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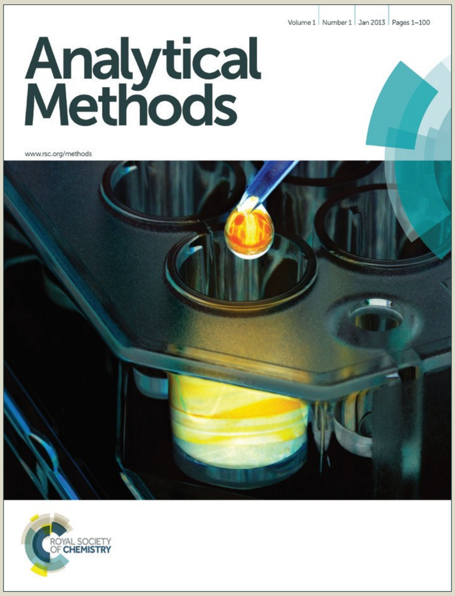

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Determination of trace mercury(II) in wastewater using on-line flow injection spectrophotometry coupling with supported liquid membrane enrichment

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An on-line flow-injection spectrophotometric method coupling with supported liquid membrane enrichment was developed to determine trace Hg(II) in water. Tributyl phosphate (TBP) dissolved in kerosene was used as the flow carrier in supported liquid membrane extraction system. The effect of various parameters on Hg(II) measurement was investigated in this developed system. The optimum conditions were determined as 20% TBP in membrane phase, 0.02 mol L^{-1} NaOH in accepting phase, 0.8 mol L^{-1} HCl in feeding phase, 0.2 μm PTFE membrane in enrichment process, and 20 min enrichment time. Under these optimum conditions, the linear range for Hg(II) measurement was from 0.2 to 30 μg L^{-1} with a detection limit of 0.06 μg L^{-1}. Additionally, this system was also demonstrated to be feasible to determine trace Hg(II) in wastewater.

1. Introduction

Mercury has attracted considerable attention as a serious pollutant due to its toxic and bio-accumulative properties.[1] The most toxic form of mercury is the highly reactive Hg(II) salts, which pose a significant health risk to humans and wildlife through the aquatic food chain, even at a trace level.[2]The Hg(II) accumulation in human body can not only lead to disease of heart, liver and thyroid, but also result in disorder of nervous system and mental retardation. Many countries have enacted legislation and written regulations with the goal of reducing mercury emissions to air, land and water. As a consequence, accurate quantification of trace Hg(II) in water or wastewater is much critical.

Various methods, such as atomic spectroscopy,[3,4,5,6] spectrophotometric,[7,8,9,10,11] and electrochemical analysis[12], have been developed to measure Hg (II) concentration in water or air, but all of them have substantial disadvantages. For example, spectrophotometric determination of Hg(II) usually adopts dithizone extraction, which is not only time and reagent consuming, but also has an unsatisfactory selectivity. Additionally, this method also uses highly toxic potassium cyanide, which could result in a secondary pollution. Furthermore, determination of Hg(II) concentration in water using these methods may be more difficult due to interference from other complex constituents in contaminated water as well as much low Hg(II) concentration typically found in water.

Supported liquid membrane-flow injection union technology (SLM-FI) is a novel method for sample pretreatment.[13,14] In this method, liquid membrane is used for separate and concentrate Hg(II) in samples, while flow-injection technology can determine concentrated Hg(II). This method can separate and concentrate desired metals effectively to avoid interference from other constituents.[15,16] Therefore, it would be expected that SLM-FI coupling with a specific detection method can be applied for analysis of trace metal in polluted water.

This study aims to develop an on-line supported liquid membrane enrichment-flow injection spectrophotometric system for determination of trace Hg(II) in water. Ethyl violet was used as the chromogenic reagent in this system, as it has high sensitivity and selectivity for Hg(II). The operating conditions were optimized both in SLM enrichment process and flow injection system. Furthermore, different samples were tested using this developed system including from real wastewater such as industrial sewage.

2. Experimental

2.1. Reagents and equipments

Standard Hg(II) solution was prepared using $HgCl_2$(analytical grade) stock solution (1 mg mL^{-1}) with distilled water. 1000 μg mL^{-1} standard Hg(II) sample (GBW08617) was supplied by National Standard Material Center of Beijing, and was diluted distilled water before use. The mixture of 20% KI and 2% ascorbic acid was dissolved with polyvinyl alcohol,[16] 0.125 g ethyl violet was dissolved in 250 ml deionized water to prepare 0.05% ethyl violet solution, which was kept in the dark

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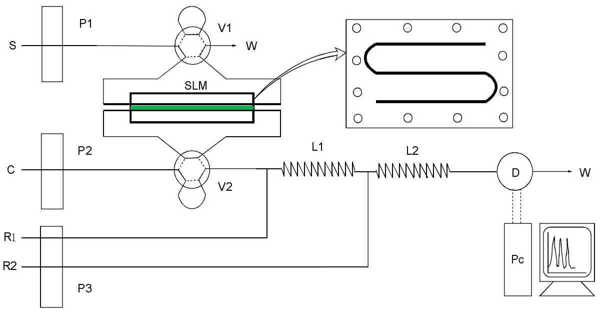
condition to prevent being degraded. After washed using sulfuric acid, kerosene solvent was distilled and its distillate at 200-220°C was collected. Other reagents including tributyl phosphate, hydrochloric acid, sodium borohydride, sodium hyposulfite were all analytical grade.

XF-1 automatic metallic element analyzer was used in flow injection system for Hg(II) detection.[15,17] Flow cell with a 2.0 cm optical path (Modern Separation and Analysis Laboratory of the Light Textile and Food School of Sichuan University, Sichuan) was equipped in the analyzer. Liquid reagents were transported to the analyzer using a HL-2 constant-flow pump (Huxi Analyzer Co., Shanghai). The element analyzer was connected to a computer for signal processing. PTFE membrane with 50 μm thickness, 0.2 μm porous diameter and 70% porosity (Beijing Plastic Institute, Beijing) was used for extraction and enrichment of Hg(II). Fabrication of the supported liquid membrane (SLM) extraction equipment with 0.5mm depth, 2 mm width, and 400 mm length was shown in a previous study.[15] PE6-2 Hydride Genration AFS (Puxi Universal Equipment Co., Beijing) was used for Hg(II) relative analysis with the SLM-FI method.[18]

2.2. Experimental method

The flow diagram of the developed method is shown in Fig. 1.



S: Sample; P1，P2，P3: Pump; C: Re-extraction solution; SLM: Supported liquid membrane; R1: KI solution; R2: ethyl vio1ct solution; V1, V2: Valve; D: Detector； L1, L2: Reaction coil; Pc: Computer system; W: Wastewater.

Fig.1. Schematic diagram of supported liquid membrane-flow injection analysis (SLM-FIA) system

The PTFE microporous membrane was immersed into tributyl phosphate (TBP) kerosene solution for 18-24 h, and then it was fixed in SLM equipment after removing kerosene from surface using filter paper. The flow channels were connected to a PTFE tube with a 0.5 mm inner diameter, and the flow rate of each channel can be adjusted individually. Standard solutions or samples were extracted and re-extracted for 20 minutes, and then the valve of XF-1 analyzer was changed to the detection state to measure Hg(II) concentration in the re-extraction solution. At this point, the re-extraction solution C was mixed with solution R1 in L1, following reaction with R2 (ethyl violet solution) in L2. Afterwards, the mixing solution was pumped into detection tank D and its absorbance was measured at 540 nm due to dye generation. Finally, Hg(II) concentration in water was quantified using the height of peaks at 540 nm.

The effect of various parameters for Hg(II) enrichment was investigated by changing each variable in turn while keeping others constant, including HCl concentration (0.01-0.03 mol L^{-1}), TBP concentration (5%-15%), sodium hyposulfite concentration (0.005-0.025mol L^{-1}), enrichment time (5-30min) and the membrane porous diameter (0.1-0.3 μ m). In the flow injection system, both ethyl violet and KI were added and reacted with Hg(II) in the chromogenic reaction, therefore their effects on Hg(Ⅱ) detection were also evaluated . When all the reagents are present, the chromogenic reaction will take place within a few minutes and there will be a colour change. Thus, in our study, the change of absorbance (λmax =540 nm) was taken as an indication of the amount of mercury(Ⅱ) present in the samples. Additionally, the effect of PVA concentrtion was also taken into account in this study as its addition can enhance the colour variation in the chromogenic reaction. Furthermore, the flow rates of pump P2 and P3 were also tested in the range of 0.5 to 1.5 mL min^{-1} and 0.1 to 1.0 mL min^{-1}, respectively.

After optimization, a 1000 mL real wastewater sample was taken from a metallurgical refinery sewage and its pH was adjusted to 1-2 with HCl solution and then diluted to 50 mL with distilled water. Parallel measurements and standard addition tests were carried out using the developed method.

3. Results and discussion

3.1. Hg(II) extraction principle

The separation capability of supported liquid membrane is mainly depended on carrier properties. When TBP was used as a carrier to migrate Hg(II) in this study, TBP and Hg(II) generated a neutral complexing compound in the interface of donor (feed liquid) phase and membrane phase (Eq. 1).

$$HgCl_2 + TBP = TBP\cdot HgCl_2 \qquad (1)$$

Through membrane phase, this complexing compound reacted with $Na_2S_2O_3$ to form another complexing compounds in the interface of membrane phase and accepter phase (Eq. 2, 3, 4 and 5), and TBP was released to membrane phase.

$$TBP\cdot HgCl_2 + S_2O_3^{2-} = HgS_2O_3 + TBP + 2Cl^- \qquad (2)$$

$$TBP\cdot HgCl_2 + 2S_2O_3^{2-} = [Hg(S_2O_3)_2]^{2-} + TBP + 2Cl^- \qquad (3)$$

$$TBP\cdot HgCl_2 + 3S_2O_3^{2-} = [Hg(S_2O_3)_3]^{4-} + TBP + 2Cl^- \qquad (4)$$

$$TBP\cdot HgCl_2 + 4S_2O_3^{2-} = [Hg(S_2O_3)_4]^{6-} + TBP + 2Cl^- \qquad (5)$$

Hg(II) migration was enhanced significantly because of a strong complexes ability between Hg^{2+} and $S_2O_3^{2-}$ ($lg\beta_1$=29.86, $lg\beta_2$=32.26, $lg\beta_3$=33.61), which resulted in a good separation of Hg(II) from solution.

3.2. Parameter optimization for extraction and enrichment

The extraction and enrichment of Hg(II) from samples depends on the relative concentrations of reagents (such as HCl, TBP and $Na_2S_2O_3$), enrichment times and porous diameter of membrane. As shown in Fig. 2, peak height was increased with the increase of HCl concentration to 0.02 mol L^{-1} and then dropped with the further increase of HCl concentration to 0.03 mol L^{-1}. A maximum relative peak value of 210×10^{-3} a.u. was found when HCl concentration was 0.02 mol L^{-1} in samples.

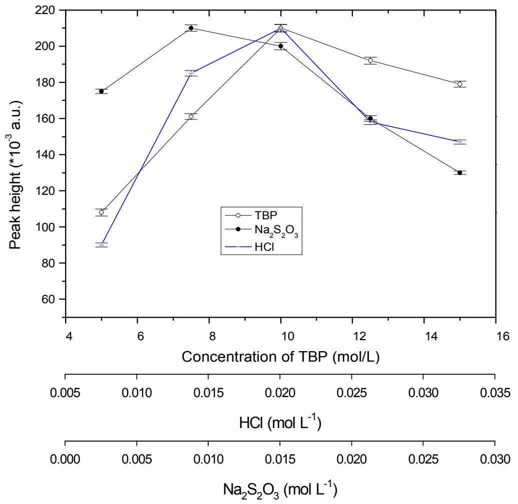


Fig. 2. Effect of TBP, HCl and $Na_2S_2O_3$ concentration on Hg(II) measurement

Sodium hyposulfite was used as extraction solution due to the following two reasons. First, it has a good complexing capability with mercury, which can enhance mercury migration. Second, it can improve sensitivity of the developed system. Fig. 2 shown that the relative peak value was increased to 210×10^{-3} a.u. with the increase of hyposulfite concentration to 0.01mol L^{-1}, then decreased with further increasing hyposulfite concentration. The optimum sodium hyposulfite concentration was observed at 0.01 mol L^{-1} in re-extraction phase with a maximum relative peak at 210×10^{-3} a.u.

The effect of TBP concentration on Hg(II) mobility was investigated in the range of 5% to 15%. The result shown the relative peak reached a maximum value of 210×10^{-3} a.u. when carrier (TBP) concentration was 10% (Fig. 2).

A linear relationship between relative peak value and enrichment time was observed in the range of 5 to 30 min, but the optimum enrichment time was selected at about 20 min when considering analysis frequency (Fig. 3). For extraction and enrichment, but its stability was getting worse at the same time by the wastage of kerosene solvent. According to our experiments, if the membrane diameter over 0.3 μm(0.4 or 0.5), the extraction and enrichment was terrible and their reproduction quality was not so good. Therefore, the PTEE membrane with 0.2 μm diameter was the best option for the balance of stability and capability of extraction and enrichment.

The produced liquid membrane had a good stability within 24 h, which can be used for Hg(II) analysis. However, its stability was gradually decreased after 24 h, which could be due to run off of carrier in membrane phase. Therefore, further study is needed to investigate how to improve the stability of liquid membrane as well as prolong its longevity.

The PTEE membrane with 0.1 μm diameter had a preferable stability, but its capability for extraction and enrichment was relatively unsatisfactory. On the contrary, the PTEE membrane with 0.3 μm diameter had a high capability

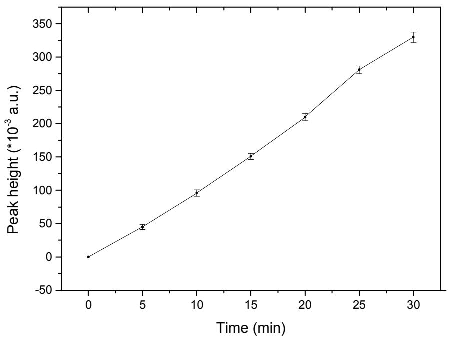


Fig. 3. Effect of enrichment time on Hg(II) measurement

3.3. Optimization of flow injection system

As shown in Fig. 4,Taking into account of compromise between the conflicting demands of reproducibility, sensitivity and noisily, the optimum flow-rates of P2 and P3 were selected at 1.0 and 0.5 mL min^{-1} respectively, as shown in Table 1.

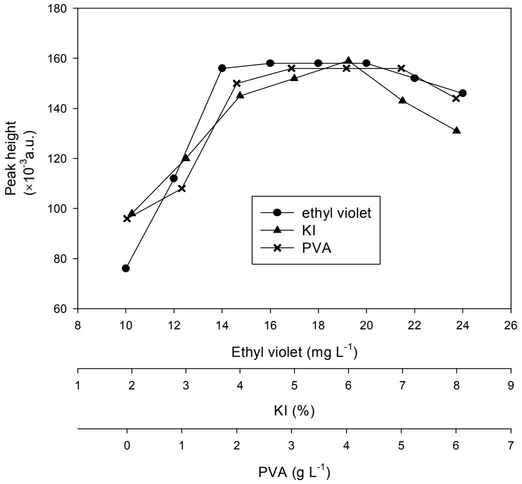


Fig. 4. Effect of ethyl violet, KI and PVA concentration on Hg(II) measurement

Table 1 Optimized conditions for FIA

Conditions	Experimental range	Optimum value
Reaction coil L1 (m)	1-6	3
Reaction coil L2 (m)	1-6	3
Flow velocity P2 (mL min^{-1})	0.5-1.5	1.0
Flow velocity P3 (mL min^{-1})	0.1-1.0	0.5

Additionally, the result indicated the sensitivity of the developed system was improved with length increase of reaction coil to 3 m, then decreased with further length increase of reaction coil. Thus, two 3-m coils were chosen for flow injection system (Table 1).

3.4. Linear range and detection limit

Quantitative analysis was based on the maximum relative peak under optimized experimental conditions when the baseline was stable. A good linear relationship with high regression coefficient was observed between the maximum relative peak value and Hg(II) concentration within 0.2-30 μg L^{-1} as follows: H (×10^{-3} a.u.) = 2.130 C (μg L^{-1}) + 9.313. r=0.9994. The detection limit was 0.06 μg L^{-1}, which is three times higher than background noise. Five parallel measurements were carried out for 10 μg L^{-1} Hg(II) standard solution, and the relative standard deviation was only 2.38%, indicating the high accuracy of the developed method in this study.

3.5. Effect of coexistent ion

In order to ensure an insignificant interference of various ions on Hg(II) measurement using the developed system, i.e., relative measurement error less than ±5%, the maximum times of their concentration higher than 20 μg L^{-1} was determined at the optimum conditions , and the investigating results of the interference of other ions listed in Table 2.

Table 2 The following concentration of ions do not interfere the developed mercury determination (concentration in mg L^{-1}) [a]

Ion	Concentration	Ion	Concentration
K^+	40	Zn^{2+}	100
Na^+	40	Al^{3+}	100
SO_4^{2-}	40	Pb^{2+}	40
Cl^-	40	Ni^{2+}	40
Mg^{2+}	200	Cr^{3+}	40
Ca^{2+}	200	Mo^{5+}	40
NH_4^+	160	Cu^{2+}	1
CO_3^{2-}	160	Ag^+	1
NO_3^-	160	Bi^{3+}	1
HCO_3^-	160	Sn^{4+}	1
Mn^{2+}	100	Cd^{2+}	1
Fe^{3+}	100		

[a] Concentration of mercury was 20 μg L^{-1}

In addition, although several other ions such as Sn^{4+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} were demonstrated a major interference in chromogenic system, the upper limit of their concentration has also been significantly improved in this developed system.

3.6. Determination of water samples

The results for standard water sample analysis using the developed method at the optimized conditions are shown in Table 3.

Table 3 Determination of Hg(II) concentration in certified reference materials using the developed method (n = 3)

	Certified (μg L^{-1})	Measured (μg L^{-1})	RSD (%)
GBW 08617 (1)	5	4.9±0.2	3.10
GBW 08617 (2)	10	10.1±0.2	2.52
GBW 08617 (3)	20	19.9±0.5	2.51

The measured results are much consistent with the values of the certified reference materials, and the RSD (n=3) is less than 3.10%. Additionally, this system was applied to determine Hg(II) concentration in real wastewater samples, and a standard method (HG-AFS) was applied to test the same samples. Results obtained by the developed method and that of standardised method (HG-AFS) compare well. All the results are shown in Table 4.

Table 4 Determination of Hg(II) concentration in two types of wastewater using the developed method (n = 3)

Samples	Measured (μg L^{-1})	Added (μgL^{-1})	Total (μg L^{-1})	Recovery (%)	HG-AFS (μg L^{-1})
Waste water1	12.4±0.4	10	22.6±0.5	102.0	12.3±0.2
Waste water2	12.5±0.4	10	22.3±0.6	98.0	12.6±0.2
Waste water3	15.4±0.5	10	25.0±0.5	96.0	15.9±0.2
Waste water4	13.8±0.5	10	23.2±0.5	94.0	13.9±0.2
River water1	1.2±0.3	5	6.1±0.3	98.0	1.2±0.1
River water2	——	5	4.9±0.2	98.0	——
River water3	——	5	4.8±0.3	96.0	——
Tap water1	——	5	5.1±0.2	102.0	——

Recovery tests were carried out on samples with adding known amounts of Hg(II) inside. The Hg(II) recovery at different concentration levels was varied from 94% to 102%, indicating the method developed in this study could be applied to determine trace Hg(II) in wastewater, and other environmental water samples with a satisfactory result.

4. Conclusion

An flow injection spectrophotometric system coupling with on-line supported-liquid-membrane enrichment method has been developed successfully for determination of trace Hg(II) in water. The developed system demonstrated the promising results in terms of accuracy (94% to 102% recovery) and precision (RSD≤3.10%) for Hg(II) measurement. Moreover, high sensitivity in this system was achieved with a detection limit of 0.06 μg L^{-1}.

This developed SLM-FI method is suitable for the determination of mercury greater than 0.2 μg.L^{-1} in water, river water, surface water and waste water. The time needed for the complete method including the extraction, enrichment, and determination is less than 25 min. Results obtained by the developed SLM-FI method and those of the standardized methods (standard samples) compare well. Thus it is possible to elate and detect mercury at very low concentration.

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