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Short communication

Fast speciation of mercury in seawater by short-column high-performance liquid chromatography hyphenated to inductively coupled plasma spectrometry after on-line cation exchange column preconcentration

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ABSTRACT

A simple and fast method for trace speciation analysis of mercury (Hg^{2+}), methylmercury ($MeHg^{+}$) and ethylmercury ($EtHg^{+}$) in seawater has been developed by short-column high-performance liquid chromatography hyphenated to inductively coupled plasma spectrometry (HPLC–ICP-MS) after on-line cation-exchange column (CEC) preconcentration. The analytes were firstly adsorbed on the CEC without any extraneous reagent, and then were eluted rapidly (within seconds) and completely with a very low concentration of L-cysteine solution, which provides the conveniency for the on-line coupling of the preconcentration method and detection technique. To our best knowledge, it is for the first time to employ the CEC preconcentration technique to trap all of the three mercury species simultaneously at their positive charged status for the purpose of speciation analysis. Under the optimized conditions, a very high preconcentration factor up to 1250 has been obtained with 30 mL sample solution, which leads to the very low detection limits of 0.042 ng L^{-1} for Hg^{2+}, 0.016 ng L^{-1} for $MeHg^{+}$ and 0.008 ng L^{-1} for $EtHg^{+}$ (as Hg), respectively. With the established method, three seawater samples were also analyzed, and all the three mercury species have been found in each sample, albeit at a very low concentration.

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1. Introduction

Seafood products have always been one of the main food sources for human beings, while problem of the discharged heavy metals accumulated in the seafood becomes more and more severe today. Among the most concerned heavy metals, mercury has been considered as one of the most toxic elements for human health, while methyl mercury has been proved to be the most toxic mercury species. It is reported that [1] the concentration of mercury is normally in the range of 1–20 ng L^{-1} in the open-ocean water, while up to 100 ng L^{-1} is usually found in the coastal water owing to the anthropogenic discharges. As mercury is liable to enter and finally be accumulated in human body through the food chain, detecting the level of mercury, as well as analyzing its species in the seawater is of great importance to evaluate the risk of mercury exposure to human beings. In comparison with other water sources, such as lake water and well water, analysis of the seawater is a more challengeable task, because of the relative complicated matrix components [2].

Diversified analytical techniques have been developed for the speciation of mercury over the past decade; among them, chromatographic separation combined with spectroscopic detection [3–6] has been highlighted. Predominately, high performance liquid chromatography (HPLC) is adopted in the chromatographic separation techniques, as mercury species normally are nonvolatile compounds in the benign conditions, while inductively coupled plasma mass spectrometry (ICP-MS) is preferred in the spectroscopic detection, due to its high sensitivity and rapidness. Therefore, the combined HPLC–ICP-MS technique has been well used for the speciation of mercury in various edible, biological and environmental water samples [7–11]. However, suffered from poor instrument tolerance towards total dissolved salts (TDS) content, matrix separation instead of sample dilution is also required to obtain a sufficient analytic sensitivity when samples with high matrix contents (such as seawater) are analyzed [12]. Another concern is that the preconcentration of the analytes is usually required prior to HPLC–ICP-MS as the original level of mercury in most samples is far from being detected (the sensitivity for Hg is relative low owing to its high ionization energy). Thus, various extraction and preconcentration methods, including hollow fiber liquid–liquid–liquid microextraction (HF-LLLME) [13], dispersive liquid–liquid microextraction (DLLME) [14], cloud point extraction

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(CPE) [15,16] as well as solid phase extraction (SPE) [17,18] have been reported for the enrichment of mercury species. Comparatively, SPE is more environmental friendly as it is free of toxic organic extraction reagent, most importantly, the stronger tolerance to complex matrices endows it with a more capability of online application.

In the preconcentration of mercury species by SPE, nonpolar material such as C-18 has been widely adopted as the adsorbent as already reviewed by Leopold et al. [19], thus, a diversity of complexing agents (mostly sulfur containing reagents) such as ammonium pyrrolidinedithiocarbamate (APDC), diethyldithiocarbamate (DDTC), sulfhydryl, 2-mercaptoethanol and dithizone were selected for sorption of mercury species on C-18 solid phase cartridges [20]. Also, materials immobilized with chelating reagent as active sites at the column packing [21] or other were also employed as the absorbent for mercury species based on the similar principle. Accordingly, atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) have been generally adopted as the most suitable detection systems either for off-line SPE [22,23] or on-line flow injection SPE [24,25] because sulfur-reagents/HCl solution was generally selected to elute the target analytes, while for UV–vis [26] or diode array detector [27], more than 50% organic reagent (such as methanol and acetonitrile) as the eluent was usually required. However, the eluents used above could be incompatible with the HPLC–ICP-MS used in this work. In either case, it is a time-consuming chelating adsorption procedure and possibly brings contamination for the measurement; what is worse, these preconcentration systems suffer undesirable interferences from coexisting transition metals probably arising from their competition for the complexing agent and/or active sites at the column packing [28] when running the real sample. Therefore, a more simple and fast preconcentration method is anticipated to be combined with HPLC–ICP-MS.

For this purpose, sulfonic acid based cation-exchange resin is chosen as the adsorbent instead of C-18 material since the analytes can be efficiently and quickly adsorbed on the resin without any extraneous reagent. There are only few studies reported on the use of ion-exchange materials as adsorbent previously [29,30]. Another highlight here is the L-cysteine (Cys) is deliberately selected for elution based on its unique amphoteric and complexation properties (by adjusting the charge of Cys, instantaneous elution can be achieved). Despite Cys has been introduced as chelating reagent in many previous studies [31–33], it was only used for the purpose of separation in most cases; while for elution, the importance of pH cannot be ignored. Thus, without use hydrochloric acid or toxic reagent as others, and without adsorption on the column, the elution and separation can be achieved simultaneously only with an appropriate acidity solution of Cys. To our best knowledge, this is the first report on utilization of the charged resin for the speciation of mercury by on-line SPE hyphenated to HPLC–ICP-MS. By this technique, on-line sample preconcentration and matrix removal have been achieved simultaneously just by replacing the sample injection loop of HPLC with a cation-exchange column. No loss of sample and the analytical time (within 7 min) can be reduced for analytes when a pump rather than a syringe is adopted to load the sample on the column, which is quite different from Cairns et al.'s [2] work. Besides, the fast determination for daily analysis can be realized by using a short-column as the separation column in this work, which is also quite few [34] for the separation of mercury species in the previous studies. In this study, Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ were selected as the targeted analytes. The experimental parameters including the eluent type, the pH value, the sample volume, the flow rate as well as the matrix effects were investigated and optimized. The established method was well applied for the determination of mercury species in three seawater samples, and spike tests were also performed for each sample. Finally, the accuracy of the method has been verified by analyzing a standard reference material of seawater (GBW (E) 080042).

Table 1
Operating conditions of the HPLC–ICP-MS system.

Parameters	Value
ICP-MS system	
RF power (W)	1500
Nebuliser gas flow (L min^{-1})	0.90
Auxiliary gas flow (L min^{-1})	0.80
Cooling gas flow (L min^{-1})	13.0
Sampling cone (mm)	1.0, nickel cone
Skimmer cone (mm)	0.7, nickel cone
Isotopes monitored	^{202}Hg
Dwell time (ms)	100
Resolution	0.7 amu
Acquisition mode	Time resolved analysis
HPLC system	
Column	C18 reversed phase (50 mm × 4.6 mm i.d, 5 μm)
Mobile phase	4% (v/v) methanol, 10 mM cysteine, pH 8
Flow rate of the mobile phase	1.0 mL min^{-1}
Sample loop	CEC

2. Experimental

2.1. Apparatus

An X series II ICP-MS (Thermo Fisher Corp., USA) was operated in the time-resolved analysis (TRA) mode. IonPac CG5A guard column (50 mm × 4 mm id) (Dionex Co., Ltd., USA) was introduced as a sample preconcentration column. The chromatographic system consisted of a Waters 626 pump, and the sample loop of HPLC was substituted by the CEC in this study. Separation was achieved using an Aichrom C18 column (50 mm × 4.6 mm id, 5 μm) (Beijing Ba Fang Century Technology Co., Ltd., China). The outlet of the LC column was directly connected to the sample introduction system of ICP-MS via a 50 cm of 0.18 mm i.d. Peek tubing. The optimized ICP-MS and HPLC operating conditions were summarized in Table 1. A P3000 pump (Beijing Tong Heng Innovation Technology Co., Ltd., China) was employed to load the sample solution on to the CEC. A schematic diagram of the on-line CEC enrichment system coupled to HPLC–ICP-MS for the determination of trace mercury species in seawater samples is shown in Fig. 1.

The pH values were measured with a PHS-3C pH-meter (Shanghai Precision & Scientific Instrument Co., Ltd., China).

2.2. Standard solutions and reagents

Ultrapure water (18.2 MΩ cm, prepared by Millipore, Simplicity 185) was used throughout the experiment. A stock standard solution of 1000 mg L^{-1} Hg^{2+} prepared in 5% nitric acid was obtained from National Standard Material Center (GSB G 62069-90, Beijing, China). Stock standard solutions of methylmercury (1000 mg L^{-1}, as Hg) were prepared by dissolving CH_3HgCl, which was purchased from Dr. Ehrenstorfer (Augsburg, Germany) in HPLC methanol. Stock standard solution of C_2H_5HgCl was supplied by National Institute of Metrology (Beijing, China). All the stock solutions were kept in amber glass bottles and stored at 4 °C in the dark. Working standard solutions were prepared by successive dilution of the stock solution. Certified reference material (CRM) of seawater was obtained from National Standard Material Center (GBW (E) 080042, Beijing, China), the matrix of the CRM is the ocean water, and the acidity was adjusted to pH 1 with H_2SO_4 to stabilize the trace amount of mercury.

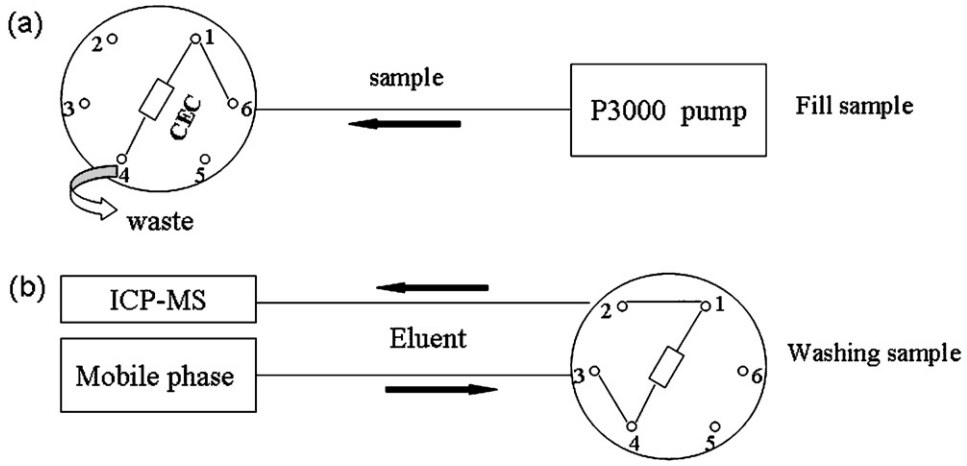

Fig. 1. Schematic representation of the on-line SPE sample enrichment system coupled to HPLC–ICP-MS: (a) fill the sample on the CEC, (b) elution of the sample.

L-Cysteine (Cys) as chelating reagent was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and HPLC grade methanol (Fisher Scientific, USA) was used as organic modifier in the mobile phase. All of the other chemicals were of analytical-reagent grade at least.

2.3. Sample collection and preparation

Seawater samples were collected in pre-cleaned polypropylene from three coastal regions (Qingdao, Dalian, Shenzhen) of China, then were transported (the samples were kept in low temperature) to the laboratory for immediate analysis. Before on-line CEC preconcentration, the samples were filtrated through a cellulose acetate filter with 0.22 μm pore size and transferred to clean amber glass vials. For the standard reference material, fifty-fold dilution was made prior to analysis due to its high acidity and the high preconcentration factors of the established on-line CEC method. For spike-recovery tests, the three mercury species were added prior to any sample treatment including dilution and filtration.

2.4. Preconcentration

The original sample loop on the rotary injection valve (6 channel) was replaced with CEC, as shown in Fig. 1(a). With aid of the pump (P3000), three replicates of 30 mL sample solution containing the analytes were loaded on to the CEC, then Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ were adsorbed on the sulfonic acid based resin quickly due to the strong electrostatic affinity. The valve was then switched, as shown in Fig. 1(b), thus, the analytes carried by eluent were directly transported into the ICP-MS for determination.

3. Results and discussion

3.1. Optimization of the eluent type and mobile phase for HPLC

Due to the sulf-ligand in the molecule of L-cysteine, it was used as the chelating reagent for elution in this study. As we know, amphoteric molecules called zwitterions contain both positive and negative charges depending on the functional groups present in the molecule. The net charge on the molecule is affected by pH of their surrounding environment and can become more positively or negatively charged due to the loss or gain of protons (H^{+}). The pI is the pH value at which the molecule carries no electrical charge or the negative and positive charges are equal. For Cys, at a pH below their pI (5.2), proteins carry a net positive charge; above their pI they carry a net negative charge.

As the positive charged Cys^{+} (pH < 5.2) adsorbed on the cation-exchange column will be chelated with mercury species in the next analytic run, the pH value of the eluent was adjusted to about 8 by 25% NaOH aqueous solution to make the L-cysteine existed as Cys^{-}, thus, the CEC can be used repeatedly without any effect on the next adsorption. The concentration of L-cysteine has been exclusively optimized to realize completely elution. The influence of the concentration on the elution efficiency was evaluated in the range of 4–14 mM (at 2 mM interval) with other experimental conditions constant. The results indicated that, when the concentration of Cys was lower than 10 mM, the peak area of organic mercury was decreased, the reason might be that the amount of Cys is not enough to be chelated well with all the adsorbed analytes, however, when the concentration was higher than 10 mM, no obvious change was observed. Thus it can be seen, the elution procedure was effortless and instantaneous since the strength of coordination bond is much higher than that of ionic bond, thereby, without the addition of inorganic acid (such as HCl or HNO_3 used in many precious studies), an absolutely elution could be achieved only with a very low concentration of Cys solution.

In the meantime, the mobile phase for HPLC is also required to be optimized for shortening the separation time and reducing the level of carbon and salt entering the ICP torch. Herein, methanol as organic modifier should be added to reduce the retention time and improve the peak type. Thus, a solution containing 4% methanol and 10 mM L-cysteine (pH 8) was finally selected as the mobile phase as well as the eluent. The results showed that baseline separation of the three mercury species can be achieved, and the retention time for the analytes was greatly reduced by using a short separation column (less than 2.5 min for Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$). Fig. 2 illustrates the chromatographic separation of a mixed standard solution containing 50 μg L^{-1} Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ by the HPLC–ICP-MS.

3.2. Optimization of the pH value

Rabenstein and Fairhurst [35] have reported that the sulfhydryl group binds CH_3Hg most strongly with a formation constant for CH_3Hg cysteine complexes of 5.0×10^{15} but that at pH < 2 this complex disassociates due to competition of protons for the sulfhydryl group. Moreover, the basicity of the sample is also required to below the tolerable upper levels of the separation column. Thus, the adsorption procedure was performed at different pH values in the range of 2–8 (adjusted with 25% HNO_3 and $NH_3{\cdot}H_2O$) while keeping other experimental conditions constant. However, the results indicated that the pH value has little effect on the adsorption and determination. Finally, in order to avoid the exogenous

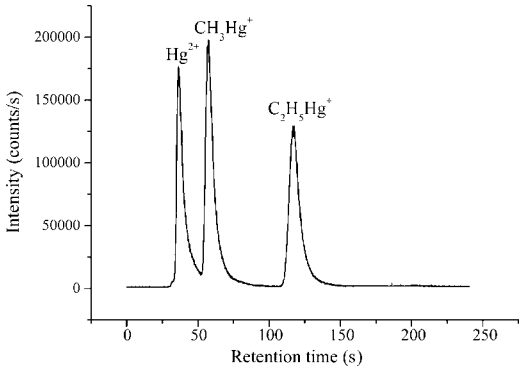

Fig. 2. Chromatogram showing the separation of Hg^{2+}, $MeHg^+$ and $EtHg^+$. The concentration of each mercury species was 50 μg L^{-1} (as Hg). The mobile phase contains 4% (v/v) methanol and 10 mM L-cysteine, pH 8.

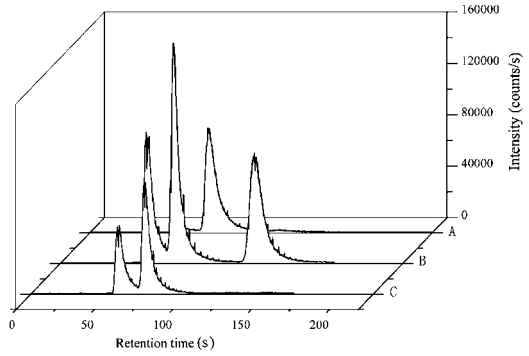

Fig. 3. Chromatograms of the enriched Hg^{2+}, $MeHg^+$ and $EtHg^+$ from (A) seawater from Dalian, Liaoning, (B) seawater spiked with 50 ng L^{-1} per mercury species, and (C) standard reference material of seawater (sample was diluted fifty-fold before analysis). Peaks of 1–3 represent Hg^{2+}, $MeHg^+$ and $EtHg^+$, respectively.

contamination and consequently minimize the background, the experiment was performed at pH 7 without the addition of any other reagents.

3.3. Effect of flow rate and sample volume

The influence of the sample flow rate on the preconcentration factors (PFs) and recoveries (>95%) of Hg^{2+}, $MeHg^+$ and $EtHg^+$ were investigated in the ranges of 1–9 mL min^{-1}, while keeping the other conditions constant (the maximal flow rate is depended on the maximal tolerable pressure of the pump). The results demonstrated that the PFs and recoveries of mercury species were almost kept constant till 9 mL min^{-1}, no obvious change was observed with altering of the flow rate, thus, all the experiments were carried out at a flow rate of 9 mL min^{-1} in this study to reduce the analytical time.

It is also necessary to examine the maximum applicable sample volume especially when the practical samples containing very low level analytes were analyzed. The influence of sample volume on the recoveries of a mix solution of 50 ng L^{-1} Hg^{2+}, $MeHg^+$ and $EtHg^+$ standard were investigated in the range of 5–50 mL. The results showed that, the recoveries were found to be stable only till 30 mL, then it will decrease. It might be due to the limited adsorptive capacity of CEC and the loss of adsorbed analytes rinsed by the larger volume of sample. Therefore, 30 mL was selected as the breakthrough volume for this work.

3.4. Effect of wash time after adsorption

There were still some residual analytes inside the system especially at the piping and interfacing after the adsorption of mercury species, which probably affect the subsequent measurement. Moreover, for real samples with complex matrices such as seawater, if without washing the system after sample preconcentration, the large content of salt in seawater will induce the instability of the plasma, and may be deposited on the sample cone and/or skimmer cone, thus, the washing procedure is indispensable. Ultrapure water was selected as the washing reagent since the adsorbed analytes on the CEC cannot be cleared by the common water. The results showed that at the flow rate of 9 mL min^{-1}, 1 min was sufficient to completely get rid of the residue with negligible effect on the next analytical run.

3.5. Matrix effects

The effects of common coexisting ions in real seawater samples on the recoveries of Hg^{2+}, $MeHg^+$ and $EtHg^+$ were also studied. For this experiment, 30 mL of the solution contained 50 ng L^{-1} each of the three mercury species and various amounts of interfering ions (5000 mg L^{-1} of Na^+, 200 mg L^{-1} of K^+, Ca^{2+}, Ba^{2+}, Al^{3+}, Sr^{2+}, CO_3^{2-}, NO_3^- and Br^-, 2000 mg L^{-1} of Mg^{2+} and SO_4^{2-}, and 10,000 mg L^{-1} of Cl^-) were treated with the on-line analytical procedure. The results showed that the recoveries of Hg^{2+}, $MeHg^+$ and $EtHg^+$ were in the range of 89.7%–103.6%, which meant that the interference from coexisting ions can be ignored by this on-line enrichment method.

3.6. Analytical figures of merit and practical sample analysis

The analytical characteristics of the optimized method were summarized in Table 2. Calibration curves were obtained between the peak area of signal after preconcentration and the concentration of primary mercury species in the spiked standard solution c (ng L^{-1}). The PFs were calculated as the concentration of analytes after the on-line CEC procedure and without preconcentration. The limit of detection (LOD) was defined as $C_L = 3S_B/m$ (where C_L is the limit of detection, S_B is standard deviation of the blank values and m is the slope of the calibration graph). The LOD for organic mercury is better than that for inorganic mercury, the reason is that the LOD is blank limited as there is inorganic mercury present in almost all the reagents used in the analytical process.

In comparison with other methods, the established method has its unique predominance including very low detection limits (0.008 ng L^{-1} for $EtHg^+$) as well as very short sample preparation time (3.5 min for preconcentration of the mercury species on CEC), as shown in Table 3; moreover, the analytes can be baseline separated within 2.5 min since a short-column was adopted in this work. Hence, for the daily analysis of water samples, the proposed sample pre-treatment method is very compatible with the subsequent detection technique, and will not affect the fast performance of ICP-MS. In addition, the established method is simpler due to the minimum analytical steps, and almost no contamination from external since the only introduced reagent was L-cysteine.

For practical application, the method was applied for determination of Hg^{2+}, $MeHg^+$ and $EtHg^+$ in three Chinese seawater samples, and spike tests were also performed. The chromatograms were shown in Fig. 3 and the results in Table 4 indicated that, all the mercury species were detected by the established method due to its low limit of quantification. The content of $MeHg^+$ and Hg^{2+} detected in three replicates of a standard reference material of seawater (GBW (E) 080042) were found to be 0.34 ± 0.02 ng mL^{-1} and 0.63 ± 0.04 ng mL^{-1}, respectively, and the sum of these two mercury species was in good agreement with the certified value of 1.00 ± 0.06 ng mL^{-1} for total Hg.

Table 2
Analytical characteristics.

Parameters	Hg^{2+}	$MeHg^{+}$	$EtHg^{+}$
Linear range (ng L^{-1})	0.5–100	0.5–100	0.5–100
Correlation coefficient (R^2)	0.9993	0.9997	0.9999
Response function	$y = 6.06E^{+7}x - 2538$	$y = 9.20E^{+7}x - 3607$	$y = 8.45E^{+7}x - 694$
Limit of detection (ng L^{-1}) (3σ, $n = 7$)	0.042	0.016	0.008
Repeatability (R.S.D.[a], %) ($n = 10$)	5.1	4.4	3.6
Preconcentration factors (EFs)	1250	1250	1250
Sample volume (mL)	30	30	30
Extraction time (min)	<3.5	<3.5	<3.5

[a] The solution containing 50 ng L^{-1} of Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ was analyzed.

Table 3
Comparison with other method.

Method	LOD (ng L^{-1})	Preconcentration factors	Sample consumption (mL)	Procedure time (min)	Reference
CPE-HPLC–ICP-MS	13 ($MeHg^{+}$) 8 ($PhHg^{+}$) 6 (Hg^{2+})	18 ($MeHg^{+}$) 46 ($PhHg^{+}$) 57 (Hg^{2+})	25	>20	[15]
CPE-HPLC–ICP-MS	4 (Hg^{2+}) 10 ($MeHg^{+}$)	42 (Hg^{2+}) 21 ($MeHg^{+}$)	25	>20	[16]
SPE-HPLC–ICP-MS	3 (Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$)	27.8 (Hg^{2+}) 31.2 ($MeHg^{+}$) 23.9 ($EtHg^{+}$)	100	>50	[17]
SPE-HPLC-AFS	800 (Hg^{2+}) 4300 ($MeHg^{+}$) 1400 ($EtHg^{+}$)	1000	100–500	>7	[20]
On line CEC-HPLC–ICP-MS	0.042 (Hg^{2+}) 0.016 ($MeHg^{+}$) 0.008 ($EtHg^{+}$)	1250	30	3.5	This work

Table 4
Analytical results of Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ in some environmental water samples.

Water sample	Mercury species	Concentration (ng L^{-1}), mean ± S.D.[a]	Added (ng L^{-1})	Recovery (%)
Seawater 1[b]	Hg^{2+}	1.21 ± 0.13	5.00	89
	$MeHg^{+}$	6.87 ± 0.74	5.00	100
	$EtHg^{+}$	0.65 ± 0.06	5.00	101
Seawater 2[c]	Hg^{2+}	2.41 ± 0.18	5.00	87
	$MeHg^{+}$	68.0 ± 4.50	5.00	98
			50.0	100
	$EtHg^{+}$	0.58 ± 0.04	5.00	97
			50.0	99
Seawater 3[d]	Hg^{2+}	1.16 ± 0.10	5.00	92
	$MeHg^{+}$	4.41 ± 0.52	5.00	101
	$EtHg^{+}$	0.93 ± 0.06	5.00	102

[a] Standard deviation ($n = 3$).
[b] From Qingdao city, Shandong province.
[c] From Dalian city, Liaoning province.
[d] From Shenzhen city.

4. Conclusion

An on-line simple and rapid method for the determination of Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ in seawater samples has been demonstrated. The sample loop in the injection valve of HPLC was replaced by a cation-exchange column packed with sulfonic material. Without derivatization and complexing reagent, the three mercury species were adsorbed on the CEC absolutely. High PFs were obtained and low LOD were achieved within only 3.5 min for enrichment and 2.5 min for separation and determination. This technique has distinctive advantages over conventional preconcentration methods with respect to very short sample preparation time and free of toxic organic extraction solvent. For the above reason, the proposed method is satisfied for the mercury speciation of many real environmental water samples without using complicated sample treatment procedures.

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