Cold Vapor Atomic Absorption Determination of Hg in Crude Oil and Gasoline Samples after Solid Phase Extraction Using Modified Disks

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ABSTRACT: *A facile and highly efficient method have been developed for the preconcentration of the mercury content in crude oil and gasoline samples after digestion with microwave-assisted digestion. Octadecyl silica membrane disk has been modified by the recently synthesized triazene ligand, (E)-1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triaz-1-ene (ENT), then the modified membrane was used for the preconcentration of mercury(II) ions and Cold Vapor Atomic Absorption Spectrometry (CV-AAS) have been used to determine the Hg (II) ion. Solution studies of ENT with a series of metal ions have been done in advance, and the results showed a strong affinity of ENT to the mercury ion. For solid phase extraction, pH of sample 6.0, flow rates 3.0 mL / min, enrichment factor 240, capacity of modified disk 690 µg Hg per 8.0 mg of ligand, eluent solvent 5.0 mL, 1.5M* $HClO_4$*, and the amount of the ligand 8.0 – 10.0 mg, have been optimized. A linear calibration curve has been obtained in the range of 0.80 – 65 µg / L with* $R^2 = 0.9991$ *and the Limit Of Detection (LOD) based on three times the standard deviation of the blank was 0.25 µg / L. The Relative Standard Deviation (RSD) for the determination of 50 mL aqueous solution containing 0.5 µg / L Hg (II) found to be 1.0 % while a RSD value of 1.9% have been obtained for the determination of 0.1 µg / L Hg (II) (n=3). The characteristic concentration is 1.2 µg / L in the original samples. The newly developed method was successfully applied to the determination of mercury ion in real crude oil samples, which are very important in environment and industries process.*

KEY WORDS: *Mercury, Crude oil, Solid phase extraction, Triazene, Cold Vapor Atomic Absorption Spectroscopy (CV-AAS).*

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INTRODUCTION

Crude oil and its derivatives are complexes matrix composed predominantly of saturated and aromatic hydrocarbons. Heteronuclear compounds, emulsified water and minerals are also presented [1]. Considering this fact that crude oil has been in touch with the earth layers for several million years, different kind of metals in different concentration ranges are expected [2]. Unfortunately knowledge of the mercury concentrations in crude oil is much less certain. Estimates of the average total mercury concentrations in crude oil have ranged widely from 10 ng / g of oil to 3500 ng / g of oil [3]. Another reference has suggested concentration range of 0.01 ng / g to 10 μg / g for total mercury and emphasizes that these amounts are highly depended upon geological location [4]. Thus, the determination of mercury content in crude oil and oil derivatives has environmental and industrial importance, because this metal can deposit in the equipment, which could affect the maintenance and operation [5]. On the other hand, mercury poisons catalysts used in oil refining [6-8]. In all kinds of petrochemical processes regarding human health, mercury could concentrate in fish body and eventually causes different diseases and death.

There are many different techniques for determination of mercury such as spectrophotometry [9, 10], coated magnetic nanoparticle adsorbent [11], inorganic sorbent and adsorbent [12, 13], neutron activation analysis [14] and so on. However, Cold Vapor Atomic Absorption Spectrometry, (CV-AAS) is widely accepted technique for the determination of mercury because of its simplicity, higher sensitivity, and selectivity [15-17]. American Society for Testing and Materials (ASTM), offers two different methods; ASTM D7622 and ASTM D7623 for mercury concentration ranges of 5.0-350 μg / L to 5.0-400 μg / L respectively [18,19]. Recently, several methods have been reported for even lower detection limit [20-24].To achieve lower limit of detection in metal analysis various separation-preconcentration techniques including solvent extraction [25], Electro-deposition [26], coprecipitation [27], cloud point extraction [28], membrane filtration [29] and solid phase extraction [30-32] had been used in analytical studies. Among these methods, solid phase extraction is still more interested because of its simplicity, higher preconcentration factor, rapid phase separation, time and cost saving [33, 34].

The aim of this work is to develop a simple and inexpensive procedure step after the microwave-assisted digestion of crude oil and gasoline samples in order to: (i) eliminate interfering species from sample matrix to ensure accurate results and (ii) enrich mercury content in sample leading to better detection ability. In this regard, a newly synthesized ligand with high affinity to Hg (II) ions was used as a disk modifier in solid phase extraction of mercury (II) ions from digested sample.

EXPERIMENTAL SECTION

Instruments

A Varian AA 240 atomic absorption spectrometer equipped with VGA 77, (Australia) was used for all absorption measurements. A photron mercury hollow cathode lamp was used as light source. The operation condition of the instrument was adjusted according to the manufacturer instruction (current 3.0 mA, absorbance wavelength at 253.7 nm, spectral bandwidth at 0.5 nm). Samples were digested in Analytik Jena Microwave Digestion System TOP Wave (Germany), equipped with the high performance vessels CX 100 (100 mL, max. 300°C, and max. 100 bars). HP spectrophotometer, (USA) (Agilent 8453) equipped with thermostated bath (Huber Poly-state CC1) was used for electronic absorption spectra recording. Extraction was achieved by ME1 pump from Vacuurand company. The pH adjustment was done by a Metrohm digital pH meter, (Switzerland) model 632 equipped with a combined glass – calomel electrode. Extraction was performed with Empore high performance extraction membrane disk (47 mm diameter × 0.5 mm thickness) containing octadecyl bonded silica (8μm particles, 6 nm pore size) from 3M Company. The disk was used in conjunction with standard Millipore 47 mm filtration apparatus. Hamilton sampler (100, 500 μL) was used for all solution preparation.

Reagents and solutions

Methanol, acetonitrile, and other organic solvents used in this work, were of ACS grade, and all acids and water were of pro analysis from Merck. All salts were of the highest purity available from Merck and used as received without purification. A 1000 mg / L stock solution of Hg (II) was prepared by dissolving 0.1349 g $HgCl_2$ in 5 mL concentrated nitric acid and diluting to 100 mL

Table 1: Operation program of microwave digestion system.

Condition	Step		
	1	2	3
Temperature (ºC)	130	160	230
Max. pressure (bar)	80	80	100
Heat ramp (min)	10	10	10
Hold time (min)	10	10	30

with deionized water. Working solutions were prepared daily from the stock solution by successive dilution with water. A solution of 20% (w/v) stannous chloride was prepared by dissolving $SnCl_2$ powder in 10% HCl solution. (E)-1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triaz-1-ene ligand (ENT) was synthesized and purified according to the reported procedure [35]. All glassware was kept in 10% (v/v) nitric acid and washed three times with doubly distilled water before use.

Preparation of modified disk

After placing the membrane in the filtration apparatus, it was first washed with 10 mL methanol, then with 10 mL acetonitrile to remove all contaminations arising from the manufacturing process and the environment, followed by washing with 20 mL deionized water. After drying the disk by passing air through it for several minutes, a solution of 8 mg ENT ligand was dissolved in 5 mL acetonitrile and introduced to the reservoir of the apparatus and drawn slowly through the disk by applying a slight vacuum. Then, 5 mL water was added to the test tube and the resulting solution was again introduced to the reservoir and passed through the disk slowly. The filtration step was repeated until the filtrate solution was completely clear. Finally, the disk was washed with 25 mL water and dried by passing the air through it. The membrane disk modified by the ENT ligand was then ready for sample extraction. There was no significant change in the membrane performance by using them up to 3 times. They were modified and reused after conditioning in methanol for 10 min.

Sample digestion

Before digesting, to ensure homogenous sampling, each sample was mixed in a clean beaker using a magnetic stirrer. Accurately a pair of 500 µL of sample was transferred to two pre-cleaned digestion vessels by using a 500µL sampler. 6mL nitric acid, 2mL hydrochloric acid and 2mL hydrogen peroxide were added to each sample vessel and the temperature program shown in Table 1 was imposed. After completing the digestion time and passing several minutes as cooling period, the content of two vessels were transferred quantitatively to a 50mL volumetric flask and neutralized by using diluted NaOH solution. The resulted solution was used for the preconcentration step.

Preconcentration step

The pH of 50mL digested sample solution was adjusted to 6.0 by adding 5 mL of phosphate buffer solution. This solution was prepared by dilution of 12.1 mL from solution 1/15 mol / L $Na_2HPO_4.2H_2O$ and was brought up to 100mL with solution 1/15 mol / L KH_2PO_4. Then, this solution was passed through the modified membrane disk at a flow rate of 50 mL / min with the aid of a pump. After extraction, the disk was dried by passing air through it. A test tube was then placed under the extraction funnel and the retained mercury was eluted with 5 mL of 1.5 mol / L $HClO_4$ at a flow rate of 3 mL / min. The final solution was acidified with HCl 10% and then mixed with $SnCl_2$ 20% using online vapor generation apparatus (VGA 77). In this condition, Hg (II) ions in the extracted solution are converted to metallic Hg^0. Then the resulted Hg^0 was sent to a quartz tube located in the optical path of the spectrometer with the aid of argon carrier gas. Peak height of resulted signals was used for both calibration and measurements.

RESULTS AND DISCUSSION

Complexation study and preconcentration

A powerful and reliable sample preparation method for the elemental analyses, microwave-induced digestion ovens have been frequently used in analytical laboratories

***Table 2: Formation constants of different metal-ENT Complexes in acetonitrile*.**

Metal	Log k_f
Hg(II)	7.30 ± 0.02
Ag(I)	4.12 ± 0.02
Cu(II)	6.65 ± 0.03
Pb(II)	2.67 ± 0.02
Cd(II)	4.24 ± 0.02
Mn(II)	3.11 ± 0.03
Zn(II)	2.65 ± 0.04
Ni(II)	3.03 ± 0.04
Co(II)	2.18 ± 0.02
V(V), Fe(II), Fe(III)	

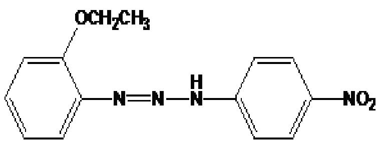

Fig. 1. Structure of (E)-1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triaz-1-ene (ENT).

in different industrial fields [36]. However, preparation of crude oil and its fractions with the aid of microwave digestion ovens for the analysis of mercury content mainly resulted in two undesirable phenomenon which are practically touchable: (i) decreasing of mercury concentration in resulted solution with the factor of approximately 50 to 100 and (ii) large blank signal in CV-AAS determination due to various interfering species which are produced during the digestion step. As a result, CV-AAS is not straightforward and an applicable method for the mercury determination in the resulted solutions when a low amount of analyte is available. Thus, a reliable preconcentration step is essential for quantitative separation and enrichment of mercury ions from digested samples. Sample pretreatment is a key step in a real sample analysis that improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results and facilitates the calibration procedure.

The spectroscopic results have shown that the complexation of mercury and ENT ligand was accompanied by decreasing in the absorption band of the ENT at 370 nm, and increasing absorption band at 460 nm. The mole ratio plot (absorbance versus $[Hg^{2+}]/[ENT]$) at of 370 nm for ENT has been shown that the curve is leveled off at mole ratio of 0.5. This emphasizes that the formation of complex can occur at ratio of 1:2 (metal to ligand) in the solution. The strength of ENT interactions with different metals was also investigated and the results have been listed in Table 2. As it can be seen, ENT forms the most stable complex with Hg (II) ion. So, it was expected that ENT could act as a selective solid phase modifier for Hg (II) separation. The formation constants of the resulting ENT- metal complexes were evaluated by Stability Quotients "SQUAD", software for curve fitting in order to determine k_a and k_f of acids and complexes respectively, thus researchers used this software before [37].

Effect of pH

The effect of pH on the preconcentration of 1.0 µg / L mercury ion was investigated in the range of 1.0-7.0. The pH was adjusted by either diluted nitric acid or sodium hydroxide. Fig. 2 shows that the sorption of mercury ion is quantitative and constant in the pH range of 5.5 to 6.5. In more acidic media, pH lowers than 5.0 nitrogen atoms of ENT are likely protonated. Thus, these donors do not have any pairs available to form a complex with mercury ion. Finally, pH 6.0 was selected as an optimum value for the further studies. To maintain the optimized pH, phosphate buffer solution pH 6.0 was used. Higher pH values (> 7.0) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.

Effect of reducing agent concentrations

The influence of the $SnCl_2$ concentration on the cold vapor generation was evaluated within the range of 10- 25% (w/v). Table 3 shows that the maximum absorbance for analyte is obtained at concentrations between 20 and 25% (w/v). Thus, $SnCl_2$ concentration of 20% was selected for further experiments.

Effect of ligand amount

The optimal amount of, (E)-1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triaz-1-ene (ENT) for proper modification of

Table 3: The effect of stannous chloride concentration on the absorbance of 1.0 μg / L of Hg (II).

$SnCl_2$ percentage	Signal	Standard deviation
10	0.1611	0.0049
15	0.1643	0.0035
20	0.1721	0.0011
25	0.1723	0.0011

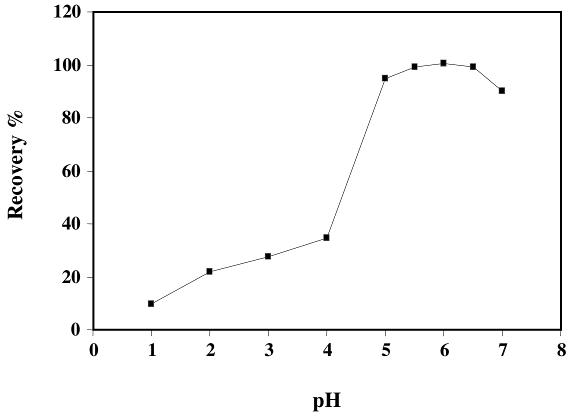

Fig. 2: The effect of pH of the sample on extraction recovery of Hg (II) ion.

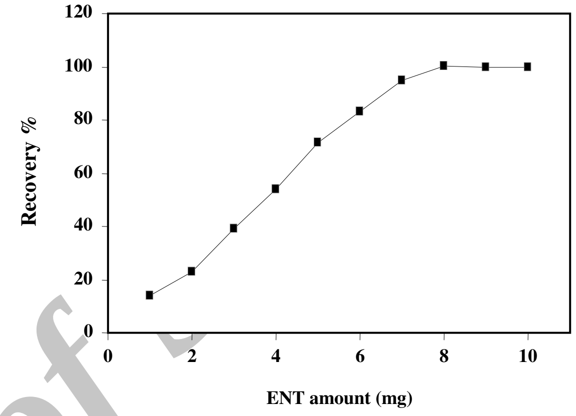

Fig. 3: The effect of amount of the ENT on extraction recovery of Hg (II) ion.

the octadecyl silica membrane disk for the quantitative extraction of 50 ng mercury (II) ion from 50mL of aqueous sample was investigated. The results of this study are shown in Fig. 3 and indicate that with 8 mg or more of the ENT, the extraction of mercury was quantitative while the use of less amount of ligand resulted in considerable decrease in the extraction of analyte. Therefore for subsequent work the disk was modified with 10 mg of ENT.

Choise of eluent type and concentration of elution Solution

In order to choose a proper eluent for the retained mercury ions, after the extraction of 50 ng of mercury ion from 50 mL sample solution by the modified disk, the mercury ions were stripped with 5 mL of various stripping agents and the results are summarized in Table 4. The results of the study revealed that, among different stripping agents being examined, 1.5 mol / L $HClO_4$ solution provided a quantitative elution of mercury from the modified disk.

Effect of flow rate

The flow rate of the Hg (II) solution through the disk is a very important parameter for time controlling of adsorption and analysis. Using the disk procedure, the effect of flow rate on the sorption of 1.0 μg / L of Hg (II) in the range of 10 – 100 mL / min was investigated. The results showed that Hg (II) can quantitatively be retained on the disk with flow rates in the range of 10 – 90 mL / min. Thus, to achieve a higher speed of operation, a sample rate of 50 mL / min was selected as a more controllable value. The effect of the eluent flow rate was also studied in the range of 1-10 mL / min and it was found that the recovery remained constant at the flow rates up to 5 mL / min. Then, to achieve maximum control of stripping step, a flow rate of 3 mL / min was selected for the eluent.

Effect of divers ions

In order to investigate the selective separation and determination of Hg (II) ion from its binary mixtures with divers ion, an aliquot of aqueous solutions (50 mL)

Table 4: Recovery of 1.0 μg / L Hg (II) from modified disk using different stripping solutions.

Stripping solution	Recovery percentage
HNO_3 (0.1 M)	19.3
HCl (0.1 M)	38.8
$HClO_4$ (0.1 M)	82.7
$HClO_4$ (1.0 M)	98.0
$HClO_4$ (1.5 M)	100.4

Table 5: Effect of diverse ions on the preconcentration of 1.0 μg / L of Hg (II).

Diverse ion	Concentration (mg L^{-1})	Recovery %
Ca^{2+}	1000	98.8
Mg^{2+}	1000	99.3
Na^+	1000	100.1
Ag^+	50	97.7
Cu^{2+}	50	99.1
Pb^{2+}	50	98.9
NO_3^-	1000	99.8
Cl^-	1000	96.3
SO_4^{2-}	1000	97.5

containing 0.05 μg Hg (II) and given amounts of other ions was taken and the recommended procedure was followed. A relative error of less than 5 % was considered to be within the range of experimental error. The results are summarized in Table 5. The data shows that the mercury ions in the binary mixtures are retained completely by the modified membrane disk, even in the presence of high concentration of different ions.

Breakthrough volume

The breakthrough volume refers to the maximum sample volume passes through a given mass of sorbent until analyte retention is no longer quantitative. The breakthrough volume of the sample solution was tested by dissolving 0.5 μg mercury in different volumes of water and the recommended procedure was conducted under optimal experimental conditions. The extraction was found to be quantitative in all cases up to 1200 mL of sample. Thus, the breakthrough volume for the method should be greater than 1200 mL. Consequently, by considering the final elution volume of 5 mL and the breakthrough volume of 1200mL, an enrichment factor of 240 was easily achievable.

Capacity of the Modified disk

In order to determine the maximum amount of Hg (II) ion retained on the modified disk, 50 mL of a solution containing 1000 μg of Hg (II) was passed through the disk at the optimized flow rate and pH. Because of the high mercury concentration in the resulted solution, 25 mL of this solution was diluted to 500 mL with water. Then, mercury concentration in diluted solution was determined. As a result, the maximum capacity of the disk was found to be 690±7 μg mercury per 8 mg of ligand. In other words, 8 mg ligand can retain around 690 μg Hg (II) ions.

Analytical Performance

The detection limit of mercury (II) ion based on three times the standard deviations of the blank (k=3, n=5) was 0.005 μg / L in digested sample solution and 0.25 μg / L in original crude oil and petroleum samples. The linear

Table 6: Comparison of the different methods performance for the determination of mercury content in crude oil and related products.

Sample	Method and detection system	LOD	RSD	Reference
	CV-AFS oxidant/acid solution: BrCl/HCl	0.01 ng / g	7.5% (n=3) Average of 7 samples	24
Gasoline	CV-AAS direct reduction in micro emulsion media	0.1μg / L	5% (n=10) (1μg / L Hg)	38
	CV-AAS Solid Phase Extraction	0.25 μg / L	8.5% (n=3) (0.82 μg / L)	this work
Crude oil	CV-AFS Thermal decomposition	0.2 ng / g	10.3% (n=2) (2.9 ng / g)	21
	CV-AAS Solid Phase Extraction	0.25 μg / L	1.8% (n=3) (17.9 μg / L)	this work

Table 7: Figures of merits of the analysis of mercury content in digested crude oil and gasoline samples with and without using developed solid phase extraction.

Parameter	Without SPE	With SPE
Mean of blank signals[a]	0.0258	0.0030
Blank signal standard deviation[a]	0.0013	0.0003
Characteristic concentration (μg / L)	12	1.2
Slop of the calibration curve	0.0181	0.1798
LOD (μg / L)	10.7	0.25
LOQ (μg / L)	33	0.80
Linear Dynamic Range (μg / L)	33 - 950	0.80 – 65

[a] *N=3.*

calibration curve was obtained in the range of 0.80 – 65 μg / L in the original samples. The linear equation for aqueous solution was A= 0.1798C – 0.0002 with R^2 = 0.9991 (n = 6) where, A and C are absorbance and concentration of mercury in μg/L respectively. If dilution factor of 50 for the digestion step taken into account, the slop of calibration curve for original samples would be 0.0036. The improvement factor (defined as the slope of calibration curve after preconcentration divided by the slope before preconcentration) was obtained 9.9.

The Relative Standard Deviations (RSD) for the determination of 50 mL of 0.1 and 0.5 μg / L of Hg (II) in aqueous solution (corresponding to 5.0 and 25 μg / L mercury in original gasoline and crude oil samples) after applying recommended extraction step were 1.9 and 1.0 % (n=3), respectively. Read amounts of 4.9 and 25.3 for mentioned samples ensured accurate determination of ultra-trace amounts of mercury (II) ions in aqueous sample solutions. Table 6 is a brief comparison of suggested method and some previously reported methods. Summarized data indicates a similar performance for this simple and low cost method compared with moderately sophisticated mentioned methods.

Improvements over Direct analysis

In order to investigate the performance of the both recommended extraction procedure and direct analysis in real samples, several samples with different concentration of Hg (II) ion were digested (according to 2.4 sections) and determined with and without applying extraction step. Table 7 indicates the obtained results and confirms a dramatic improvement in all analytical parameters for the use of the recommended extraction step. In addition to lower the limit of detection and wider linear dynamic range, it is worth to mention that with extraction step, the magnitude and standard deviation of signals for the sample and standard blank were obtained similar. This similarity firstly guarantied the LOD of 0.25 μg / L in real samples analysis and secondly allowed to determine the real samples with no need to blank determination. Although the developed solid phase extraction step can enrich mercury (II) ions with coefficient of 10, however

Table 8: Determination of total mercury in gasoline and a crude oil sample before and after the desalination after applying recommended extraction procedure.

Sample	Hg^{2+} added (μg / L)	Found (μg / L)	RSD (n=3, %)	Recovery (%)
Crude oil	□	18.4	2.2	□
	10.0	28.0	1.9	96
	20.0	39.1	1.5	103.5
Crude oil after desalination	□	17.9	1.8	□
	10.0	28.1	1.4	102
	20.0	37.7	1.1	99
Gasoline	□	0.82	8.5	□
	1.00	1.80	3.3	98.0
	2.00	2.75	2.5	96.5

the LOD and LOQ were improved by factor of 43. The improvement of 43 times in LOD and LOQ corresponded to the 9.9 times increasing of the slope of calibration curve and the 4.3 times lower the fluctuations of the blank determination by using of the recommended extraction.

Validation and analysis of real samples

Crude oil samples were collected from south oil resources of Iran and gasoline sample was bought from a gas station located it Tehran. In order to determine total mercury in samples recommended procedure were followed. In addition, after spiking samples with 10 and 20 μg / L Hg (II) the performance of the method were examined. The results are presented in Table 8, indicating that the modified disk is able to determine total mercury content in gasoline and crude oil samples even in ppb levels with a high level of accuracy and reliability. The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

CONCLUSSIONS

The developed preconcentration-separation procedure for mercury (II) ion and applying it after the digestion of samples followed by cold vapor atomic absorption determination was described. Availability, simplicity and cost effectiveness of the used facilities can made it convenient choice for the determination of total mercury content in some petroleum products. (E)-1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triaz-1-ene (ENT) was used as modifier for the octadecyl silica disk in solid phase extraction of a mercury ion. The results showed that even in high concentration of other spices the recovery of mercury (II) ion is quantitative. Therefore, in complicated Medias like microwave assisted digested samples with high concentration of ions, proposed extraction technique is able to separate Hg (II) ion from solution. The highly selective and sensitive recovery of mercury ion in such complicated matrix originates from the high affinity ENT to form a complex compound with Hg (II). The results obtained from real samples analysis (section 4.5) certify excellent performance of the method in enrichment of Hg (II) ion and simplification of sample matrix simultaneously.

Although LOD of 0.25 μg / L is a little more than some recently reported methods [39] but it is quiet enough for the determination of total mercury in gasoline samples. On the other hand, wider linear dynamic range in established method has provided more flexible analysis of mercury content of samples with expanded concentration range. Considering maximum of 10 min for a cycle of the extraction (including washing apparatus, ligand deposition, passing the sample and stripping), sample throughput of 6 h^{-1} is legible for the 43 times better detection ability compared with direct analysis.

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