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Determination of mercury(II) in water samples using dispersive liquid-liquid microextraction and back extraction along with capillary zone electrophoresis

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Abstract We have developed a method for the determination of mercury in water samples that combines dispersive liquid-liquid microextraction (DLLME) with back-extraction (BE) and detection by capillary zone electrophoresis. DLLME is found to be a simple, cost-effective and rapid method for extraction and preconcentration. The BE procedure is based on the fact that the stability constant of the hydrophilic chelate of Hg(II) with L-cysteine is much larger than that of the respective complex with 1-(2-pyridylazo)-2-naphthol. Factors affecting complex formation and extraction efficiency (such as pH value, concentration of the chelating agent, time of ultrasonication and extraction, and type and quantity of disperser solvent) were optimized. Under the optimal conditions, the enrichment factor is 625, and the limit of detection is 0.62 μg L^{-1}. The calibration plot is linear in the range between 1 and 1,000 μg L^{-1} (R^2=0.9991), and the relative standard deviation (RSD, for n=6) is 4.1%. Recoveries were determined with tap water and seawater spiked at levels of 10 and 100 μg L^{-1}, respectively, and ranged from 86.6% to 95.1%, with corresponding RSDs of 3.95–5.90%.

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Introduction

Mercury is one of the prevalent toxic heavy metals with significant environmental concern because of its persistent accumulation, high toxicity, wide use and large distribution [1, 2]. Its measurement is a challenging task by its trace level presence in complicated matrices and the interference of other elements. Therefore, in order to determine the trace level mercury ions and to improve the detection sensitivities, high-efficiency preconcentration methods and high selective and sensitive analysis techniques are urgently required.

Various preconcentration methods have been used for extraction of mercury from environmental samples, such as liquid liquid extraction (LLE) [3, 4], liquid-liquid micro-extraction (LLME) [5–7], cloud point extraction (CPE) [8, 9], solid phase extraction (SPE) [10, 11] and solid phase microextraction (SPME) [12, 13]. Also, other sequential and parallel extraction methods, formation of complexes and chelates and indirect methods have been much used in mercury ion studies [14–17]. Interestingly, speciation identification and determination are usually included, such as EtHg, MeHg and PhHg, together with Hg^{2+} [5, 6, 8, 9, 11, 14, 15, 18].

Recently, a new LLME method called dispersive liquid-liquid microextraction (DLLME) was firstly introduced in 2006 by Rezaee and co-workers [19] and it was successfully applied for the extraction and the preconcentration of organic and inorganic compounds from water samples [20–22]. In DLLME, a mixture containing appropriate amounts of extraction solvent and disperser solvent was injected

rapidly into an aqueous sample with a syringe. Then, a cloudy solution (water/disperser solvent/extraction solvent) was formed and the analyte was extracted into the interior of the droplets of the extraction solvent. After a very short extraction time (a few seconds), the phase separation was accomplished by centrifugation, and the analyte was sedimented in the bottom and removed by syringe and analyzed by various techniques like gas chromatography (GC) [23, 24], liquid chromatography (LC) [25, 26], flame and electrothermal atomic absorption spectrometry (FAAS, ETAAS) [27, 28], and inductively coupled plasma optical emission spectrometry (ICP-OES) [29] and UV–vis spectrophotometry [30]. Lately, the DLLME combined with high performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS) was developed for the speciation of mercury in water samples [31], in which the high sensitivity and excellent linear range were attained for Hg^{2+} but with high ICP-MS cost.

Capillary electrophoresis (CE) for metal analysis has the advantages of low cost, robustness, rapidity, and versatility [32]. However, CE-UV suffers from poor sensitivity because of the small injection volumes and narrow optical path length, as well as weak UV–vis absorbance of metal ions. Consequently, preconcentration methods in conjunction with CE represent a promising tool especially for sensitive determination of metals at trace levels [33]. Recently, mercury speciation analysis by CE has been greatly performed and summarized [14, 15], indicating the possible trend that more research will focus in quantification of mercury species in real samples and in identification of potential interferences, by virtue of various derivatization and sample pretreatment methods used [34–40].

In this work, a new method combining DLLME-back extraction (DLLME-BE) with capillary zone electrophoresis (CZE) was developed for the determination of trace Hg^{2+} in water samples, using 1-(2-Pyridylazo)-2-naphthol (PAN) and L-cysteine (L-Cys) as chelating reagents for DLLME and BE, respectively. The aim of BE was to enable L-Cys to displace the hydrophobic Hg-PAN complex and then form hydrophilic Hg-L-Cys one. More importantly, the aqueous sample solution was naturally compatible with aqueous CZE determination. To the best of our knowledge, this is the first demonstration for the determination of Hg^{2+} by DLLME-BE with CZE. Several major influence factors of the extraction efficiency were systematically investigated. Under optimized extraction conditions, excellent analytical performances were attained, such as wide linear range, low detection limit, high precision, and high enrichment factor. The DLLME-BE with CE-UV was proved potentially applicable for efficient extraction and high sensitive determination of Hg^{2+} in water samples.

Experimental

Reagents

Mercury ion standard stock solutions were prepared by dissolving metal salts $HgCl_2$ in ultrapure water of a concentration of 1,000 mg L^{-1}. 1-(2-Pyridylazo)-2-naphthol (PAN) as the chelating agent was dissolved in ethanol solution. L-cysteine (L-Cys) (0.1%, w/v) was used to back-extract mercury species into aqueous phase at the back extraction procedure. The above three reagents were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China. http://www.reagent.com.cn). Carbon tetrachloride (CCl_4), chlorobenzene (C_6H_5Cl), boric acid, methanol, acetonitrile and acetone were all obtained from Tianjin Kermel Chemical Reagent Factory (Tianjin, China. http://www.chemreagent.com).

Instrumentation

Capillary electrophoresis (CE) measurements were carried out on a Beckman P/ACE™ MDQ Capillary Electrophoresis System (Beckman Coulter, Fullerton, CA, USA. http://www.beckmancoulter.com.cn) equipped with a diode array detector (DAD). Uncoated fused-silica capillaries (Yongnian Optical Fiber Co. Ltd., Hebei, China. http://www.rui-feng.com) with 60.2 cm total length, 50 cm effective length and 75 μm i.d. were used as separation column. The pH value measurements were made with a Rex pH meter (Shanghai Precision Scientific Instrument Corporation, Shanghai, China. http://www.lei-ci.com). The phase separation was conducted using a centrifuge with a relative centrifugal force of $2,200 \times g$ (Xiangyi Centrifuge Instrument Co. Ltd., Hunan, China. http://www.xiangyilxj.com).

Electrophoretic procedures

A new capillary was conditioned firstly with methanol for 15 min, followed by 1 mol L^{-1} NaOH for 20 min, 0.1 mol L^{-1} NaOH for 10 min, ultrapure water for 15 min, and the running buffer for 10 min. Prior to start of daily experiments, the capillary was further rinsed with methanol, water, 1 mol L^{-1} NaOH, 0.1 mol L^{-1} NaOH and running buffer for 5 min, respectively. Between two successive CE runs, the capillary was rinsed with the running buffer for 2 min, which consisted of 100 mmol L^{-1} boric acid and 10% (v/v) methanol (pH= 8.5). The detection wavelength was set at 200 nm and the capillary temperature was maintained at 25 °C. The operating power supply was positive polarity at 22 kV, and pressure injection was performed using 0.5 psi for 5 s (1 psi= 6894.76 Pa). All electrolytes and samples were filtered through a 0.45 μm membrane filter and degassed by ultrasonication prior to analysis.

DLLME-BE procedure

The DLLME-BE procedure is schematically shown in Fig. 1. The aqueous sample solution of 10 mL containing Hg^{2+} and PAN (as chelating reagent) was placed in a 15 mL conical centrifuge tube and 1 mL of 0.1 mol L^{-1} boric acid buffer solution with pH value of 6.5 was added. 800 μL ethanol (as disperser solvent) containing 30 μL chlorobenzene (as extraction solvent) was placed in a 1.5 mL centrifuge tube and was shaken well. Then the mixture was rapidly (within approximate 3 s) injected into the sample solution by using a 1.00 mL syringe, and then the solution was gently shaken. A cloudy solution (water/ethanol/chlorobenzene) was formed in the tube. After centrifugation for 3 min at 3,000 rpm, the dispersed fine droplets of chlorobenzene were sedimented in the bottom of conical tube. The sedimented phase was removed with 25 μL microsyringe and injected into a 0.5 mL centrifuge tube. Ten microliter (10 μL) 0.1% (w/v) L-Cys was injected into the tube and then ultrasonicated for 5 min. In this step, L-Cys displaced PAN to form the complex of Hg-L-Cys, because mercury could form more hydrophilic and stable complexes with L-Cys over their PAN counterparts (Hg-PAN) [38]. After centrifugation, the hydrophilic Hg-L-Cys was extracted into the upper aqueous phase which was prepared for CE analysis.

Results and discussion

CE separation of mercury

In the procedure of DLLME, mercury ion reacted with PAN to form Hg-PAN complex which was extracted into the sedimented phase after the addition of disperser and extraction solvents and centrifugation. Then in the back extraction, L-Cys was added into the sedimented phase and it can displace PAN from the hydrophobic Hg-PAN complex after ultrasonic and centrifugation. Hg^{2+} can form more hydrophilic and stable complex with L-Cys and it can easily be separated by CZE.
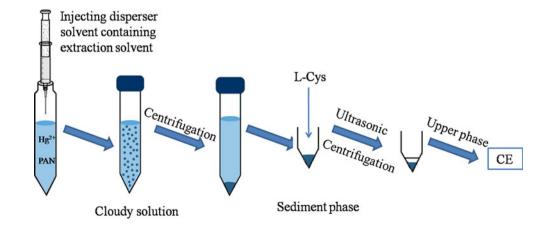
The CZE separation conditions were investigated, such as the nature, concentration, pH value of the electrophoresis buffer, the applied voltage and the sample injection time. The boric acid and methanol system was mostly used according to previous reports [37, 38, 41]. In this work, the buffer pH, the concentration of boric acid and methanol in the buffer solution were examined. Excellent base-line separation between L-Cys and Hg-L-Cys complex was obtained by using the optimized running buffer of methanol of 10% (v/v) in 100 mmol L^{-1} boric acid (pH=8.5). So, the buffer was used in the further study. The excellent base-line separation of Hg-L-Cys complex and L-Cys were achieved within 6 min, which was consistent with the standard solution without DLLME-BE.

Optimization of DLLME-BE conditions

Study of the chelation reaction

Effect of pH value The pH value of the sample solution played an important part in metal-chelate formation and the subsequent DLLME. The pH of the mercury solution was varied by using boric acid buffer solution in the pH value range of 5–8.5. The peak height of the complex increased as the pH value increased to 6.5, and slightly decreased as the pH value increased from 6.5 to 8.5. Hence, the sample solution at pH 6.5 adjusted by boric acid buffer was selected for better chelation reaction.

Effect of PAN concentration PAN was used as chelating agent for Hg^{2+} to produce a hydrophobic complex which was extracted into chlorobenzene. The influence of PAN concentration was evaluated in the concentration range of 0.01–0.05 mmol L^{-1}. The results showed that the peak height of metal-chelate was increased with the PAN concentration up to 0.02 mmol L^{-1} and decreased in the range of 0.02–0.05 mmol L^{-1}. Because of the small volume

Fig. 1 Scheme of the DLLME-BE procedure

of the sedimented phase, PAN can easily be saturated at high concentration. Therefore, the PAN concentration of 0.02 mmol L^{-1} was selected for the further study.

Reaction time

The reaction time was calculated between injection of PAN and then mixture of disperser solvent and extraction solvent. It was investigated from 1 to 10 min. The results showed that the reaction efficiency increased from 1 to 5 min and significantly decreased with the time increasing because of the instability of the formed PAN complex. Therefore, 5 min was selected as reaction time. Then, it is worth pointing out that, the obtained complex formation remained sable over the time needed to make repetitions and confirmed the reliability and repeatability of the DLLME-BE-CE analysis. Although it has not been studied in detail, derivatization and subsequent separation of the former complexes by CE might cause potential transformations of various species [42]. It would therefore be worth investigation whether the complexes formed are sufficiently stable under CE conditions, but so far no such study has been conducted [15].

Study of DLLME conditions

Effect of type and volume of the extraction solvent In DLLME, the extraction solvent should have special characteristics. Firstly, it should form a cloudy solution with water and the disperser solvent. Then it should have higher density than water which can easily enable to separate the extraction solvent from the water phase by centrifugation. Also it should have high extraction efficiency, selectivity and low solubility in water. Therefore, type and volume of the extraction solvent was studied. Carbon tetrachloride and chlorobenzene were selected for the determination of Hg^{2+}. Between the two kinds of extraction solvents, chlorobenzene exhibited higher enrichment factor (EF), which is defined as the ratio between the analyte concentration in the final aqueous phase and the initial concentration of the sample solution, and formed a well stable cloudy solution. Therefore, chlorobenzene was chosen as the extraction solvent.

To investigate the effect of extraction solvent volume, a series of sample solutions were tested using 800 μL ethanol containing different volume of chlorobenzene (20–40 μL at 5 μL intervals). Experimental results suggested that the peak height increased with increasing volume of chlorobenzene up to 30 μL, and then it decreased slightly owing to the increase of sedimented phase volume. So, 30 μL was chosen as the optimal extraction solvent volume for the further study.

Effect of type and volume of disperser solvent The disperser solvent should be miscible in the extraction solvent and the aqueous sample. Methanol, ethanol, acetonitrile and acetone were investigated. Several sample solutions were studied using 800 μL of each disperser solvent, which contained 30 μL chlorobenzene. Finally, ethanol was chosen as the most suitable solvent because of the higher extraction efficiency and its lower toxicity and lower cost.

The effect of the disperser solvent volume was also studied. The peak height increased initially up to 800 μL ethanol, while, afterwards, it decreased as the ethanol volume further increased. The volume variation of the disperser solvent might affect the formation of an emulsion system of "water/ethanol/chlorobenzene", and then lead to different dispersion degree of the extractant in water, thereby influencing the extraction efficiency. When using low volume of ethanol, the cloudy sediment phase was not formed well, thereby, the extraction efficiency decreased. However, excessive ethanol caused the solubility increase of the complex, so the extraction efficiency also decreased. Thus, 800 μL ethanol was selected for the following work.

It was observed that different volume of ethanol caused the variation of the sedimented phase, at the constant volume of chlorobenzene (30 μL). The volume of the disperser solvent and the volume of the extraction solvent should be changed simultaneously in order to obtain the same volume of the sedimented phase as reported [28, 43–45]. Calculated from experimental results, the volume difference was obtained in about 4% after centrifugation.

Study of back extraction conditions

Effect of L-Cys volume L-Cys of 0.1% (w/v) was chosen as the extraction solvent as reported [37, 38]. In this process, Hg^{2+} formed more hydrophilic and stable complex with L-Cys over its PAN counterpart [38]. The volume of L-Cys was investigated from 10 to 25 μL with 5 μL interval under constant extraction conditions. The result showed that when the volume increased, the peak height decreased. So, we chose 10 μL in the further experiment.

Ultrasonic time

After L-Cys was added to the sediment phase, in order to accelerate the substitution reaction between Hg-PAN and Hg-L-Cys, ultrasonication was employed. Then, the solution was emulsified and must be centrifuged. The solution was separated into two phases and the upper aqueous phase was employed for analysis. The ultrasonic time was investigated in the range of 1–10 min. The results showed

Table 1 Comparisons of analytical performance for mercury determination by using different CE-hyphenated techniques and other techniques

Detection techniques	Pretreatment techniques	Migration time (min)	LOD (μg L^{-1})	Linear range (μg L^{-1})	RSD [a] (%)	EF [b]	Ref.
CZE-UV	DLLME-BE	5.6	0.62	1–1000	4.07	625	This work
CZE-UV	dCPE [c]	10	10	—	5.0	52	[38]
CZE-UV	SPE	10	2.41		—	—	[35]
MEKC [d]-UV	Off-column derivatization	10	130	—	—	—	[46]
CZE-UV	FASI [e]	16.5	0.14	0.69–13.8	5.07	813	[34]
CZE-UV	HF-LLLME-LVSS [f]	8.5	0.03	0.1–10	16.40	4580	[40]
CE-FHF-AAS [g]	Off-column derivatization	9	53	—	2.0	—	[36]
Chip-CE-AFS [h]	Off-column derivatization	1.1	53	—	1.5	—	[37]
CE-amperometric detection	IE [i]	8	1.7		—	—	[39]
HPLC-UV	IL-SDME [j]	24	22.8	80–480	11.6	3	[6]
ETV-AAS [k]	SDME	—	0.01	0.1–50	6.7	970	[5]
HPLC-ICP-MS [l]	CPE	13.4	0.006	0.2–200	4.4	57	[47]
HPLC-ICP-MS	DLLME	15	0.0014	0.005–2	4.4	350	[31]

[a] Relative standard deviation for peak height

[b] Enrichment factor

[c] Dual-cloud point extraction

[d] Micellar electrokinetic chromatography

[e] Field-Amplified Sample Injection

[f] Hollow fiber-based liquid-liquid-liquid microextraction-large-volume sample stacking

[g] Flame-heated furnace atomic absorption spectrometry

[h] Atomic fluorescence spectrometry

[i] Ion exchange

[j] Ionic liquid single-drop microextraction

[k] Electrothermal vaporization atomic absorption spectroscopy

[l] Inductively coupled plasma mass spectrometry

that there was no significant signal increasing with the time increasing. So, 5 min was chosen for sonication.

Interference study

In order to demonstrate the selectivity of the developed method, the effect of alkali and alkaline earth metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}) and heavy metal ions (Pb^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}), which usually coexist in environmental water samples were tested. Under the optimized conditions of DLLME-BE-CZE, the test standard solutions containing 100 μg L^{-1} Hg^{2+} and the criterion for interference was set at ±10% in the signals observed in absence of any foreign metal ions. Na^+, K^+, Ca^{2+}, Mg^{2+} are inert, and even at 500 times higher concentration (50 mg L^{-1}) their effects on the extraction of Hg^{2+} can be neglected, since the recoveries of Hg^{2+} was in the range of

99.0–99.8%. Pb^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Co^{2+} and Cd^{2+} individual at 2 mg L^{-1}, and Cu^{2+} at 1 mg L^{-1}, did not cause significant interferences with the recoveries of Hg^{2+} ranging from 95.7% to 100.6%. In addition, the organomercury compounds (methyl mercury (MeHg), ethylmercury (EtHg) and phenlmercury (PhHg)) were found no interferences, since their migration times were much different from that of Hg-L-Cys. Therefore, the developed method showed high specificity and reliability for Hg^{2+} determination.

Method performance

Under the above optimized DLLME-BE conditions, a series of experiments were performed for obtaining good method performances. The calibration curves were linear in the range of 1–1,000 μg L^{-1} of Hg^{2+}. High preconcentration efficiency was obtained with the calculated EF of 625. And the relative

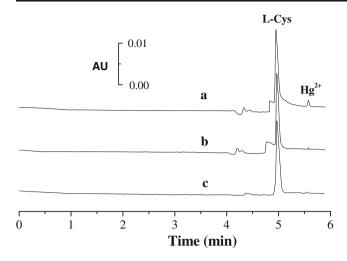**Fig. 2** Electropherograms of Hg^{2+} of the extract obtained by the present DLLME-BE method from (**a**) seawater sample spiked with 2 µg L^{-1} standard Hg^{2+} solution, (**b**) seawater sample without spiking, and (**c**) tap water sample without spiking. Experimental conditions: DLLME: 800 µL ethanol as disperser solvent containing 30 µL chlorobenzene as extraction solvent, 0.02 mmol L^{-1} PAN as chelating reagent, 5 min as reaction time; BE: 10 µL L-Cys of 0.1% (w/v) as extraction solvent and 5 min as sonication time; CE: capillary, total length of 60.2 cm and effective length of 50 cm; voltage applied, 22 kV; running buffer: 100 mmol L^{-1} boric acid and 10% (v/v) methanol (pH=8.5); sample injection: 0.5 psi, 5 s; detection wavelength, 200 nm

standard deviation (RSD) was 4.07% based on the peak height for six replicates of a standard solution at 500 µg L^{-1} Hg^{2+}. The limit of detection (LOD) was obtained based on the signals as three folds of the baseline noise (S/N=3), attaining the favorable LOD of 0.62 µg L^{-1}. The detection limit is lower than the maximum contaminant level (MCL) for Hg^{2+} in drinking water, namely 2 µg L^{-1} formulated by the United States Environmental Protection Agency (EPA) and 1 µg L^{-1} by the Health Department of the Chinese Government.

Comparisons of analytical performances with other reported CE-hyphenated techniques are shown in Table 1 for the determination of Hg^{2+}. As can be seen from Table 1, the DLLME-BE assisted to obtaining 4 and 16 times higher sensitivity, 12 times higher EF in a shorter time than those

Table 2 Recovery and precision of the DLLME-BE-CZE method for the determination of Hg^{2+} in the two spiked real water samples (*n*=6)

Sample	Added (µg L^{-1})	Found (µg L^{-1})	Recovery (%)	RSD (%)
Tap water	10.0	9.51±0.56	95.1	5.90
	100.0	91.2±3.9	91.2	4.24
Seawater	10.0	8.66±0.34	86.6	3.95
	100.0	93.6±4.8	93.6	5.10

of dCPE and SPE, all three followed by CZE-UV detection [35, 38]. Furthermore, using the same UV detection, the presented sensitivity was even above 2 orders of magnitude higher than that of off-column derivatization [46]. Several CE-UV applications after sample stacking also referenced in two recent reviews [14, 15], show the same or even better sensitivity and EF for Hg^{2+}, respectively, such as 0.14 µg L^{-1} and 813 using FASI [34], and 0.03 µg L^{-1} and 4580 using HF-LLLME-LVSS [40], using longer migration time (Table 1). In addition, compared with generally recognized element specific detection methods, such as atomic absorption spectrometry (AAS) [36], atomic fluorescence spectrometry (AFS) [37] and amperometry [39], coupled to off-column derivatization [36, 37] or ion exchange (IE) [39], the developed method still offered about 3 and 85 times higher sensitivity with high precision in a short time.

Besides the CE analysis, as seen from Table 1, other hyphenated techniques are also included for comparison. The obtained linear range was the similar to or wider than the listed ones even ICP-MS [31, 47] or AAS [5]. The obtained LOD was lower than that reported by using HPLC-UV with IL-SDME [6]. Also, it is noted from Table 1 that the CPE assisted HPLC-ICP-MS can detect two orders of magnitude lower Hg^{2+} concentrations [47], and even lower down to 0.0014 µg L^{-1} by using DLLME assistance [31] (Table 1). Nevertheless, the benefits of CE are still obvious and well-known that, it is easy to use and the running costs are low and running time is short. Therefore, the developed DLLME-BE was demonstrated an ideal sample preconcentration method and its coupling with CZE-UV indicated great potential for the analysis of Hg^{2+} in real water samples.

Application to water samples

To evaluate the feasibility of DLLME-BE-CZE, the developed method was applied to the tap water and seawater samples. The electropherograms from the extracts of tap and seawater samples are shown in Fig. 2. Analysis of the seawater sample spiked with Hg^{2+} standard solution at 2 µg L^{-1} (MCL formulated by EPA) shows two resolved peaks in Fig. 2a at *ca.* 5.1, and 5.6 min, corresponding to L-Cys and Hg-L-Cys, respectively. On the other hand, the endogenous Hg^{2+} was not detected in the seawater (Fig. 2b) and tap water (Fig. 2c) samples.

To further evaluate the method performance in complex matrices, the recovery was investigated by spiking the Hg^{2+} standard at two levels (10 and 100 µg L^{-1}) and analyzing six replicates for each concentration. Recoveries were between 86.6% and 95.1%, with the RSD lower than 5.90% (Table 2). The developed DLLME-BE-CZE method proved greatly applicable for the determination of Hg^{2+} in water analysis.

Conclusions

This work demonstrated the first application of the DLLME-BE coupled to CZE for the determination of Hg^{2+} in water samples. By use of the two-step preconcentration procedure, the enrichment factor for the metals investigated was 625. Besides preconcentrating trace Hg^{2+}, this procedure could significantly eliminate the interference from foreign ions and matrix. The present DLLME-BE-CE with simple UV detection obtained similar or higher detection sensitivity to/than some hyphenation methods with simple instrumental setup and obviously low costs, as a rapid, simple, accurate, and environmental friendly analysis methods. With the advantages it has, further research focusing on novel ligands will be promising for trace analysis of various heavy metals in water samples.

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