Division Control No. ECD-134B

This manuscript has been presented at
the Dalhlem Workshop on
"The Importance of Chemical Speciation
in Environmental Processes"
Berlin, 1984.

ANALYTICAL ASPECTS OF ORGANOMETALLIC SPECIATION IN FRESHWATER SYSTEMS

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NWRI Contribution No. 86-188

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EXECUTIVE SUMMARY

Analytical Aspects of Organometallic Speciation in Freshwater Systems

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A review is given on the recent techniques and developments on species analysis of molecular and ionic organometals and organometalloids in the aquatic environment. Technique for quantitative extraction of ionic organometals, methods of derivatization, and digestion of biological samples are discussed.

The best methods are combination methods consisting of a separation technique and an element-specific detection system. Gas chromatography and atomic absorption spectrometry (GC-AAS), Liquid chromatography and atomic absorption spectrometry (HPLC-AAS) are the most commonly used combinations.

This is a background overview prepared for the Dahlem Workshop, Berlin on "The Importance of Chemical Speciation in Environmental Processes", of which the author was an invited lecturer. We have done a good deal of forefront research on speciation of organolead and organotin in the environment, as well as on the GC-AAS techniques. Many of the state-of-the-art extract and digestion techniques are originated and developed in NWRI.

ASPECT ANALYTIQUE DE L'IDENTIFICATION DES ORGANOMÉTALLIQUES DANS LES MILIEUX D'EAU DOUCE

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Résumé Les techniques et progrès récents dans la détermination des espèces moléculaires et ioniques des organométalliques dans l'environnement aquatique sont passés en revue. On discute des techniques d'extraction quantitative des organométalliques ioniques, des méthodes de préparation de dérivés et de la digestion des échantillons biologiques qui doit précéder l'identification des composés. A l'heure actuelle, la meilleure technique pour identifier les composés organométalliques est une séparation chromatographique couplée à un détecteur spécifique aux éléments.

INTRODUCTION

L'étude des composés organométalliques dans l'environnement est un sujet relativement nouveau en dépit du fait que ces composés sont utilisés depuis longtemps dans de nombreuses industries et en agriculture. Suite aux effets catastrophiques des intoxications par le mercure au Japon, des recherches intensives ont mené à la découverte que des micro-organismes présents dans les sédiments peuvent effectuer la méthylation biologique du mercure inorganique.

Au cours des dix dernières années, des rapports portant sur la méthylation dans l'environnement de nombreux autres métaux, comme le plomb, l'étain, l'arsenic et le sélénium, de même que sur la toxicité des composés méthylés, ont continué d'être publiés. On a retrouvé des organométalliques comme les dérivés alcoylés de l'étain et du plomb dans l'air, l'eau, les sédiments et les biotes. En 1978, l'American Chemical Society a organisé un colloque spécial sur les organométalliques et les organométalloïdes, sur leur présence et leur devenir dans l'environnement pour discuter ce nouveau domaine de la chimie. Toutes ces études effectuées au cours des dix dernières années ont donné naissance à de nouvelles techniques d'analyse qui permettent de doser les organométalliques aux concentrations auxquelles on les retrouve dans l'environnement. On doit aux spécialistes en chimie analytique la conception de nouveaux systèmes hybrides d'analyse qui nous renseignent sur le devenir des organométalliques, des composés qui, il n'y a pas si longtemps, n'étaient même pas censés exister dans les milieux aquatiques.

ANALYTICAL ASPECTS OF ORGANOMETALLIC SPECIATION IN FRESHWATER SYSTEMS

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Abstract The recent techniques and developments applicable to the determination of molecular and ionic organometallic compounds in the aquatic environment are reviewed. Techniques for quantitative extraction of ionic organometals, methods of derivatization, and digestion of biological samples prior to speciation are discussed. Chromatographic separation coupled to an element specific detector is currently the best technique for organometallic speciation.

INTRODUCTION

The study of organometallic compounds in the environment is a relatively new subject, in spite of the fact that organometals have long been used in many industries and in agriculture. After the catastrophic mercury poisonings in Japan, intensive research led to the discovery of biological methylation of inorganic mercury by microorganisms in sediment. During the last decade, reports about the environmental methylation of many other metals, such as Pb, Sn, As and Se, and the toxicity of the methylated compounds continued to appear in the literature. Organometals such as alkyltin and alkyllead compounds were found in air, water, sediments and biota. A special symposium on organometals and organometalloids, and their occurrence and fate in the environment was held under the auspices of the American Chemical Society in 1978, to discuss this new area of chemistry. All these studies during the last decade have given impetus to the development of a new type of analytical technique useful for the determination of organometals at environmental concentrations. Credit must be given to analytical chemists who design new hybrid analytical systems for the investigations of the fate of organometallics, which not long ago were considered not even to exist in aquatic systems.

RÉSUMÉ A L'INTENTION DE LA DIRECTION

Aspects analytiques de l'identification des composés organométalliques dans les milieux d'eau douce

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On passe en revue les techniques et les progrès récents dans l'analyse des espèces moléculaires et ioniques d'organométalliques et d'organométalloïdes dans le milieu aquatique. On présente une technique d'extraction quantitative des organométalliques ioniques, des méthodes de préparation de dérivés et de digestion des échantillons biologiques.

Les meilleures méthodes sont des méthodes combinées qui font appel à une technique de séparation et à un système de détection spécifique aux éléments. On utilise le plus souvent une combinaison de la chromatographie en phase gazeuse et de la spectrométrie par absorption atomique et la chromatographie en phase liquide et la spectrométrie par absorption atomique.

L'auteur a été invité à donner un exposé général sur cette question à l'atelier Dahlem, à Berlin, qui porte sur l'importance de l'identification des composés chimiques dans les processus

environnementaux. Nous avons fait beaucoup de travaux de recherche de premier plan sur l'identification des composés organiques à base de plomb et d'étain dans l'environnement ainsi que sur les techniques faisant appel à la chromatographie en phase gazeuse et à la spectrométrie par absorption atomique. Bon nombre des techniques d'extraction et de digestion utilisées couramment dans le domaine ont été mises au point au INRE.

TECHNIQUES FOR SPECIATION

Many techniques are available for the determination of a particular species of an organometal, but not too many techniques are suitable for the simultaneous determination of several species in the same sample at environmental concentrations. In the latter case, sensitivity as well as specificity is of prime importance. The method should directly identify and quantitate a species in the form in which it is present in the sample with as little chemical modification as possible. Thus, many methods that determine one species and obtain the concentrations of other species by difference, are not desirable, because of the possibility of accumulation of errors and the absence of affirmative identification. Of all the available methods, those using combinations of a separation technique and an element-specific detector are currently most suitable for the determination of organometals. The systems combine mainly chromatographs, such as gas chromatographs (GC), and liquid chromatographs (LC), with atomic spectrometers in the absorption (AAS), emission (AES) or fluorescence (AFS) modes as the detectors. The following are the most common and widely used systems.

Gas Chromatography-Atomic Absorption Spectrometry (GC-AAS)

The interfacing of a GC to an AAS detection system is simple requiring very little or no structural modification of the individual instrument. The instruments can be easily decoupled as required. The column exit of the GC at the detector base is connected with a transfer line to the atomization device of the AAS. Both flame and furnace modes have been successfully used.

GC-Flame AAS

To combine a GC with a flame AAS, the transfer line can either be connected to the nebulizer or directly fed into the flame at the burner head. The latter arrangement gives better sensitivity because the analyte is not diluted by the nebulizer gases. The sensitivity of flame AAS is generally poorer than that of the graphite furnace. Recently, Ebdon et al. (1982) increased the residence time of the atoms in the absorption path by feeding the GC effluent, mixed with

hydrogen, into a flame-heated ceramic tube. This system has excellent sensitivity of 17 pg for tetramethyllead. Fig. 1 illustrates the configuration of the atomization device.

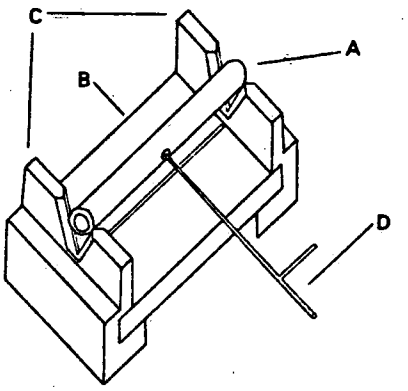

Fig. 1 - Flame heated ceramic tube atomizer. A- ceramic tube; B- air-acetylene burner head; C- stainless steel supporters; D- glass-lined T-piece (Ebdon, Ward and Leathard, 1982, with permission).

The height of the ceramic tube above the burner is critical. The device is simple, sensitive, and low in cost. However, some operational inconveniences may be encountered in its use. These include the optimization of many gas flow rates and the continuous operation of a dry flame for several hours a day. The effect of long operation times on the burner and the nebulizer coatings has yet to be assessed.

GC-Graphite Furnace AAS (GC-GFAAS)

Furnace AAS provides much better sensitivity than flame AAS. Several designs are available for GC-GFAAS systems. Segar (1974) used a tungsten tube to deliver the GC effluent into a heated GF tube at ca. 1700°C. In the analysis of mixed tetraalkyllead compounds in gasoline he achieved detection limits of 10 ng Pb. The sensitivity was improved by the use of a specially designed carbon rod atomizer

operated at a constant temperature of 2000°C. The detection limit for tetramethyllead under these conditions was 0.1 ng Pb.

Other designs used the inert gas purge tubes leading to the furnaces. The GC effluent was introduced into the furnace either through a T-fitting from both ends or through the central injection opening of the furnace tube. The sensitivity was much enhanced and a detection limit of 0.04 ng Pb was reported by De Jonghe et al. (1980) for tetraalkyllead. Commercial furnaces are not designed for continuous operation. The graphite furnace in a GC-GFAAS must be kept at the atomization temperature (1500-2000°C) during the course of chromatography. The average life of a graphite furnace tube is about 10-15 hrs. Thus, the operation of a GC-GFAAS system could become very expensive. Furthermore, graphite tubes deteriorate on prolonged heating over period of hours as indicated by a gradual loss of sensitivity.

Electrothermal Silica Tube Furnace

A simple, electrothermally heated, open-ended furance made of a silica tube (Fig. 2A) was used (Chau and Wong, 1977; Chau, Wong, and Bengert, 1982) for the determination of organolead and organotin compounds. The silica tube (7 mm, i.d.; 4cm long) is wrapped with 26 gauge resistance wire (5 ohms) and insulated with asbestos tape. The unit is housed in a block of preshaped fire brick that is mounted on top of the burner assembly. Hydrogen, air or mixtures of both can be introduced to the furnace through a side arm to enhance atomization as required. Twenty Volt a.c. applied to the furnace assisted by the hydrogen flame produce temperatures as high as 900°C. Such a temperature is sufficient for the atomization of organometals such as alkyltin, alkyllead and alkyl selenides. The furnace can be operated at its maximal temperature continuously for several hours per day for up to one month without deterioration. A layer of metal oxide may form in the interior walls of the furnace after long use causing loss of sensitivity. At that time, the furnace should be replaced.

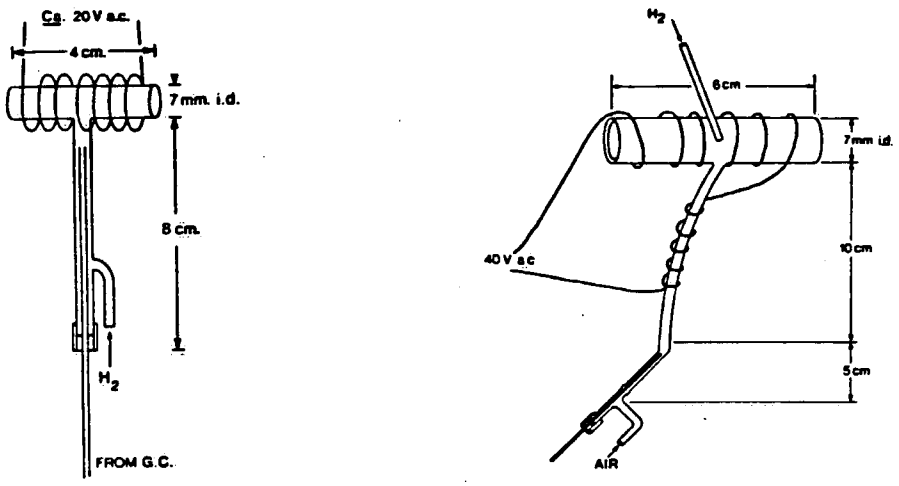

Fig. 2 - (A) Silica furnace (B) Silica furnace with precombustion section (Chau and Wong, 1977, with permission)

Solvents, particularly chlorinated hydrocarbons that are trapped with the sample may interfere with the determination of elements with absorption lines in the far UV region. Under certain conditions, the broad band absorbance may be so high as to be unmanageable by deuterium background correction. A precombustion section made from a silica tube with an air inlet can be installed as part of the furnace to burn off the contaminants (Fig. 2B).

The transfer line is a stainless steel tube, 1.6mm i.e., joining the furnace and the GC column exit. Several kinds of tubing meterials can be used, such as teflon-lined aluminum, glass-lined stainless steel, and teflon. The transfer line is wrapped with heating tapes to control its temperature and prevent condensation of the analytes. The GC-electrothermally heated silica furnace system is schematically shown in Fig. 3. The 4-way valve installed between the carrier gas inlet and the injection port makes it possible to use a cold trap for volatile samples, whereas samples contained in a solvent can still be injected through the injection port.

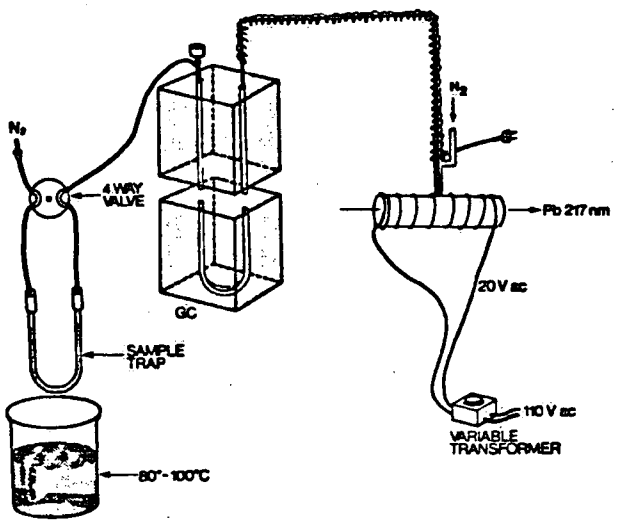

Fig. 3 - Schematic diagram showing the interface of GC-AAS (Chau and Wong, 1983, with permission)

Other Systems

The other commonly used spectrometric instruments for element-specific detection are atomic emission spectrometers. Braman et al. (1977) used a d.c. arc discharge spectrometer for the determination of methylarsines at the nanogram level. Higher sensitivity was achieved by the same research group for methyltin compounds using a hydrogen-rich flame in the emission excitation (Braman and Tompkin, 1979). Recently plasmas were used as excitation sources (Talmi and Bostick, 1975; Reamer, Zoller, and O'Haver, 1978) to detect picogram quantities of arsenic and lead. Similarly, microwave excited helium plasma was used to attain the same sensitivity in the determination of alkyllead compounds (Estes, Uden, and Barnes, 1982). Plasma is a more effective source of excitation for emission.

Gas Chrmoatography-Mass Spectrometry (GC-MS) systems do not receive wide application in the analysis of organometallic compounds probably because these instruments have high installation cost and require special skills for operation. The sensitivity of MS is not particularly superior to any of the spectrometric methods. Only a few reports on GC-MS determination of organometals appeared in the literature.

Liquid Chromatography-Atomic Absorption Spectrometry (LC-AAS)

Certain organometals are polar and may exist in solution as hydrated cations. These compounds may not have adequate volatility for GC separation. Liquid chromatography can separate these species without chemical modification. The latitude in choosing solvent systems and elution modes has made LC a very versatile technique for the separation of organic compounds. However, the application of LC to organometallics is still in its infant stage.

LC-AAS Systems

An LC-AAS system is more complicated than a GC-AAS system because a continuous liquid flow is not always compatible with a high temperature furnace. Different modes of AAS have been interfaced with LC. When flame AAS is used, the LC effluent can easily be routed to the nebulizer of the burner. The LC flow rate should be slightly higher than that of the nebulizer in order to achieve better sensitivity. The overall sensitivity of IC-flame AAS system is in the µg range which limits its extensive use in environmental analysis.

Much sensitivity can be gained with furnace ASS. In coupling LC with GFAAS, the most difficult part is the introduction of the effluent into the furnace. Several designs, that are still far from perfection, are available. One design uses an automatic sampler to take aliquots from the effluent stream. A sequencer-controlled multiport sampling valve was used by Cantillo and Segar (1975). A commercial AA sampler was employed by Brinckman et al. (1977) to sample the effluent from a micro flow-through well. Similarly, Stockton and Irgolic (1979) sampled the LC effluent with a sequencer-controlled slider injector. All these techniques give chromatograms in pulse form. The sum of the signals in a chromatographic peak quantifies the analyte. The precision of the measurement will depend on the number of signals in a peak, which is determined by the cycle time of the furnace. The commercial furnaces generally operate in three cycles: drying, ashing and atomizing. The minimal time to complete these cycles and cool the furnace is 40 seconds. Thus, if a band has a width of only 1-2 min, the chromato-

graphic peak is not well defined. The precision of the results is also influenced by the synchronization of the autosampler with the GFAAS cycle.

A second approach is the peak storage technique suggested by Vickrey et al. (1983). Fractions of the effluent containing the components and separated by plugs of an inert gas were stored in capillary tubes. The fractions were analyzed off-line by GFAAS. More aliquots can be analyzed in this manner to quantify a peak. This method has better precision and accuracy than the pulse, and on-line analysis method, but is quite cumbersome. A detection limit of 0.048 ng was obtained for tetraphenyllead with a 20 µl sample injection onto the LC column.

The third approach does not involve discrete sampling of the effluent, but isolation of the analytes from the effluent stream in volatile forms. This technique can be applied to organometals that readily form covalent hydrides, such as that of As, Ge, Sn, Pb, and Sb. A post-column hydride generator is installed on-line and the volatile hydrides are continuously fed to a heated silica furnace. A recent report by Burns et al. (1981) described the combination of a HPLC and an electrothermally heated silica furnace AAS via an automatic hydride generator. A mixture of methyltin compounds was analyzed with detection limits of 2-20 pg. An automatic system has also been developed by Ricci et al. (33) for the analysis of As(III), As(V), monomethylarsonic, dimethylarsinic and p-aminophenylarsonic acids using ion chromatographic separation and determination of the hydrides by AAS. Fig. 4 shows the interfacing of the two systems. Detection limits were less than 10 ng ml^{-1} for each species. Similarly, a conventional gravity-flow column chromatograph coupled to an automatic hydride system was used for the determination of methylarsenic acids and inorganic As (Chau and Wong, 1983). The post-column hydride formation has certain advantages over the batch hydride generation. The molecular rearrangement (Talmi and Bostick, 1975) during the hydride reaction can be avoided. In addition on-line automatic hydride generation gives more uniform and reproducible results than

the manual batch system. The on-line hydride generation is at present the best interface for LC and furnace AAS, but is applicable only to compounds reducible to volatile derivatives. Consumption of the whole sample during analysis provides high sensitivity.

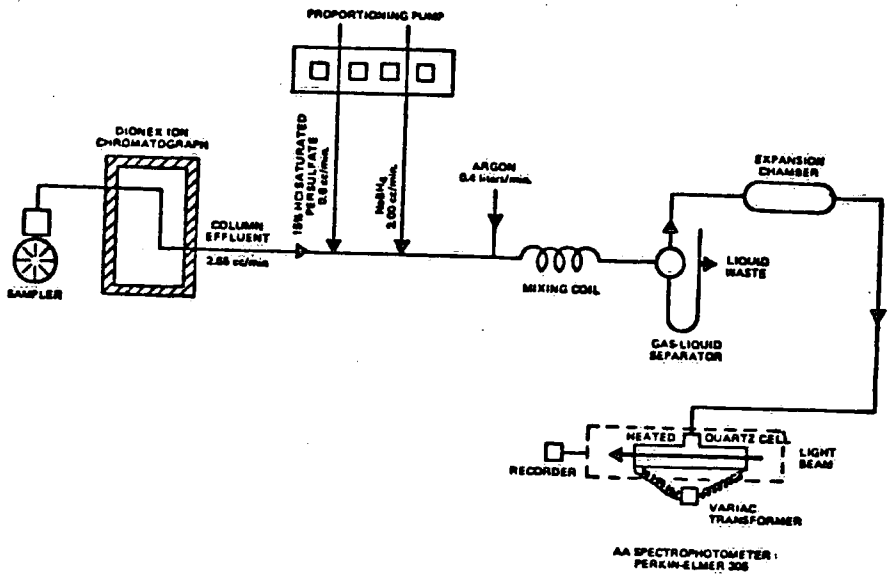

Fig. 4 - Dionex ion chromatograph coupled with automatic arsine generator and AAS detector (Reprinted with permission from Ricci, Colovos and Hester, 1981. Copyright (1981) American Chemical Society).

Other LC-Element Specific Systems

A d.c. argon plasma emission detector was used with a HPLC (Uden, Quimby, Barnes, and Elliott, 1978) for determination of several transition metal complexes. The use of inductively coupled plasma emission spectrometers (ICP) as element-specific detectors is described in the analytical background papers of this volume (Irgolic and Brinckman, 1985). An on-line, post column, and continuous hydride generation technique coupled to an ICP has been developed for the analysis of methyltin species (Krull and Panaro, 1984). A review on

the use of ion chromatography and liquid chromatography coupled to element specific detectors such as atomic emission and atomic fluorescent spectrometry for inorganic speciation studies has also been provided in this volume (Krull, 1985).

Electrochemical detectors based on oxidation and reduction of the analytes have been used for organic analysis. These detectors have good sensitivities but generally lack element-specificity and versatility in comparison to the spectrometric detectors. A cyclic voltammetric detector was used with HPLC (MacCrehan, Durst, and Bellama, 1977) for the determination of alkyl- and phenyl-derivatives of Hg, Sn, and Pb with submicrogram sensitivity. Using the differential pulse mode of the amperometric detector further improved the sensitivity and selectivity (MacCrehan and Durst, 1978). The method was applied to the determination of methylmercury in fish with a detection limit of 40 pg Hg. Reviews on the use of electrochemical detectors in liquid chromatography are available (Buchta and Papa, 1976; Pungor, Toth, Feher, Nagy, and Varadi, 1975). Although electrochemical detectors have not been used very frequently with LC, they are expected to find wider application in the future.

Electrochemical Methods

Electrochemical methods have been used for the determination of organometals in natural waters. These methods are sensitive, relatively specific, if the sample matrix is known, and require very little or no sample preparation. Most methods developed earlier were based on the determination of one of the organometals and obtained the concentrations of other compounds by difference. For example, Plazzogna and Pilloni (1967) determined the R_2Sn^{2+} and R_3Sn^{+} species in solution by titrating their total amounts potentiometrically with alkali and then determining the R_2Sn^{2+} in another aliquot by amperometric titration with standard 8-hydroxyquinoline solution. In mixtures of R_2Pb^{2+} and R_3Pb^{+} compounds, dialkyllead ion can be titrated amperometrically with ferrocyanide solution and trialkyllead ion with tetraphenylboron solution. Hodges and Noden (1979), using two different plating potentials in anodic stripping voltammetry, were

able to determine the concentrations of dialkyl- and triaklyllead in solution. These methods, however, differentiate only the dialkyl- and trialkyl-metals as a class without identifying the alkyl groups. At the same time, a similar stripping voltammetric method was developed by Columbini et al. (1981) for consecutive determinations of Me_4Pb, Et_4Pb, Me_3Pb^+, Et_3Pb^+, Me_2Pb^{2+}, Et_2Pb^{2+}, and Pb(II) in natural waters with detection limits in the nanomolar range. The species were separated by selective solvent extraction. This method is sensitive and relatively specific, but is tedious and complex, involving many steps of calculation by difference. Despite these disadvantages, this method represents the current state-of-the-art for speciation by electrochemical techniques.

ANALYSIS OF MOLECULAR AND IONIC ORGANOMETALS

Molecular Organometals

Volatile, molecular organometallic compounds such as tetraalkyllead, tetraalkyltin, methylarsines, and methylselenides, either generated in experimental systems or in the ambient atmosphere can be collected cryogenically at ca. -150°C in a trap containing non-polar chromatographic column materials (OV-1, OV-101, glass beads). For very volatile compounds such as methylarsines and dimethyl sulfide, the cold trap can serve as GC allowing fractional volatilization of the components into the detector in the order of their boiling points. A GC would give more accurate control of temperature and gas flow and could produce more accurate retention times.

For the determination of volatile organometals in natural waters, the purge and trap techniques with an inert gas and cryogenic trap are often used. Andreae and Barnard (1983) determined dimethyl sulfide in seawater with a flame photometric detector. Jackson et al. (1982) determined the extremely volatile methyltin hydrides in an estuary with a tin-selective photometric detector. An alternate method is to extract the molecular organometals such as tetraalkyllead from water or sediment with a non-polar solvent, the extract is then analyzed by GC-AAS.

Ionic Organometals

Ionic organometal species behave like aquated metal ions or salts in solution. Typical examples of such compounds are the dialkyllead, trialkyllead and a variety of alkyltin cations. These organometals are difficult to determine, because they are not easily extracted from aqueous media or biological tissues. In addition, the thermal instability of these compounds complicates the chromatographic separation. Both problems have to be resolved before reliable analyses can be performed. Previous methods were based on the salting-out extraction of Bolanowska (1967) for trialkyllead compounds followed by spectrometric determination with dithizone or gas chromatographic determination with an electron capture detector.

Several methods were published that used GC-microwave helium plasma, GC with flame ionization detector, and GFAAS after sequential extraction of samples. The results were not satisfactory. The main difficulty lies with the incomplete extraction of these compounds from aqueous medium. Recently, the method of quantitative extraction and determination of dialkyl- and trialkyllead compounds was improved (Chau, Wong, and Kramar, 1983; Forsyth and Marshall, 1983). This improved method made it possible for the first time to establish the presence of dialkyllead and trialkyllead in a variety of environmental materials (Chau, Wong, Bengert, and Dunn, 1984).

Extraction of Ionic Alkyllead Compounds

The extraction of dialkyl and trialkyllead compounds has been difficult because of the highly polar nature of these species. Triethyllead species can be extracted almost quantitatively into benzene in the presence of saturated sodium chloride (Bolanowska, 1967) but only 20 percent of trimethyllead were recovered under the same conditions. The addition of potassium chloride made the quantitative extraction of trimethyllead possible (Noden, 1980). In spite of these improvements, only 30-40 prcent of dialkyllead species and especially of dimethyllead could be extracted. Many attempts were made in enhancing the recovery of dialkyllead. Additions of inorganic lead salt, sodium benzoate, and other compounds were largely

ineffective (Birnie and Hodges, 1981). Recently, sodium diethyldithiocarbamate was found to extract quantitatively all dialkyl- and trialkyllead species from an aqueous medium into benzene (Chau, Wong, and Kramar, 1983). Tetraalkyllead and lead(II) species were also extracted. Similarly, dithizone was used for the quantitative extraction of the dialkyl- and trialkyllead from a variety of media including water, buffer solutions and eggs (Forsyth and Marshall, 1983).

Ionic butyltin species were extracted from water into benzene by tropolone solutions (Meinema, Burger-Wiersma, Versluis-de Haan, and Giver, 1978). The more polar methyltin species are not quantitatively recovered unless sodium chloride is added to the medium. Once the ionic alkyl metals are isolated from the matrix, they can be derivatized for final determination.

Methods of Derivatization

For GC-AAS analysis, the polar and high-boiling ionic organometals must be converted to more volatile yet stable derivatives. Two methods are currently used.

Conversion to Hydrides

Compounds readily converted to covalent hydrides can be isolated as volatile derivatives and then determined. Hydride techniques were used to analyze mixtures of methylarsenic acids (Andreae, 1977; Braman, Johnson, Foreback, Ammons and Bricker, 1977). In a similar manner, methyltin, dimethyltin and trimethyltin were converted to form the corresponding hydrides and Sn(IV) to stannane (Braman and Tompkin, 1979; Hodge, Seidal and Goldberg, 1979). The hydrides were collected in a trap cooled by liquid nitrogen and were then vaporized into the detector. The hydride derivatization can be extended to alkyl derivatives of metals such as Pb(IV), Ge(IV), and Sb(V). This method has advantages and disadvantages. Isolation of the analytes from the sample matrix in volatile forms is a great advantage. All of the analyte is collected and the sensitivity is, therefore, improved. A disadvantage is the possibility of molecular rearrangement during the

reduction. Such rearrangements were observed during the reduction of organoarsenic compounds and methyltin compounds (Y.K. Chau, personal communication). The cause of molecular rearrangement is not fully known. Talmi (1975) suggested the use of sodium borohydride tablets instead of borohydride solution to minimize rearrangements. Another disadvantage observed in the author's laboratory is a mysterious contamination, which occurs now and then, even when the most stringent precautions are exercised. The hydride might be such a reactive agent that it acts on anything it contacts. Laboratories not equipped with clean-room facilities may find it difficult to successfully use the hydride generation technique.

Alkylation

Alkylated metals of group IV, $R_nM^{(4-n)+}$, readily acept further alkyl groups from a Grignard reagent to form stable tetraalkyl derivatives, $R_nMR'_{(4-n)}$, that are more volatile than their parent compounds. Methylation was used (Meinema, Burger-Wiersma, Versluis-de Haan, and Giver, 1978) to determine butyltin compounds. Pentyl Grignard was employed to derivatize butyltin species (Maguire and Huneault, 1981) and butyl Grignard for the determination of methyltin speciation (Chau, Wong, and Bengert, 1982), The butylation reactions (Eq. 1) were also used to prepare volatile derivatives of dialkyl- and trialkyllead compounds.

$$R_nPb^{(4-n)+} + (4-n)\ BuMgCl \rightarrow R_nPbBu_{(4-n)} + (4-n)Mg^{++} + (4-n)Cl^- \qquad (1)$$

The butyl derivatives, $R_nPbBu_{(4-n)}$ (R = Me or Et) have relatively low boiling points and high thermal stability. The GC-AAS chromatograms of the butyl derivatized dialkyl-, trialkyllead and Pb(II) and tetraalkyllead species are shown in Fig. 5.

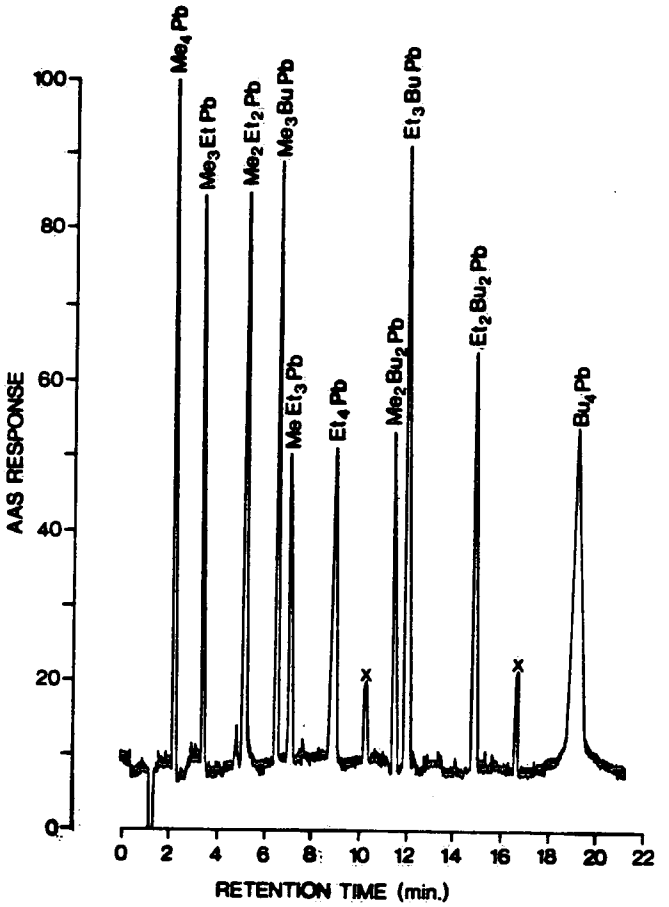

Fig. 5 - GC-AAS chromatograms of five R Pb (10 ng each); four butyl derivatives of R PB^{++} and R Pb^{+} (8 ng each) and Pb(II) (15 ng) expressed as Pb. x - unidentified Pb compound (Chau, Wong, and Kramar, 1983, with permission).

Phenylmagnessium bromide was used for the determinations of alkyllead compounds extracted by dithizone (Forsyth and Marshall, 1982). Alkylation is easy to control and gives uniform and consistent results. The Grignard reagents can also be contaminated, but are generally purer than the hydride reagent. This technique does not use all of the analyte for the analysis. The derivatization is carried out in a non-aqueous medium of which only a small aliquot is injected to the analytical system. However, the extraction used to isolate the analytes for alkylation, generally concentrates the analytes.

SAMPLING, SAMPLE PRESERVATION AND SAMPLE PREPARATION

Sampling of Surface Microlayers

Surface microlayers are important strata at which water and air meet. This natural interface consists of a thin hydrophobic layer that has been known to concentrate metals and organics through various processes. Hydrophobic organometals, such as tetraalkyllead and tetraalkyltin, and the naturally occurring metal hydrides, are believed to be concentrated in this layer. We observed high concentrations of mixed alkyllead species in the microlayer that were not found in the adjoining water.

Special samplers are available to collect surface microlayers. The most convenient and simple collector is a glass plate, 40x40 cm, that is manually dipped into the water. The adhering film is scraped into a container with a neoprene blade. Though cumbersome, this sampler is simple and economical. A more elaborate sampler (designed by the National Water Research Institute, Burlington, Ontario, Canada) consists of a motor-driven rotating ceramic drum of ca. 1 m length, 40 cm diameter mounted in the front of a small boat. While the boat is trolling at about 1-2 knots, the drum is rotating at ca. 10 rpm. The depth of immersion of the drum in the water is kept at 2-3 cm with adjustment cranks. The surface film adhering to the drum is scraped by a blade and collected in a bottle. The drum is far more efficient than the glass plate. A 4-litre sample can be collected in ca. 10 min.

A regular trace metal sampler can be used for taking water samples. Contamination in sampling for organometals is not as serious as for heavy metals because organometals are not universal contaminants. However, precautions must be taken to obtain representative samples. For example, plastic ware should not be used for organotin sampling because of the alkyltin stabilizers they contain. Boat paints normally contain butyltin antifouling agents. Tetraalkyllead in gasoline used in boat motors can be a source of alkyllead contamination.

Sample Preservation

Some organometals are unstable in the presence of light. Alkyllead compounds were observed to degrade slowly in water to inorganic lead. However, lake water samples enriched with dimethyllead and trimethyllead chlorides are stable for at least one month if refrigerated and stored in glass bottles in the dark (Chau, Wong, and Kramar, 1983). Alkyltin compounds are stable in water. Because extraction of methyltin compounds required saturated sodium chloride, Chau et al. (1982) recommended to add the sodium chloride to samples at the time of sampling to reduce the risk of adsorption of inorganic tin and alkyltin onto the container walls.

Acidification of water samples with hydrochloric acid has been proposed to reduce adsorption loss. Maguire (personal communication) also found it desirable to acidify water samples to pH 1 to preserve butyltin and inorganic tin species during short time storage. In general, storage in glass containers and in the dark are essential. If volatile species are to be determined, the samples should be immediately extracted. It is convenient to add a layer of hexane to seal off the surface for subsequent processing in the laboratory.

Digestion of Biological Samples

Digestion of samples without altering the chemical nature of the analytes is indeed a most challenging analytical problem. For some samples that contain the organometals in a physical mixture, straight extraction may be sufficient to separate the analytes. In biological samples, the organometals could be part of the tissue. Under these circumstances extraction would not recover them efficiently. This is particularly the case for ionic organometals such as dialkyl- and trialkyl-lead compounds. The addition of various salts during extraction can recover the trialkyllead species but cannot adequately recover dialkyllead compounds. Recently, two digestion procedures were published. Chau et al. (1984) digested fish, algae, and macrophytes in tetramethylammonium hydroxide, and Forsyth and Marshall (1983) used a mixture of lipases and proteases to hydrolyze egg homogenates. Both methods were effective in releasing the alkyllead compounds chemically unchanged from biological tissues.

Extraction of Sediments

Organometals in sediments are derived from anthropogenic sources, or formed by the biological and chemical processes of alkylation or dealkylation. For the determination of organometals in sediments, total digestion is not necessary. An effective extraction procedure can often recover the organometals.

Tetraalkyllead species can be recovered by extraction with hexane. The ionic alkyllead species can be extracted with sodium diethyldithiocarbamate after addition of sodium chloride, sodium iodide and sodium benzoate (Chau, Wong, Bengert, and Dunn, 1984). Similarly, methyltin compounds can be extracted from sediments with a solution of tropolone in benzene in the presence of sodium chloride (Y.K. Chau, personal communication). For complete extraction of butyltin compounds, the sediment has to be refluxed for two hours with a benzene solution of tropolone (R.J. Maguire, personal communication).

DIFFICULTIES AND RESEARCH NEEDS

Difficulties encountered in speciation analyses of environmental samples for organometals arise mainly from sample preparation which includes incomplete recovery of individual analytes and interferences caused by sample matrix. Polarity of the organometallic molecules varies according to the nature of the organic component parts and the degree of the organic substitution which control the efficiency of recovery. It is not unusual to experience variations of extraction efficiency among a series of organometals of the same homolog. Matrix interferences can be serious with biological samples such as eggs and fish tissues during the extraction and final determination.

Data interpretation is another difficult area in dealing with transient and labile species whose half lives may not be in the same scale as that of the analytical processes. For example, the measurement of volatile tetraalkyllead species in natural water may not have any significance if their degradation products were not simultaneously measured.

Further research needs in the chromatography-element specific detection systems include several aspects. Liquid chromatography and furnace atomic absorption spectrometry are not fully compatible and further improvements are desirable. Electrochemical detection systems for chromatography have not yet been fully developed. Atomic fluorescence detectors have not been widely applied in spite of their multielement capability and sensitivity. Complexation with a flurogenic ligand after column separation can be a sensitive technique for organometals and its selectivity should be further investigated. The feasibility of interfacing a micropore HPLC directly into a micro emission flame or a graphite furnace should also be explored.

In the sample treatment aspect, recovery of organometals from biological matrices without destruction of their chemical forms has been a challenging problem for analytical chemists. Many organometallic compounds are involved in bio-geochemical reactions under environmental conditions, their interactions with other organometals and their environmental pathways and metabolism require further investigations and assessment.

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