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## Direct hydride derivatization of methyl- and ethylmercury chlorides in aqueous solution with $\text{KBH}_4$

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**Abstract:** A convenient hydride derivatization procedure of methyl- and ethylmercury chlorides to volatile hydrides was reported. In sealed vials methylmercury and ethylmercury compounds in acidic aqueous solutions were converted into their volatile forms by the reaction with potassium tetrahydroborate ( $\text{KBH}_4$ ) and evolved to the headspace of the vials. The gaseous analytes in the headspace were extracted and concentrated by solid phase microextraction (SPME) and injected into gas chromatography (GC) for separation and identified by mass selective detector (MS).

**Key words:** hydride derivatization; methyl- and ethylmercury; gas chromatography; mass selective detector

### Introduction

Rapid and sensitive analytical methods for the determination of mercury and related compounds in environmental samples are imperatively demanded since various chemical forms of mercury in the natural environment can behave differently, thereby affecting its biogeochemical behavior and toxicity to organisms. However, most of alkylmercuries exist in non-volatile polar forms which have relatively high boiling points and often poor thermal stability and are not suitable for separation by gas chromatography (GC). They must be converted to non-polar and volatile species. Up to date, the most commonly used derivatization methods are ethylation, Grignard reaction and hydride generation.

First synthesized by Honeycutt and Riddle, sodium tetraethylborate ( $\text{NaBEt}_4$ ) was introduced to derivatize methylmercury (MeHg) by Craig's group and widely used in conversion of organomercuries. However, this method can not be used for the speciation of monoethyl- and diethylmercury. Derivatizations with Grignard reaction are versatile because of the diversity of Grignard reagents but require an organic solution medium. Although they remain primary method for lead and tin, application for organomercury is an interesting curiosity.

Since methylmercury has been demonstrated to be converted to hydride form, hydride generation has been an alternative derivatization method for the determination of methylmercury. However, information of hydride generation of ethylmercury (EtHg) has been scarcely reported.

Solid phase microextraction (SPME) as a promising technique for sample preparation and pretreatment was originally developed at the end of 1980's and has become one of the most important research areas in modern analytical chemistry. It is a kind of solvent-free and environmental-friendly procedure and can be combined with GC to analyze trace level of volatile and semi-volatile compounds efficiently and quickly.

The aim of this paper was to identify the formation of volatile hydride derivatives by the reaction of methyl- and ethylmercury chloride in acidic aqueous solutions with  $\text{KBH}_4$ . The hydrides were volatile enough and evolved to headspace and can be extracted by SPME, then separated and identified by gas chromatography (GC) on-line coupled with mass selective detector (MS).

# 1 Experimental

## 1.1 Apparatus

Separation and identification of methyl- and ethylmercury hydrides was taken by a model of HP 5890 II/HP 5971A gas chromatography with mass selective detector (Hewlett-Packard, USA) which controlled by a HP chemstation. A  $30\text{ m} \times 0.25\text{ mm i. d.} \times 0.25\text{ }\mu\text{m}$  thickness capillary column was used throughout the experiment. The GC injector temperature was kept at  $200^\circ\text{C}$  and the oven temperature was set at  $65^\circ\text{C}$  for MeHgH and  $105^\circ\text{C}$  for EtHgH. Helium as carrier gas was controlled at flow rate of 1 ml/min.

A laboratory-assembled SPME device including an approximately 15 cm of capillary fused-silica fiber and a stainless-steel tube projection part of Hamilton microsyringe was used throughout the experiment. Of the 15 cm long fiber, only the bottom 4 cm, which was pretreated by dipping in concentrated hydrofluoric acid for 3.5 h, was used to absorb the sample. The fiber inserted inside the syringe needle was put through the septum of a headspace vial by the protection of the syringe needle and the bottom 4 cm was exposed just above the surface of the sample solution.

## 1.2 Reagents

A 1.000 mg/ml of organomercury standard solutions were prepared by dissolving amount of methyl- and ethylmercury chloride (Merck-Schuchardt) in 10 ml benzene and diluting with cyclohexane to 25 ml, respectively.

A 6% (m/v) of potassium tetrahydroborate solution was prepared daily by dissolving  $\text{KBH}_4$  (Shanghai Chemical Reagent Factory) in water and the solution was used without filtration and without the use of a stabilizing reagent.

A 0.1 mol/L solution of acetic acid-sodium acetate (HAc-NaAc) buffer was prepared by dissolving 4.1 g of NaAc in a final volume of 500 water containing 2.86 ml of glacial acetic acid. The acidity of the buffer was adjusted by a pH meter type PHS-2.

## 1.3 Procedure

A 20 ml of pH3 HAc-NaAc buffer solution containing  $100\text{ }\mu\text{g}$  MeHg (for EtHg, the pH is 4) was added to a 100 ml vial sealed with a rubber septum and then 1 ml of 6% aqueous  $\text{KBH}_4$  was injected into the vial through the septum. The organomercury hydrides were produced, evolved to the headspace of the vial. Then two transportation methods were used: first, 5 ml aliquot of MeHg or 2 ml aliquot of EtHg was taken for analysis using a gas-tight syringe; second, a 4 cm length of pretreated SPME fiber was exposed to the headspace by piercing the septum with the needle of the fiber assembly and then depressing the plunger linked to the fiber. Care must be taken to ensure that the fiber did not contact the liquid surface. After extraction, the fiber was removed and injected into the chromatograph injector under the protection of the needle.

# 2 Results and discussion

The reaction medium is adjusted using HAc-NaAc buffer solution to pH3 for methylmercury and pH4 for ethylmercury. Derivatization of MeHgH and EtHgH took place immediately after the injection of  $\text{KBH}_4$ . The spectra of the mass-spectral analysis at the retention time of  $\text{MeHg}^+$  and MeHgH are shown in Fig. 1a and Fig. 1b. The spectrum of MeHgH showed in Fig. 1b was similar to that previously reported by Filippeli. Compared with the highest peak of  $\text{MeHg}^+$  at  $m/z$  217, the peak at  $m/z$  218 corresponding to MeHgH is the highest. Direct identification of EtHgH was achieved by hydride generation with  $\text{KBH}_4$ , as shown in Fig. 2. The cluster mass spectrum peaks at  $m/z$  227–233 due to  $\text{EtHg}^+$  in Fig. 2a were replaced by peaks at  $m/z$  228–234 corresponding to EtHgH in Fig. 2b, supporting the formation and thermal stability of the

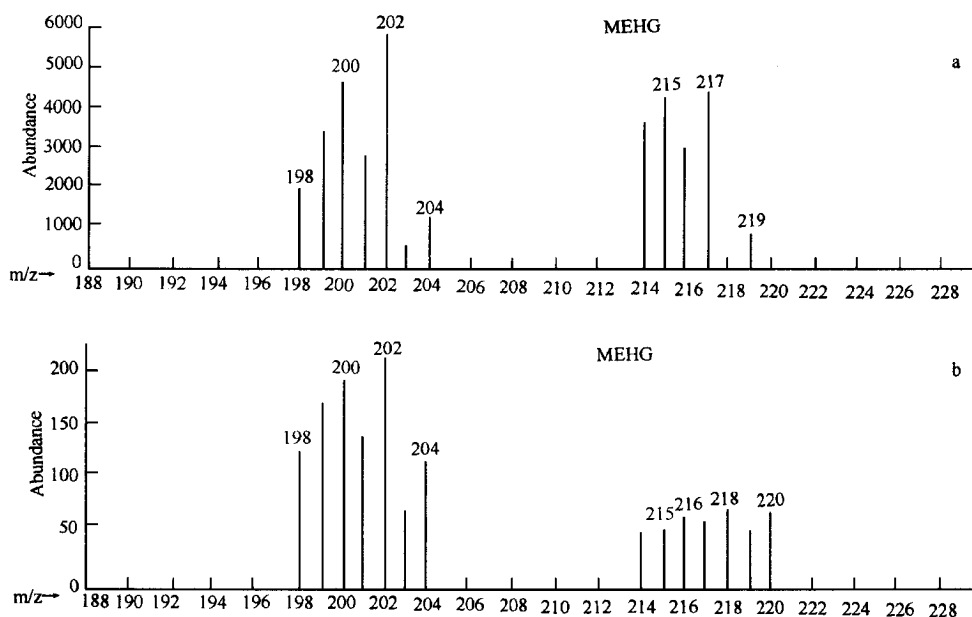


Fig.1 Mass spectrum  
 a. MeHgCl b. MeHgH

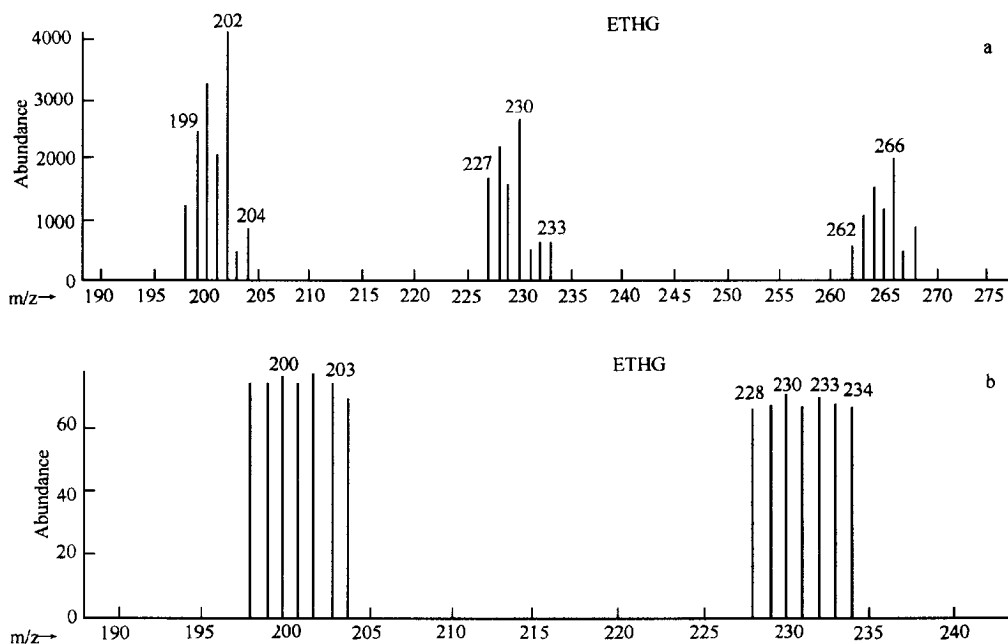


Fig.2 Mass spectrum  
 a. EtHgCl b. EtHgH

ethylmercury hydride. No traces of cluster near  $m/e$  252 for MeHgCl and  $m/e$  266 for EtHgCl was observed. All MeHgCl and EtHgCl were transformed into volatile hydrides within one

reaction. No further production of MeHgH and EtHgH were detected upon addition a second aliquot of  $\text{KBH}_4$  to samples.

Metal hydrides are known to be produced by  $\text{NaBH}_4$  additions, but those from Hg have long been regarded to yield only unstable compounds. We tested the molecular stability of MeHgH and EtHgH and found that, MeHgH has a half-life of approximately 1.5 h whereas EtHgH has 1h. But extracted by SPME, the half-life of both MeHgH and EtHgH can be postponed 0.5 h. This may be due to the physical bond of MeHgH and EtHgH to the fiber coating.

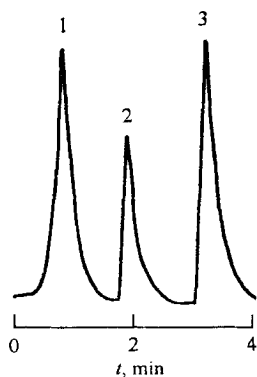


Fig. 3 Chromatogram of MeHgH and EtHgH

1. solvent; 2. MeHgH;
3. EtHgH

Following the derivatization with  $\text{KBH}_4$ , mixed MeHgH and EtHgH can be extracted by headspace solid phase microextraction (SPME). Then the derivatives are injected into a Shimadzu GC-9A gas chromatograph (Japan), separated on a  $30 \text{ m} \times 0.32 \text{ mm i. d.} \times 0.25 \mu\text{m}$  SPB-1 capillary column and detected by a modified Perkin-Elmer 503 atomic absorption spectrometer (USA) with a mercury hollow cathode lamp at  $253.7 \text{ nm}$ . The column temperature was programmed at  $45^\circ\text{C}$  for 1 min, increased to  $65^\circ\text{C}$  at  $40^\circ\text{C}/\text{min}$  and held for 1 min, then increased to  $150^\circ\text{C}$  at  $40^\circ\text{C}/\text{min}$  and held for 2 min. As shown in Fig. 3, MeHgH and EtHgH could be base-line separated with the retention time of 2.2 min for MeHgH and 3.7 min for EtHgH, respectively. The detection limits of 23 ng for MeHgH and 17 ng for EtHgH were achieved using this GC-AAS method.

### 3 Conclusion

In acid buffer solution, ethylmercury chloride as well as methylmercury chloride can be converted to volatile hydride forms with  $\text{KBH}_4$ . The important application of this method is that, it can be used, solvent-freely, in the speciation analysis of monomethyl-, dimethyl-, monoethyl- and diethylmercury by GC interfaced with elemental specific detector, such as AAS and AES. A SPME-GC-AAS method based on hydride derivatization for the determination of methyl- and ethylmercury in environmental samples has been established in our laboratory and will be reported.

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