution to aqueous layer, back-extract twice with toluene. 2. **MeHg+**: Add to wet sample 1.5 mol/L HBr and 1 mol/L CuSO$_4$, extract with CH$_2$Cl$_2$, to organic phase add 20 mL high purity water, heat to 80°C and evaporate CH$_2$Cl$_2$ under a stream of N$_2$, use ethylation in aqueous layer to convert MeHg+ into volatile form, introduce analyte into chromatographic system in a stream of N$_2$; **Hg$_{total}$**: sample was decomposed in H$_2$SO$_4$/K$_2$Cr$_2$O$_7$ mixture at 140°C for 2 h and immediately analyzed. | 1. **MeHg+**: GC ECD; 2. **MeHg+**: GC /pyrolysis/ CVAFS; **Hg$_{total}$**: CV AFS | Sample matrix- sediment; concentrations observed: MeHg+: 0.13-45 ng/g dry mass, Hg$_{total}$: 0.2-250 μg/g dry mass. | [34] |
| MeHg+ | Extract 1-2 g dry sample with 10 mL HNO$_3$ (15 mol/L) or HCl (1.2.4.6.8.10.12 mol/L), 60 W, 3 min, centrifuge extract (2000 rpm, 5 min), wash residue three times with water and extract MeHg+ with 10 mL 6 mol/L HNO$_3$ to test extraction efficiency using HNO$_3$ or HCl with various concentrations. To aliquot of extract (0.2 – 3 mL) add 50 mL high purity H$_2$O, adjust pH to about 3 using KOH and acetate buffer. Ethylation in aqueous phase was used to convert MeHg+ into volatile form. | CT-GC QFAAS | Sample matrix- sediment | [35] |
| MeHg+ | Leach with KBr/H$_2$SO$_4$, extract MeHgBr with toluene, clean up extract with cysteine solution, back-extract MeHg+ with benzene. | GC ECD | Sample matrix – soil, detection limit 0.01-0.05 ng/g | [36] |
| Organo-mercury compounds | Slurry 1-4 g dry sample with10 mL 0.1 mol/L acetate buffer (pH 4) and leave for 24 h (add 3 drops of concentrated HNO$_3$ in case of sediment samples). Next, to 2 mL of extract add 8 mL acetate buffer containing 1 g NaCl, adjust pH to 4 using KOH solution, and then add 1 mL 6% KBH$_4$ solution, and stir magnetically. Use SPME to isolate analytes. | SPME-GC AAS | Sample matrix- soil, sediment; Detection limit: CH$_3$Hg+ - 16 ng (as Hg), C$_2$H$_5$Hg+ - 12 ng (as Hg), C$_6$H$_5$Hg+ - 7 ng (as Hg), Recoveries of the investigated organomercury compounds were 93.6–105.2% | [8] |
| MeHg+, Hg$^{2+}$ | Extract with CH$_2$Cl$_2$, then ethylate with NaBEt$_4$, isolate analytes using a Tenax fiber | GC MIP AED | Sample matrix – sediment, soil Detection limit: MeHg+ - 0.1 ng/g | [37] |
| MeHg+, Me$_2$Hg, Hg$^{2+}$ | Use NaBEt$_4$ to generate hydrides, enrich on sorbent (Chromosorb), desorb thermally analytes. | PTI GC MIP AED | Sample matrix – soil, sediment Detection limit: < 1 ng/L | [37] |
| Me$_2$Hg, Et$_2$Hg, Ph$_2$Hg | 1. Direct solid-phase microextraction (SPME) 2. Headspace SPME | GC MIP AED | Sample matrix – soil, sediment Detection limit: 1. Me$_2$Hg- 144 pg/mL (as Hg) Et$_2$Hg- 30 pg/mL (as Hg) 2. Me$_2$Hg- 30 pg/mL (as Hg) Et$_2$Hg- 25 pg/mL (as Hg) | [37] |

Table 2. continued

| Analytes | Extraction conditions | Separation (and determination) technique | Additional comments | References |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| $MeHg^+$ | Supercritical fluid extraction, distillation with mixture $KCl-H_2SO_4$ | GC MIP AED | Sample matrix – sediment Detection limit: 0.1 ng/g | [37] |
| $MeHg^+$ | Acid hydrolysis (HCl) + cysteine + aqueous acetate solution + toluene | GC MIP AED, GC ECD | Sample matrix – sediment Detection limit: $MeHg^+$ - 1.2 pg | [37] |
| $Me_2Hg$, $Et_2Hg$ | Solid-phase microextraction (SPME) Fiber- 100µm PDMS Extraction time- 20min Extraction mode- HS | MIP AES | Sample matrix – soil Detection limit: 3.5-5 µg/L Chromatographic column: 25 m x 0.32 mm x 0.25 µm HP-1 Temperature program: 40°C (5min)-40°C to 200°C (1min) | [38] |
| $MeHg^+$, $EtHg^+$, $PhHg^+$ | Solid-phase microextraction (SPME) Fiber- glass fiber Extraction time- 1.5-2h Extraction mode- HS Derivatizing agent- $NaBH_4$/acetate buffer | AAS | Sample matrix – soil Chromatographic column: 30 m x 0.32 mm x 0.25 µm SPB-1 Temperature program: 50°C (1min)-40°C/min to 65°C (1min), 150°C (1min), 200°C (1min) | [39] |
| $MeHg^+$, $Me_3Pb^+$, $BuSn^{3+}$, $Bu_2Sn^{2+}$, $Bu_3Sn^+$ | Solid-phase microextraction (SPME) Fiber- 100µm PDMS Extraction time – 10 min Extraction mode – HS Derivatizing agent- $NaBEt_4$/acetate buffer, pH 5.3 | ICP-MS | Sample matrix – sediment Detection limit: $BuSn^{3+}$- 0.34 ng/L, $Bu_2Sn^{2+}$- 2.1ng/L, $Bu_3Sn^+$- 1.1 ng/L, $MeHg^+$ -4.3 ng/L, $Me_3Pb^+$- 0.19 ng/L Chromatographic column: 30 m x 0.25 mm x 0.50 µm (polydimethylsiloxane), Temperature program: 60°C (1min)-20°C/min to 200°C (0.5 min) | [40]] |
| $MeHg^+$ | Microwave assisted extraction of sample with $CH_3OH$ and HCl (30% power for 20 min). Dilute of the sample using DI water, then inject through a 0.45 mm syringe filter into a sample loop. | IC-ICP-MS | Sample matrix- soil Detection limit: 73 pg/mL | [41] |

pounds have to be extracted from the sample matrix and converted into volatile and thermally stable derivatives [52].

Most often, derivatization of mercury, lead, tin, arsenic and selenium compounds involves converting them into [6]:

 – volatile hydrides using sodium tetrahydroborate,
 – ethyl derivatives using sodium tetraethylborate,
 – butyl derivatives using tetrabutylammonium tetrabutylborate,
 – higher alkyl or aryl derivatives using Grignard reagents,
 – volatile complexes.

The formation of halogen derivatives, finding use in speciation analysis of tin compounds, is not used in the determination of lead and mercury species. The derivatization techniques most commonly used in gas chromatography are compiled in Table 3.

Reduction of nonvolatile compounds to volatile hydrides using sodium tetrahydroborate is one of the most common methods of derivatization in speciation analysis of Hg, Pb, Sn, As, and Se [53], although some authors question the notion of formation of volatile hydrides by

Se and Pb [54]. Mono- and dimethylarsenic acids can be determined simultaneously as $MeAsH_2$ and $Me_2AsH$, respectively. Trialkyllead compounds easily form volatile hydrides in the presence of $NaBH_4$, while dialkyllead compounds do not react with this reagent. The technique has found most use in speciation analysis of organotin compounds due to the possibility of simultaneous chromatographic determination of ionic methyl and butyl forms of tin [55].

The conversion of organometallic compounds into volatile hydrides using sodium tetraborate can be carried out in a separate vessel (*off line*), from which the products are transferred into the GC column via layer absorbing water, or *on-line*. The external reactor is often connected to the GC column through an additional module enabling preliminary separation of species by means of the purge-and-trap technique. In the *online* mode the first segment of the GC column constitutes the zone of reaction with $NaBH_4$ or the reaction is carried out in the injection chamber in front of the column, which contains a minireactor with this reagent. Following separation from the post-reaction mixture using an inert carrier gas (argon, helium), volatile hydrides are directed to the atomization (AFS,

Table 3. Comparison of selected methods of derivatization of organometallic compounds [5, 52, 56-58].

| Reduction with $NaBH_4$ | Ethylation with $NaBEt_4$ | Alkylation with Grignard reagents |
|---|---|---|
| Method description | | |
| Mix acidified sample solution with derivatizing agent ($NaBH_4$). Purge reaction mixture with an inert gas to transfer hydrides formed to gaseous phase. | Add buffer (pH 3-5) to sample solution and mix with $NaBEt_4$. Purge reaction mixture with an inert gas to transfer derivatized analytes to gaseous phase. | Reaction is carried out in organic solvents. Excess of derivatizing agent is removed by adding an acid to the sample. |
| Reaction time | | |
| Very short | 2-10 min | 30-180 min |
| Advantages | | |
| – Reaction takes place in aqueous medium compatible with most samples<br>– Reactions are fast<br>– Low cost<br>– High yield<br>– Simplicity and high sensitivity<br>– Shorter times of reaction and purge of volatile derivatives compared to ethylation with $NaBEt_4$<br>– Method well described in literature. | – Reaction takes place in aqueous medium compatible with most samples<br>– High yield<br>– Short reaction time<br>– No need to remove organic solvent (required in Grignard reaction)<br>– Method well described in literature. | – Low volatility of analytes<br>– High yield<br>– Possibility of use in derivatization of various alkyl groups (propyl, butyl, pentyl, hexyl, methyl or ethyl) and phenyl<br>– Method well described in literature. |
| Disadvantages | | |
| – Susceptibility to all kinds of interferences (affects precision and speed of determination)<br>– Derivatives can be too volatile (possible analyte losses)<br>– Method limited to elements which can form volatile hydrides in reaction with $NaBH_4$ (hydrides are not formed by compounds with high b.p., e.g. phenyltin)<br>– Lability and possibility of dismutation of hydrides of lead, mercury, arsenic and tin | – Expensive reagent<br>– Not as well characterized as $NaBH_4$ reduction<br>– Cannot be used in speciation analysis of ethyl derivatives of lead (they lose their chemical identity)<br>– Incomplete derivatization due to interference from matrix components of the sample. | – Slow derivatization process<br>– Lack of compatibility with procedures based on aqueous extracting agents (recommended change of solvent)<br>– Tediousness and time consumption, associated with using nonaqueous medium.<br>– Large solvent consumption. |

AAS) or excitation (ICP, MIP) system and determined using a specific detector.

The greatest advantage of this approach is its simplicity and high sensitivity. Moreover, the procedure has shorter times of reaction and purging volatile derivatives from the reactor compared with the ethylation in the aqueous phase technique [56]. However, the applicability of this procedure to speciation analysis is limited to the elements which are capable of formation of volatile hydrides in reaction with NaBH$_4$ (such volatile hydrides are not formed by the compounds with high boiling points, such as phenyltin [57]). Another disadvantage of the generation of volatile hydrides is its susceptibility to all kinds of interference, which adversely affects precision and speed of analysis. In addition, one should remember that hydrides of lead, mercury, arsenic and tin are unstable and easily undergo dismutation [56].

Alkylation using **Grignard reagents** (alkylmagnesium halides) resulting in the formation of alkyl derivatives is carried out in nonaqueous media, mainly after extracting the investigated species into organic phase in the presence of complexing agents (tropolone, dithiocarbamates). Derivatives with lower molecular masses have found wider application due to their higher volatility. Grignard reagents are used in speciation analysis of selenium, arsenic, tin, lead and mercury [56], although in speciation analysis of tin they are being replaced with easier and less time consuming derivatization with NaBH$_4$.

The main advantage of derivatization with Grignard reagents is its high yield, the possibility of using a variety of alkyl groups (propyl, butyl, pentyl, hexyl and phenyl in addition to methyl and ethyl) [52], as well as applicability to samples having a complex composition of matrix.

The shortcoming of the method is its tediousness and time consumption resulting from the necessity of using nonaqueous media [5].

Ethylation with **sodium tetraethylborate (STEB)** can be carried out in the aqueous medium (as opposed to the alkylation using Grignard reagents), which makes the technique more attractive thanks to shorter time of analysis and no need to remove organic solvent. However, the technique can only be used to distinguish among inorganic and methyl lead and mercury species. Ethyllead species and inorganic lead species are converted solely into tetraethyllead and lose their chemical identity [56]. Ethylation is also successfully used for the derivatization of organotin compounds prior to their GC separation [69-26]; however, butyl- and phenyltin species must be extracted from solution after derivatization due to their lower volatility compared with methyltin [54]. Also in this case, there are difficulties in obtaining quantitative conversion to ethylated species resulting from interference by some matrix components of the analyzed sample.

Specific derivatization of organometallic compounds prior to their introduction into the capillary or during

Table 4. Selected derivatization techniques used in speciation analysis of Pb, Hg, As, Sn and Se (literature data).

| Separated species | Method/Derivatizing agent | Literature |
|---|---|---|
| Organometallic compounds of Hg, Pb, Sn, As | Grignard reagent, NaBH$_4$, NaBR$_4$, where R- C$_2$H$_5$,C$_3$H$_7$, C$_6$H$_5$ | [52] |
| MBT, DBT, TBT, MMHg | NaBEt$_4$ | [60] |
| Organometallic compounds of Hg, Pb, Sn | NaBEt$_4$ | [61] |
| Organometallic compounds of Hg, Pb, Sn, As, Se MMHg | NaBH$_4$ NaBEt$_4$ | [53] |
| Organometallic compounds of Hg, Sn, Pb | NaBEt$_4$, NaBPr$_4$ | [62] |
| Organotin compounds | Grignard reagent, NaBH$_4$ | [63] |
| Organotin compounds | NaBEt$_4$ | [23, 25, 57] |
| MMHg | NaBH$_4$, NaBEt$_4$ | [64] |
| MMHg, DMHg | NaBEt$_4$ | [65, 66] |
| MMHg, EtHg | NaBEt$_4$, NaBPr$_4$, NaBPh$_4$ | [67] |
| MMHg, PrHg | NaBEt$_4$, NaBPr$_4$ | [68] |
| MMHg | NaBEt$_4$ | [69] |
| MMAA, DMAA | NaBH$_4$ | [70] |
| MMAA, DMAA, TMAO | NaBH$_4$ | [14] |
| Organometallic compounds of Hg, Pb, Sn, As, Se | NaBH$_4$ | [54, 71] |
| Hg, Sn, As, Se | NaBH$_4$ | [72] |
| Hg, As, Se | NaBH$_4$ | [73] |

separation is also carried out using electrophoretic methods. Complexation of metal ions with different oxidation numbers allows differentiating their charge density, thus facilitating separation. Sometimes anionic and cationic species are converted into complex ions with like charges, thus simplifying electrophoresis. The efficiency of separation of organometallic species is also improved by complexing them prior to their introduction into the capillary (e.g. complexing various mercury species with cysteine or dithizone) or by modifying the electrolyte with weak ligands, such as cyclodextrin [59].

Precolumn derivatization is rarely used in liquid chromatography. The species to be separated are modified using ion-pair chromatography; complexing agents are sometimes added to the mobile phase in reverse phase chromatography. The fundamental role in liquid chromatography is played by postcolumn derivatization. It aims to convert the separated species into the form best suited for the detection system used: colored complexes (for UV-vis detection), fluorescent (fluorimetry), volatile compounds (spectral detectors). In the last case any method suitable for precolumn derivatization in GC can be used; the cold vapor technique for the determination of mercury also is important [6].

The literature data on various derivatization methods for organometallic compounds are compiled in Table 4.

## Methods of Separation and Determination of Organometallic Compounds

Speciation analysis makes use of analytical methods allowing selective determination of various chemical species present in a sample, often at very low concentrations. Selective determinations of elemental species can be carried out by preliminary separation of the species, followed by their quantitative determination using the same techniques as those employed at this stage for the determination of total contents of elements [76]. The methods primarily applied for this purpose are chromatographic techniques, such as liquid, gas or supercritical fluid chromatography as well as other separation techniques, e.g. capillary electrophoresis.

### Role of Chromatographic Techniques in Speciation Analysis

Chromatography can be used in a variety of modes, thus allowing for the selection of the best technique in speciation analysis, depending mostly on chemical properties of the species to be separated. Liquid chromatography is best suited for nonvolatile or thermally unstable compounds as well as polar and ionic substances; gas chromatography is appropriate for the separation of volatile and thermally stable compounds. Supercritical fluid chromatography is complementary to gas and liquid chromatography. Each technique, particularly liquid chromatography, can be further classified into subgroups

differing with respect to the type of stationary and mobile phases [6]. It should be pointed out that in some cases liquid chromatography allows speciation analysis without prior derivatization of the analytes [5].

In speciation analysis of organometallic compounds the following chromatographic techniques have found the widest use:

– gas chromatography [75, 53, 56, 61, 76-82],
– normal or reverse phase liquid chromatography [75, 56, 82-88],
– supercritical fluid chromatography [89, 90, 83, 91,],
– ion-pair chromatography [82, 87],
– micellar chromatography [82, 87],
– ion exchange chromatography [82, 87],
– exclusion chromatography [82, 87].

Typical instrumentation employed in speciation analysis of organometallic compounds involves techniques combining the process of chromatographic separation of mixtures with the selective detection of analytes in the column effluent. The main technical problems in combining chromatography with selective detectors are interferences taking place during separation and detection that affect the detector signal as well as the long time needed for data acquisition (required to characterize many transient signals composing a chromatogram) [58].

The majority of determinations of organometallic compounds are carried out by gas chromatography. The advantages of GC include very high resolution, low background resulting from high purity of the carrier gas, relatively low cost of the instrumentation and the ease of coupling GC to a variety of systems of final determination and identification of the analytes. The disadvantage of this approach is the fact that the majority of organometallic compounds occurring at trace levels cannot be directly separated by GC due to their thermal lability, high reactivity and ionic nature. Consequently, the analyte derivatization step is required prior to analysis [58].

Due to the fact that the majority of species of organometallic compounds are ionic or polar, mainly occurring in water, the application of liquid chromatography as a separation technique would seem to be a natural choice. However, the number of detectors used for speciation analysis is limited and many of them require sample nebulization, which can cause a loss of up to 98% of the analyte [3]. The type of sample matrix can also limit the choice of detector. Consequently, detection limits for the methods based on liquid chromatography [88, 92, 93] are usually higher by several orders of magnitude compared to those based on GC (e.g. the detection limit for methylmercury is about 50 ng/g when using the CV-AAS detector [94]). On the other hand, the coupling of LC with the detectors such as atomic fluorescence spectrometer (AFS) or inductively coupled plasma – mass spectrometer (ICP-MS) enables reaching low detection limits, which is especially important in speciation analysis of the elements that cannot be directly determined by GC.

Properties of supercritical fluids and their application to extraction of different elemental species from solids

were discussed in the section dealing with the extraction and enrichment of organometallic compounds from solid matrices. Supercritical fluids are also used as mobile phases in chromatographic separations. Compared with other chromatographic methods, SFC offers a number of advantages; on the other hand, the properties of the most common supercritical fluid, carbon dioxide, limit the method to the separation of nonpolar and electrically neutral species. The use of polar fluids (water, ammonia) requires much higher temperatures and pressures. This problem can be solved by adding modified agents, for example methanol, to carbon dioxide, which increases its polarity.

The main reason for a very limited use of SFC, also in cases of separation of organometallic compounds, seems to be the high cost of instrumentation compared to other chromatographic techniques [95].

### Electrophoretic Techniques [3, 5, 6, 96]

One of the most interesting separation techniques that have recently been introduced in analytical chemistry is capillary electrophoresis (CE). The process of separation of sample components is based on the phenomena of electrophoresis and electroosmosis taking place in capillaries of small diameter upon applying a high voltage (10-30 kV). The technique is characterized by its high resolution, short analysis time and low cost of operation due to low reagent and sample consumption. Capillary electrophoresis systems can be readily automated and are easy to couple to a variety of detectors (spectrophotometric, mass, fluorescence, conductometric, etc.), thus finding a wide applicability.

Three modes of capillary electrophoresis have found use in speciation analysis [9]:
  – capillary zone electrophoresis,
  – micellar electrokinetic capillary chromatography,
  – capillary gel electrophoresis.

In addition, the newest technique combining the advantages of liquid chromatography and capillary electrophoresis – capillary electrochromatography may prove useful in speciation analysis. In this technique, the separation process is carried out in packed columns (like in LC)

but of greatly reduced diameters; the driving force is the electroosmotic flow (like in CE).

Thus far, the electrophoretic techniques mentioned above have had marginal application in speciation analysis of organometallic compounds. One of the reasons for this is the need for highly sensitive detectors as a result of very small sample volumes that can be transported to the detector.

### Analytical Techniques Used for the Detection and Quantitative Determination of Organometallic Compounds

The most commonly used techniques in speciation analysis are hyphenated methods (Fig. 2) – chromatography as a separation technique coupled to atomic spectroscopy methods – atomic absorption spectroscopy (**AAS**) [7, 8, 9, 43, 39, 97], atomic fluorescence spectroscopy (**AFS**) [66, 98, 99], microwave induced plasma- atomic emission spectroscopy (**MIP-AES**) [65, 77, 100], inductively coupled plasma – atomic emission spectroscopy (**ICP-AES**) [58-47, 96-85] or inductively coupled plasma – mass spectrometry (**MS, ICP-MS**) [14, 54, 72, 76, 84, 93, 98, 101, 102, 103]. The flame photometric detector (**FPD**) can also be used [104, 105, 106], particularly for the determination of volatile organotin derivatives. Thus, the hyphenated methods are an extension of chromatographic techniques in which "classical" GC and LC detectors have been replaced by the methods of selective determination of elements with low detection limits [74]. The majority of hyphenated methods offers the power of high resolution chromatography combined with high sensitivity and element specificity.

Selected references on most common hyphenated techniques used for the separation and determination of some organometallic compounds are compiled in Table 2.

### Summary

Trace elements are important components of the biosphere. Proper functioning of all living organisms depends on their concentration, kind of species and mutual ratio
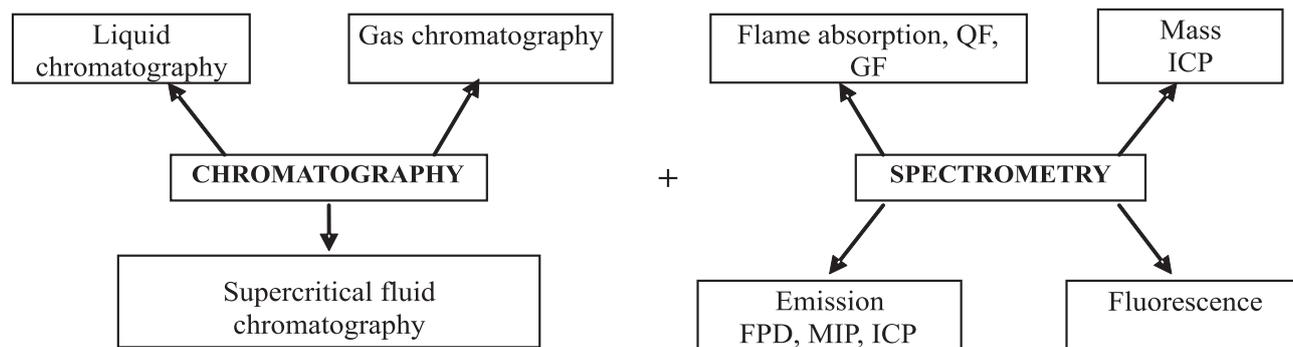


Fig. 2 Selected hyphenated techniques used in speciation analysis of organometallic compounds present in samples of soil and sediments [107].

in the tissues. Many trace elements are known for playing an essential role in maintaining system homeostasis. The natural cycle of trace elements in the environment is generally balanced, whereas all the elements introduced through anthropogenic activity undergo a variety of transformations, migrations and gradual inclusion into the natural cycles. Hence, human activity affects directly or indirectly chemical changes of individual components of the environment and food products, thus influencing human health.

The determination of total content of trace elements in biological and environmental samples is often insufficient for the evaluation of their effect on living organisms and the environment. Various species of a given element have different chemical and physicochemical properties, which results in their diverse effect (including toxicity) on living organisms. This calls for the application of speciation analysis, which allows both the identification of different elemental species occurring in a specific material and their quantitative determination. Speciation analysis has become one of the most important trends in the development of trace analysis.

Organometallic compounds, being persistent and biologically available and therefore undergoing bioaccumulation, are a special kind of anthropogenic pollutant. Based on a search of the available literature it can be concluded that there are no universal procedures of collection, preparation and determination of organometallic compounds of Hg, Sn, Pb, As and Se in soils and sediments. The selection of analytical procedure is limited by the form of analytes and type of matrix as well as the concentration range of analytes; hence, each sample requires an individual approach.

Speciation analysis of organometallic compounds in environmental samples faces a number of problems, which presents a serious challenge to the analysts. These include:

– the possibility of change in sample composition during their collection, storage and analysis due to transformation and degradation of the analytes affected by external factors (temperature, light, exposure to air);
– limited availability of reference materials, which makes validation of analytical procedures more difficult;
– necessity of usage of very sensitive determination methods due to low concentration levels of the analytes in the sample.

The data regarding methods of extraction and determination of organometallic compounds of Hg, Sn, Pb, As and Se in soils and sediments are compiled in Table 2. The compiled data reveal that there are a variety of procedures for the determination of such compounds in solid matrices.

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