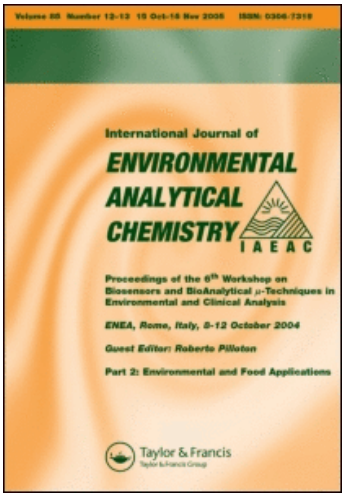


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# New Speciation Approaches in the Biogeochemical Cycles of Organometallics in the Environment

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**To cite this Article** Rapsomanikis, S. and Andreae, M. O.(1992) 'New Speciation Approaches in the Biogeochemical Cycles of Organometallics in the Environment', International Journal of Environmental Analytical Chemistry, 49: 1, 43 — 48
**To link to this Article: DOI:** 10.1080/03067319208028125
**URL:** http://dx.doi.org/10.1080/03067319208028125

*Intern. J. Environ. Anal. Chem.*, Vol. 49, pp. 43-48
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# NEW SPECIATION APPROACHES IN THE BIOGEOCHEMICAL CYCLES OF ORGANOMETALLICS IN THE ENVIRONMENT

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*(Received, 19 November 1991; in final form 23 March 1992)*

In situ aqueous ethylation of fish tissue samples containing inorganic and methylmercury compounds or sediment samples containing butyltin compounds produced molecular, volatile mixed alkyls of predictable composition. Dynamic purging, cryogenic trapping on a chromatographic packing, thermal desorption to an electrically heated quartz furnace and AAS detection effected their analysis. The procedure for mercury compounds is simplified and absolute detection limits for $CH_3Hg^+$ and $Hg^{2+}$ are 12 pg and 230 pg, respectively. Detection limits for the ethylated butyltins are comparable to the ones for the hydride derivatives.

**KEY WORDS :** Ethylation, methylmercury, butyltin, sodium tetraethyl borate



## INTRODUCTION

A framework for studying the mass balance of biogeochemical processes requires information about the strength of sources and sinks. It also requires information about species concentrations in different environmental compartments, about their reactivities and about the influence of human activity. A large data base is required to understand the global biogeochemical cycle of an element and specific information about its chemical form in the different environmental compartments is also needed. The latter necessity has created a refinement in chemical analysis termed "SPECIATION". The chemical identity or the molecular formula or part of it, is the information sought. Selective extractions or chromatography coupled with an element specific detector may achieve the desired result. We have chosen the latter method for the speciation of metals and metalloids in our studies of their biogeochemical cycles. For a number of these metals and metalloids, speciation is achieved by *in situ* derivatising to hydrides using $NaBH_4$ or to alkyls using Grignard reagents. However, in some cases, derivatisation by $NaBH_4$ may not be efficient, or the resulting hydrides may not be stable enough for high precision analysis. Derivatisations using Grignard reagents, on the other hand, involve solvent extractions and numerous handling steps. This is time consuming and may also result in low analytical precision. Previously,

analysis of ionic methyllead and methylmercury compounds involved Grignard derivatisation procedures for the former or direct chromatography for the latter. An *in situ* derivatisation technique reported recently[1] overcame the methyllead and methylmercury hydride's instability by employing $NaB(C_2H_5)_4$ and forming the more stable ethyl derivatives:

$$Pb^{2+} + 2NaB(C_2H_5)_4 \text{ —— } (C_2H_5)_2Pb \text{ —> } 1/2\ (C_2H_5)_4Pb + 1/2Pb^{\circ} \quad (1)$$

$$Hg^{2+} + 2NaB(C_2H_5)_4 \text{ —> } (C_2H_5)_2Hg \quad (2)$$

$$(CH_3)_3Pb^{+} + NaB(C_2H_5)_4 \text{ —> } (CH_3)_3PbC_2H_5 \quad (3)$$

$$(CH_3)_2Pb^{2+} + 2NaB(C_2H_5) \text{ —> } (CH_3)_2\ Pb(C_2H_5)_2 \quad (4)$$

$$CH_3Hg^{+} + NaB(C_2H_5)_4 \text{ —> } CH_3HgC_2H_5 \quad (5)$$

These carbon to metal forming reactions occur in aqueous media under conditions optimised for maximum yield of the predicted derivatives. Reaction (1) has been utilised in the determination of inorganic lead in natural waters and biological tissues after trapping the produced $(C_2H_5)_4Pb$ on the surface of a graphite furnace[2]. Reactions (2) and (5) have been used for the speciation of mercury in fish tissue, and in fresh and marine waters in a two stage purge and trap system coupled to an atomic fluorescence detector[3]. Reactions (1) (3) and (4) in conjunction with the respective reactions for ionic ethyllead or mixed methyl-ethyl lead compounds have been used in a HPLC-AA postcolumn derivatisation technique[4]. In another case, $NaB(C_2H_5)_4$ has been used to form $(C_2H_5)_2$ Cd which is eventually detected in a hydrogen rich flame of an atomic fluorescence set-up[5]. One of the more important findings from the utilisation of $NaB(C_2H_5)_4$ as derivatisation reagent is that it produces a higher yield of derivative ethylated butyltins than hydride formation with $NaBH_4$[6]. Butyltins in sediment samples were determined after extraction, preconcentration, methanolic phase ethylation and analysis by a conventional GC-AAS system. The same system was employed for the determination and speciation of mercury compounds in standard reference materials[7]. In the present study we employ the derivatisation-purge and trap-AAS procedure because it is simple and very sensitive to methylmercury and butyltin compounds in environmental samples. *In situ* aqueous ethylation of samples containing inorganic mercury, methylmercury, methyltin and butyltin compounds produces molecular, volatile, mixed alkyls of predictable composition. Dynamic purging , cryogenic trapping on a chromatographic packing, thermal desorption to an electrically heated quartz furnace and AAS detection effects their speciation.

## EXPERIMENTAL

A simplex optimisation programme[8] was used to optimise parameters for the analyses of organotin and organomercury compounds. Aliquots of standards or samples where placed in the reaction flask and the volume was made up to 20 $cm^3$ using acetate buffer of pH 4.05. After the addition of 100 µl 1% w/v aqueous $NaB(C_2H_5)_4$ solution, the mixture was stirred

for 10 minutes at room temperature and purged for 6 minutes. Then the reactor was bypassed, the liquid nitrogen removed and the temperature programme started. Sediments were extracted with 0.5 M methanolic NaOH and analysed for methyl and butyltin compounds. Tuna fish muscle was dissolved in 25% w/v methanolic KOH and analysed for inorganic and methylmercury. Quantification was effected by the method of standards addition. The organomercury derivatives where purged by a stream of helium from the reaction phase to the liquid nitrogen cooled trap which contained 3% OV-101 on Chromosorb HP 60-80 mesh. Species were separated by heating the trap from -198°C to 120°C in 2 minutes. Additional hydrogen and air were not necessary in the atomisation process of organo-mercurials. The derivative organotin compounds were processed in a similar manner but species were separated by heating the trap from -198°C to 120°C in 2 minutes and from 120°C to 200°C in 1 minute. Details of the apparatus and standards are given elsewhere[9].

## RESULTS AND DISCUSSION

Previous results for the speciation of mercury in fish tissues employing a two stage trapping[3]



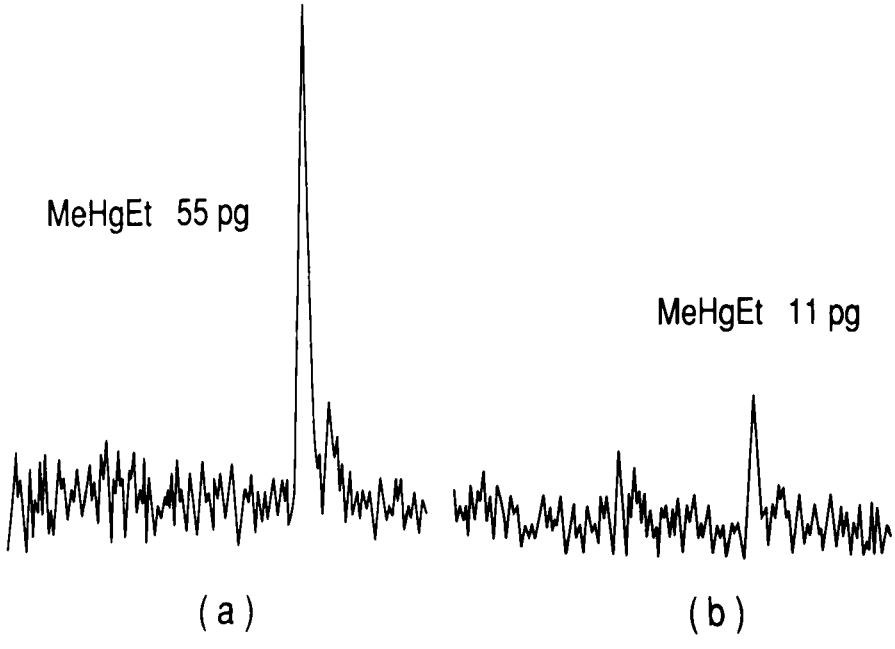


**Figure 1** (a) Chromatogram of 55pg $CH_3Hg^+$ derivatised to $CH_3HgC_2H_5$
(b) 11pg $CH_3Hg^+$ derivatised in a similar manner. Total chromatographic time, 2 minutes.

or conventional GC coupled to AAS[7] warranted the investigation of the simple purge and trap GC-AAS system. The reaction conditions had been optimised earlier[1] and the extraction procedure already established[3]. Calibration graphs of aqueous $Hg^{2+}$ and $CH_3Hg^+$ standards were produced and from them absolute limits of detection were calculated according to a literature procedure[10]. The limit of detection is defined as the analyte concentration giving a signal equal to the blank signal, $Y_B$, plus three standard deviations of the blank, $S_B$. However, the intercept of the calibration line with the y axis is taken as $y_B$ and the statistic $S_{Y/X}$ (standard deviation of the residuals from the calculated regression line) as $s_B$. A chromatogram of two methylmercury standards is presented in Figure 1.

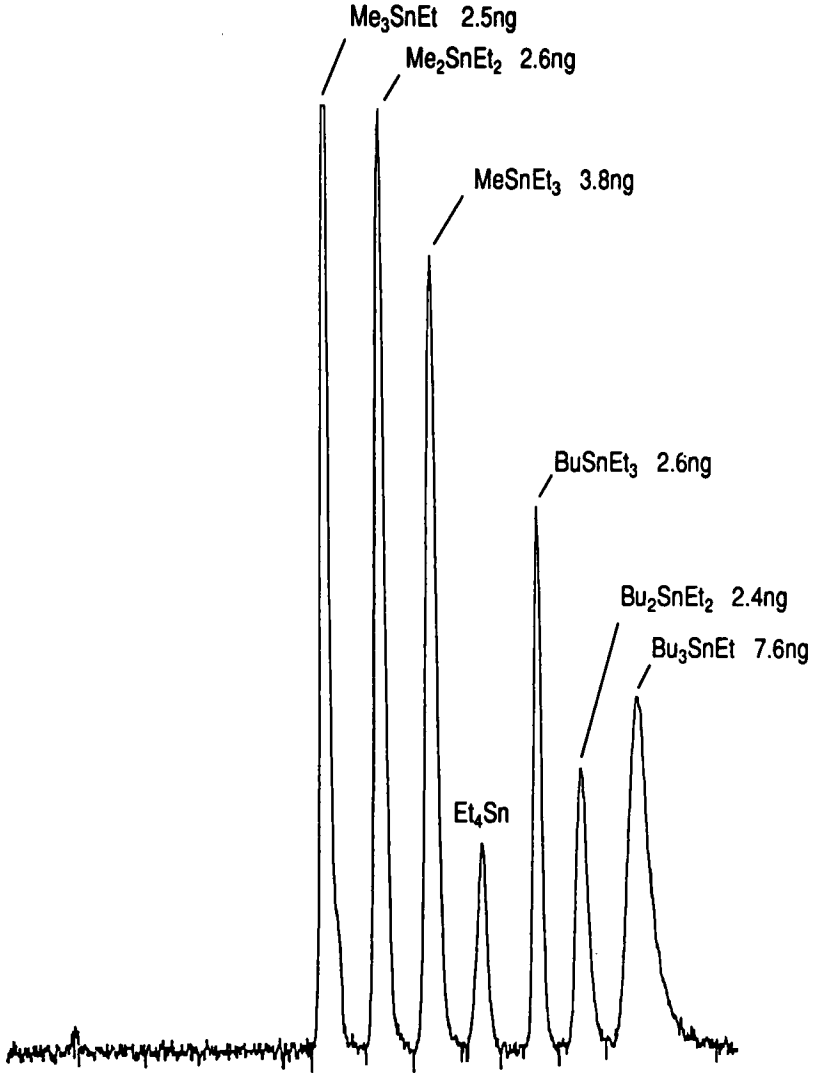


**Figure 2** Chromatogram of mixed alkyltin standard with absolute amounts shown as Sn. Total chromatographic time, 5 minutes.

The tuna fish muscle tissue was analysed in triplicate and was found to contain 4.12 ± 0.24 μg $CH_3Hg^+$ $g^{-1}$ and 3.30 ± 0.19 μg $Hg^{2+}$ $g^{-1}$ dry weight. As a future reference material it was analysed in an laboratory intercallibration exercise organised by the BCR (Bureaux of Community Reference Materials; European Economic Community, Brussels, Belgium). The mean of all individual values for the analysis of the same sample, presented by 11 laboratories employing different techniques, was 4.23 ± 0.62 μg $CH_3Hg^+$ $g^{-1}$ dry weight. The mean of all mean values was 4.16 ± 0.59 μg $CH_3Hg^+$ $g^{-1}$ dry weight. The quantification of $Hg^{2+}$ was not a requirement in the exercise.

The detection limit for the tuna fish muscle as dry weight proved to be 100 ng of $CH_3Hg^+$ $g^{-1}$ if 0.1 g of dry weight is dissolved in 40ml extracting solution and 50 μl of extract is analysed. Clearly better concentration detection limits can be achieved if larger amounts of extract are analysed. However, the absolute detection limit of $CH_3Hg^+$ remains 12 pg even for the tuna fish muscle extract. The linearity range is shortened from up to 5 ng for aqueous standards to 1 ng for the tuna fish muscle extract. There was never a need for second stage desorption prior to analysis, nor was there ever evidence of dismutation reactions taking place in the reaction vessel. As reported previously[7], it was not necessary to add hydrogen or air to the cuvette to improve the atomisation efficiency.

The experimental set-up can also be used for the analysis of methyl and butyltins after their derivatisation to ethyl-methyl or butyl-ethyl molecular compounds (Figure 2). Here we report preliminary results on the *in situ* ethylation of these compounds and their analysis using the simple purge and trap GC-AAS apparatus. Detection limits calculated in a similar way to those for the mercury compounds are comparable to hydride derivatives[9] (varying between 50 and 200 ng as Sn/g dry sediment weight for all methyl- and butyl-ethyltin derivatives) but with improved precision because, once formed, the metal to carbon bond is stable. The applicability of the method to sediments spiked with $(C_4H_9)_3SnCl$ is shown in



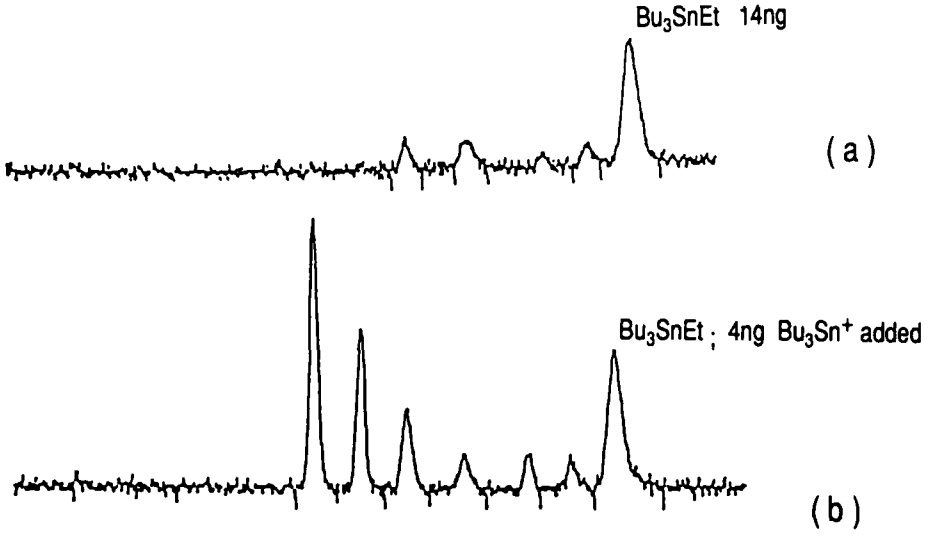


**Figure 3** (a) Extract of spiked river Main sediment.
(b) Addition of standard containing 4 ng of $Bu_3Sn^+$, to the extract.

Figure 3. The heating programme for the elution of these compounds is different to the programme for the elution of the tin hydrides, because of their higher boiling points. Thermal control of the reaction vessel and of the transference lines could increase the analytical signal and the precision of the method even more.

There are many advantages to this method. First, there is the simplicity of the apparatus. Second, handling is kept to a minimum. Third, rather than labouring through many steps, clean-up is effected by the separation of the liquid ("dirty") phase and the gaseous phase containing the analyte stream. Fourth, preconcentration is achieved *in situ* and under an inert atmosphere. These combine to make this method an invaluable tool in the analysis of environmental samples containing naturally occurring or pollutant organometallics. Comparison between the method for the analysis of $CH_3Hg^+$ in fish tissue described here and the classic method of the 1960's[11] confirms the advantages listed above. *In situ* aqueous ethylation is a novel derivatisation technique that opens new research possibilities in aqueous phase organometallic chemistry and points to ways in avoiding Grignard reagents.

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