

Rapid Determination of Mercury Species in Sewage Sludge by High-Performance Liquid Chromatography On-line Coupled with Cold-Vapor Atomic-Fluorescence Spectrometry after Ultrasound-assisted Extraction

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So far, no research has been focused on the determination of organomercuries in sewage sludge. Here, an ultrasonic extraction method for the rapid determination of methylmercury (MeHg) and ethylmercury (EtHg) in sewage sludge after ultrasound-assisted extraction is proposed. Using TMA (tetramethylammonium hydroxide) as the extractant with 3.0 g copper powder, ultrasonic extraction for 30 min at 70°C demonstrated to be highly efficient, and was shown a satisfied extraction efficiency for MeHg and EtHg from sewage sludge samples. Determination of mercury species was carried out by high-performance liquid chromatography on-line coupled with cold-vapor atomic fluorescence spectrometry (HPLC-CV-AFS). The obtained results from quality control samples were excellent. The proposed method was also validated by the application to five real samples. The results showed that the developed methodology was practicable and highly reliable. Due to the high toxicity of organomercuries and huge amounts of sewage sludge discharged every year, people should pay particular attention to pollutions from sewage sludge.

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Introduction

Mercury is a toxic element that is present in the environment in different kinds of forms. Totally, there are organic and inorganic species. Among these species, people pay particular attention to methylmercury (MeHg) and ethylmercury (EtHg). They are more toxic than other species, and can be transported and transformed under different kinds of environmental conditions.¹⁻³ They can be accumulated through food chains, and both of them have been detected in biological and environmental samples.⁴⁻⁶

Sewage sludge is a by-product of waste-water treatment plants. It contains many toxic components, such as heavy metals, pesticides, PCB (polychlorinated biphenyls), PBDE (polybrominated diphenyl ethers), PAHs (polycyclic aromatic hydrocarbons) and bacteria. Due to the relatively high contents of toxic components and huge amounts of sewage sludge discharged every year, the disposal of sewage sludge is a great problem all over the world, and many researchers have focused on the biological and environmental risks of sewage sludge.^{7,8}

Mercury species in environmental and biological samples are usually determined by hyphenated techniques based on on-line coupling chromatography separation with element-specific detectors. The most frequently used element-specific detectors are atomic fluorescence spectrometry (AFS) and inductively coupled plasma mass spectrometry detectors. Since AFS is relatively cheaper, and its running cost is lower, it has become a very popular detector in mercury determination.^{9,10} The

advantages of high-performance liquid chromatography (HPLC) are the separation of mercury species without prior derivatization and operations at ambient temperature. Therefore, determination using HPLC on-line coupled to AFS (HPLC-AFS) is a most useful technique for mercury speciation analysis.^{11,12}

For mercury speciation analysis in environmental and biological samples, the vital step is to extract the target species from sample matrices in their original forms without any disturbances. For environmental and biological samples, there are two main methods: acid leaching and alkaline digestion. Acid leaching is to use the mineral acid (such as HCl or H₂SO₄) together with several assisted extractants (such as Cu²⁺, Cl⁻, Br⁻) to chelate or replace the mercury species from the original sample matrices.¹³⁻¹⁵ This method is usually used for soil or sediment samples. The following procedures are conducted to clean and preconcentrate the target mercury species before their analysis. Usually, organic solvents are added to extract the organic forms and to eliminate the inorganic mercury from the acidic matrices.¹⁶⁻¹⁸ Na₂S₂O₃ is thus for the back-extraction of the target species from organic solvents. The Na₂S₂O₃ phase can be directly injected into the instrumental analysis system or cleaned for further use. Alkaline digestion is to use KOH (or NaOH) in an organic solvent (usually CH₃OH) or TMA (tetramethylammonium hydroxide) solution to extract the mercury species from the original sample matrices.^{19,20} This method is usually used for biological samples. The following procedures for alkaline digestion are almost the same to those of acid leaching. The only difference is that the alkaline sample matrices should be neutralized to the acidic condition before organic solvents are added.

Ultrasonic extraction is widely used for different sample

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matrices. It is highly effective, requires less extraction time and is not laborious compared to routine extraction methods.²¹⁻²³ So far, no literature has been published on the determination of organomercuries in sewage sludge samples. Furthermore, the detection of organomercuries will help us to understand the processes of the waste water treatments and the pollutions from sewage sludge disposals. Therefore, it is very necessary to develop a systematic, rapid and sensitive ultrasonic method for the determination of mercury species in sewage sludge samples.

The aim of the present work was to set up a systematic, simple, rapid and sensitive method for the determination of mercury species in sewage sludge samples after ultrasonic extraction. The experiments were based on comparing different extractants, including TMA, KOH/CH₃OH, HCl, and CuSO₄/KBr for different extraction times at different temperatures.

Experimental

Apparatus

The chromatographic system was an Agilent 1100 Model (Santa Clara, CA) with a Rheodyne Model 7725i injection valve (Oak Harbor, WA) including a 20- μ l sample loop. For mercury speciation, a reversed phase column (Agilent ZORBAX XDB-C18, 2.1 \times 50 mm, 5 μ m) was used during the experiments. The mobile phase was composed of 5% (v/v) CH₃OH, 60 mM CH₃COONH₄ and 0.1% (v/v) 2-mercaptoethanol in ultra-pure water.

A CV-AFS system comprising an AF-610D nondispersive atomic fluorescence spectrometer (Beijing Raileigh Analytical Instrument Co., Beijing, China) equipped with a high-intensity hollow cathode lamp, two peristaltic pumps and a gas-liquid separation chamber was employed. The effluent of the separation column was mixed with an oxidizing agent (K₂S₂O₈ in HCl) and introduced to a PTFE digestion coil (i.d. 0.8 mm) that was wrapped around an 8 W UV lamp. The organic mercury species were decomposed to the inorganic form in this digestion coil under UV irradiation. Then, the reducing agent (KBH₄ in KOH) was introduced into the effluent of the digestion coil. The inorganic mercury was reduced to mercury vapor. The produced vapor was separated by a gas-liquid separation chamber, delivered by argon gas, and detected by AFS. AF-610D software was installed into a personal computer to control the whole system and to record the detection signals. All HPLC-CV-AFS conditions are given in Table 1.

All ultrasonic extractions in this experiment were made by an ultrasonic generator (KUDOS, 250 W power, 50 Hz, Shanghai, China).

Reagents and chemicals

Stock solutions of 1000 mg L⁻¹ methylmercury chloride (Merck, Whitehouse Station, NJ) and ethylmercury chloride (Merck) were prepared in methanol and stored at 4°C. Working solutions were prepared on the day of use.

Acidic KBr solution: 18 g of KBr and 5 ml of concentrated H₂SO₄ were dissolved in water, and then diluted to 100 ml.

1 mol L⁻¹ CuSO₄ solution: 25 g of CuSO₄·5H₂O was dissolved in water, and then diluted to 100 ml.

0.5% KBH₄ (m/v) solution: 5 g of KBH₄ and 2 g of KOH in 1 L ultra-pure water.

0.8% K₂S₂O₈ (m/v) solution: 8 g of K₂S₂O₈ and 100 ml of concentrated HCl in 1 L ultra-pure water.

All reagents used were of at least analytical grade. Ultra-pure water was obtained from EASYpure LF system (Dubuque, IA) and used throughout this experiment.

Table 1 HPLC-CV-AFS conditions in the experiment

HPLC	
Column	Agilent ZORBAX XDB-C18 column, 2.1 \times 50 mm, 5 μ m
Mobile phase	5% (v/v) CH ₃ OH; 60 mmol l ⁻¹ CH ₃ COONH ₄ ; 0.1% (v/v) 2-mercaptoethanol
Flow rate of mobile phase	0.4 ml min ⁻¹
Injection volume	20 μ l
Cold vapor generation	
Oxidizing solution	0.8% (m/v) K ₂ S ₂ O ₈ in 10% (v/v) HCl, 3.0 ml min ⁻¹
Reducing solution	0.5% (m/v) KBH ₄ in 0.2% (m/v) KOH, 2.4 ml min ⁻¹
AFS	
Lamp	Hollow cathode mercury lamp, 253.7 nm
PMT voltage	280 V
Primary current	30 Ma
Carrier gas	Argon, 500 ml min ⁻¹

Sample extraction

Sewage sludge samples were all freeze-dried, crumbled, pulverized with a mill into powder and stored at -20°C.

Four extraction solvents: TMA in water (25%, m/v), KOH/CH₃OH (25%, m/v), 6 M HCl and acidic KBr/CuSO₄ (3:1, v/v), were used for the extraction of organic mercury species from sewage sludge samples in the experiment. Sample blanks were simultaneously done. For spiked recovery experiments, 10 ng of MeHg and EtHg standard solutions were added into homogenized samples 12 h before extractions.

Ultrasonic extraction

Final 2.0 g of sewage sludge sample was weighed inside a 40-ml glass centrifuge tube. In each case, 5 ml of water with 4 ml of acidic KBr/CuSO₄, 5 ml of 6 M HCl, 4 ml of TMA or 4 ml of KOH/CH₃OH were used as the extractant, respectively. After the tube was ultrasonicated for 30, 60, 90, 120, 150, 180 min, respectively, 10 ml CH₂Cl₂ was added in order to extract the organic mercury species from the water phase (for TMA and KOH/CH₃OH, 3 ml concentrated HCl was added before CH₂Cl₂). The tube was mechanically shaken for 1 h and centrifuged for 20 min at 3500 rpm. After 4 ml of the organic phase was transferred into a 10-ml glass centrifuge tube, 1 ml 10 mM Na₂S₂O₃ was added into the 10-ml tube to extract the mercury species from the organic phase. The tube was shaken for 1 h and centrifuged for 20 min at 3500 rpm. After 0.8 ml of the Na₂S₂O₃ phase was transferred into a 2-ml PE centrifuge tube, the 2-ml tube was centrifuged for 20 min at 12000 rpm. Finally, the tube was stored at 4°C before direct injection into the HPLC-AFS system.

Speciation of mercury

The speciation of mercury was performed by a HPLC-CV-AFS on-line coupling system. Mercury species in Na₂S₂O₃ phase were directly injected into the HPLC-CV-AFS system. Their signals were recorded by the software. Sample peaks in the chromatograms were identified by their retention times. Standard chromatograms of MeHg and EtHg at 100 ng ml⁻¹ in standard solution are shown in Fig. S1. The sensitivity for MeHg was higher than that for EtHg due to the relatively long retention time and peak tailing of EtHg.

Results and Discussion

Optimization of HPLC-AFS parameters

The oxidant was $K_2S_2O_8$ in 10% HCl (v/v) and the reductant was KBH_4 in 0.2% KOH (m/v). Their concentrations significantly influenced the generation efficiency of mercury vapor. A relatively high $K_2S_2O_8$ concentration would lead to higher background and poor sensitivity, and a low concentration would result in a low organic mercury decomposition efficiency under UV irradiation. Figure S2 shows the optimization results of the $K_2S_2O_8$ concentration in 10% HCl (v/v) and KBH_4 concentration in 0.2% KOH (m/v) in order to obtain the highest sensitivity. $K_2S_2O_8$ (0.8%, m/v) in 10% HCl (v/v) and 0.5% KBH_4 (m/v) in 0.2% KOH (m/v) were chosen as the optimized concentrations for MeHg determination. Similar results were also obtained for EtHg determination. These optimized concentrations were used throughout this experiment.

Argon was used as a carrier gas to deliver the generated mercury vapor for detection. The flow rate of argon would influence the sensitivity of AFS and the retention time of the mercury species. Figure S3 shows the optimized flow rate of argon gas. The result was 500 ml min^{-1} . This optimized flow rate was used throughout this experiment.

Other parameters were also optimized, and are listed in Table 1.

Extraction efficiencies for ultrasonic methods

For ultrasonic extraction, the organic mercury compounds would be unstable, and decomposed by ultrasound.²⁴ Thus, when the extraction time was increased to a specific value, the extraction recovery would increase to be the highest.

Acidic KBr/CuSO₄. The extraction recoveries of MeHg and EtHg using acidic KBr/CuSO₄ as the extractant for different durations of ultrasonic treatment from sewage sludge samples are shown in Fig. S4. The highest recoveries for MeHg and EtHg were 57.1 ± 4.0 and $52.4 \pm 3.7\%$ for an extraction time of 120 min, respectively.

6 M HCl. The extraction recoveries of MeHg and EtHg using 6 M HCl as the extractant for different durations of ultrasonic treatment from sewage sludge samples are shown in Fig. S5. The highest recoveries for MeHg and EtHg were 63.9 ± 2.5 and $58.1 \pm 3.6\%$, respectively.

TMA and KOH/CH₃OH. The extraction recoveries of MeHg and EtHg using TMA or KOH/CH₃OH as the extractant for different durations of ultrasonic treatment from sewage sludge samples are shown in Fig. S6. The highest recoveries for MeHg and EtHg were 71.5 ± 4.6 and $67.9 \pm 3.6\%$, respectively.

Changing the ultrasonic extraction temperature

The previous ultrasonic extractions were all performed at room temperature (about 19.8°C). The temperature was an important factor that would influence the extraction efficiency of mercury compounds.²⁵ In this experiment, we chose 0°C , room temperature (about 19.8°C), 45 and 70°C to investigate whether satisfactory recoveries of MeHg and EtHg could be obtained.

Figure S7 shows the extraction recoveries of MeHg and EtHg from sewage sludge samples using acidic KBr/CuSO₄ as the extractant for different ultrasonic times at different temperatures. The highest recoveries for MeHg and EtHg were 72.1 ± 3.1 and $72.6 \pm 3.9\%$ for 180 min at 70°C , respectively.

Figure S8 shows the extraction recoveries of MeHg and EtHg from sewage sludge samples using 6 M HCl as the extractant for different ultrasonic times at different temperatures.

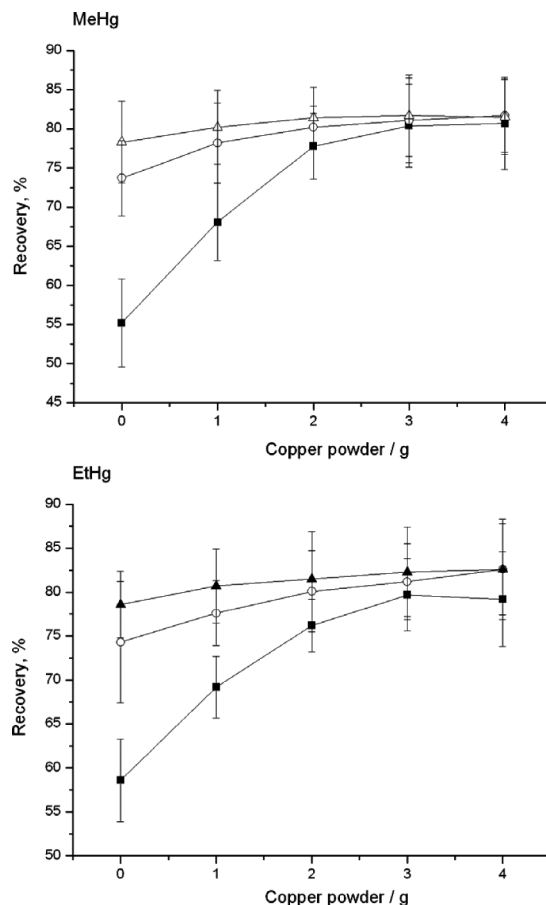


Fig. 1 Extraction recoveries of MeHg and EtHg from sewage sludge using TMA as the extractant at 70°C for 30, 60 and 90 min of ultrasonic treatment by adding different mass of copper powder. ■, 30 min; ○, 60 min; △, 90 min.

The highest recoveries for MeHg and EtHg were 79.7 ± 4.6 and $79.2 \pm 4.2\%$ for 180 min at 70°C , respectively.

Figure S9 shows the extraction recoveries of MeHg and EtHg from sewage sludge samples using KOH/CH₃OH as the extractant for different ultrasonic times at different temperatures. MeHg and EtHg could be extracted in less than 150 min for recoveries of 80.1 ± 3.7 and $80.5 \pm 3.5\%$, respectively.

Figure S10 shows the extraction recoveries of MeHg and EtHg from sewage sludge samples using TMA as the extractant for different ultrasonic times at different temperatures. MeHg and EtHg could be extracted in less than 120 min for recoveries of 80.9 ± 7.2 and $80.0 \pm 5.5\%$, respectively.

Among these four extractants, TMA was chosen to be the most suitable extractant due to its shorter extraction time for 120 min and satisfactory extraction efficiency of 80.9 ± 7.2 and $80.0 \pm 5.5\%$ for MeHg and EtHg, respectively.

Copper powder

We then investigated other chemicals added to accelerate the extraction process. Sulfur is abundant in sewage sludge, and mercury species usually bind to this element. Copper powder was always used to replace the mercury species from the sample matrices.²⁶ Here, we added the copper powder to find whether the extraction process could be accelerated.

Figure 1 shows the extraction recoveries of MeHg and EtHg from sewage sludge samples using TMA as the extractant at 70°C for 30, 60 and 90 min of ultrasonic treatment by adding

Table 2 Some analytical features of the HPLC-AFS system

Compound	Calibration curve	Correlation coefficient (R^2)	Detection limit (ng mL ⁻¹)/ng	RSD ^a , %
MeHg	$y = 117x - 195$	0.9942	0.1/0.002	2.7
EtHg	$y = 85x + 102$	0.9934	0.2/0.004	3.1

a. Standard concentration, 5 ng mL⁻¹, $n = 5$.

Table 3 Determined values of MeHg and EtHg in IAEA-405 (Estuarine Sediment) (mean \pm SD, ng g⁻¹, $n = 3$)

Certificated material	MeHg		EtHg	
	Recommended value	Determined value	Recommended value	Determined value
IAEA-405	5.49 ± 0.549	5.23 ± 0.319	NA	ND

NA: Not available.

ND: No detection.

different masses of copper powder. For a 30-min ultrasonic treatment, the critical value for the added copper powder was 3 g, and the extraction recoveries reached to satisfactory values of 80.4 ± 5.3 and $79.7 \pm 4.1\%$ for MeHg and EtHg, respectively. For 60 and 90 min ultrasonic treatments, the critical values were 2 and 1 g, respectively. Here, the added copper powder of 3 g accelerated the ultrasonic extraction remarkably, and the extraction time was greatly reduced to only 30 min for satisfactory recoveries.

In these experiments, using TMA as the extractant with 3.0 g of copper powder for 30 min ultrasonic treatment was proved to provide the most efficient and satisfactory extraction efficiencies of MeHg and EtHg from sewage sludge samples. The recoveries of MeHg and EtHg were 80.4 ± 5.3 and $79.7 \pm 4.1\%$, respectively. The extraction time of the proposed method was greatly reduced to only 30 min.

Evaluation of analytical performance

Quality-control samples with the proposed methods were analyzed to evaluate the analytical performance. Excellent results of analyses were obtained. Some analytical features of the HPLC-AFS system are given in Table 2. The absolute detection limits of HPLC-AFS, which were defined as three-times the background, were 2 pg of MeHg and 4 pg of EtHg during a method validation period of 5 analytical batches. The method detection limits in a 2.0-g sewage sludge sample were evaluated at 125 pg g⁻¹ for MeHg and 250 pg g⁻¹ for EtHg. When the extracted sample was 2.0 g, and the added amount of organomercuries was 2.0 ng of Hg as MeHg or EtHg, the precisions were 6.1 and 5.1% RSD, and the mean recoveries were 80.2 and 80.1%, respectively. The analytical performances of the proposed method were comparable with other systems.^{27,28}

Validation of the method

The final sample matrices for injection contained 0.01 mol L⁻¹ Na₂S₂O₃. The influence of the Na₂S₂O₃ matrices on separation and detection was investigated. The results showed that 0.01 mol L⁻¹ Na₂S₂O₃ had no impact on the separation and detection of mercury species. Since there is no certificated reference material (CRM) of sewage sludge available, a certificated reference material (CRM) of IAEA-405 (Estuarine Sediment) was chosen for analysis to validate the proposed

Table 4 Determined results for MeHg and EtHg of five real samples (mean \pm SD, mg g⁻¹, $n = 3$)

Sample	MeHg concentration	EtHg concentration
S1	1.12 ± 0.13	ND
S2	ND	ND
S3	1.03 ± 0.09	ND
S4	0.92 ± 0.09	ND
S5	ND	ND

ND: No detection.

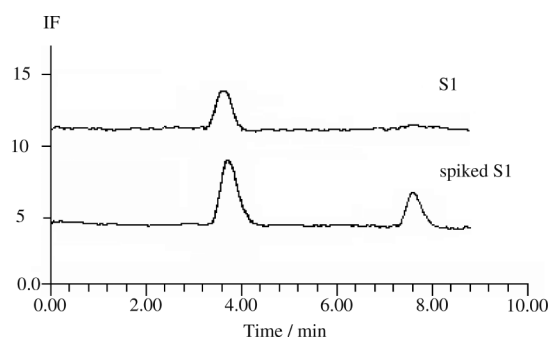


Fig. 2 Chromatograms of sample S1 and spiked S1 (S1 spiked with 2.5 ng MeHg and EtHg).

methodology. The determined values in triplicate of the IAEA-405 and the recommended values are given in Table 3. The obtained concentrations of MeHg in IAEA-405 were in good agreement with the recommended values, and no EtHg was detected in the CRM. The results showed that the developed methodology was practicable and highly precise. Five real samples were analyzed by the proposed ultrasonic extraction method to validate the analytical methodology. The determined results are indicated in Table 4, and two chromatograms are shown in Fig. 2. MeHg was detected in three of five samples. No EtHg was detected in the samples.

Conclusions

The ultrasonic extraction of MeHg and EtHg in sewage sludge samples by comparing different extractants at different temperature using the HPLC-CV-AFS system was successfully performed. Using TMA as the extractant with 3.0 g of copper powder, ultrasonic extraction for 30 min at 70°C was chosen to be suitable for the extraction of MeHg and EtHg from sewage sludge samples with satisfactory recoveries. Excellent results from quality-control samples were obtained. The CRM IAEA-405 was analyzed to validate the proposed methodology. Five real samples were also determined. Because ultrasonic extractions have the advantages of simple pretreatment procedures with less extraction time and high extraction efficiency, and the HPLC-AFS system is highly sensitive with low price and low running cost, ultrasonic extraction coupled with the HPLC-AFS system will have good and wide application prospects in environmental analysis. Besides, due to the high toxicity of organomercuries and huge amount of sewage sludge discharged every year, pollutions from organomercuries of sewage sludge should be paid particular attentions. The results will also help us to understand the processes of waste-water treatment.

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Supporting Information

Figures S1 to S10 are available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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