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Speciation analysis of mercury in natural water and fish samples by using capillary electrophoresis–inductively coupled plasma mass spectrometry

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ABSTRACT

A environment-friendly microwave-assisted extraction used to extract trace mercury compounds from fish samples, and a ultra-sensitive method for the analysis of Hg(II), methylmercury (MeHg) and ethylmercury (EtHg) by using capillary electrophoresis–inductively coupled plasma mass spectrometry (CE–ICP–MS) were described in this study. The extraction method is environment-friendly, simple, effective, and can be used to extract trace mercury compounds in fish samples with a satisfied recovery within several minutes. The CE–ICP–MS analytical method has a detection limit as lower as 0.021–0.032 ng Hg/mL for MeHg, EtHg and Hg(II), and can be used to determined ultratrace MeHg, EtHg and Hg(II) in natural water and fish samples directly without any preconcentration. With the help of the above methods, we have successfully determined MeHg, EtHg and Hg(II) in dried fish (*Tapertail anchovy*) muscle and natural water within 25 min with a RSD (relative standard deviation, $n=6$) <5% and a recovery of 94–103%. Our results showed that dried muscle of *T. anchovy* contained only one species of mercury, MeHg, indicating that MeHg is easier to be accumulated by aquatic organisms.

1. Introduction

Mercury is one of the most toxic elements impacting on human and ecosystem health, the United State Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) have listed mercury and its compounds in the third place on the "Priority List of Hazardous Substances". So far, a lot of researches have shown that any mercury released into the environment undergoes biogeochemical transformation processes and can be converted into the more toxic organic mercury form [1,2]. Therefore, there is a wide range of mercury species exists within natural water, and the chemical form of mercury not only controls its bioavailability and toxicity but also controls its transport and persistence. It was well known that the concentrations of mercury escalate up the food chain because of its high bioaccumulation. For example, predatory fish can have up to 10^6 times higher mercury concentrations than the ambient water and up to 95% of this mercury can be in the form of organic mercury [2]. For above reasons, the World Health Organization (WHO) recommends a maximum intake of methylmercury of 1.6 μg/kg per week and the organomercury compounds were banned from agricultural use in the 1970s in the world [3]. In order to control the effectiveness of these legal provisions and to ensure the safety of aquatic organisms for consumption, it is very important to develop a sensitive and accurate analytical method for the quantification of each species of mercury in natural water and aquatic organisms.

So far, the main techniques used for the speciation analysis of mercury are based on the combination of separation technology and sensitive element-selective detectors. For example, liquid chromatography (LC) and gas chromatography (GC) coupled with atomic fluorescence spectrometry (AFS) [4–8], atomic emission spectrometry (AES) [9,10], and inductively coupled plasma mass spectrometry (ICP–MS) [8,11–14]. However, for ionic Hg species, GC-based techniques require a previous derivatization step due to its low volatility and LC-based techniques require a previous complexation step in order to form non-polar [2]. The derivatization is one of the most critical steps in the speciation analysis of mercury, low yield as well as degradation phenomena in derivatization can heavily affect the quality of the results. LC-based techniques also suffer from the inadequate stability (combined with ICP–MS) and second environmental pollution due to the usage of much organic solvent. In addition, chromatographic separations provide interactions of species between stationary and mobile phase, probably resulting in the destruction of complexes [15,16].

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In comparison with chromatographic techniques, capillary electrophoresis (CE) has several advantages such as higher separation efficiency for all ionic and neutral species, much smaller sample and reagent consumption, no interaction between the sample and the stationary phase, various separation modes and low operating cost etc. [17–19]. Combined with different detectors such as UV-spectrometry [20–22], atomic fluorescence spectrometry (AFS) and ICP–MS [23–27], CE has been tried to use in the analysis of various mercury compounds. However, the combination of CE and UV or AFS has obvious limitations such as lower sensitivity, poorer stability and so on, and CE–ICP–MS methods reported previously can not separate methylmercury (MeHg) and ethylmercury (EtHg) completely and have a lower sensitivity and poorer stability [25–27]. In addition, most chromatography-based methods previously reported are focused on natural water samples whose matrix is relatively simple, the speciation analysis of mercury in aquatic organisms has been few reported [11,12].

The main aim of the present study is to develop a novel method for the simultaneous determination of ultratrace level of MeHg, EtHg and Hg(II) by using CE–ICP–MS and establish a environment-friendly extraction method for the extracting of all species of mercury in aquatic organisms, in hope of providing a realistic approach for the evaluation of safe consumption of seafood.

2. Experimental

2.1. Chemicals and reagents

The analytical grade of three species of mercury compounds, namely mercuric chloride, methylmercury-chloride and ethylmercury-chloride, were purchased from Best Chengdu Reagent Co., Ltd. (Chengdu, China). The 1000 μg/mL stock standard solution of mercuric chloride was prepared by dissolving above standard matter in Milli-Q water. The 1000 μg/mL stock standard solution of methylmercury-chloride and ethylmercury-chloride were prepared by dissolving above standard matters in methanol solution. Mercaptoacetic acid (MAA) was obtained from Sigma Co., Ltd. (China). All the stock standard solutions were stored at 4 °C. Working standard solutions were prepared by diluting the stock solutions to the desired concentration with Milli-Q water. The analytical grade sodium tetraborate ($Na_2B_4O_7{\cdot}10H_2O$) and sodium dihydrogenphosphate ($NaH_2PO_4{\cdot}2H_2O$) were purchased from Shanghai Reagents Co. Ltd. (Shanghai, China). The running buffer solution of 50 mmol/L H_3BO_3–12.5 mmol/L $Na_2B_4O_7$ (pH 9.20) was prepared by dissolving above reagents in Milli-Q water. All solutions were treated by ultrasonic agitation and filtered through a 0.22 μm membrane filter before use.

All experiments were performed at room in which the temperature was regulated in 25–27 °C by an air conditioner, and water used in this experiment is Milli-Q water (18.2 MΩ/cm) prepared by a Milli-Q equipment (Millipore, Bedford, USA).

2.2. CE–ICP–MS system

The CE–ICP–MS system consists of a CEi-SP20 CE–Interface system (Reeko Instrument Co. Ltd., Xiamen, China) and an Agilent 7500ce ICP–MS (Agilent Technologies, USA). The CE–Interface was made according to the principle reported in our previous paper [28]. The CE capillary was conditioned daily by purging with Milli-Q water for 10 min, 0.1 mol/L NaOH solution for 10 min, Milli-Q water for 10 min and running buffer solution for 10 min, respectively. Between each run, the CE capillary was flushed with Milli-Q water and running buffer solution for 2 min respectively in order to clean any analyte or matrix adsorbed on the surface of capillary.

2.3. Determination of MeHg, EtHg and Hg(II) in natural water and dried fish muscle

Natural water sample was collected from Minjiang river in Fuzhou of China. The water was immediately filtered through a 0.22 μm membrane filter after sampling, and then was used for CE–ICP–MS analysis directly. Mercury in dried fish (*Tapertail anchovy*) muscle was extracted with dilute hydrochloric acid. Firstly, about 0.5 g sample was accurately weighed and put into a 100 mL Teflon beaker, which coupled with a screwed cover, and 20.0 mL of 1 mol/L HCl solution was added into it. Then, the beaker, which closed with screwed cover, was put into a microwave digester (Sineo Microwave Chemical Technology Co. Ltd., Shanghai, China). The microwave system was programmed to heat the whole at 70 °C for 5 min under 400 W power. After the whole was cooled to room temperature, the extract was separated by filtering it through a 0.22 μm membrane filter, and the residue was repeatedly extracted once again with the same manner. Then, the total extract was evaporated to near dryness by using a pressured nitrogen blowing concentrator with a moderate stream and the residue was diluted to the appropriate volume with buffer solution again (according to the mercury content in the sample). The final solution was used for the CE–ICP–MS analysis with continuous sample-introduction mode.

For the determination of MeHg, EtHg and Hg(II) with CE–ICP–MS, above 10 μL of above sample solution or mixed standard solution of MeHg, EtHg and Hg(II) was firstly put into a microtube, and 40 μL of 0.1% MAA solution was added. Then, the whole was plenty agitated for 10 min in order to complex mercury compounds with MAA. Finally, the whole solution was diluted to 100 μL with running buffer solution, and the final solution was injected into CE–ICP–MS for determination with electro-migration injection.

3. Results and discussion

3.1. Optimization of CE–ICP–MS conditions for the analysis of MeHg, EtHg and Hg(II)

The CE separation of MeHg, EtHg and Hg(II) is still a very difficult problem because these mercury compounds in solution are present as undissociated molecules [29]. It has been reported that an effective way to solve this problem is to complex mercury compounds with an ionic agent having thiol group [21]. In this study, the effect of complexing agents on the separation of MeHg, EtHg and Hg(II) was studied by using cysteine and MAA as complexing agent, and the results showed that MAA is more suitable. After complexing with MAA, MeHg, EtHg and Hg(II) can be completely separated within 25 min by CZE (capillary zone electrophoresis).

In CE-based analysis, the buffer solution including its chemical components, pH and concentration greatly affected the separation of analytes by affecting the electroosmosis flow (EOF). In the experiment, several different buffer solutions including H_3PO_4–NaH_2PO_4, NaH_2PO_4–$Na_2B_4O_7$, H_3BO_3–$Na_2B_4O_7$ were used to separate MeHg, EtHg and Hg(II). The result showed that MeHg, EtHg and Hg(II) can be more completely separated when the H_3BO_3–$Na_2B_4O_7$ solution ($H_3BO_3/Na_2B_4O_7$ = 4/1, mole concentration) was used as buffer solution.

The pH of buffer solution greatly affects the migration times/resolution. The relationship between migration time/resolution and pH was studied in detail in the range of 9.00–9.40 with 50 mmol/L H_3BO_3–12.5 mmol/L $Na_2B_4O_7$ as buffer solution. From the results shown in Fig. 1A, we found that higher pH is favorable to prolong the migration time and improve the separation of MeHg, EtHg and Hg(II), three mercury compounds

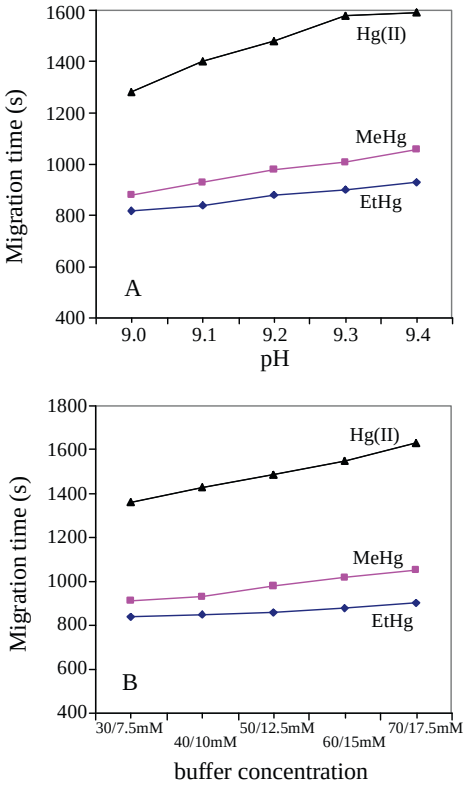

Fig. 1. (A) The effect of pH on the separation of Hg(II), MeHg and EtHg. Data were obtained by determining 3.0 ng/mL of EtHg, Hg(II) and 2.0 ng/mL of MeHg under the optimal CE–ICP–MS conditions except pH. (B) The effect of buffer concentration on the separation of Hg(II), MeHg and EtHg. Data were obtained by determining 3.0 ng/mL of EtHg, Hg(II) and 2.0 ng/mL of MeHg under the optimal CE–ICP–MS conditions except buffer concentration.

can be baseline separated when pH is higher than 9.1. Considering the analytical time and electrophoretic resolution, we selected pH 9.20 as the optimum pH for the separation of MeHg, EtHg and Hg(II).

The effect of concentration of running buffer solution on the separation was also studied by using different concentration of H_3BO_3–$Na_2B_4O_7$ buffer solution (H_3BO_3:$Na_2B_4O_7$ = 30.0:7.5, 40:10, 50:12.5, 60:15 and 70:17.5 mmol/L) at pH 9.20, and the results are shown in Fig. 1B. The result revealed that the resolution was improved and the migration times became longer with the increase of the concentration of running buffer solution. However, higher concentration also led to a higher current and finally resulted in a bigger noise and a poorer reproducibility. Considering the analytical time and electrophoretic resolution, 50 mmol/L H_3BO_3–12.5 mmol/L $Na_2B_4O_7$ (pH 9.20) was selected as the running buffer solution.

The effect of the separation voltage on the migration time and electrophoretic resolution was investigated in detail in the range of +16 to +20 kV with 50 mmol/L H_3BO_3–12.5 mmol/L $Na_2B_4O_7$ (pH 9.20) as buffer solution. The experimental results revealed that a higher voltage was favorable to shorten migration time of all MeHg, EtHg and Hg(II), which leads to a bad electrophoretic resolution. In addition, a higher voltage also leads to a poorer reproducibility and bigger noise due to the Joule heating effect. Considering the reproducibility, analytical time and electrophoretic resolution, +18 kV was selected as the separation voltage.

In this experiment, the solution was injected into CE–ICP–MS for determination with electro-migration injection. Different injection times (5, 10, 15, 20 and 25 s) were tested in this experiment at +18 kV, and the results showed that the sensitivities of three

Table 1
Running parameters of CE–ICP–MS.

Parameters	Value
CE voltage	+18 kV
Sample injection time	10 s
CE capillary	i.d. 75 μm; o.d. 365 μm; 85 cm long
Lab temperature	23–25 °C
Running buffer solution	50 mmol/L H_3BO_3–12.5 mmol/L $Na_2B_4O_7$, pH 9.20
Velocity of pump 1	11 μL/min
Velocity of pump 2	6 μL/min
RF power	1300 W
Outer plasma gas	15 L/min
Intermediate plasma gas	0.90 L/min
Carrier gas	0.75 L/min
Makeup gas	0.30 L/min
Monitored isotope (m/z)	^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg
Nebulizer type	MCN (optimum flow is 20–35 μL/min)

mercury compounds become higher with the increase of injection time. However, longer injection time also broaden the peaks and finally degrade the electrophoretic resolution. Considering both the sensitivity and separation efficiency, we selected 10 s as sample's injection time.

At above optimum conditions (see Table 1), MeHg, EtHg and Hg(II) were baseline separated within 25 min under continuous sample-introduction mode (see Fig. 2).

3.2. Reproducibility, linear relationship and detection limits

At the optimal CE–ICP–MS conditions shown in Table 1, the same experiment was repeated for six times in order to investigate the reproducibility of our method. The RSD (relative standard deviation, n = 6) of migration times was calculated to be smaller than 3% and that of peak areas is smaller than 5% for all MeHg, EtHg and Hg(II). A series of different concentrations of mixed standard solutions (0.5, 5, 10, 20, 50 and 100 ng/mL) were determined in order to obtain calibration curves. The linear correlation coefficients between counts (peak area) and concentrations were better than 0.995 for all MeHg, EtHg and Hg(II) in the concentration range of 0.5–100 ng/mL (see Table 2). The instrument detection limits ($3\sigma/S$, the concentration necessary to yield a net signal equal to three times the standard deviation of the background) were calculated to be 0.021, 0.032 and 0.027 ng/mL for MeHg, EtHg and Hg(II) respectively, much lower than those previously reported [25–27]. Higher sensitivity, as well as higher separation efficiency, much less

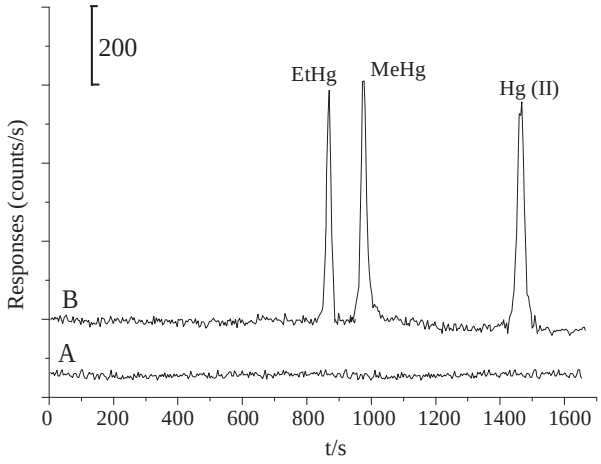

Fig. 2. The electropherograms of the mixed standard solution of Hg(II), MeHg and EtHg. Data were obtained by determining 3.0 ng/mL of EtHg, Hg(II) and 2.0 ng/mL of MeHg under the optimal CE–ICP–MS conditions. (A) Blank and (B) mixed standard solution.

Table 2
Linear relationship and detection limits.

Analyte	[a]Regression equation	Correlation coefficient	Liner range (ng/mL)	[b]Detection limit (ng/mL)
MeHg	$y = 8141.8x + 769$	0.995	0.5–100	0.021
EtHg	$y = 5347.2x - 547$	0.995	0.5–100	0.032
Hg(II)	$y = 6355.9x - 174$	0.999	0.5–100	0.027

[a] x = concentration (ng/mL), y = counts.
[b] Instrument detection limt

sample and reagent consumption, low operating cost, water-phase separation system that is suitable for biological sample and moderate separation conditions that is favorable to prevent the change of species during separation process, make our method a valuable technique to the speciation analysis of mercury.

3.3. The extraction of mercury compounds in fish muscle sample

To perform the speciation analysis of mercury compounds in fish muscle sample, the extraction of mercury compound is another key point. The extraction method must be capable of quantitatively extracting each mercury species from samples without altering the individual mercury species. So far, various methods including traditional liquid extraction, supercritical fluid extraction and microwave-assisted extraction etc. have been developed to extract different mercury compounds in sediments and fish muscle [4,30,31]. However, in these methods, the toluene, which has intense toxicity to health, was used as extracting solvent. Considered that dilute HCl solution has a good solubility for all MeHg, EtHg and Hg(II) and has a much lower toxicity than toluene, in this study, a microwave-assisted extraction with 1 mol/L HCl as solvent was used to extract mercury compounds in fish muscle.

The effect of extracting temperature on the extracting efficiency was investigated in 50–80 °C, and the results showed that higher temperature helps to improve the extracting efficiency. The extracting efficiency increased with the increase of extracting temperature in the range of 50–70 °C, and then the microwave-assisted extraction keeps a highest and stable extracting efficiency when extracting temperature in the range of 70–80 °C. In this study, we selected 70 °C as the optimum temperature.

The power of microwave digester, ratio (mL/g) of extracting solvent volume to the mass of sample and extracting time are also important factors for the extraction of mercury. In our experiments, a 400 W microwave digester was used for the extraction, and the effect of power on the extracting efficiency was not studied in detail since the power of microwave digester cannot be adjusted. The ratio (mL/g) of extracting solvent volume to the mass of sample was also optimized in this study, and the experimental result showed that the best ratio was 40. Higher ratio will increase the background of reagent blank and harm the detection limit of the method, whereas, lower ratio will decrease the extracting efficiency of MeHg, EtHg and Hg(II). Using 1 mol/L HCl as extracting solution, under 70 °C, 400 W and 40 times of solvent, mercury in the dried fish muscle can be completely extracted within 10 min after twice extraction.

3.4. Determination of mercury compounds in river water and dried fish muscle samples

In order to verify the reliability of our methods, the MeHg, EtHg and Hg(II) in river water samples were analyzed directly with the proposed method under Table 1 conditions. The MeHg, EtHg and Hg(II) in dried fish (*T. anchovy*) muscle samples were extracted with above extraction method and then their concentrations were determined with the same method. The recoveries were also obtained by determined river water and fish muscle samples, which spiked with different concentration of MeHg, EtHg and Hg(II), by using the same procedure described as above. The analytical results and their electropherograms were shown in Tables 3 and 4 and Figs. 3 and 4, respectively. From Table 3 and Fig. 3, it was clearly observed that the concentration of MeHg, EtHg and Hg(II) in the water sample

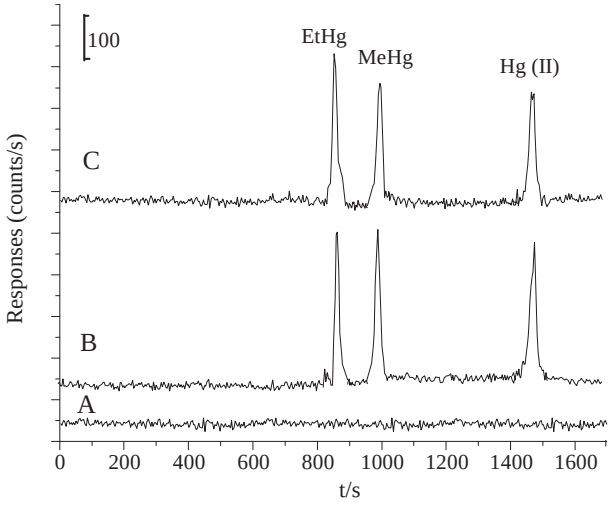

Fig. 3. The electropherograms of river water under the optimal CE–ICP–MS conditions. (A) River water collected from Minjiang rever; (B) mixed standard solution of Hg(II), MeHg and EtHg; and (C) river water spikded with 2.0 ng/mL of EtHg, Hg(II) and 1.0 ng/mL of MeHg.

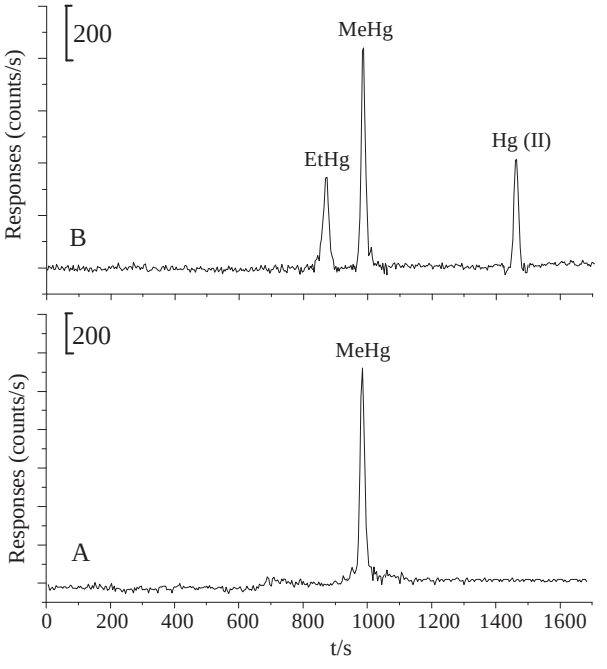

Fig. 4. The electropherograms of fish muscle under the optimal CE–ICP–MS conditions. (A) Fish muscle sample, 60 mL extracting solution of 0.2 g sample was used for detection; (B) fish muscle spiked with 0.5 μg/g of EtHg, Hg(II) and 1 μg/g of MeHg, 60 mL extracting solution of 0.08 g sample was used for detection.

Table 3
The analytical results of river water samples.

	River water											
	Sample 1				Sample 2				Sample 3			
	[a]Added con.	[a]Detected con.	RSD ($n=6$)	Rec. (%)	[a]Added con.	[a]Detected con.	RSD ($n=6$)	Rec. (%)	[a]Added con.	[a]Detected con.	RSD ($n=6$)	Rec. (%)
MeHg	0	<DL			0	<DL			0	<DL		
	1.00	0.941	3%	94%	2.00	1.901	4%	95%	3.00	3.086	4%	103%
EtHg	0	<DL			0	<DL			0	<DL		
	1.00	1.039	5%	104%	2.00	1.962	5%	98%	3.00	2.792	3%	93%
Hg(II)	0	<DL			0	<DL			0	<DL		
	1.00	1.031	4%	103%	2.00	1.880	4%	94%	3.00	2.847	5%	95%

[a] Unit is ng Hg/mL.

Table 4
The analytical results of fish muscle samples.

	Fish muscle											
	Sample 1				Sample 2				Sample 3			
	[a]Total con.											
	1.24 ± 0.01				1.27 ± 0.02				1.22 ± 0.01			
	[b]Added con.	[b]Detected con.	RSD ($n=6$)	Rec. (%)	[b]Added con.	[b]Detected con.	RSD ($n=6$)	Rec. (%)	[b]Added con.	[b]Detected con.	RSD ($n=6$)	Rec. (%)
MeHg	0	1.180	3%		0	1.221	4%		0	1.170	5%	
	0.50	1.690	2%	102%	1.00	2.181	3%	96%	2.00	3.230	3%	103%
EtHg	0	<DL			0	<DL			0	<DL		
	0.50	0.479	4%	96%	1.00	0.948	4%	95%	2.00	1.918	4%	96%
Hg(II)	0	<DL			0	<DL			0	<DL		
	0.50	0.475	3%	95%	1.00	1.009	5%	101%	2.00	1.882	3%	94%

[a] The concentrations determined with ICP–MS after samples were completely decomposed with 7 mol/L HNO_3, unit is μg Hg/g dried weight.
[b] Unit is μg Hg/g dried weight.

is lower than detection limit. The recovery is in the range 94% to 104% and RSD ($n=6$) was smaller than 5% for all three mercury compounds. As we mentioned above that the instrument detection limits of our method were 0.021, 0.032 and 0.027 ng/mL for MeHg, EtHg and Hg(II) respectively, whereas, the maximal residue limit (MRL) of Hg in drink water is 1 ng/mL in China. Therefore, our method can be used to directly detect mercury in water samples. No MeHg, EtHg and Hg(II) were detected in the water sample revealed that water collected from Minjiang river is safe in mercury index.

In fish (*T. anchovy*) muscle samples (see Table 4 and Fig. 4), only MeHg was detected and its concentration is in the range of 1.117–1.221 μg Hg/g dried weight. The recovery was in the range of 94–103% and RSD ($n=6$) was smaller than 5% for all three mercury compounds.

It was well known, whether all mercury compounds in samples were completely extracted and if each mercury species keep no change during extraction and analysis process are two key points to the speciation analysis of mercury compounds. From the results shown in Table 4, we found that the sum of the concentrations of each mercury species was consistent well with the total concentration of mercury (the concentration determined with ICP–MS after sample was completely decomposed with 7 mol/L HNO_3), indicating that all mercury had been completely extracted using our method. The approximately 100% of recovery for all MeHg, EtHg and Hg(II) obviously indicated that each mercury species kept no change during extracting and analytical process, since the recovery of at least one mercury species should excessively deviated from 100% if any mercury species was changed during extracting and analytical process. The detection limits of analytes in samples can be calculated according to the detection limits of instrument and the preconcentration times of sample. In the case of dried fish muscle, 5 mL extracting solution of 0.5 g sample can be directly analyzed using our method without any pre-treatment, therefore, the method detection limits of each mercury compound in dried fish muscle were calculated to be 0.21, 0.32, and 0.27 ng Hg/g dried weight for MeHg, EtHg and Hg(II), respectively.

4. Conclusion

A environment-friendly microwave-assisted extraction used to extract trace mercury compounds from fish samples, as well as a ultra-sensitive method for the simultaneous analysis of MeHg, EtHg and Hg(II) by using CE–ICP–MS were first reported in this study. The extraction method is simple, effective and can be used to extract trace mercury compounds in fish samples with a satisfied recovery within several minutes. Compared to previous method, the CE–ICP–MS analytical method has a much lower detection limit of 0.021, 0.032 and 0.027 ng Hg/mL for MeHg, EtHg and Hg(II) respectively, and can be used to determine ultratrace MeHg, EtHg and Hg(II) in natural water and aquatic organisms directly without any preconcentration. With the help of the above methods, we have successfully determined MeHg, EtHg and Hg(II) in dried fish muscle and river water within 25 min with a RSD ($n=6$) <5% and a recovery of 94–103%. Our results showed that dried fish (*T. anchovy*) muscle contained only one species of mercury, MeHg, indicating that MeHg is easier to be accumulated by aquatic organisms. Higher sensitivity, as well as much less sample and reagent consumption, low operating cost, water-phase separation system and moderate separation conditions, make our method a valuable technique to the speciation analysis of mercury.

Acknowledgments

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