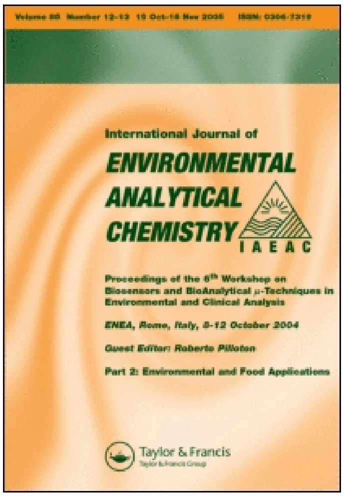

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Determination of Methyl Mercury in Lake Water

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KEY WORDS: Methyl mercury, ethyl mercury, phenyl mercury, lake water, gas chromatography

A gas chromatographic method is described for the determination of methyl mercuric compounds in lake water. Methyl mercuric compounds are extracted by benzene in a continuous extractor followed by a selective extraction with l-cysteine. The methyl mercury in cysteine is converted to a chloride and back-extracted to benzene for gas chromatography determination using ^{63}Ni electron capture detector. Ethyl mercury and phenyl mercury can also be determined by the method, but their extraction from lake water is not quantitative. Results of analyses of several lake water samples are reported.

INTRODUCTION

The significance and high toxicity of methyl mercury in the aquatic environment has been well documented[1,2] and the bacterial synthesis of methyl mercury in sediments has also been described.[3,4] Additional organo mercurials such as ethyl mercuric chloride and phenyl mercuric chloride have been introduced into the system as a result of their application as fungicides and for industrial use. It is also known that the different forms of mercury input are eventually converted to methyl mercury under anaerobic conditions by bacterial action, and that the methyl mercuric compound is readily dispersed in the overlying water and concentrated by aquatic organisms. The level of methyl mercury in water is therefore very low. Because of its potential as an environmental hazard, it is most desirable to have a sensitive method to determine methyl mercury in natural waters. This paper describes a GC technique for the determination of nanogram quantities of methyl mercury in lake water; the recovery and analyses of ethyl and phenyl mercuric compounds in lake waters were also studied.

EXPERIMENTAL

A continuous upward liquid–liquid extractor of 6-1 capacity was used for the extraction of organic mercury compounds from water. A Micro-Tek Gas Chromatograph model 220 equipped with a ^{63}Ni electron capture detector was used for the analysis of mercury.

Reagents

Methyl mercuric chloride was obtained from MC/B Manufacturing Chemist; ethyl mercuric chloride from K and K Rare and Fine Chemicals, and phenyl mercuric chloride from Eastman Kodak. The benzene used was pesticide grade, further purified by vacuum distillation. ^{203}Hg-labelled methyl mercuric chloride was obtained from Amersham-Searle Corp.

Procedure

Filter 5 l of sample through a 0.45-micron membrane filter immediately after collection and acidify with 15 ml of concentrated sulfuric acid. Extract the sample in the continuous extractor with 300 ml of benzene for 5–6 hr. Shake the benzene layer with four 5-ml aliquots of a 0.2% l-cysteine solution in a separatory funnel with the aid of a mechanical shaker. Combine the cysteine solution (20 ml) and adjust to 0.6N in hydrochloric acid. Extract the acidified cysteine solution with four 5-ml aliquots of benzene in a separatory funnel. Separate the benzene extract and concentrate it to 2 ml under reduced pressure. Inject 5 mcl of the benzene solution into the gas chromatograph.

RESULTS AND DISCUSSION

Extraction of methyl mercury from lake water

The extraction procedure is based on the method developed by Nishi and Horimoto,[5] modified for the determination of methyl mercury in lake water at the nanogram level. Since the amount of material present in water is expected to be extremely small, the use of a continuous extractor was thought to be desirable and its efficiency was investigated using the radio-isotope technique. Aliquots (5 l) of membrane-filtered lake water were spiked with ^{203}Hg labelled methyl mercuric chloride containing *ca.* 35 mcg of methyl mercuric chloride as carrier, and taken through the extraction procedure as mentioned above for different lengths of time. The benzene extracts were then extracted with four 5-ml aliquots of 0.2% cysteine solution. The cysteine extraction serves as a clean-up step for methyl mercury, which is absolutely necessary when electron capture detector is used in the gas chromatographic determination. The recovery of methyl mercury in the cysteine solution was assessed by γ-radiometry. Recovery of 96% to 98% was observed after 5 to 6 hr of extraction. In the 2-hr extraction experiment the recovery was only 45–50%.

For gas chromatographic analysis, the methyl mercury in cysteine was back-extracted to benzene by multiple extractions using four 5-ml aliquots of benzene after acidification of the cysteine solution. The hydrochloric acid used for acidification was reduced to a minimum in order to avoid possible decomposition of the mercury compounds. Acidity of 0.6N in hydrochloric acid was found suitable and the back-extraction of methyl mercury was quantitative.

As the volume of the final benzene solution has to be reduced to a minimum for chromatographic analysis, the loss of methyl mercury in the evaporation process was also investigated with isotope. When the benzene extract (20 ml) was reduced to 2 ml with vacuum distillation at 60°C and 18″ Hg, the loss of methyl mercury was 10%. The gross recovery of the multi-stage operations assessed by radio-isotope was *ca.* 88%.

Gas chromatography

The GC determination of methyl mercury is based on the extraction of the organo mercurial from water by benzene followed by a selective extraction with cysteine. The methyl mercury in cysteine solution is converted to chloride form and back-extracted to benzene for chromatography. Electron capture detector is used to detect the chloro-mercury compound. The gas chromatographic procedure was basically that of Nishi and Horimoto,[6] with modifications of parameters to achieve the highest sensitivity required for lake water analysis. Methyl and ethyl mercuric chloride show different peaks on the same chromatogram under the same set of instrument conditions. For phenyl mercuric chloride, a shorter column and lower loading of the stationary phase has to be used. The following are the instrument conditions for the analysis of methyl, ethyl and phenyl mercuric chlorides.

Methyl and ethyl mercuric chloride: column: 6 ft. U-shape, glass o.d. 6 mm, packed with 5% DEGS (Diethylene glycol succinate) on Chromosorb W 60/80, acid-washed, and pre-coated with 5% NaCl; temperature: oven

130°C, injection port 145°C; carrier gas: N_2 at 70 ml/min; detector: ^{63}Ni electron capture detector operated at 50 V pulse mode at 200°C; electrometer attenuation: 4×10^2; retention time: methyl mercuric chloride 2.5 min, ethyl mercuric chloride 4.5 min.

Phenyl mercuric chloride: column: 4 ft. U-shape, glass, o.d. 6 mm, packed with 2% DEGS (Diethylene glycol succinate) on Chromosorb W 60/80, acid-washed, and pre-coated with 5% NaCl; temperature: oven 180°C, injection port 200°C; carrier gas: N_2 at 60 ml/min; detector: ^{63}Ni electron capture detector operated at 50 V pulse mode at 230°C; electrometer attenuation: 2×10^2; retention time: 1.5 min.

Figure 1 shows the chromatogram of methyl and ethyl mercuric chloride; Figure 2 shows a separate analysis of phenyl mercuric chloride. Under the above-mentioned operation conditions, the sensitivity for the analysis of methyl mercury in lake water is 0.003 ng (absolute) which is equivalent to 0.24 ng/l when 5 l of sample is used. For ethyl and phenyl mercury, the absolute sensitivities are 0.003 ng and 0.035 ng, respectively. The recoveries of ethyl and phenyl mercury from lake water were low and erratic, and the method is not quantitative for their analysis. It has been mentioned, rather, as a potential application for the determination of ethyl and phenyl mercury.

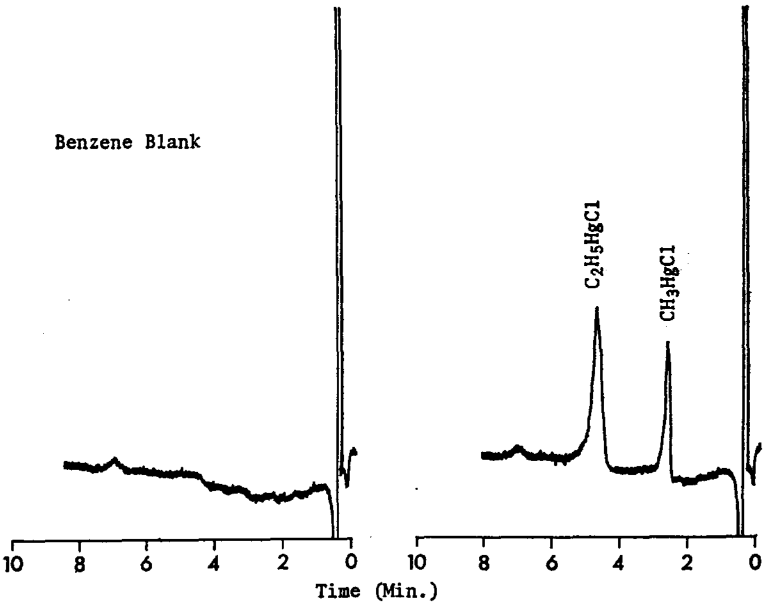

FIGURE 1 Chromatograms of benzene blank, methyl and ethyl mercuric chloride in benzene (0.25 ng injected). GC conditions given in text.

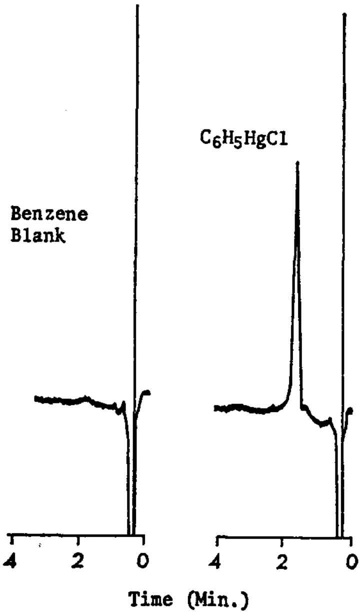

FIGURE 2 Chromatogram of phenyl mercuric chloride in benzene (0.5 ng injected). GC conditions given in text.

Confirmation tests

The methyl mercuric chloride peak on the chromatogram was identified by the confirmation tests of Jensen[7] and Nishi and Horimoto.[8] As the level of these mercury compounds in water is extremely low (*ca.* 1 ng/l) and the quantities injected into this gas chromatograph are at the picogram level (*ca.* 25 pg), it is not feasible to have the GC peaks identified by the more positive confirmation method using the GC/MS system as described by Johansson *et al.*[9] It is customary that about 10^{-8} g of material injected is required for satisfactory GC/MS identification.

Recovery of methyl mercury and other organomercurials at low levels

The recovery of sub-ppb levels of methyl, ethyl and phenyl mercuric compounds from lake water by the above extraction procedure was evaluated by the GC technique. These compounds were individually and simultaneously spiked to 5 l of filtered lake water, then acidified and extracted accordingly. To assess the recoveries of each compound the GC peak heights of the

TABLE I

Recovery of organic mercury compounds from lake water samples (5 l)

Mercury compound	Spiked (mcg)	Found (mcg)	% Recovery
CH_3HgCl	0.05	0.05	100
CH_3HgCl	0.25	0.21	84
CH_3HgCl	0.50	0.45	90
CH_3HgCl	0.75	0.65	87
C_2H_5HgCl	0.40	0.23	57
C_6H_5HgCl	1.0	0.26	26
C_6H_5HgCl	2.0	0.32	16
Multiple spikes			
CH_3HgCl	0.4	0.33	82
C_2H_5HgCl	0.4	0.23	57
C_6H_5HgCl	3.0	0	0
Multiple spikes in distilled water			
CH_3HgCl	0.4	0.37	92
C_2H_5HgCl	0.4	0.38	94
C_6H_5HgCl	3.0	2.61	87

recovered compounds were compared with those of standard solutions which are made up by dissolving weighed amounts of these compounds in benzene. Results (summarized in Table I) indicated that the recovery of methyl mercuric chloride was satisfactory. Neither ethyl nor phenyl mercury were quantitatively recovered from lake water, probably due to hydrolysis of these compounds.

The precision of the method was evaluated by five replicate analyses of the same sample spiked with 0.004 ppb of methyl mercury. The coefficient of variation was 10%.

The technique has been applied to samples from several lakes in Canada, *viz.*, Lake St. Clair, St. Clair River, Saskatchewan River, Pinchy Lake, B.C., and Clay Lake, Kenora, where very high mercury in fish has been previously reported.[10] Methyl mercury was found only in the following samples: Lake St. Clair, 0.6 ng/l; Clay Lake, Kenora, 0.5 ng/l (central lake), 1 ng/l (near shore); Pinchy Lake, B.C., 1.7 ng/l. No ethyl or phenyl mercury was found. No methyl mercury has been found in any of the four Great Lakes.

Interference

Sulfides, thiosulfate and organic thio-compounds interfere seriously with the extraction of methyl mercuric compounds. Several studies[11,12] have been reported regarding the elimination of these interferences. However, all these compounds have not been found to be present in significant quantities in lake water and such interferences are not expected in lake water analysis. For the analysis of these compounds in industrial effluents, sulfur compounds have to be removed.

Storage of samples

Methyl mercuric compounds are stable in acidic medium but will change to dimethyl mercury in alkali solution and become volatile.[13] It is for this reason that methyl mercury should be kept in acidic solution.

The storage of samples was investigated by spiking 0.05 mcg/l of methyl mercuric chloride to a filtered lake water sample and acidified to 0.1 N with sulfuric acid. It was found that the sample can be stored in polyethylene bottles for up to at least one week without loss of methyl mercury. Because of the low and erratic recoveries of ethyl and phenyl mercury compounds in lake water their storage was not investigated.

Acknowledgments

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