



# Dithizone-functionalized solid phase extraction–displacement elution–high performance liquid chromatography–inductively coupled plasma mass spectrometry for mercury speciation in water samples

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## ABSTRACT

A novel and simple solid phase extraction (SPE)-high performance liquid chromatography (HPLC)-inductively coupled plasma mass spectrometry (ICP-MS) method was developed for determination of inorganic mercury (IHg), methylmercury MeHg and ethylmercury (EtHg) in water samples in the present work. The procedure involves pre-functionalization of the commercially available C18 SPE column with dithizone, loading water sample, displacement elution of mercury species by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, followed by HPLC-ICP-MS determination. Characterization and optimization of operation parameters of this new SPE procedure were discussed, including eluting reagent selection, concentration of eluting reagent, volume of eluting reagent, effect of NaCl and humic acid in sample matrix. At optimized conditions, the detection limits of mercury species for 100 mL water sample were about 3 ng L<sup>-1</sup> and the average recoveries were 93.7, 83.4, and 71.7% for MeHg, IHg and EtHg, respectively, by spiking 0.2 μg L<sup>-1</sup> mercury species into de-ion water. Stability experiment reveals that both the dithizone-functionalized SPE cartridge and the mercury species incorporated were stable in the storage procedure. These results obtained demonstrate that SPE-HPLC-ICP-MS is a simple and sensitive technique for the determination of mercury species at trace level in water samples with high reproducibility and accuracy.

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## 1. Introduction

Mercury, known as a global pollutant, present as different species in different environmental media including atmosphere, soil, sediment and water body [1]. Mercury pollution in water has negative impact on the aquatic organism and human. Methylmercury (MeHg) is the most toxic mercury species and the mainly form of mercury in fish and other mammals. Mercury pollution in fish is mainly from bio-concentration of MeHg from water and/or bio-accumulation from aquatic food web. Speciation of mercury in water is very important for evaluation of mercury pollution. Therefore, developing reliable, sensitive and easily operating methods are of great interest for the determination of mercury species in environmental water samples. Because of low concentration of mercury species and complexity of the environmental samples matrix, an enrichment step is usually necessary before separation and detection. Different methods have been developed to enrich and determine mercury species in water samples in the past years.

The EPA 1630 method, i.e. distillation, aqueous ethylation, purge and trap, and cold vapor atomic fluorescence spectrometry, was usually used for MeHg determination [2]. However, this method is relatively tedious and MeHg artifact was found in the distillation procedure. Moreover, the ethylation-based method cannot be used for ethylmercury determination. In recent years, other pre-concentration methods were reported including solid phase micro-extraction [3–5], liquid phase micro-extraction [6–8], cloud point extraction [9,10] and solid phase extraction (SPE) [11–19]. For solid phase micro-extraction, derivatization procedure such as hydride, ethylation or phenylation derivatization is often necessary to transform inorganic mercury (IHg) and organomercurials into their volatile species. While, liquid phase micro-extraction is difficult to become a routine analytical procedure because of short of commercial available instrumentation. Solid phase extraction is relatively simple, convenient and easy to automate. In past decade, various synthesized chelating sorbents have been reported to concentrate IHg and MeHg by using solid phase extraction mode [12,13]. Dithizone-anchored poly(ethylene glycol dimethacrylate–hydroxyethylmethacrylate) microbeads were synthesized to pre-concentrate inorganic and organic mercury compounds. However, elution by CuSO<sub>4</sub>/acidic potassium bromide

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or HNO<sub>3</sub> solution and extraction with benzene were needed to adapt with gas chromatography–atomic absorption spectrometry determination [20]. Recently, a simple pre-functionalization of home-made or commercially available C18 SPE procedure with hydrophobic pyrrolidinedithiocarbamate (PDC) or dithizone was reported for trapping IHg and MeHg in water samples followed by high performance liquid chromatography–mass spectrometry (HPLC–MS) or UV determination [14,18]. While, high percentage organic solvent in mobile phase was needed to elute and separate the hydrophobic mercury–PDC/dithizone complexes, which is not compatible with element-specific inductively coupled plasma mass spectrometry (ICP–MS) detection.

The present work developed a novel dithizone-functionalized SPE procedure followed by HPLC–ICP–MS for mercury speciation in water samples. Mercury species in water sample were firstly trapped on the dithizone-functionalized commercial SPE column, eluted by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> through replacement and further determined by HPLC–ICP–MS. The proposed method will be applied to different environmental water samples to search for its reliability.

## 2. Experimental

### 2.1. Instrumentation

Agilent 1100 HPLC and Agilent 7500ce ICP–MS hyphenated system was used for separation and detection of mercury species (Agilent Technologies, Palo Alto, CA, USA). Solid phase extraction apparatus was from Agilent (Agilent Technologies, Palo Alto, CA). 3 mL C18 SPE columns (Supelclean™ LC-18 SPE, Supelco, Bellefonte, PA) were used for pre-concentration of mercury species.

### 2.2. Reagents

Dithizone (≥98%) and 2-mercaptoethanol (≥98%) were purchased from Alfa Aesar (Ward Hill, MA, USA). Methanol was of HPLC grade from J.T. Baker (Phillipsburg, NJ, USA). Analytical grade HCOOH, HCOONa, NH<sub>3</sub>·H<sub>2</sub>O, NH<sub>4</sub>Ac, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, cysteine, NaCl as well as GR grade KOH, HCl, HNO<sub>3</sub> were from Beijing Chemical Factory (Beijing, China). Humic acid was from Aldrich (Aldrich, Milwaukee, Wisconsin).

Stock solution of inorganic mercury (IHg) (1 mg mL<sup>-1</sup> as Hg) was prepared by dissolving HgCl<sub>2</sub> (≥99.5%, Beijing Chemical Factory, Beijing, China) in 5% (v/v) HNO<sub>3</sub>. Individual stock solutions of organomercury chloride (1 mg mL<sup>-1</sup> as Hg) were prepared by dissolving methylmercury chloride (MeHg) and ethylmercury chloride (EtHg) in methanol, respectively. All the organomercuric compounds were obtained from Merck (≥98%, Darmstadt, Germany).

The dithizone solution was prepared by dissolving 5.0 mg of dithizone in 0.5 mL 25% ammonium hydroxide firstly, then the pH was adjusted to 9.0 by adding the adequate volume of formic acid, making a final volume of 100 mL with de-ion water.

All the aqueous solutions were prepared with water purified by a Barnstead ultra-pure water system (Barnstead International, Dubuque, IA).

### 2.3. Solid phase extraction procedure for mercury species

*Pre-treatment of SPE column:* The C18 cartridge was flushed with 5 mL of methanol, 5 mL of 0.5 mol L<sup>-1</sup> sodium formate–formic acid (pH 4.0), and 4 mL 0.05% dithizone solution. Dithizone was totally retained on the column and a dithizone-functionalized SPE column can be obtained. Then, the SPE column was washed with 3 mL 0.5 mol L<sup>-1</sup> sodium formate–formic acid buffer (pH 4.0), and 3 mL 0.05 mol L<sup>-1</sup> sodium formate–formic acid buffer (pH 4.0) to maintain adequate pH of the column. In this procedure, acetate

**Table 1**

Experimental conditions of HPLC–ICP–MS system for mercury speciation.

Parameter	Optimized value
<b>HPLC</b>	
HPLC pump	Agilent 1100
HPLC column	Zorbax XDB-C18, 50 mm × 2.1 mm × 5 μm
Mobile phase	5% (v/v) CH <sub>3</sub> OH, 60 mmol L <sup>-1</sup> NH <sub>4</sub> Ac, 0.1% 2-mercaptoethanol (pH 6.8)
Flow rate of mobile phase	0.4 mL min <sup>-1</sup>
Injection volume	20 μL
<b>ICP–MS</b>	
ICP–MS	Agilent 7500ce ICP–MS
Nebulizer	Babington Nebulizer
Isotope	202
RF power	1500 W
Replicates	1
Plasma gas flow rate	15.0 L min <sup>-1</sup>
Auxiliary gas flow rate	0.22 L min <sup>-1</sup>
Nebulizer gas flow rate	0.82 L min <sup>-1</sup>
Dwell time	100 ms

was avoided because of the possibility of chemical methylation of inorganic mercury [21].

*Loading of water samples:* In the parameter optimization procedure, de-ion water spiked with 0.2 μg L<sup>-1</sup> mercury species was used as sample. 1 mL 5 mol L<sup>-1</sup> sodium formate–formic acid buffer (pH 4.0) was added into 100 mL water sample to adjust the pH and ionic strength. Then, the water sample was loaded on the SPE column at a flow rate of 2.0 mL min<sup>-1</sup>. The mercury species were trapped on the SPE column via the adsorption of on-column formed mercury–dithizone complexes. Then dry the column with air for 2 min to remove water.

*Elution of mercury species:* 3 mL 100 mmol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was used to elute mercury species trapped on the column. The hydrophilic mercury species–Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> complexes was formed and eluted, while hydrophobic dithizone was retained on the column. Then the eluted solution was injected into HPLC–ICP–MS for mercury speciation.

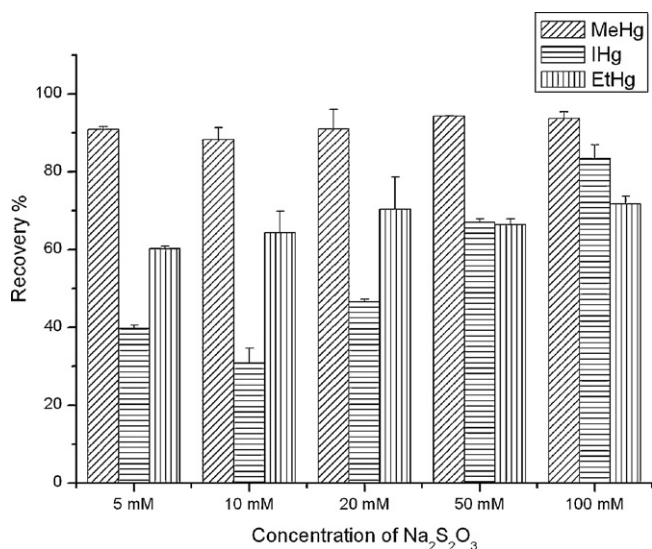
### 2.4. Analytical procedure for mercury species

The conditions of HPLC–ICP–MS hyphenated system are given in Table 1. A Zorbax XDB-C18 column (50 mm × 2.1 mm × 5 μm, Agilent, Palo Alto, CA, USA) was applied to separate mercury species with 5% (v/v) CH<sub>3</sub>OH containing 60 mmol L<sup>-1</sup> NH<sub>4</sub>Ac and 0.1% 2-mercaptoethanol (pH 6.8) as mobile phase for isocratic elution. The retention times of MeHg, IHg and EtHg are 2.5, 5.7 and 9.8 min, respectively.

## 3. Results and discussion

### 3.1. Selection of eluent

Pyrrolidinedithiocarbamate [14,17] and dithizone [18] modified-SPE cartridge were reported to pre-concentrate mercury species. In the elution procedure, pure organic solvents such as methanol were used as the eluent for desorption of the hydrophobic mercuric complex from the SPE column. In addition, mobile phase contained high percentage organic solvent was applied to separate the hydrophobic mercuric complexes. However, organic solvent in eluent and mobile phase would contaminate the sampling cone and deteriorate the sensitivity of ICP–MS. Therefore, cysteine and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> water solution without organic solvent were considered as displacement eluent. The color change by addition of cysteine or Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> into dithizone–Hg complex solution indicated that cysteine can displace mercury species from dithizone more easily than Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. However, SPE experiment revealed that the



**Fig. 1.** Effect of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> concentration on the recoveries of mercury species. Water sample volume was 100 mL and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution volume was 3 mL. Other conditions are given in Section 2.

recovery of EtHg is lower than 20% by using cysteine as eluent, owing to adsorption of EtHg–cysteine complex on the C18 SPE column. Furthermore, when cysteine present in sample matrix, MeHg and IHg cannot be separation effectively. Considering that, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> eluent was selected in the further study.

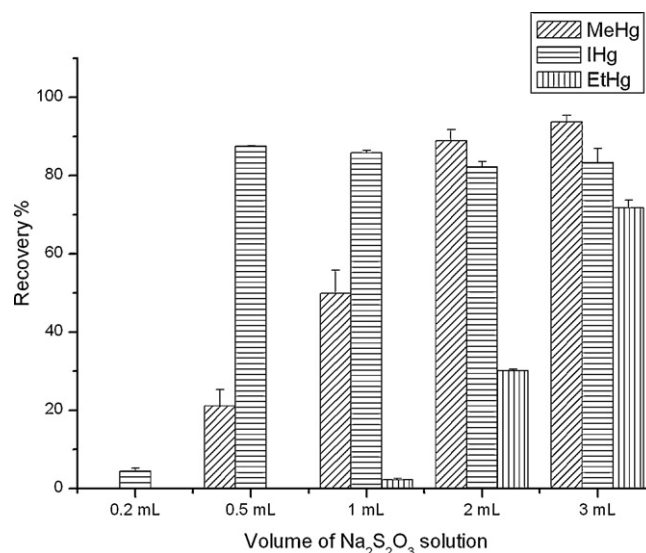
### 3.2. Effect of concentration and volume of elution solution

The effect of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> concentration in eluent on the recoveries of mercury species was investigated in the range from 5 to 100 mmol L<sup>-1</sup>, which is shown in Fig. 1. As could be seen, the recovery of MeHg reached 90% by using 5 mmol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> eluent. While, the recoveries of IHg and EtHg were relatively low. With the increasing concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> eluent, the recoveries of IHg and EtHg increased significantly. However, concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> eluent over 100 mmol L<sup>-1</sup> will deteriorate the chromatographic separation. Therefore, a 100 mmol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> eluent was selected for the rest of this work.

The effect of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> eluent volume on the recoveries of mercury species was investigated in the range from 0.2 to 3.0 mL, as given in Fig. 2. The recoveries of mercury species increased significantly with the increasing eluent volume. IHg is easy to elute than other organomercurials. The recovery of IHg reached 80% by using only 0.5 mL eluent. EtHg is difficult to elute because of its hydrophobicity. The recovery of EtHg increased over 70% by using 3.0 mL eluent. Increasing the eluent volume further will result in dilution of the analytes. Thus, the volume of eluent was optimized as 3.0 mL.

### 3.3. Effect of NaCl in sample matrix

Chloride ion exists widely in different water bodies, especially in sea water. It can form various complexes with inorganic mercury and organomercurials [22]. Therefore, chloride ion in sample matrix usually has great influence on the pretreatment and derivatization of mercury species. The effect of NaCl on the SPE was investigated in the range of 0–3% (w/v). As shown in Fig. 3, low concentration of Cl<sup>-</sup> in sample matrix has little influence on the recoveries of mercury species. While, when the concentration of NaCl is over 1%, the recoveries of mercury species decreased slowly, but were still higher than 60%. The presence of chloride ions inhibited the mercury–dithione complex formation [23], which thereby

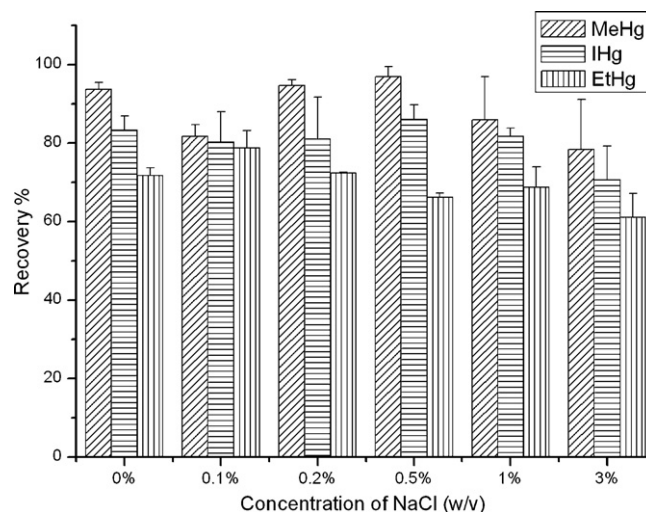


**Fig. 2.** Effect of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> volume on the recoveries of mercury species. Concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was 100 mmol L<sup>-1</sup>. Other conditions are given in Fig. 1.

reducing the adsorption of mercury in the column. The results indicated that when high chloride ion present in the sample, the method will underestimated the concentration of mercury species.

### 3.4. Effect of humic acid in sample matrix

Humic acid is one of the major components of humic substances widely present in aquatic system [24]. Mercury and organomercurials are generally bound at the acid sites of humic acid, including carboxylic acids, phenols and thiols [25]. Therefore, in this present study, the influence of humic acid in water on the SPE procedure was investigated in the concentration range of 0–20 mg L<sup>-1</sup> (as organic carbon content), which is given in Fig. 4. As could be seen, humic acid in water matrix did not significantly affect the extraction efficiency of organomercurials, but the recovery of inorganic mercury decreased slightly. Mercury species associated with the humic acid in sample solution, which decreased the extraction efficiency. Moreover, when high concentration of humic acid was present in the sample, part of humic acid was retained on the SPE column, which decreases the flow rate of water sample in loading procedure.



**Fig. 3.** Effect of NaCl in sample matrix on the recoveries of mercury species.



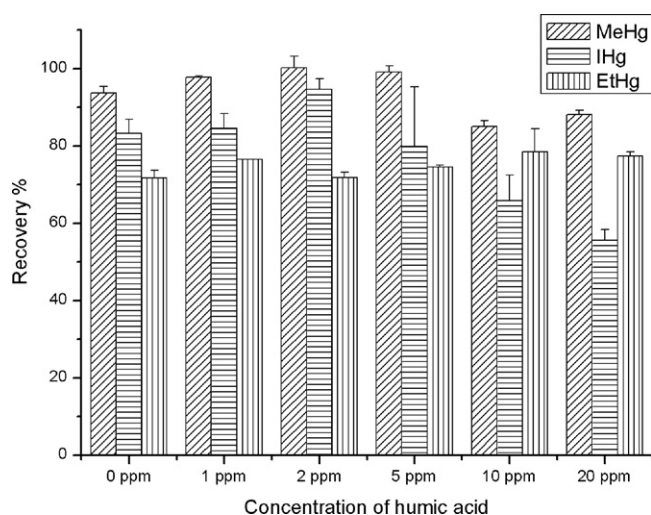


Fig. 4. Effect of humic acid in sample matrix on the recoveries of mercury species.

### 3.5. Stability of the dithizone-functionalized SPE column

Considering the feasibility of dithizone-functionalized SPE procedure for field sampling, the stability of mercury dithizonate complexes and the dithizone-functionalized SPE column was evaluated. Firstly, the dithizone-functionalized SPE column was stored at 4 °C for 7 days and then extraction was performed. The extraction recoveries of the cartridges were 94.2, 83.1 and 71.2% for MeHg, IHg and EtHg, respectively. Furthermore, the stability of the mercury dithizonate complexes immobilised on the C18 cartridges was studied. After extraction of mercury species, the SPE column was stored at 4 °C for 4 days and then the recoveries were investigated. The extraction recoveries of the cartridges were 92.5, 82.4 and 69.4% for MeHg, IHg and EtHg, respectively. These results reveal that both the dithizone-functionalized SPE cartridges and the mercury species incorporated were stable in the storage procedure.

### 3.6. Figures of merit and application to environmental water samples

From above investigation, 3 mL 100 mmol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was selected as eluent. At these optimized conditions, the pre-concentration factors based on 100 mL sample were calculated as 31.2, 27.8 and 23.9 for MeHg, IHg and EtHg, respectively. The average recoveries were 93.7 ± 1.7, 83.4 ± 3.5 and 71.7 ± 2.1% for MeHg, IHg and EtHg by spiking 0.2 μg L<sup>-1</sup> mercury species into de-ion water, respectively. The limits of detection (LODs) of mercury species were about 3 ng L<sup>-1</sup>. A comparison of LODs obtained by other liquid phase-based techniques for mercury speciation was given in Table 2. It could be seen that the LODs of this method are lower or comparable with other techniques.

In order to validate the novel method, the proposed procedure was applied for enrichment and determination of IHg, MeHg and EtHg in real environmental water samples including tap water, river water, sea water and coal-washing wastewater. The results were given in Table 3. As could be seen, only IHg species was detected in tap water, river water and sea water. However, for coal-washing wastewater relatively high concentration of MeHg was found. The concentration of IHg in coal-washing wastewater is about 10.2 μg L<sup>-1</sup>, which was determined by HPLC-ICP-MS directly without pre-concentration. The world-wide average Hg content in coal is 0.10 mg kg<sup>-1</sup> Hg [31] and MeHg and other organomercurials also present in coal [32]. MeHg detected in coal-washing wastewater should come from leaching MeHg in coal, or biological/chemical methylation of IHg. These results indicate that great importance

Table 2

Comparison of method detection limits for mercury speciation using different liquid phase-based techniques.

	Detection limits (as Hg, ng L <sup>-1</sup> )			Reference
	MeHg	EtHg	IHg	
SPE-HPLC-ICP-MS	3	3	3	This work
Dithiocarbamate resin concentration-HPLC-ICP-MS	16	–	17	[26]
SPE-slurry sampling CV-AAS	0.96	–	0.25	[27]
LPME-CE-UV	940	–	–	[7]
CPE-HPLC-ICP-MS	13	–	6	[28]
LPME-HPLC-UV	3800	700	–	[8]
Micro HPLC-ICP-MS	23	8	11	[29]
SPE-HPLC-UV	1.0	–	1.3	[30]

CV, cold vapor generation; AAS, atomic absorption spectroscopy; LPME, liquid phase micro-extraction; CE, capillary electrophoresis; UV, UV-visible spectrometry; CPE, cloud point extraction.

Table 3

Determined results of water samples by using SPE-HPLC-ICP-MS.

Water sample	Concentration found in water (μg L <sup>-1</sup> )			Spike recovery <sup>a</sup> (%)		
	MeHg	IHg	EtHg	MeHg	IHg	EtHg
Tap water	ND <sup>b</sup>	0.019	ND	96.2	127.7	82.9
River water	ND	0.025	ND	85.5	85.9	62.9
Sea water	ND	0.015	ND	95.4	86.0	79.1
Coal-washing wastewater	0.030	10.2 <sup>c</sup>	ND	108.8	<sup>d</sup>	76.6

<sup>a</sup> Concentration of each mercury species added was 0.200 μg L<sup>-1</sup> except that 0.050 μg L<sup>-1</sup> for coal-washing wastewater. Each result represents the mean of three measurements.

<sup>b</sup> ND, not detected.

<sup>c</sup> Result determined directly with HPLC-ICP-MS without pre-concentration.

<sup>d</sup> Not determined.

should be attached to mercury pollution in coal-washing wastewater. MeHg, EtHg and IHg were then spiked into the water samples to evaluate the recoveries. The results show that the concentrations of mercury species obtained with the proposed method are in good agreement with the expected values.

## 4. Conclusions

A dithizone-functionalized SPE-HPLC-ICP-MS procedure was demonstrated to be an efficient approach for concentration and determination of mercury species in environmental water samples with low detection limit. In this work, the SPE procedure can be easily realized by using a dithizone-modified C18 SPE cartridge. Furthermore, methanol is substituted by a Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution as eluent, which facilitates the use of ICP-MS detection. At optimized conditions, the detection limits of mercury species for 100 mL water sample were about 3 ng L<sup>-1</sup> and the average recoveries of MeHg, IHg and EtHg from spiked de-ion water sample were 93.7 ± 1.7, 83.4 ± 3.5 and 71.7 ± 2.1%, respectively. The simple and fast method can further contribute to understanding the fate and toxicity of mercury species in aqueous systems. Moreover, the functionalized SPE-displacement elution procedure is also expected applicable for pre-concentration of other metallic or organometallic compounds.

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