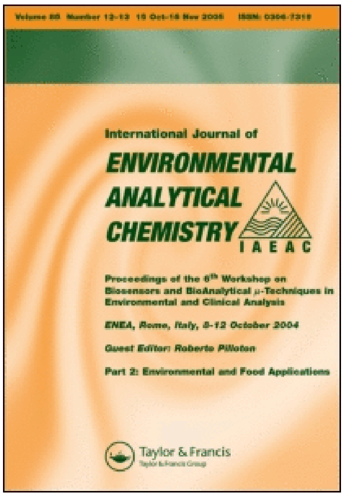

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# Differential Determination of Alkylmercury and Inorganic Mercury in River Sediment

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# Differential Determination of Alkylmercury and Inorganic Mercury in River Sediment

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Steam distillation for differentiation of inorganic mercury and alkylmercury, connected to mercury measurement by flameless atomic absorption spectrometry, was effective and suitable for river sediments. Sulfur in sediments interfered in the determination, but increasing the hydrochloric acid concentration in the procedure eliminated the interference. With this technique down to 2.5 ppb of mercury in sediment can be determined.

KEY WORDS: Mercury determination, steam distillation, river sediment, sulfur, clay.

## INTRODUCTION

In recent years, it has been reported that the methylmercury exists in river sediments, so a differential quantitative determination of alkylmercury and inorganic mercury has been sought in order to clarify the behaviour of mercury in sediment.

As a method for quantitative determination of mercury in sediments, atomic absorption photometry with a wet digestion as pretreatment has been used for total mercury and gas chromatography (electron capture detector) following extraction with benzene for alkylmercury.[1] However, the extraction process of alkylmercury is complicated, and especially there is a disadvantage that emulsion is formed in the extraction. Mitani, one of the authors, already obtained good results in the fractional determination of mercury in human blood by means of the steam distillation.[2] In this paper we investigated the applicability of this method for river sediments. As components of sediments we have clay, humic acids and sulfides which are considered to interfere with the measurement of mercury, therefore their effects on the measurement were examined and eliminated. The method was actually applied to the river sediment and good results were obtained.

# EXPERIMENTAL

## 1. Apparatus

All parts of the steam distillation equipment used for the measurement were made of glass.

The atomic absorption spectrometer (Hitachi 208) coupled with a chart recorder to measure the absorbance as peak height, was used. The closed digestion apparatus used for the residue of the distillation was described earlier.[3]

## 2. Reagents

1) Methylmercury standard solution (0.1 ppm as Hg): methylmercury standard solution was freshly prepared from the stock solution (1000 ppm as Hg) with dilution before experiments. The stock solution was kept in the dark.

Each standard solution of ethylmercury, phenylmercury and inorganic mercury was freshly prepared from each stock solution in the same manner above.

2) 40% $NH_2OH \cdot HCl$ solution: 40 g of $NH_2OH \cdot HCl$ was dissolved in distilled–deionized water to make 100 ml and the solution was rinsed with a suitable amount of a 1% dithizone chloroform solution.

3) HCl, $HNO_3$ and $KMnO_4$: These were all analytical grade.

4) All other reagents were analytical grade available commercially.

## 3. Samples

1) Clays: Bentonite and Kibushi clay were obtained from Gifu Prefectural Ceramic Research Institute. Kibushi clay was produced in the Tono district of the Gifu prefecture.

2) Humic acid: Humic acid was obtained from Nakarai Kagaku Co. as a commercial reagent.

3) Sediments: The sediment collected at a site along Suimon river, a branch river belonging to the Ibi river water system in Gifu prefecture, was wet-sieved. A part of the sediment passed through a 0.074 mm screen was used for the experiments.

## 4. Procedures

### (1) *Quantitative determination of alkylmercury*

5 to 10 g of the sediments were weighed accurately in a conical beaker, and 50 ml of 2N–HCl solution and 10 g of NaCl were added. The mixture was stirred well with a glass rod and was left to stand still for about 1 hour, and then transferred into a distilling flask with thorough washing with a small amount of distilled–deionized water. The steam distillation was continued to make the final amount of 200 ml of the distillate. The distillate was collected in the flask in which 10 ml of 2N–HCl solution was put in advance and the tip of the condenser was submerged in the solution. 50 ml of the distillate was measured and put into the reaction vessel, and 5 ml of saturated solution of NaOH, 3 ml of 1 % $CuSO_4 \cdot 5H_2O$ and 2 ml of 10 % $SnCl_2$ solution were added to the distillate, and then the vessel was closed with the lid and slightly shaken. The vessel was coupled to a measuring cell for the determination of mercury by flameless atomic absorption spectrophotometry.

### (2) *Quantitative determination of inorganic mercury*

After cooling the residue in the distillation flask, distilled–deionized water was added to make the solution a definite volume. The solution was transferred into a flat flask and attached to the closed type wet digestion apparatus. Then 20 ml of $HNO_3$ was added to the solution; the mixture was stirred and heated at 130 °C for about 2 hours. After cooling the solution, 2 g of $KMnO_4$ was directly added into the flask by dividing them into equal lots of approximately 0.5 g. In this process, the violet brown color of $KMnO_4$ should remain in the solution. After $KMnO_4$ was added, the solution was heated for about 30 minutes, and after cooling and detaching the flask from the apparatus, 40 % $NH_2OH \cdot HCl$ solution was carefully added dropwise to decolorize the $KMnO_4$ solution. Distilled–deionized water was added to the digested solution to make it a definite amount, and 50 ml of the solution was measured and put into a reaction vessel, and 10 ml of sulfuric acid solution (sulfuric acid:water = 1:1) and 2 ml of 10 % $SnCl_2$ solution were added. Mercury was measured in the same way as the alkylmercury. When too much foam was formed in the vessel, a few drops of tri-*n*-butyl phosphate was added as defoaming reagent.

### (3) *Calibration curve*

In order to verify the precision of our method, the calibration curve was obtained by performing the analysis on the standard solution of methylmercury and inorganic mercury. The calibration curves of ethylmercury and phenylmercury were also obtained.

## 5. Effect of clay on the quantitative determination of alkylmercury

As methylmercury is reported to be highly adsorbed on clays,[4] the possibility of measurement of the adsorbed methylmercury on the clay was examined.

### (a) *Adsorption of methylmercury on the clay*

1.0, 2.0 and 3.0 ml of the methylmercury standard solution were put into three stoppered Erlenmeyer flasks respectively, and distilled–deionized water was added to make each 100 ml of the aqueous solution. 5 g of the clay was added to each flask and stirred for 6 hours. Subsequently, centrifugal separation at 3000 rpm was carried out to separate the clay and the solution, and then mercury concentration in the supernatant was measured by flameless atomic absorption photometry. The same procedure except no addition of the clay was carried out. The mercury adsorption rate was calculated from these results.

### (b) *The effect of clays on the measurement*

0 (as blank), 1, 3 and 5 ml of methylmercury standard solution were put into each flask, and distilled–deionized water was added to each flask to make the solution 35 ml. 2.5 g of bentonite was put into each flask and stirred for 6 hours, and then the quantitative determination was performed by the steam distillation method described above. The recovery rate was obtained on the basis of the calibration curve. The same experiment was performed on the Kibushi clay.

## 6. Effect of humic acid on the measurement

As humic acid is known to have a high adsorption capacity for methylmercury,[5] the effect on the determination was investigated.

Humic acid was weighed in several amounts from 1 to 50 mg and each was suspended in 35 ml of water. 4 ml of methylmercury standard solution was added to each suspended solution, and left for about 12 hours with stirring. Then the steam distillation was performed to measure the mercury content. The recovery rate was calculated on the basis of the mercury content of the sample added to humic acid.

Alkylmercury was not detected in 500 mg of the humic acid.

## 7. Effect of sulfides on the determination of alkylmercury

Sodium sulfide, zinc sulfide and iron sulfide were tested. 4 ml portions of the methylmercury standard solution were added to the various amounts of sulfides varied from 0.3 to 70 mg (as sulfur) and the mercury contents were determined.

The same procedure without addition of sulfides was performed, and the mercury content found in this case was taken as 100% recovery.

## 8. Elimination of the effect of sulfides

### (1) *Increase of concentration of* $SnCl_2$ *(reducing agent) solution*

The concentration of the stannous chloride solution was increased to eliminate the interference. 10, 20 and 30% $SnCl_2$ solutions were prepared and tested on the distillate of the mixture of zinc sulfide and 4 ml of methylmercury standard solution.

### (2) *Increase of the concentration of* $CuSO_4 \cdot 5H_2O$ *solution (reducing-aid reagent)*

1, 3, 5 and 8% $CuSO_4 \cdot 5H_2O$ solution were prepared and tested.

### (3) *Increase of hydrochloric acid concentration in the case of steam distillation*

To remove sulfides in sediment samples the concentration of hydrochloric acid was increased. Mitani[2] had found that the hydrochloric acid concentration up to 5N had no effect on the steam distillation and the measurement, hence a 4N–HCl solution was adopted.

The mixture of 4 ml of the methylmercury standard solution and zinc sulfide was used as a sample, and 2N–HCl was replaced with 4N–HCl in the procedure.

## 9. Application to river sediment samples

0, 1, 2, 3, 4 and 6 ml of the methylmercury standard solution were added to each 5 g portion of the river sediment. The mixtures were analyzed by this method.

# RESULTS AND DISCUSSIONS

## 1. Calibration curves

The calibration curves of methylmercury and ethylmercury obtained with this procedure are shown in Figure I. Both curves show linearity in the range from 0.025 to 0.20 $\mu$g. If a detection limit is set on 0.025 $\mu$g Hg and

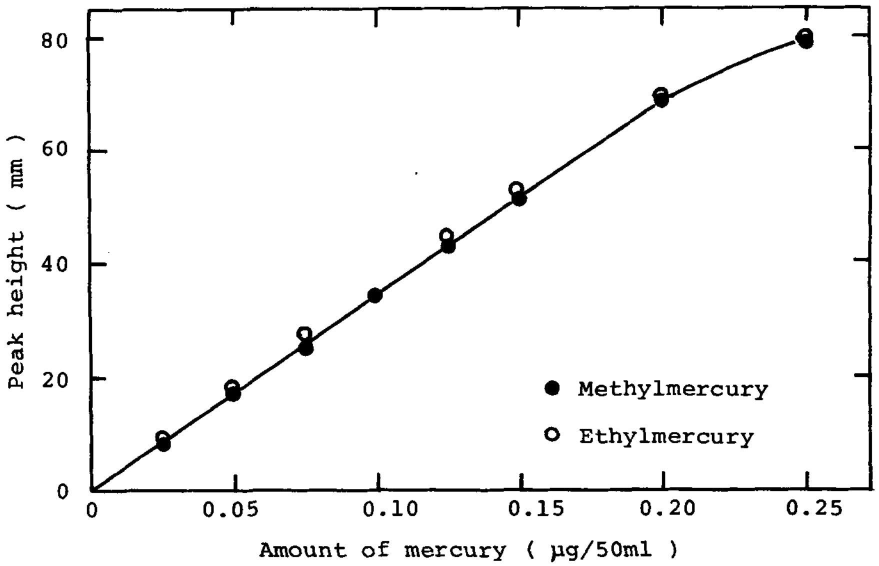

FIGURE 1 Calibration curves of methylmercury and ethylmercury.

10 g of sediment is analyzed, down to 2.5 ppb of mercury can be determined with this method in the sediment.

The calibration curve of inorganic mercury showed linearity in the range from 0.025 to 0.20 μg.

Phenylmercury was not found in the distillate.

## 2. Effect of clay on the methylmercury determination

Methylmercury up to 0.3 μg (as Hg) was completely adsorbed on 5 g of the clay.

As it was observed that bentonite and Kibushi clay had a large adsorption capacity for methylmercury, it was investigated if the adsorbed methylmercury could be completely released, distilled and measured.

As shown in Table I, the adsorbed methylmercury was well recovered by the measurement.

## 3. Effect of humic acid on the methylmercury determination

The results in Figure 2 show a slight decrease in the height of peaks when 5 to 50 mg of humic acid are added. However, when the amount of humic acid increases, an improved recovery is observed. The reason for this is

TABLE I

Recovery of the adsorbed methylmercury

| | Added and adsorbed methylmercury ng | Detected methylmercury ng | Recovery % |
|---|---|---|---|
| Kibushi clay | 50 | 48 | 96.0 |
| | 150 | 144 | 96.0 |
| | 250 | 243 | 97.2 |
| Bentonite | 50 | 54 | 108.0 |
| | 100 | 93 | 93.0 |
| | 200 | 191 | 95.5 |
| | 250 | 238 | 95.2 |

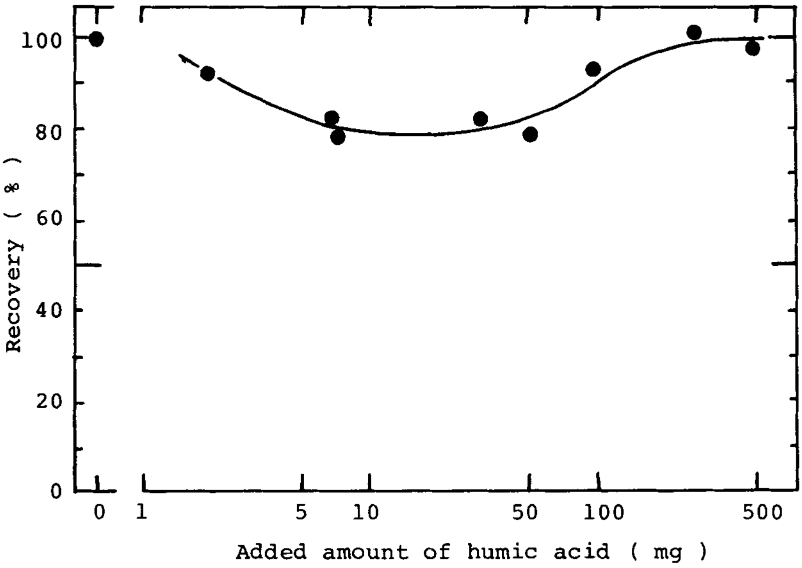

FIGURE 2 Effect of humic acid on the determination of methylmercury.

not clear, but as the recovery rate was always over 80%, no serious effect for the measurement is expected.

## 4. Effect of sulfides on the methylmercury determination

When using sodium sulfide, zinc sulfide and iron sulfide, the recovery rate became worse when the sulfur content increased over 1 mg, and the rate decreased as the sulfur content increased, as shown in Figure 3. The

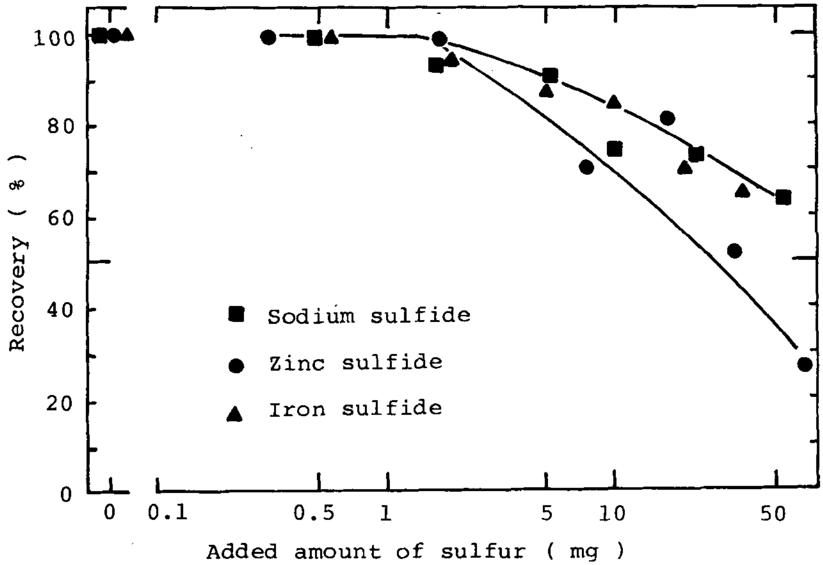

FIGURE 3 Effects of zinc sulfide, sodium sulfide and iron sulfide on the determination of methylmercury.

decrease was speculated to be caused by the sulfur in the distillate, hence the sulfur content was increased in the distillate to observe this effect. As expected, the recovery rate was reduced and there was such a strong effect that when the sulfide content in the distillate exceeded 10 mg no peaks appeared.

## 5. Elimination of the effect of sulfides

It was tried to eliminate the sulfides as $H_2S$ gas before distillation by adding a 4N-HCl solution.

The results are shown in Figure 4. The effects of up to 67.3 mg sulfur content were eliminated. The recovery rate showed 90 to 100%.

As 70 mg of sulfur corresponds to 7,000 ppm for 10 g of the sediment, the effect of sulfides can be considered negligible in sediments having high sulfur contents.

## 6. Application to river sediments

Figure 5 shows the recovery for inorganic mercury and methylmercury spiked separately in river sediments. When mercuric chloride was spiked to the river sediment with a concentration range from 0 μg/1 g of sediment to 6.0 μg/1 g of sediment, most mercury detected was in the inorganic mercury form and the spiked mercury was well recovered. Alkylmercury was detected but the concentration was nearly constant (about 20 ppb). When methylmercury was spiked to the river sediment with a concentration range from 0 μg/10 g of sediment to 0.6 μg/10 g of sediment, the

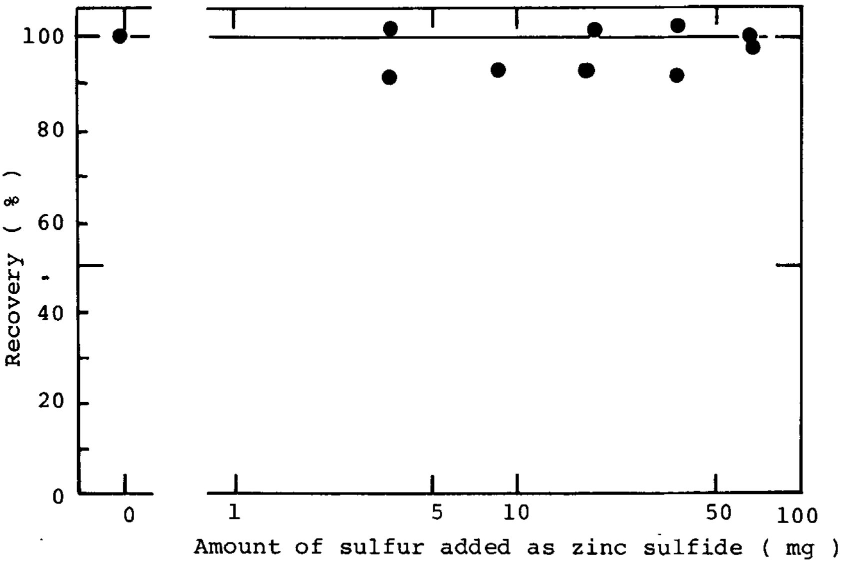

FIGURE 4 Elimination of the effect of sulfide on the determination of methylmercury by adding 4N HCl instead of 2N HCl.

methylmercury was detected as alkylmercury. The concentrations of inorganic mercury were around 100 μg/10 g of the sediment.

Several samples, which were collected along the Suimon river, were analyzed by the method and the results are shown in Table II. The concentrations are rather high, because the Suimon river used to be heavily polluted by the mercury discharged from a chemical plant.

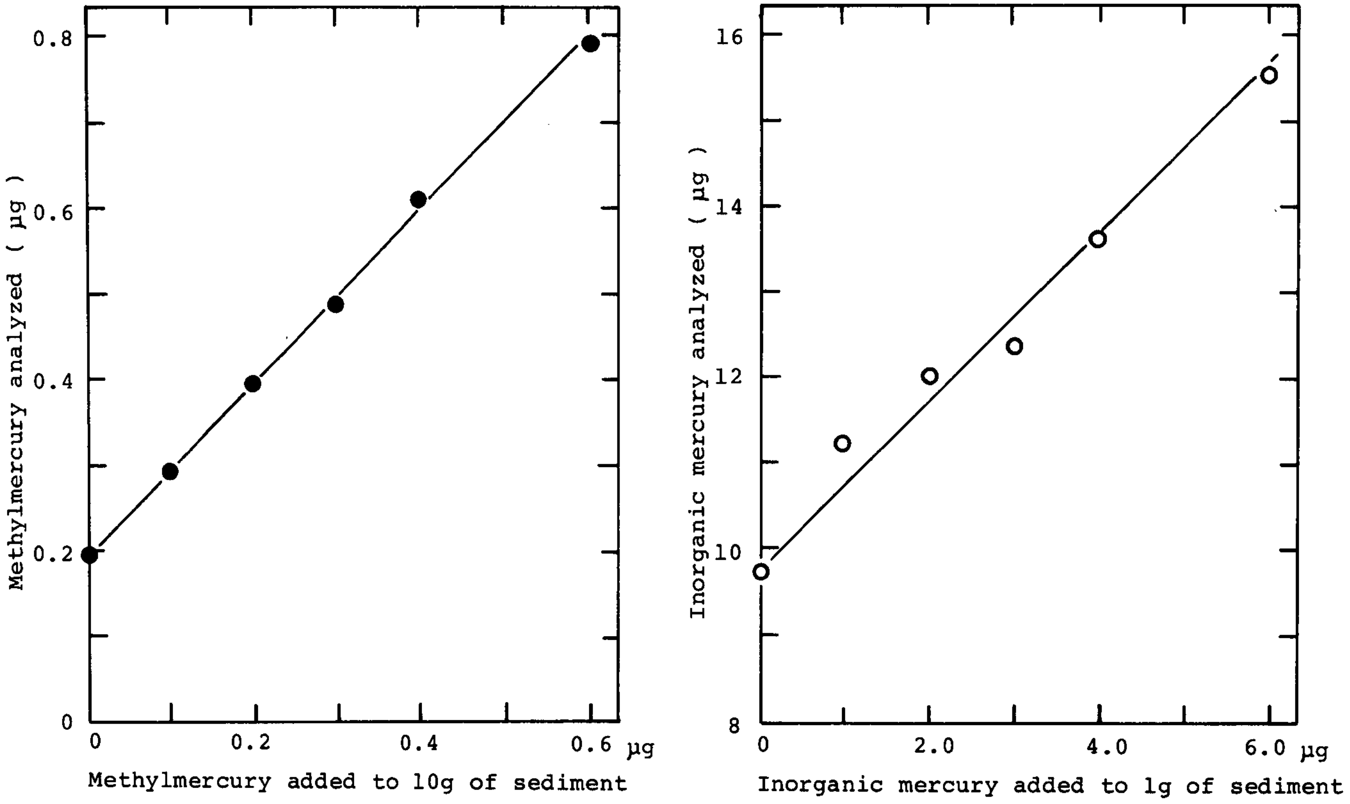

FIGURE 5 Inorganic mercury and methylmercury recovery test.

TABLE II

Mercury concentration in the river sediments

| Sample | Alkylmercury concentration (ppb) | Inorganic mercury concentration (ppm) | Proportion of alkylmercury to total mercury (%) |
|---|---|---|---|
| a | 14 | 10.46 | 0.13 |
| b | 10 | 9.43 | 0.11 |
| c | 3 | 15.95 | 0.02 |
| d | 24 | 16.95 | 0.14 |

## References

1. The Water Quality Bureau, Environment agency (Japan): *Methods for the Survey of Bottom Sediments*, pp. 6–13 (1975).
2. K. Mitani, *Journal of Hygienic Chemistry* **22,** 65 (1976).
3. *Official Methods of Analysis of A.O.A.C.* (11th edition), 418 (1970).
4. R. S. Reimers and P. A. Krenkel, *Journal of the Water Pollution Control Federation* **46,** 352 (1974).
5. H. Yoshida, K. Kumegawa and S. Arita, *Journal of the Chemical Society of Japan*, 785 (1976).