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Review

Speciation of Organometallic Compounds of Tin, Lead, and Mercury

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Abstract

This paper presents a discussion of fundamental problems of the speciation analytics of organometallic compounds occurring at low concentration levels in samples involving a complex matrix.

It points out differences in analytical procedures for speciation analyses and those for determinations of total contents of a metal present in the studied sample in a number of different species.

Keywords: organometallic compounds, speciation, sample preparation, derivatisation, separation

Introduction

The very term "speciation analysis" was initially associated with, generally, those methods of analysis which answered questions regarding the amount and forms of presence of a given metal in the investigated sample. This information does not serve to satisfy "purely academic interest" only, but it has become gradually more valuable with developments in the field of medicine, ecology, even geology.

Metals are rarely present in the environment in a native form or as free cations. Usually they occur in a bonded form, in larger molecules, formed as a result of different bio- and/or geochemical processes [1]. It is worth stressing that both *quantity* and *quality* of forms of occurrence of any given metal carry information, extremely important to understanding its bioaccessability for living organisms, as well as the cycles of its circulation in the environment.

Conclusions on a role of a given element in these or other processes, based exclusively upon the determinations of its total contents, have been (in many cases) proven insufficient, and even (in some extreme cases) misleading.

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Some examples of fields in which speciation analysis provides an important research tool are given below.

Ecological Risk Assessment

Checking the elements of the natural environment (air, waters, soils) for the presence of organometallic compounds of anthropogenic origin *(e.g.,* tetraethyllead) has been one of the major fields utilising speciation analytics. Speciation is required for a reliable evaluation of an environmental impact of existing or planned constructions or plants, due to the fact that the majority of organometallic derivatives reveal significantly higher toxicity than the corresponding metals in the form of free ions.

Ecotoxicology

Speciation analytics is employed here for identification of natural ways of detoxification, *via* microorganisms and plants, of areas polluted with heavy metals. A particular role in these processes is ascribed to metalthioneines - a group of proteins, capable of bonding many metals [2]. Other important fields remaining within

the scope of ecotoxycologists are studies on phenomena of natural biomethylation of mercury and formation of arsenobetaine and arsenosugars in organisms of marine animals.

Food industry

It is known that metals play important roles in metabolisms of living organisms. Their deficiency leads to significant changes in biochemical processes while, at the same time, their excess may cause poisoning. Some metals constitute irreplaceable components of food *{e.g.,* calcium, magnesium, iron, selenium, zinc, copper) while consumption of food containing excessive amounts of these metals may lead to serious consequences and malfunctioning of the organism. An additional complication is a diversified bioaccessability of microelements, depending on the respective chemical forms of their occurrence in food. This is a chief reason, for example, that some seafood may be consumed safely, even in quantity, despite its apparently "lethal" arsenic contents. It has been proven that practically all arsenic present in seafood occurs in the form of quite harmless arsenobetaine. This fact does not permit skipping proper control of such food.

Speciation analytics may serve in this field not only as a tool of control of the quantity and quality of harmful metals present in food, but also for the assessment of packing materials. Some types of polymers may release, undesired organometallic compounds used as their stabilizers. Also, some problems of food storage may include speciation studies of metals. For example, it has been found that positive correlation exists between the contents of free ions of copper and selenium in milk and fats and the rate of spoilage of these food products.

Medicine and Pharmacy

Metals participate in many biochemical processes of vital importance for the organism. Hemoglobin (iron), insulin (zinc), alcoholic dehydrogenase (cadmium, zinc), and β-amylase (copper), are just a few examples of proteins, hormones and enzymes containing metal atoms which are vitally important for proper functioning of human organisms. Substances labeled with isotopes of technetium are used in diagnostics, imaging techniques applied to the heart, cardiovascular system, and brain.

Organometallic compounds have found many applications in pharmacology. Compounds of platinum, ruthenium and gold are used as anticancer medicines. Speciation analytics serves in this field as a tool permitting finding such forms of the active components, which allow for an optimum intake by the organism. On the other hand, the same tool permits studying of the relevant processes in human systems.

Analytical procedures utilised in speciation analytics of organometallic compounds differ, in several important aspects, from those used in determinations of the total contents of metals present (actually in many different combinations) in an investigated sample.

First, speciation-specific problems arise already at the definition of the analytical goal. One should be aware of limitations, which methods used in speciation are subjected to and possible ambiguities, which may result from imprecise and unclear definition of the goal of analysis.

In the case of the determination of total contents of any metal, the question an analytician is asked usually reads: *"What amount of metal M is contained in a given sample?".* There is no doubt about intention of the one who asks the question, the goal of the analysis to follow is defined unambiguously. However, when speciation is involved, similarly formulated question: *"What kind of compounds of metal M and in what quantities are present in a given sample?"* gives little chance of obtaining an exact answer. There are two basic reasons of this state of matters. The first is due to the limitations of the available procedures of speciation analytics. Some of the compounds cannot be determined because the suitable procedures have not yet been developed, or their determination is too expensive or time and labour consuming. The second reason is related to the complex systems of chemical equilibria occurring in real samples.

For example, when speciation of mercury in a biological sample is discussed, it is most frequently understood as differentiation between methyl mercury (CH_3Hg^+) and inorganic mercury (Hg^{2+}). It is rather improbable, however, that the two substances are present exclusively as respective free ions. Both analytes might actually form many complexes, or remain bound to thiol groups of some amino acids which, in turn, may belong to different peptides, which may form different polypeptides, and so forth. Determination of all possible permutations of the two aforementioned analytes becomes technically impossible and, therefore, *a priori* assumptions must be made about definitions of the analytes which are relevant to the actual needs and goals. In the above example, such simplification might mean defining the analytes as sums of free ions, CH_3Hg^+ and Hg^{2+}, respectively, as well as those which may be liberated by splitting from larger molecules in the process of matrix decomposition, the latter performed by a chosen method.

Basic types of speciation analytics have been discussed in several extensive reviews [3-5].

Precisely defined goals and scopes of the analysis constitute a basis for a subsequent design of all steps or stages of a suitable analytical procedure.

Fundamental problems involved in particular stages of analytical procedures utilised in speciation analytics of organometallic compounds, especially those of lead, tin, and mercury are discussed below. The importance of this subject may be illustrated by a number of review articles published in recent years [6-14].

Analytical Procedure

Collection of Samples, Their Storage and Preservation

The general scheme of a procedure used for sampling and sample preservation in speciation analytics is ruled by the same principles as in any other type of analyses. The sampling method must ensure representativeness of the samples collected, while preservation prevents any

possible changes during storage. The latter is of special importance in the case of speciation, as the total amount of a given element may remain constant, while proportions of particular forms, both physical and chemical, may vary when compared with original sample composition. Choosing the method of preservation (or a conservant used), one should consider possible difficulties resulting from its use.

Below, the main methods used for sample preservation and storage are discussed.

Liquid samples. Liquid samples of different types (surface waters, precipitation, ground waters, urine, *etc.),* taken for subsequent analysis for their contents of organic derivatives of lead, should be preserved, according to current recommendations, without acidification, in plastic containers (Teflon, polyethylene), at 4°C, in darkness. Samples prepared in this way may be stored up to three months [15]. In the case of tetra substituted lead derivatives, addition of an organic solvent *(e.g.*, hexane) is recommended, to reduce the losses due to their volatility and instability in aqueous medium [16, 17]. Similar recommendations are valid in the case of tin [18] and mercury [19] derivatives (although in this case some authors suggest acidification of the samples [19-21] using hydrochloric acid, or freezing at -30°C [22]).

Solid samples. The same method of storage as for liquid samples is recommended, *i.e.,* polyethylene or Teflon containers, reduced temperature, no light. Wet samples may be dried in air, using ovens (50°C), by sublimation [15, 23], or just kept frozen, without removing moisture, at -20°C [24]. Samples to be analysed for the contents of volatile components should be extracted with a suitable solvent immediately after their collection [15].

Gaseous samples. In this case one should differentiate between the suspended matter (dusts, aerosols) and the gaseous phase itself. At the collection stage, the former is separated from the gaseous phase on suitable filters and is subsequently stored according to principles applied to solid samples. Analytes from the gaseous phase are usually captured from a stream of the sample on a sorbent bed. Among the sorbents utilised for these purposes are: *Porapak, Chromosorb* and *Carbotrap.* The beds are subsequently stored in the same manner as solid samples. In the case of metallic mercury and dimethyl mercury, one can utilise gold (or platinum-gold alloy) sorbents or sorbents with these metals deposited on their surfaces [25, 26].

Preparation of Samples for Analysis

Sample preparation is more or less complicated operation, depending on type of analyte, sample type and origin, utilised method and technique of final determination. This stage includes different unit processes, such as:

- sample mineralisation and/or dissolution,
- removal or masking interfering substances present in the sample,
- extraction of analytes,
- purification of the extract,
- derivatisation of the analytes,
- enrichment of the analytes.

These processes may be performed separately, although a clear tendency may be noticed to combine at least some of them into a single operation [27]. Such an approach shortens time required for sample preparation, reduces the risk of losses by elimination of multiple transfer of solutions, as well as the risk of contamination of the sample; the latter factor being of particular importance when trace analysis is required.

Figure 1 shows a general scheme of all procedures of sample preparation for subsequent analysis, utilised in speciation analytics of organometallic compounds of lead, tin, and mercury. This scheme has been compiled on the basis of several original papers [22, 26, 28-44] and a number of review articles [6, 12, 15, 18, 21, 45-47] discussing both methods of sample preparation for speciation analysis, and determination of individual organometallic compounds in samples of different types. It is important to stress that this is one generalised scheme. Not all operations shown in it are necessary in each and every actual procedure; some other schemes are also possible.

The majority of operations shown in the scheme are the same for all the three metals discussed. The only exception is derivatisation using sodium borohydride (NaBH)), which is not applicable for lead compounds, as they do not form volatile derivatives in a reaction with NaBK,.

Preliminary sample preparation. In the case of solid samples, the first stage of their preparation is, usually, their homogenisation. This is achieved by application of special mills or grinders, after drying or deep-freezing (in liquid nitrogen) the samples. Subsequently, some procedures require dissolution of a sample matrix with the purpose of liberating these portions of the analytes, which are adsorbed, complexed or otherwise, bound to the main components of the sample. This operation is most frequently met in handling biological samples, in which the analytes are, as a rule, chemically bonded to the protein chains. Similar situations may take place when soil samples are treated, taken from soils rich in humic substances, capable to form complexes with many metals. Diluted acids (HC1, CH_3COOH), their mixtures with alcohols, aqueous or alcoholic solutions of hydroxides (NaOH, KOH, tetramethylammonium hydroxide - TMAH) or enzymes containing solutions permitting partial decomposition of a protein matrix (used, for instance, in determination of metaloproteins) are most frequently utilised for sample dissolution. pH of the resulting solution is subsequently adjusted to the desired value by the addition of a suitable buffer or certain amount of acid or base solution.

Operation of matrix dissolution used in sample preparation for speciation analysis, despite its formal similarity to mineralisation of a sample in cases of the determination of total contents of a component, is usually carried out under much more gentle conditions. In the latter case, total conversion of all the forms present in the sample to free metal ions is usually required. This is most frequently achieved using concentrated mineral acids (HC1, H_2SO_4, $HClO_4$) or their mixtures, which reduce the

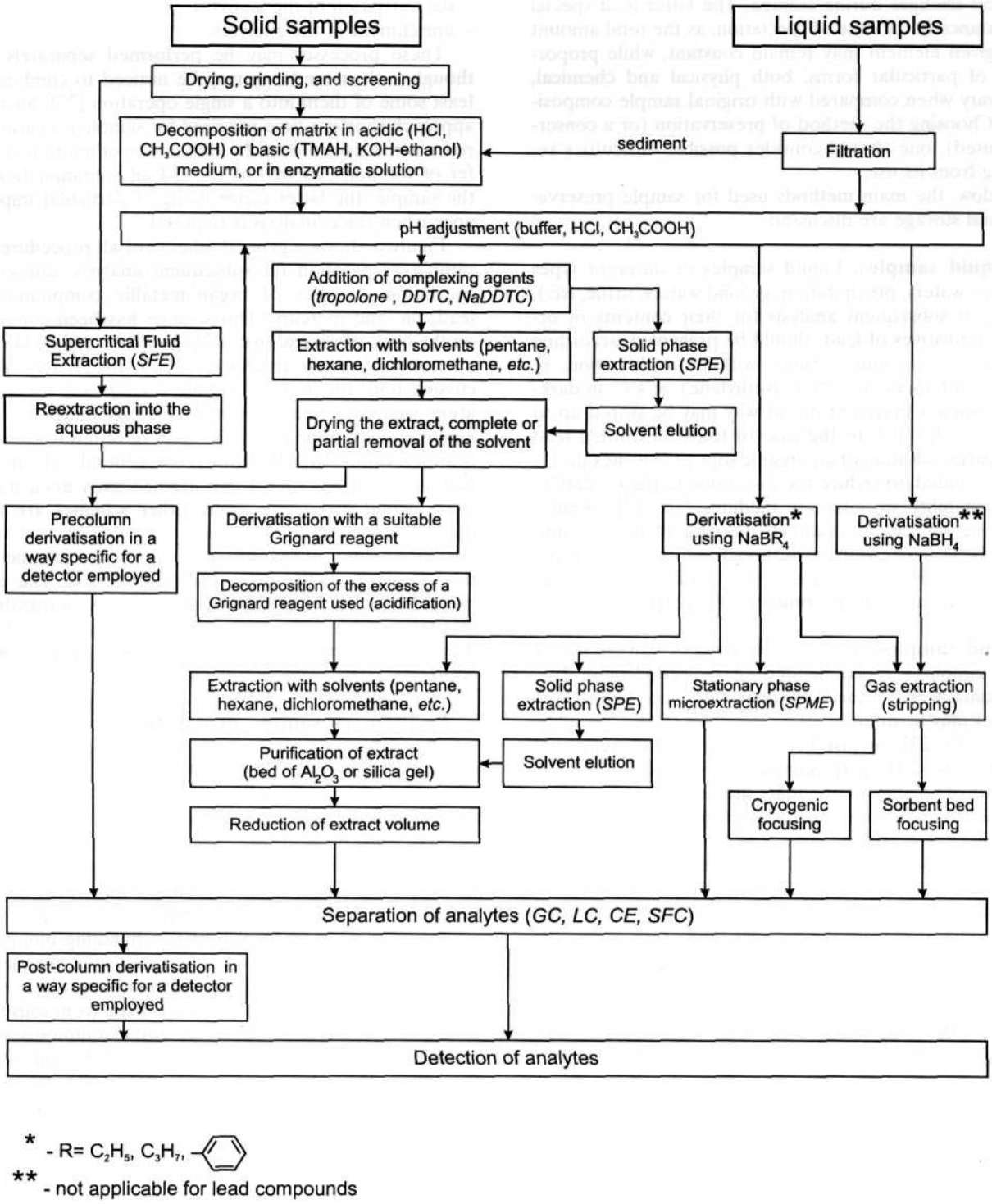

Fig. 1. A general scheme of sample preparation for speciation analysis of organometalic compounds of lead, tin, and mercury.

matrix to simple inorganic compounds. This method cannot be employed in the case of speciation analysis, as destruction of the matrix would mean losing the information belonging to the very goal of this analysis. Gentle conditions of a sample dissolution, used in speciation methods, do not result in matrix destruction, but rather in its partial decomposition and liberating the analytes from macromolecules.

Extraction of analytes. This important step of the sample preparation procedure is present in a majority (if not in all) of procedures used in trace analysis and, therefore, is inseparable from speciation analytics. Extraction of analytes may be included in different phases of the whole process of sample preparation, with different objectives to achieve. Due to the fact that organometallic compounds are usually present at very low concentrations, the principal objective is their enrichment. To this end, liquid solvent extraction, gas extraction (stripping),

solid sorbent extraction, and supercritical fluid extraction are used. Another objective of this operation is matrix exchange prior to any subsequent step of sample preparation or just before final determination. Extraction may also be treated as a possible way of removing the interfering substances. It happens quite frequently that single operation of extraction combines the three aforementioned objectives, *i.e.* analyte enrichment, change of the matrix, and removing the interfering substances [48, 49].

Extraction of analytes from aqueous solutions by organic solvents is usually enhanced by using an addition of complexing agents, like tropolone (2-hydroxy - 2,4,6-cycloheptatrienone) or sodium diethyldithiocarbamate (NaDDTC, DDTC). These enhancers form weak, non-polar complexes with ionic forms of analytes (originating from sample or as a result of a matrix dissolution), easily transferred to the organic phase. These additives offer advantageous recoveries when methods including subsequent derivatisation of analytes using Grignard reagents, or their extraction to a non-polar solid phase, are employed. In a case of derivatisation using sodium tetraalkyl or tetraarylborates (ethyl borate, propyl borate, phenyl borate), the reaction is usually carried out in a solution obtained directly in the matrix dissolution step, after a suitable pH adjustment. Some authors [34] suggest a possibility of carrying out the extraction of solid samples using supercritical fluids *(SFE)* without any previous treatment. Frequently, extraction of analytes is aided by ultrasounds or microwave field energy.

It seems worth mentioning that in cases of the determination of total metal contents, as opposed to speciation analyses, extraction of analytes is rarely necessary. It is included, as a rule, only when determination of trace amounts of metals is involved *(e.g.*, extraction of gold using ion exchanging resins before its determination from sea water).

Derivatisation of analytes. This operation is included into a definite majority of procedures of determination of organometallic compounds [50]. Its objective is to change the chemical form of an analyte which simplifies (or even enables) the subsequent analysis. As has already been mentioned, after sample dissolution the analytes are usually present in the solution in an ionic form. Separation of polar substances, which is the case when ions are involved, may lead to many problems when typical chromatographic systems usually designed for separation of non-polar substances are employed. Ionic analytes may result in peak tailing, which makes proper (or automatic) interpretation of peaks difficult, as well as gradual worsening of separation power of the column, caused by irreversible adsorption of analytes on active sites of the column. Even if some procedures are available, permitting separation of analytes without their derivatisation prior to separation on specially prepared columns [29, 41], due to their increased labour consumption (column deactivation after several analyses is required), they have never enjoyed wide popularity. It should be noted, however, that the derivatisation step might increase; on the other hand, the risk of error bearing results of analysis due to either losses of analytes or unintentional contamination of samples with analytes. Derivatisation for subsequent gas chromatography is aimed primarily at facilitating this technique of separation of a mixture of analytes. In the case of liquid chromatography, there is one more reason for derivatisation, namely, making detection possible, or, if possible, enhancing sensitivity of the final determination of analytes. While speciation analytics involving gas chromatography employs practically exclusively different types of selective detectors (chiefly spectrometric), when it comes to liquid chromatography, derivatisation may make it possible to employ common, universal detectors, *e.g.*, a UV-VIS spectrophotometric detector or fluorescence detector, thus increasing applicability of the latter separation technique.

Another important aspect of derivatisation is facilitation or enabling analyte enrichment at all. Derivatisation provides extractable forms of analytes for such processes as stripping, solvent extraction, solid phase extraction or stationary phase micro extraction.

Among the methods of derivatisation, the top approval gained the following: derivatisation utilising Grignard reagents, sodium alkyloborates and sodium hydroborate, the first method being most versatile and the third, the least versatile one. A serious disadvantage of derivatisation using Grignard reagents is its high labour consumption, due to the necessity of using non-aqueous media. While the methods using sodium alkyloborates or sodium hydroborates are much simpler (respective reactions occur in aqueous medium), their application is not always possible. Ethylation of analytes using $NaBEt_4$ does not always provide an unambiguous answer to the question of what kind of analyte was present in the original sample *(e.g.*, Pb^{2+}, $PbEt^{3+}$, $PbEt_2^{2+}$, $PbEt_3^{+}$, all will produce $PbEt_4$ after ethylation), while the reaction with sodium hydroborate is limited to analytes yielding volatile products (this fact excludes it from use it for lead compounds). Nevertheless, derivatisation in aqueous medium is such an easy method that new derivatisation reagents are being tested, like sodium tetrapropylo - [52] and tetraphenyloborate [53]. Application of these new reagents brings opportunity to eliminate the aforementioned ambiguities.

The derivatisation process may be carried out before, after or even during the extraction step. It is usually performed before the separation of analytes; sometimes it takes place prior to the detection step.

While derivatisation is present as a step of many methods of determination of organometalic compounds, it is relatively rarely included in procedures for determination of total metal contents, unless one counts as derivatisation such operations as precipitation or reduction of metals to atomic form.

Enrichment of analytes. As has already been said, enrichment of analytes, while in different manners, is embraced by all procedures of speciation analytics. Most frequently, this process occurs during solvent extraction of analytes. Other popular methods include: solid phase extraction, supercritical fluid extraction and gas extraction. Each of these ways has its own advantages and disadvantages.

Undoubtedly, solvent extraction may be counted among the most versatile methods but, on the other hand, it reveals many weak points. First of all, when high

enrichment is desired, relatively large samples must be used and, in turn, adequately large volumes of liquid solvents. This solvent (or solvents) must subsequently be separated from the analytes it contains, to achieve the desired degree of enrichment. To this end, solvent evaporation in a stream of an inert gas or distillation is usually utilised. Both these operations are time consuming and cause air pollution with substances, which are neutral neither to human health nor to the environment. Economical considerations also provide arguments against this method. Solvents used for extraction must be of suitably high purity, which means their relatively high price. Even if they may be recovered *(e.g.,* by distillation), this must be followed by the laborious process of their purification.

Despite its handicaps, enrichment by solvent extraction remains quite popular due to its simplicity and unsophisticated equipment required. Although, there is a trend in analytical chemistry to eliminate this method wherever possible, replacing it by such methods of analyte enrichment, which quitted usage of solvents altogether or, at least, use them in strictly limited amounts. Among such methods, there are: solid phase extraction, supercritical fluid extraction and gas extraction.

Solid phase extraction *(SPE)* is a method which in the foreseeable future might become a complete substitute for the solvent extraction. Unsophisticated equipment, simplicity, wide selection of sorbents and high values of the enrichment coefficient contribute to still wider application of this technique. One can count, among additional advantages, a possibility of analyte enrichment *in situ* and analyses of samples in an *on-line* mode. Among the limitations, one should mention the necessity of previous transfer of analytes to a liquid or gaseous phase, when solid samples are involved, and some difficulties in extraction of highly contaminated samples.

Supercritical fluid extraction (SFE) is a method used for analyte enrichment from solid samples. One of the great and unique advantages of this technique is an opportunity of almost complete control of extraction properties of the supercritical fluid. Unknown in other methods of extraction, this feature creates the opportunity to influence the process, even when in progress. The most common extracting agent is carbon dioxide, pure or with the addition of so-called modifiers *(e.g.,* methanol, acetone, ethanol, dichloromethane, *etc.).* Other, relatively rarely used media are freons, ethane, sulfur hexafluor-ide, nitrous oxide, methanol, ammonia, and water. The limited number of these substances does not limit versatility of SFC. Using only one of them *(e.g.*, carbon dioxide) one can find such parameters of the process (varying temperature, pressure, type and amount of a modifier used), to obtain such extracting properties of the medium which best suit our actual needs. Despite its numerous and undisputable advantages, supercritical fluid extraction is not yet common in analytical laboratories (quite the opposite situation is found in industry), which is due to the high price of the instrumentation required [54].

Gas extraction is a method of analyte enrichment, usually coupled with gas chromatography. The method is employed when analytes are sufficiently volatile or may be suitably transformed, *e.g.* by means of derivatisation. Gas extraction is one almost perfect method of enrichment, when applicable. The technique is used for analyses of both solid and liquid samples. It provides an opportunity of practically complete transfer of analytes from the sample to the separation system, at the same time permitting significant lowering of the detection limit of the method. It eliminates any need for using solvents. Additional gains are: simple equipment and its almost "natural" compatibility with *on-line* analytical systems. Its most serious limitation is its limited applicability. As mentioned before, the analytes (or their derivatives) enriched by this technique must indicate suitable volatility, which eliminates any chances for analyses of high molecular weight substances (e.g., biomolecules). A limited repertoire of derivatisation reagents also narrows the applicability of gas extraction for enrichment of analytes. Additional problems may originate not from the type of analytes present in the sample, but rather from the sample matrix, when it contains, for example, surfactants, which may lead to the formation of foam during gas extraction. From the brief summary given above, one can conclude that, while an ideal, a perfect method of analyte enrichment does not exist. The repertoire of available ways and means is sufficiently broad to permit an optimal choice of a most suitable method in a given case.

Integrated sample preparation procedures. The problem of shortening analysis time is closely related to the procedure of sample preparation chosen in a given case. Sample preparation is the bottleneck step of all analytical methods (if it is included), limiting further reduction of time required per single analysis.

Among the methods of sample preparation used in speciation analytics, special attention should be paid to integrated (accelerated) sample preparation procedures, which combines several sample preparation steps into one operation. Microwave assisted sample preparation procedure has been successfully applied for organotin [55, 56], organomercury [57] and organolead [58] compounds in samples of different origin.

Beside shortening analysis time integrated sample preparation procedures are easier for automation and less susceptible to human errors than multistep protocols.

Separation of Analytes

Separation of analytes is an imminent feature distinguishing procedures belonging to the field of speciation analytics from procedures for determination of total metal contents. The necessity of this step, or stage, is indicated by the very definition of speciation analysis. Different chromatographic methods are most commonly utilised here, gas chromatography, liquid chromatography, while the application of supercritical fluid chromatography in the field has also been described [59, 60].

Attempts are being made to apply capillary electrophoresis for speciation analytics of organometalic compounds [61]. Although up-to-date, its utilisation is rather marginal despite its high separation potential. There are several reasons for this situation; one can mention, for instance, a requirement to use a highly sensitive detector *(e.g., ICP-MS)* to ensure an adequate detection limit, due to a small volume of the sample that may be

introduced to the detector [2]. Additionally, in many cases there are no sufficiently sensitive and selective detectors for organometallic compounds.

A similar situation may be observed when one considers use of chromatography with supercritical fluid as a mobile phase. This technique combines the features of gas and liquid chromatography, yet, despite its advantages *(e.g.,* a possibility of determination of substances of significantly different boiling points, even non-volatile ones, in a single run), it has not found wide application in speciation analytics. The most probable reason is the high cost of the required instrument, much higher than is the case in competitive methods, like both gas and liquid chromatography which are, for many reasons and in many cases, better methods.

Methods of liquid chromatography (as well as capillary electrophoresis and supercritical fluid chromatography) are irreplaceable when separation of high molecular mass, non-volatile, or thermally labile substances is required. It does not mean that applications of liquid chromatography are restricted to these groups of compounds. Many cases are described [6] of utilisation of liquid chromatography for determination of derivatives usually analysed using gas chromatography. It is worth stating that sometimes liquid chromatography enables analysis of samples without previous derivatisation of analytes.

Unfortunately, the "Achilles heel" of liquid chromatography is the high value of the detection limit. This results from the fact that most frequently, detectors used in speciation analytics require introduction of the sample in a gas phase (as a vapour or aerosol) [2, 6]. This requires turning the eluate from the column into a form of spray, which leads to losses in analyte contents up to, according to some authors [2], 98% of their original amount.

The leading place among the separation methods employed in speciation analytics is, undoubtedly, occupied by gas chromatography. It is used for determination of compounds which are characterised by suitable volatility and thermal stability under separation conditions, or may be transformed in a suitable form. This group includes chiefly alkyl and aryl derivatives of such metals as mercury, lead, tin [18], arsenic [62], and selenium [63].

It seems the situation here is paradoxical, as the analytes present in real samples are basically compounds of ionic character, usually polar and of not particularly high thermal stability. Generally, these are no-good candidates for determination by gas chromatography. In the field of speciation analytics, using different reactions of derivatisation of the analytes solved the problem. These reactions yield non-polar compounds, sufficiently stable at elevated temperatures, quite suitable for separation by gas chromatographic techniques.

Utilisation of gas chromatography in speciation analytics brings several advantages. First of all, flexibility in combining this technique with different systems of final determination and/or analyte identification. As opposed to liquid chromatography, it is relatively easy to introduce a whole sample to the detector. Additional advantages favouring this technique are: moderate instrument prices, wide variety of available detectors, and one of the best separation powers.

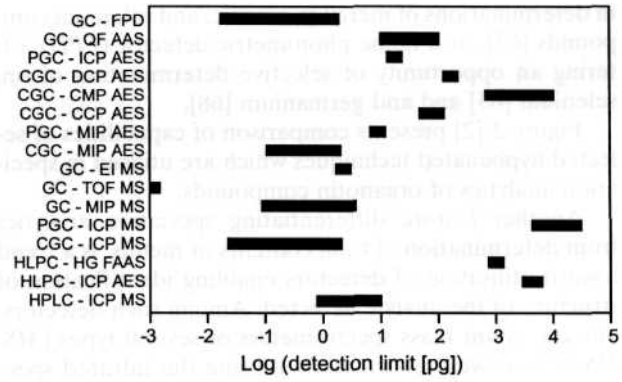

Fig. 2. Comparison of capabilities of selected hyphenated techniques utilised in speciation analytics of organotin compounds [2]-

AAS - atomic absorption spectrometry, **AES** - atomic emission spectrometry, **CGC** - capillary gas chromatography, **CMP** - capacitively coupled microwave plasma, **DCP** - direct current plasma, **EI** - electron beam ionization, **FAAS** - flame atomic absorption spectrometry, **FPD** - flame photometric detector, **GC** - gas chromatography, **HG** - hydride generation, **HPLC** - high-performance liquid chromatography, **ICP** - inductively coupled plasma, **MIP** - microwave induced plasma, **MS** - mass spectrometry, **PGC** - packed column gas chromatography, **QF** - quartz furnace, **TOF** - time-of-flight mass spectrometer.

Final Determination

The last stage of an analysis (if one skips the data handling) is identification and final determination of analytes. Different spectroscopic methods enjoy the widest application in analyses of metals. Also, occasionally detectors such as an electron capture detector *(ECD)* or a flame-photometric detector *(FPD)* are employed. The type of the detector employed is related to the technique of separation of the analytes, although some detectors are of broad or universal use. For instance, the aforementioned *ECD* and *FPD* are not used when the analytes are separated by means of liquid chromatography or capillary electrophoresis, while a fluorescence detector is not suitable for gas chromatography.

Spectroscopic methods such as mass spectrometry or atomic emission spectrometry with inductively coupled plasma (ICP-MS, ICP-AES) belong to the most universal, sensitive and selective methods of detection utilised both in speciation analytics of organometallic compounds and in determinations of total contents of metals. Due to the low detection limits offered by inductively coupled plasma, techniques of combining this detector with all major methods of analyte separation *(GC-ICP-MS, LC-ICP-MS, SFC-ICP-MS, CE-ICP-MS)* have been developed [64, 65]. In a case of a similar, gaining wider popularity, atomic emission detector with microwave induced plasma, *MIP-AED,* its coupling with gas chromatography only has been described to-date. Due to its lower (by several orders of magnitude) sensitivity, usage of the atomic absorption detector *(AAS)* is limited to *GC-AAS* [66] and *LC-AAS* combinations. For some metals, specific and highly sensitive detectors exist, like an atomic fluorescence detector *(AFS),* successfully used

in determinations of mercury, arsenic, and selenium compounds [67], or a flame photometric detector *(FPD),* offering an opportunity of selective determination of tin, selenium [63] and and germanium [68].

Figure 2 [2] presents comparison of capabilities of selected hyphenated techniques which are utilised in speciation analytics of organotin compounds.

Another feature differentiating speciation analytics from determination of total contents of metals, is a trend toward utilisation of detectors enabling identification of structure of the analyte detected. Among such detectors, one can count mass spectrometers of several types *(MS, MS-MS)* as well as detectors utilising the infrared spectrometry principles *(IR, FTIR, FFTIR).*

Conclusions

Literature studies give an impressive number of papers dealing with the speciation of tin, mercury and lead. Numerous methods of sample preparation, analyte separation and detection techniques have been developed. It seems that almost every speciation problem can be solved nowadays. However it must be stated that at present speciation analytics is not an easy task. Time and labor-consuming procedures requiring skilled personnel and lack of commercially available equipment puts the speciation analytics within the domain of academic laboratories. Development of new, simpler (integrated) sample preparation procedures and commercialization of instrumentation together with changes in legislation should change this situation in the near future.

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