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OCCURRENCE AND SPECIATION OF ORGANOMETALLIC COMPOUNDS IN FRESHWATER SYSTEMS

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EXECUTIVE SUMMARY

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This is a review paper on the environmental occurrence of organometallic compounds and the recent developments in their speciation in water, sediment and biological samples. The sources of organometallic compounds are mainly from anthropogenic inputs and from biotic and abiotic methylation processes.

The most sophisticated analytical methods for organometallic speciation are combination systems consisting of a separation technique coupled with an element-specific detector. The best systems to date are gas chromatography (GC) or liquid chromatography (LC) coupled with an atomic spectrometric detector in the absorption or emission mode with sensitivity in the sub-nanogram level.

Techniques for quantitative extraction of ionic organometals, methods of derivatization and digestion of biological samples without destruction of the original chemical form are discussed.

With these techniques, the occurrence of molecular and ionic alkyllead compounds (R= Me,Et) has been found for the first time in water, sediment and fish in areas of lead pollution.

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ABSTRACT

Organometals and organometalloids have been found in environmental samples as a result of their extensive usage and biotic and abiotic methylation processes. Alkyllead and and organotin compounds are the most widely used organometals.

In connection with studies of organometallic speciation, highly sensitive, and specific analytical techniques have been developed using combination analytical systems. At present, combination systems consisting of a separation technique coupled with an element-specific, atomic spectrometric detector are most satisfactory. A variety of atomic spectrometric detectors have been used in combination with gas chromatography and liquid chromatography.

INTRODUCTION

Metals are involved in several cycles in the environment, notably physical, chemical, biological and geological, most of which involve changes in their chemical forms. One of the most fascinating reactions is the transformation of metals and metalloids through biotic processes because it involves the formation of metal-carbon bonds in aquatic medium. Such processes have immense impact on the environment as illustrated by the methylation of mercury to methylmercury compounds. Environmental methylation of other metals such as As, Se, Pb, and Sn has been subsequently reported in the literature. The important aspects of organometal formation are alterations of toxicity and change of transport pattern of an element in the system. The change of toxicity to aquatic biota with the degree of carbon substitution and length of the alkyl groups has been demonstrated in the structure-toxicity relationship for alkyltin compounds on algae (Wong et al., 1982). The involvement of biological pathways in geochemical cycles of many elements has only recently been emphasized.

Organometals are extremely versatile in their uses and applications because their chemical and biological properties can be modified by varying the nature of the organic groups. Thus, organometals can be custom-synthesized for a specific purpose. For example, trialkyltin compounds have been synthesized for specific

biocidal action towards one class of organism without harmful affects to others. The synthesis of organometals beginning in the late twenties represents a major achievement of chemical technology. They are extensively used in medicine as chemotherapeutic agents, in biological and agricultural applications as biocides, in industries as catalysts and gasoline antiknock agents. Of all the industrial organometallic compounds organotin and organolead are the most widely used. Trialkyltin compounds are used as agricultural pesticides, in antifouling paints for ships and docks, as lumber preservatives and as slimicides in industrial cooling waters. Tetraalkyllead compounds are used in gasoline as antiknock additives. Along with the organometals research, investigators are confronted with a new challenge, speciation analytical techniques, to identify the chemical forms and to determine concentrations of compounds in environmental pathways. Many new hybrid techniques have been developed in recent years and such research will no doubt continue to flourish.

It is appropriate here to clarify the definition of the term "speciation" used in this paper. There are several meanings of the term "speciation" that environmental scientists used. Speciation is often used to describe a chemical or biological process which changes the form of an element. For example, chemical speciation, biological speciation and photolytic speciation have been used to describe the transformation of an element by these processes (Thayer, 1984). In its most common usage, speciation means the act of chemical analysis to differentiate the different forms of an element, or it is used as a

collective noun for chemical forms. Thus ambiguous meaning sometimes results. In the recent Dahlem Workshop on "The importance of chemical speciation in environmental processes" held in Berlin, 1984, suggestions were made to use "speciation" only to mean "the determination of compounds" when the intent is to emphasize that trace element compounds and not "total trace elements" are the subject of analytical investigations. Thus examples of correct use of the words "speciation" and "speciate" are "the speciation of chromium"; "efforts to speciate trace elements in aerosols were unsuccessful". Thus "speciation techniques" means chemical techniques which will identify the different chemical forms of the element studied.

SOURCES OF ORGANOMETALS IN THE ENVIRONMENT

Anthropogenic Sources

The presence of butyltin (Hodge et al., 1979) and methyltin (Braman and Tompkins, 1979; Jackson et al., 1982) species have been reported in natural waters and in rains. Similarly, butyltin and methyltin derivatives were found in rivers and lakes, surface microlayer (Maguire et al., 1982), in sediments and fish (Maguire, 1984; Chau et al., 1984a) in Ontario. The occurrence of various butyltin species particularly in harbours and marinas is attributed to its wide usage and to the successive biotic or abiotic cleavage of the

tin-carbon bonds of tributyltin to produce dibutyltin, monobutyltin and ultimately inorganic tin in the aquatic system.

The degradation can be catalyzed by photolysis. Triphenyltin acetate underwent cleavage of the Sn-C bond in natural water when irradiated by sunlight, forming diphenyl- and monophenyltin as products (Soderquist and Crosby, 1980). Bis-tributyltin oxide (TBTO) also degraded in sunlight to give dealkylation products, dibutyltin monobutyltin and Sn(IV) (Maguire et al., 1983). Freshwater algae have been found to degrade tributyltin (Maguire et al., 1984). The occurrence of the various alkyltin species in harbour and industrial localities is attributed to these degradation reactions.

Methyltin compounds are not as widely used compared to the butyl derivatives and their environmental occurrence has been attributed to biotic and abiotic methylation of both organotin and inorganic tin compounds (Chau et al., 1981; Hallas et al., 1982).

Tetraalkyllead compounds in aquatic systems also degrade slowly by photolysis to trialkyllead, dialkyllead and finally to inorganic lead(II) with varying dissociation constants, viz

$$R_4Pb \xrightarrow{k_1} R_3Pb^+ \xrightarrow{k_2} R_2Pb^{2+} \xrightarrow{k_3} Pb(II)$$

Although the rate constants have not been determined, it is known from the half life of the degradation products that the first degradation

k_1 is much faster than the second which is faster than the third, and that the trialkyllead (Me and Et) compounds are remarkably stable in aqueous solution in the absence of light. Both trimethyl- and triethyllead (1 ppm solution) are stable in the dark for a period of up to 78 days (Jarvie et al., 1981; Chau et al., unpublished data). Irradiation with UV light or sunlight speeds up the degradation. Trimethyllead and triethyllead have half-lives of only about 28 hrs and 16 hrs under direct sunlight. The photodegradation of tetraalkyllead compounds involves perhaps complicated reactions; it has been observed that irradiation of tetraethyllead in seawater caused cleavage of the Pb-C bonds, giving rise to lead(II) salts, hydrocarbons and various alkyllead compounds including n-butyltriethyllead (Charlou et al., 1980). Thus, the photolytic reactions of tetraalkyllead may not simply involve the cleavage of Pb-C bonds, but also the formation of other higher alkyl groups. All these reactions will contribute to the various alkyllead compounds in the aquatic environment.

The ionic dialkyllead and trialkyllead compounds are stable if they are not directly exposed to light. They are degradation products of tetraalkyllead as discussed above. In the case of the methyl series, they could be the intermediates of sequential methylation. Not much attention has been given to these alkyllead species in the past mainly because of the lack of suitable methodology for their determination at environmental concentrations. Recently, all these

molecular and ionic alkyllead compounds have been found in fish and sediment near alkyllead production plants (Chau et al., 1979, 1984b, 1985).

Biotic and Abiotic Methylation

The first case of environmental biomethylation was probably the "arsenic room" phenomenon when Gosio established that the garlic smelling gas liberated from green-coloured wallpaper (containing arsenic dyes) by the growth of moulds was an organoarsenic compound later identified by Challenger (1935) as trimethylarsine. It was found that the methyl groups were supplied by the moulds, hence the term "biomethylation" was introduced. Subsequent investigations discovered that many other moulds and bacteria also generated methylarsenic compounds from inorganic arsenic (Cox and Alexander, 1973a). Methanogenic bacteria under anaerobic conditions can methylate inorganic arsenic to volatile dimethylarsine (McBride and Wolfe, 1971). Lake sediments as well as three pure bacteria cultures incubated with inorganic arsenic compounds produced monomethyl- and dimethyl arsenic acids (Wong et al., 1977). Both marine and freshwater green algae are capable of methylating arsenic (Andreae, 1979; Baker et al., 1983). High levels of phosphate have been formed to inhibit the methylation of arsenite by the yeast Candida humicola (Cox and Alexander, 1973b). A study has indicated that both As(III) and As(V) ingested by man were converted to mono- and dimethyl

arsenic acids and excreted in urine (Crecelius, 1977). Because the methylated arsenic compounds are considerably less toxic than the inorganic arsenic compounds, arsenite and arsenate, and are more readily excreted and show less tendency to bind to protein, arsenic methylation has been suggested as a detoxification mechanism for living organisms.

Although biomethylation has been known for some 50 years, research interest in this area was only intensified after the Minamata Bay tragedy in the fifties. Environmental biomethylation leading to the formation of highly neurotoxic compounds, methylmercury (CH_3Hg^+) and dimethylmercury ($(CH_3)_2Hg$), from inorganic mercury was identified as the cause of the intoxification when the fish were consumed by inhabitants in that area.

Biomethylation of mercury has been proposed as a detoxification mechanism for unicellular microorganisms. Monomethylmercuric compounds are soluble both in water and in lipids, facilitating their excretion. Dimethylmercury is highly volatile, thus readily diffusing away to the surrounding atmosphere. For multicellular organisms or higher animals, however, methylation of mercury is not considered a detoxification mechanism.

Biomethylation of lead in sediment since it was first reported (Wong et al., 1975) has generated much controversy over the past years. Several studies have found that lead(II) and trimethyllead(IV) acetate was converted to tetramethyllead in sediment (Schmidt and Huber, 1976; Dumas et al., 1977; Thompson and Crerar, 1980). Other

reports claimed that the methylation processes were abiotic, and the conversion of trimethyllead to tetramethyllead was by chemical disproportionation (Jarvie et al., 1975; Craig, 1980; Reisinger et al., 1981). Under sterilized conditions, methylation of trimethyllead to tetramethyllead involved formation of a sulfide complex, $[(CH_3)_3Pb]_2S$, which subsequently disproportionated to tetramethyllead. The sulfide is a biogenic compound and has a biological origin. Under these conditions, it becomes difficult to differentiate sharply between biotic and abiotic processes. Therefore, lead methylation may occur through an abiotic route mediated by biological processes.

Biomethylation of other metals have been studied (Ridley et al., 1977). Trimethyltin hydroxide was converted biologically to tetramethyltin in sediment (Guard et al., 1981). Inorganic Sn(II) and Sn(IV) were methylated to different methyltin species in sediment (Chau et al., 1981; Hallas, 1982; Jackson et al., 1982). Methyltin species have been found in natural waters (Braman and Tompkins, 1979; Hodge et al., 1979; Maguire et al., 1982; Chau et al., 1984a); and in algae (Ishii, 1982). Microbial methylation of selenium was observed when Se(IV) and Se(VI) were incubated with sediment (Chau et al., 1976c; Reamer and Zoller, 1980). The products were volatile dimethylselenide, dimethyldiselenide and dimethylselenone. These compounds have subsequently been found in environmental samples (Jiang et al., 1983). All these processes have been identified as biological methylation although abiotic processes may occur simultaneously.

Occurrence of other methylated metals such as methylgermanium species (Lewis et al., 1985), methylstibonic and methylstibinic acids (Andreae et al., 1981) in natural waters have been reported; however, proof is not yet available to confirm their environmental methylation. Methyl derivatives of sulfur are also present in natural waters (Lovelock et al., 1972; Andreae and Barnard, 1984). Their formation mechanisms have yet to be investigated.

At least two methyl donor compounds have been found in the biological system, namely, S-adenosylmethionine (CH_3^+ donor) and methylcobalamin (CH_3^- donor), which play important roles in the biomethylation of metalloids (As, Se) and metals (Hg), respectively. Other methylating agents which are present in biological systems are methyliodide, methylmethionine, betaine and trimethyl sulfoxo iodide. Table 1 lists some methyl donors of biological significance.

TABLE 1.

Methyl Donor	Methyl Group
S-adenosylmethionine	CH_3^+
Methyl cobalamin	CH_3^-
Methyl iodide	CH_3^+
Trimethyl sulfoxo iodide	CH_3^+
Betaine	CH_3^+
Methylmethionine	CH_3^+

Environmental processes often consist of a complex interplay of biotic and abiotic mechanisms, so that it becomes difficult to classify whether a process is purely chemical or biological in nature.

Photochemical reactions may be involved in the formation of metal-carbon bonds. Irradiation of mercuric sulfide solution in the presence of acetate ions resulted in the formation of methylmercury (Akagi and Takabatake, 1973). Chemical methylation of lead(II) and tin(II) can occur by oxidative addition mechanisms of methyliodide, a biogenic compound in natural water (Ahmad et al., 1981; Jarvie and Whitmore, 1981; Craig and Rapsomanikis, 1985; Rapsomanikis and Weber, 1985). Transmethylation reactions are another possible mechanism in the environment for the formation of organometals. Under laboratory conditions, transfer of methyl groups from methyltin to mercuric ion to form methylmercury (Jewett et al., 1982), from methyllead to tin(II) to form methyltin species (Chau et al., unpublished data), have been observed. Thus, organometals can be formed through abiotic pathways which are highly probable in the environment.

DETERMINATION OF ORGANOMETALS

While many techniques are available for the determination of organometals, there are only few techniques that can differentiate the chemical speciation of the compound. Certain methods which were considered specific have to depend on a series of chemical separations

before the analysis is finally determined, usually after destruction of the compound. Thus, these methods are indirect and the specificity will depend on how specific the separation is. Of all the methods available, only those with adequate specificity and sensitivity for environmental samples are included in this discussion. For this reason, many spectrophotometric methods based on colour development of the metal element, or of the organometallic compound with a reagent, or the determination of the metal element by atomic absorption techniques are not included in the discussion.

The best methods currently used for speciation analysis of organometals and organometalloids are combination methods consisting of a separation technique with gas or liquid chromatography coupled to a specific detection system such as atomic spectrometry. Thus, these systems are highly sensitive and specific. The atomic spectrometric detectors used include atomic absorption, atomic emission, and atomic fluorescence spectrometry. The excitation techniques include flame, furnace for atomic absorption, and various forms of plasma excitation for atomic emission. The following are the most commonly used element-specific systems for the determination of organometallic compounds in the freshwater and estuarine environments.

Gas Chromatography-Atomic Absorption Spectrometry System (GC-AAS)

The most common and widely used combination is the GC-AAS system (Chau and Wong, 1976a). The interfacing of a GC to an AAS is simple

and straightforward without any structural alteration of both instruments. The interface can be readily achieved by connecting the GC column outlet and the atomization device with a stainless steel transfer tube (diameter 2 mm). The transfer tube is wrapped with heating tape so that the temperature can be adjusted to avoid condensation during operation. Both flame and furnace atomizers have been used in the determination of alkyllead compounds. When flame atomization is used, the GC effluent can simply be fed into the nebulizer through the regular liquid sampling port (Kolb et al., 1966; Harrison et al., 1974; Chau et al., 1976b). If the nebulizer has a plastic surface (Penton in Perkin-Elmer nebulizer), it is advisable to install a glass lining inside the nebulizer chamber to avoid contamination of the nebulizer by the organometallic analytes (Chau et al., 1976b). Flame atomization AAS is about three orders of magnitude less sensitive than the furnace mode and is therefore not widely used for environmental analysis.

Furnace AAS has sensitivity at the nanogram and lower level for most metals and is therefore far superior for detecting organometals. In serving as a GC detector, the AA furnace has to be continuously heated to the required temperature of about 900°C for most of the organometals. The commercial graphite furnaces are operated on drying, ashing and atomizing cycles and are not suitable for use without modification. The most suitable furnace is an electrothermally heated, open-ended quartz furnace (ca. 4 cm long, 7 mm i.d.) used

in organolead detection (Chau et al., 1976a). The introduction of hydrogen to the furnace is important in enhancing the atomization of certain organometals such as alkyllead and alkyltin compounds. The enhancement has been explained by the formation of metal hydrides inside the furnace (Forsyth and Marshall, 1985). Another design of silica furnace with a precombusion tube to burn off any hydrocarbons or solvents before the sample enters the main furnace has been used (Chau and Wong, 1977). This type of furnace is particularly useful with elements whose absorption lines are in the ultra-violet region.

Commercially available graphite furnaces have been made use of by several workers using the inert gas purge passageway of the graphite furnace for introduction of the GC effluent (Segar, 1974; Robinson et al., 1977; Parris et al., 1977). Using such a device, Radziuk et al (1979) and DeJonghe et al. (1980) determined tetraalkyllead compounds with absolute detection limits of about 0.04 ng. The graphite furnace can be operated at a higher temperature (2000°C) than the silica furnace (900-950°C), however, the sensitivity gain is only by a factor of 2. One of the major disadvantages of graphite furnace operation is the necessity to maintain the furnace temperature at 2000°C during the course of chromatography. The life time of a graphite tube under these conditions is only about 10-15 hrs (Radziuk et al., 1979). Thus the operation can be expensive in comparison with the silica furnace which lasts over a period of one month on a daily operation basis. The highest sensitivity a furnace ever achieved is

the flame-heated ceramic tube used by Ebdon et al. (1982) which detects 17 pg of Pb in the chromatographic effluent mixed with hydrogen. This is indeed the most simple and low-cost furnace reported to date.

Other forms of atomic spectrometry include emission and fluorescence. A d.c. arc discharge emission spectrometer was used for methylarsenic compounds at the nanogram level (Braman et al., 1977). Enhancement of sensitivity was achieved by using a hydrogen-rich emission spectrometer in the determination of methyltin compounds (Braman and Tompkins, 1979). The sensitivity of emission spectrometric detection depends very much on the excitation source. Several forms of plasma excitation such as microwave plasma emission (Talmi and Bostick, 1975; Reamer et al., 1978; Estes et al., 1982) have been used to achieve higher sensitivity. Although emission spectrometry has the capability of multi-element detection, not much work has been developed in this aspect.

Table 2 summarizes some combination systems using gas chromatograph and atomic spectrometric detectors.

Derivatization Techniques

Combination systems using GC as separation technique are limited to organometals of relatively low boiling points. For ionic and hydrophilic organometals such as dialkyl- and trialkyllead,

monoalkyl-, dialkyl-, and trialkyltin (R = Me,Et), which have relatively high boiling points, they must be rendered volatile by derivatization. The derivatization used must be one that does not change the original structure of the metal-carbon bonds such that the speciation identity remains unaltered. Hydride conversion and alkylation to convert the ionic organometals to their corresponding hydrides, and tetraalkylated forms are the most commonly applied techniques. The reactions are as follows:

(1) $R_nSn^{(4-n)+}$ + Excess BH_4^- ---→ $R_nSnH_{(4-n)}$

(2) $R_nPb^{(4-n)+}$ + (4-n) RMgCl -----→ $R_nPbR'_{(4-n)}$ + (4-n)$MgCl^+$

The hydride derivatization technique is applicable to a number of metals and ionic alkyl metals, e.g. Ge, As, Se, Sn, Sb, Te, Pb, Bi (Robbins and Caruso, 1979) and the hydride formed generally have enhanced sensitivity during the atomization process because of the readily ruptured bonds of the metal hydrides. Hydride derivatization has been used to determine organoarsenic compounds (Andreae and Klumpp, 1979; Braman et al., 1977) and methyltin compounds (Braman and Tompkins, 1979).

TABLE 2. Gas Chromatograph-Atomic Spectrometer Systems

System	Compounds	D.L. (ng)	Reference
GC-AAS(flame)	R_4Pb (R=Me,Et)	0.2	Harrison et al., 1974
GC-AAS(flame)	R_4Pb (R=Me,Et)	100	Chau et al., 1976b
GC-AAS(flame)	R_4Pb (R=Me,Et)	1.5	Radziuk et al., 1979
GC-QFAAS	R_4Pb (R=Me,Et)	0.1	Chau et al., 1976a
GC-GFAAS	R_4Pb (R=Me,Et)	0.1	Robinson et al., 1977
GC-GFAAS	Me_3AsH, Me_4Sn, Me_2Se,	5,7,12	Parris et al., 1977
GC-GFAAS	$Me_nGe^{(4-n)+}$	0.075-0.150	Hambrick III et al., 1984
GC-GFAAS	R_4Pb (R=Me,Et)	0.04	DeJonghe et al., 1980
GC-QFAAS	$R_nSn^{(4-n)+}$	0.1	Chau et al., 1982
GC-QFAAS	Me_2Se, Me_2Se_2	0.1	Chau et al., 1975
GC-AFS	R_4PB (R=Me,Et)	0.1	Radziuk et al., 1973
GC-MES	MMA,DMA	0.02	Talmi and Bostick, 1975
GC-MES	R_4Pb (R=Me,Et)	0.006	Reamer et al., 1978
GC-MES	R_3Pb^+ (R=Me,Et)	0.56-3.5	Estes et al., 1982
GC-QFAAS	R_3Pb^+, R_2Pb^{2+}	0.1	Chau et al., 1984a
GC-MES	$MeHg^+$,$EtHg^+$,Me_2Hg	0.02×10^{-3} g/s	Chiba et al., 1983

QFAAS - Quartz furnace AAS
GFAAS - Graphite furnace AAS
MES - Microwave emission spectrometry
D.L. - Detection limit in ng of element

In batch hydride generation prior to the GC separation, molecular rearrangement of the alkyl group sometimes occurs, giving confusing results in species identification (Chau, unpublished data). When the hydride generation is applied after chromatographic separation, such rearrangement is totally eliminated. Unfortunately, post-column hydride generation is only applicable to liquid chromatography. Thus, the hydride technique is an ideal interface for liquid chromatography and furnace AAS. This aspect will be discussed in the subsequent sections.

Alkylation to tetraalkylated forms of a metal or a partially alkylated metal in Group IVA by a Grignard reagent can result in the formation of volatile derivatives suitable for GC separation. Methylation, butylation and pentylation (Meinema et al., 1978; Chau et al., 1982; Maguire and Huneault, 1981) have been applied to alkyltin compounds, and butylation and phenylation (Estes et al., 1983; Chau et al., 1984b; Forsyth and Marshall, 1983) have been applied to ionic alkyllead species. The chromatograms of a GC-AAS system for the separation and determination of ten alkyllead species (Chau et al., 1983) illustrates the analytical capability of such a combination (Fig. 1).

LIQUID CHROMATOGRAPH-ATOMIC SPECTROMETER SYSTEMS (LC-AAS)

Liquid chromatography including High Performance Liquid Chromatography (HPLC), and ion chromatography (IC) provides powerful separation capability for molecular and ionic organometal species in solution. These techniques can usually separate organometallic species without the required volatility necessary for GC separation, thus there is no need to derivatize the analytes. The advantages of liquid chromatographic techniques over other separation techniques have been fully discussed by Krull (1985). The most used, already commercially available HPLC detector: UV-VIS, atomic fluorescence (AFS), refractive index, electrochemical and conductivity have adequate sensitivity but do not at all offer element-specificity for detection. Only atomic spectrometric detectors are truly element-specific for speciation purposes. The atomic spectrometric devices used are atomic absorption (AAS), atomic emission (AES), and atomic fluorescence (AFS). Plasma excitation is the most sensitive technique for emission. Various forms of plasma have been used. Reviews on HPLC systems using GFAAS and inductively coupled plasma (ICP) and other element specific detectors for molecular and inorganic speciation are available (Irgolic and Brinckman, 1985; Krull, 1985).

The interfacing of HPLC to continuously operating detectors such as flame AAS and ICP is relatively simple. The adjustment of the HPLC flows to match the detector requirement is the only important

parameter for compatibility of the two components. The mobile phase of HPLC operation must not interfere with the atomization process. The sensitivity of the HPLC-flame AAS is generally in the μg/L level, limited by the sensitivity of the flame atomization. Flame AAS therefore is not a useful detector for environmental analysis.

Furnace type atomization devices such as graphite furnaces, electrothermal quartz furnaces, etc. offer higher sensitivity, and are readily applicable for environmental samples. When used in tandem combination with liquid chromatographs, the graphite furnace suffers from incompatability because of its discontinuous operational nature. For this reason, an interfacing device is necessary to couple a liquid chromatograph and a furnace AAS.

There are at present three HPLC-furnace AAS interface devices in use, all of which make use of an autosampler to take discrete samples from the liquid chromatograph effluent for injection to the furnace (Brinckman et al., 1977; Stockton and Irgolic, 1979; Vickrey, 1983). The designs of Stockton and Irgolic and Vickrey involved storage of aliquots in capillary tubes for subsequent injections to the AA furnace off-line. Such designs increase the number of determinations to define a chromatographic peak. All these systems give pulsed signals the sum of which represents the quantity of analyte in a chromatographic peak. These systems, however, do not provide a continuous, on-line, real-time analysis, although they have the adequate sensitivity for environmental work. The best approach to

achieve continuous and on-line HPLC-AAS interface is the post-column on-line hydride generation (Burns et al., 1981; Ricci et al., 1981). The hydride generation unit not only converts the analytes to volatile forms, but also isolates them from sample stream in gaseous forms to reach the furnace. Matrix interference is thus reduced to minimal. Furthermore, post-column hydride generation reduces the analytes after they are separated, thus it is free from molecular rearrangement.

Atomic emission spectrometric detectors are continuous operating units which can be directly coupled to liquid chromatographs. Such systems have been used in the determination of metals and inorganic speciation (Jones and Manahan, 1976; Hausler and Taylor, 1981; Krull, 1985); however, they have not been widely applied to organometallic compounds. The coupling of atomic emission spectrometric detectors (AES) such as inductively coupled plasma (ICP), microwave-induced plasma (MIP) and direct current plasma (DCP) to liquid chromatographs is expected to be exceedingly useful in the analysis of organometals and organometalloids. In this type of combination, the choice of mobile solvent in HPLC is critical, because many of the organic phases commonly used such as methanol and acetonitrile extinguish the plasma (Ibrahim et al., 1984). HPLC-ICP has been used to determine tetra-alkyllead in gasoline with mixed solvents of butanol:ethanol: water in 15:35:50 ratio, to increase the aspiration rate of the mobile phase and to stabilize the plasma. Direct ICP detection has also been successfully used in the analysis of a mixture of methylated arsenic

acids, As(III), As(V) and arsenobetaine (Morita et al., 1981). Figure 2 illustrates the clean separation of three organoarsenic and two inorganic arsenic species.

The use of post-column hydride generation has been applied to HPLC-ICP system to enhance sensitivity in arsenic speciation and to eliminate mobile phase effects on the plasma (Bushee et al., 1984). A direct current plasma emission detector has been used to detect methyltin species after HPLC separation and hydride conversion (Krull and Panaro, 1984). Some sensitive high pressure liquid chromatograph-atomic spectrometer systems used in environmental analysis are summarized in Table 3.

Digestion Techniques for Biological Samples

Sample digestion or dissolution is an important process in environmental analysis. Difficulties are often encountered with labile species in most digestion procedures which result in breaking down of the chemical form of the analytes. Thus the form analyzed does not represent the form present in the sample. For biological samples such as tissues, plants, animal organs, etc. the commonly used acid digestion is totally unsuitable.

Two sample digestion/dissolution methods suitable for speciation work have so far been published for biological materials. Forsyth and Marshall (1983) used a mixture of enzymes, lipase and proteases for

TABLE 3. Liquid Chromatograph-Atomic Spectrometer Systems

System	Compounds	D.L. (ng)	Reference
HPLC-GFAAS	R_3Sn (R=C_6H_5-,C_4H_9-C_3H_7-)	316	Brinckman et al., 1977
HPLC-GFAAS	MMA,DMA,As(III),As(V)	0.1	Brinckman et al., 1980
HPLC-GFAAS	AsB,AsC,As(III),As(V)	10	Stockton and Irgolic, 1979
HPLC-GFAAS	R_nSnCl_{4-n} (R=Me,Pr, Bu,Ph)	n/a	Vickrey et al., 1980
HPLC-GFAAS	MMA,DMA,As(III),As(V)	5	Woolson and Aharonson, 1980
IC-QFAAS	MMA,DMA,AS(III),As(V)	10	Ricci et al., 1981
HPLC-QFAAS	R_nSnCl_{4-n}	2-20pg	Burns et al., 1981
LC-AAS(flame)	R_4Pb (R=Me,Et)	10	Messman and Rains, 1981
HPLC-ICP	$MeHg^+$,$EtHg^+$,$PrHg^+$ $Hg(II)$	ng/L range	Gast et al., 1978
HPLC-ICP	MMA,DMA,As(III), As(V),AsB	2.6ng/s	Morita et al., 1981
HPLC-ICP-Hy	DMA,As(III),As(V)	10-20	Bushee et al., 1984
HPLC-ICP	R_4Pb		Ibrahim et al., 1983

IC - Ion chromatography
Hy - Hydride generation
ICP - Inductively coupled plasma
GFAAS - Graphite furnace AAS
QFAAS - Quartz furnace AAS
MMA - Monomethylarsonic acid
DMA - Dimethylarsinic acid
AsB - Arsenobetaine
AsC - Arsenocholine
D.L. - Detection limit in ng of element

hydrolysis of egg homogenates. Chau et al. (1984b) digested fish tissue, algae and aquatic plants in a tissue solubilizer, tetramethylammonium hydroxide. Both procedures were effective in releasing alkyllead species from biological tissues without altering their chemical forms. Sample clean-up is desirable for biological materials because residual fats and protein in sample matrices can gum up GC columns and transfer lines and even deposit on the furnace. For example, cleaning-up of the final extract of butylead derivatives of alkyllead species in fish can be achieved by passing the extract through a silica gel column and eluting the alkylleads with pentane (Chau et al., unpublished data). The alkylleads are eluted first leaving the fats and organics behind in the column which can be cleaned up by further elution.

Sample Preservation

Some organometals and organometalloids such as methyltin, methyllead, methylmercury and methylarsenic acids have been found to be involve in life processes. It is known that tetraalkyllead ingested by mammals would dealkylate to form trialkyllead in vivo. Thus preservation of samples in their authentic state becomes difficult. It is our experience that water samples can be preserved without change of the methyltin and alkyllead species (R=Me,Et) if stored in glass bottles at 4°C and in the dark for a period of up to

one month. Biological samples and sediments are normally frozen after collection to slow down microbial activities. Whether there is any change in species distribution in biological samples with respect to time is not known because of the difficulties in obtaining homogeneous samples to follow small changes in concentration.

Contamination in the course of sampling and analysis is not a serious problem for most organometals because they are not ubiquitous contaminants. It is important to avoid using plastic ware in taking storage of samples and reagents for organotin analysis because of the dialkyltin stabilizers used in some plastic manufacture. Antifouling paints used in boats is another possible source of contamination of trialkyltin compounds.

CONCLUSION

The occurrence of organometals and organometalloids in the environment and their participation in biotic and abiotic cycles have attracted much research effort in their related areas, which has opened up new research frontiers in environmental chemistry of metals. Many organometallic compounds previously not known to be stable in aqueous medium have been, and will continue to be, identified as new analytical techniques continue to develop. Such information often directs us to discover new pathways and cycles of elements which have not been explored before. Many organometals are closely related

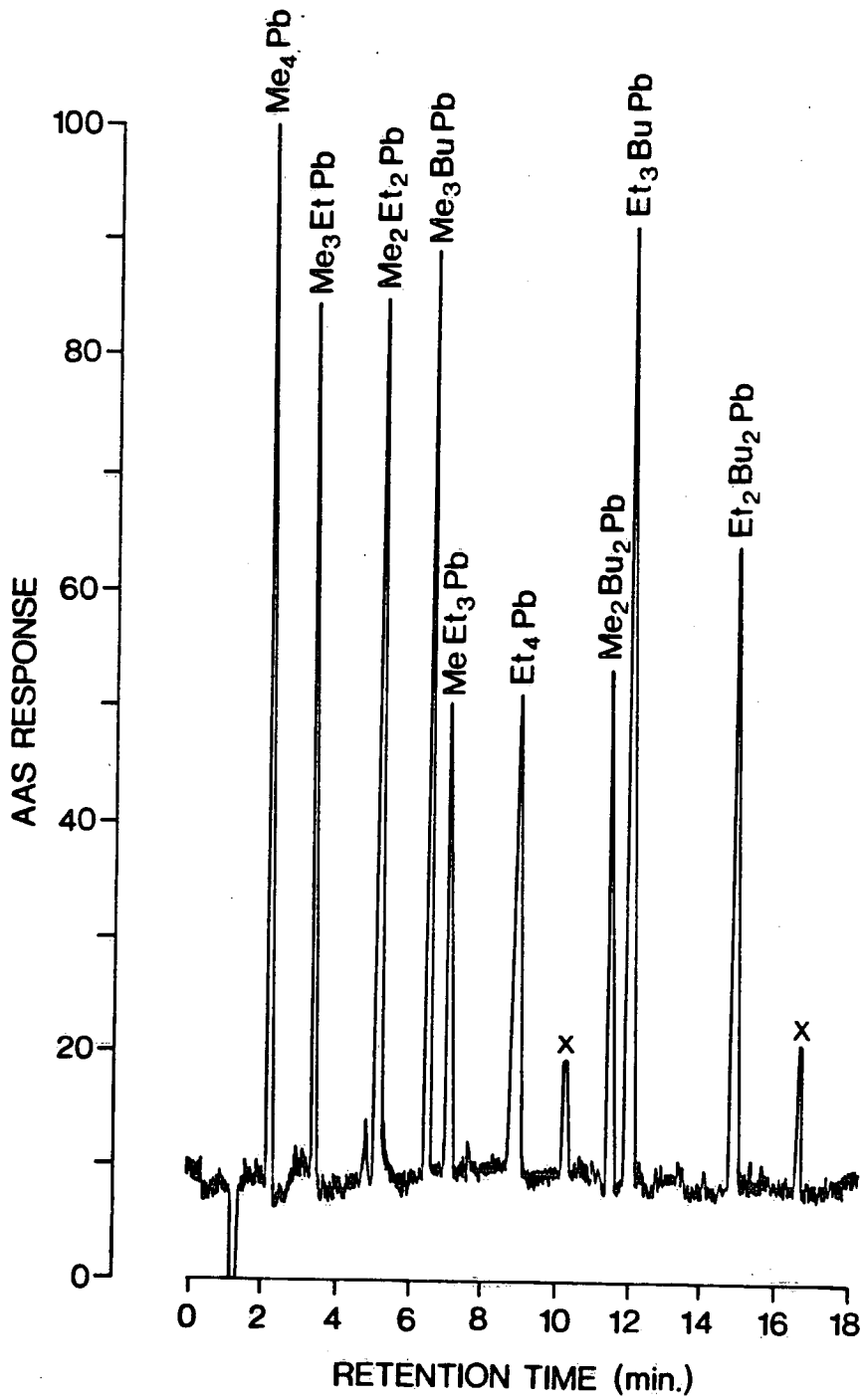
to biogenic processes; they are key species for closing the gaps between biology and chemistry. These are exemplified by the transformation and biomethylation of elements which truly represent biogeochemical processes.

Combination analytical systems are currently the best instrumentation for element-specific analysis of organometals. A quantitative approach in metal toxicity prediction will become more reliable as the knowledge of speciation and structure of organometallic compounds advances.

Legends:

Fig. 1 GC-AAS chromatograms of five tetraalkylead compounds (10 ng each), four butyl derivatized dialkyl- and trialkyl-lead (8 ng each) (R=Me,Et) and Pb(II). x - unidentified lead compounds. (Reprinted with permission from Chau *et al.*, 1983).

Fig. 2 LC-ICP chromatograms of As(III), As(V), methylarsenic acids and arsenobetaine (350 ng each). (Reprinted with permission from Morita *et al.* 1981; Copyright (1981) American Chemical Society).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80
60
40
20
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Me_3EtPb
Me_2Et_2Pb
Me_3BuPb
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Et_4Pb
Me_2Bu_2Pb
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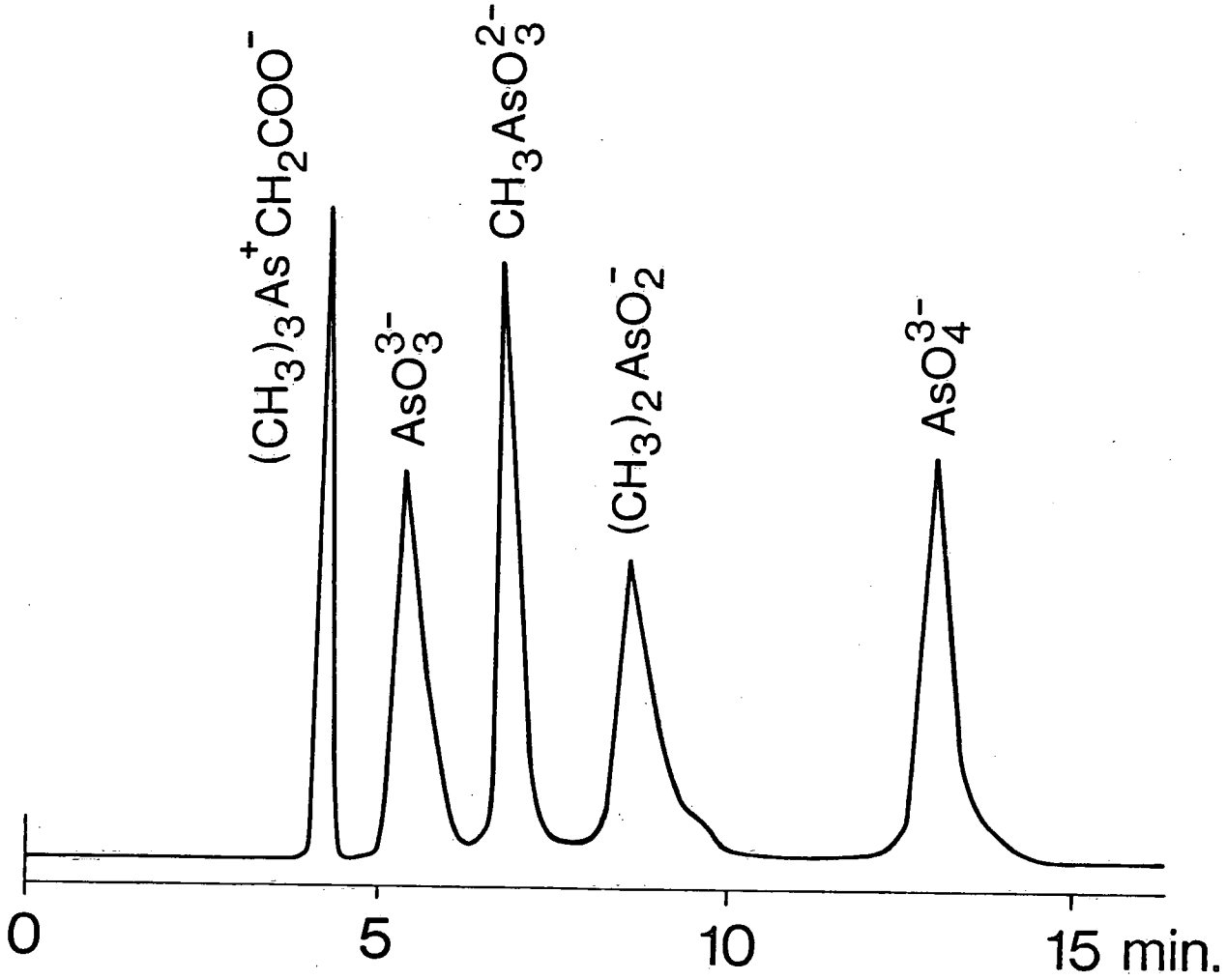
X
X
0
2
4
6
8
10
12
14
16
18
RETENTION TIME (min.)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AsO_3^{3-}
$CH_3AsO_3^{2-}$
$(CH_3)_2AsO_2^-$
AsO_4^{3-}
0
5
10
15 min.

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Legends:

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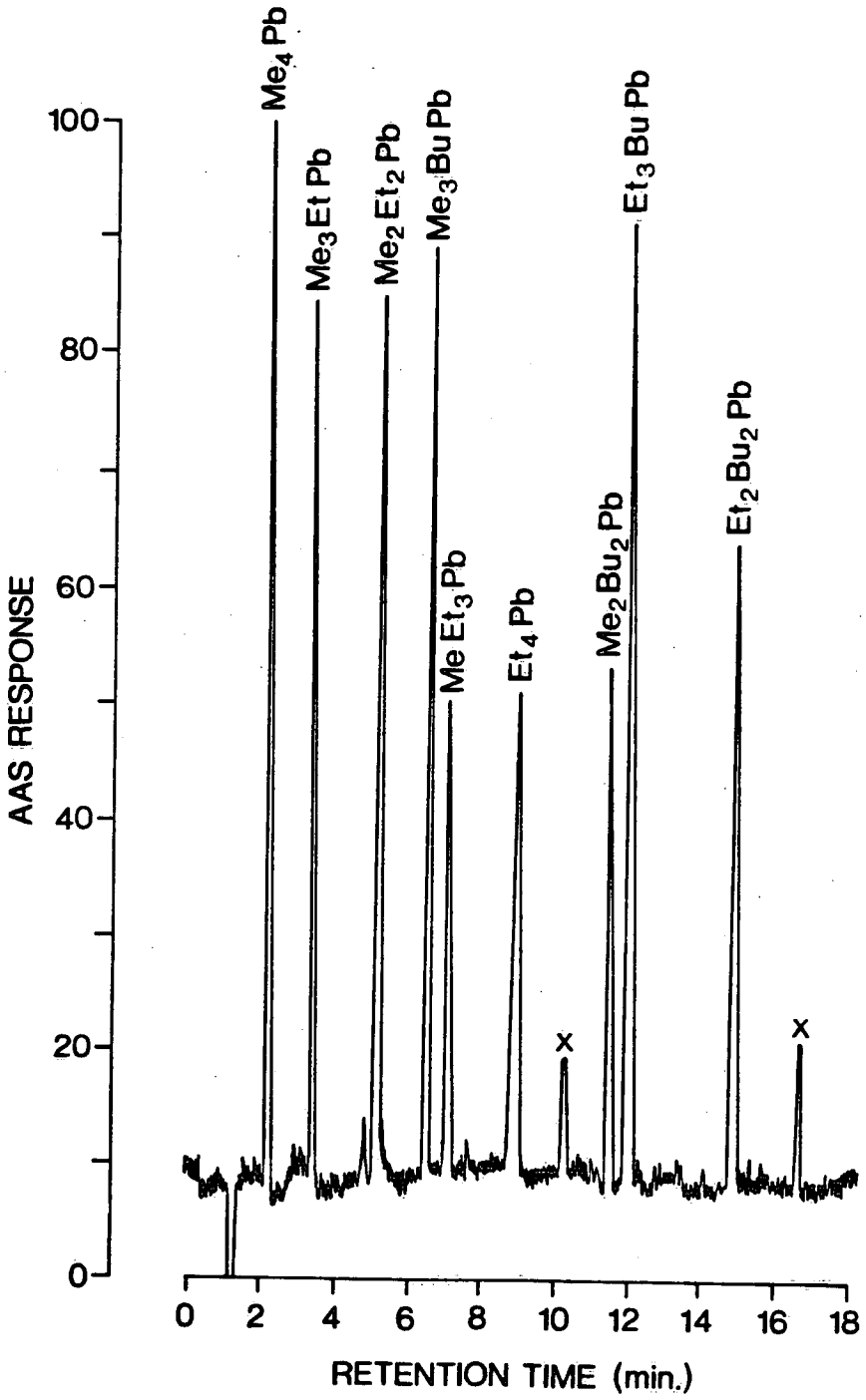
Fig. 2 LC-ICP chromatograms of As(III), As(V), methylarsenic acids and arsenobetaine (350 ng each). (Reprinted with permission from Morita *et al.* 1981; Copyright (1981) American Chemical Society).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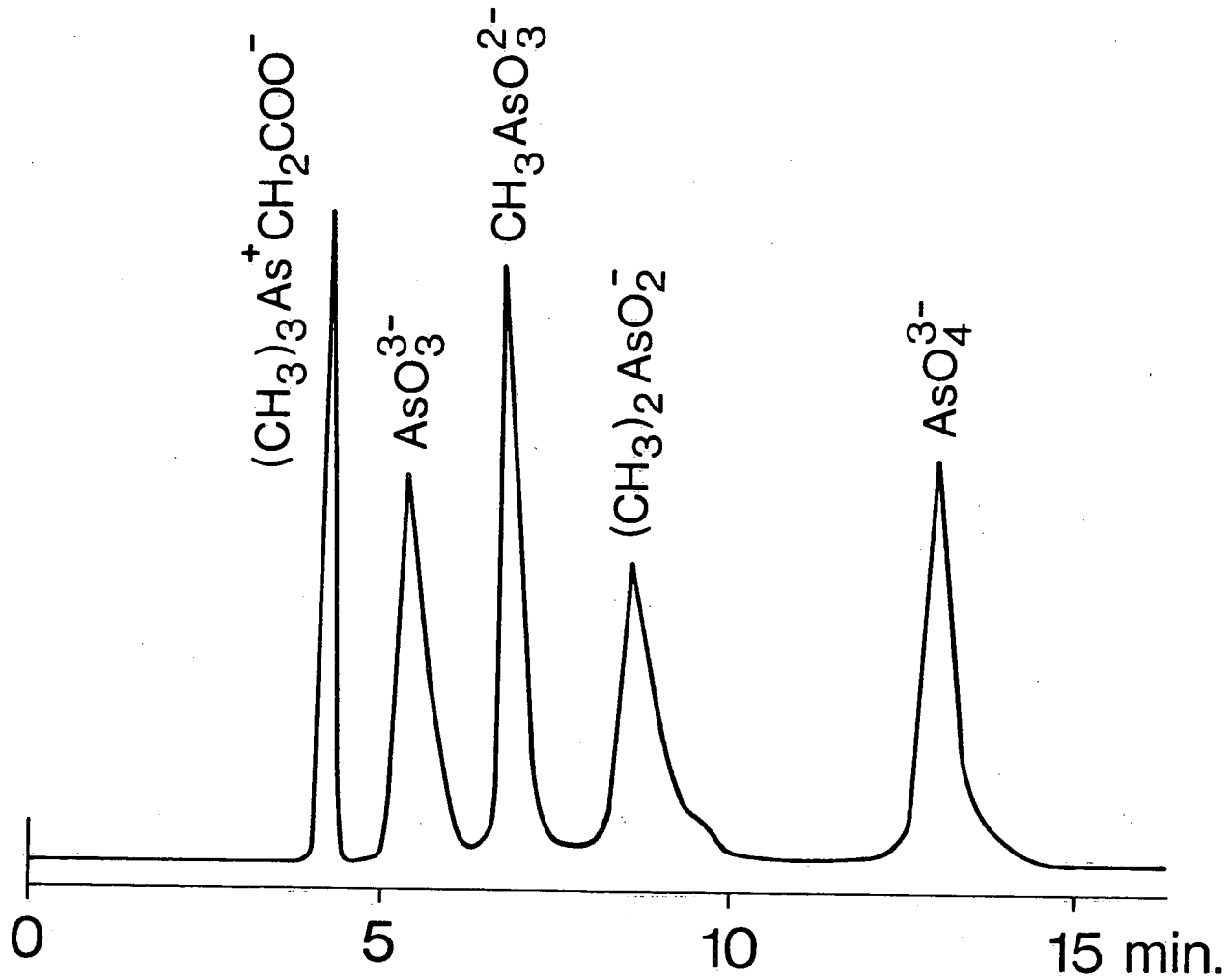
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