



Solid phase extraction of ultra traces mercury (II) using octadecyl silica membrane disks modified by 1,3-bis(2-ethoxyphenyl)triazene (EPT) ligand and determination by cold vapor atomic absorption spectrometry

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ABSTRACT

A facile and highly efficient method was developed for the preconcentration of the ultra trace amounts of mercury (II) ions. Octadecyl silica membrane disk was modified by the recently synthesized triazene ligand, 1,3-bis(2-ethoxyphenyl)triazene (EPT), and cold vapor atomic absorption spectrometry was used to determine the resultant preconcentrated Hg(II) ions. Solution studies with EPT and a series of metal ions were done in advance, and the results showed a strong affinity of EPT to the mercury ions. To perform solid phase extraction, various parameters such as pH of the sample, flow rates and the amount of the ligand were optimized. A linear calibration curve was obtained in the range of 0.02–1.90 $\mu\text{g L}^{-1}$ with $r^2 = 0.9990$ ($n = 8$), and the limit of detection (LOD) based on three times the standard deviation of the blank was 10.6 ng L^{-1} . The relative standard deviation (RSD) for the determination of 0.1 $\mu\text{g L}^{-1}$ Hg(II) found to be 2.9% while a RSD value of 1.1% was obtained for the determination of 1.0 $\mu\text{g L}^{-1}$ Hg(II) ($n = 8$). The preconcentration and improvement factors were 380 and 74, respectively. The newly developed method was successfully applied to the determination of mercury ions in real water samples.

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1. Introduction

It is well known that mercury is one of the most toxic heavy metals in the environment. Different forms of mercury can be accumulated in animals and plants. Mercury can damage central nerve by entering into human body from food cycle [1]. As an environmental widely dispersed element, mercury can be destructive to natural metabolism, increment and procreate of organism, leading to maladjustment in hormone secretion. Therefore, determination of trace amounts of mercury in real samples is of more interest in environmental pollution monitoring.

Several analytical techniques such as spectrophotometry [2,3], inductively coupled plasma mass spectrometry (ICP-MS) [4], inductively coupled plasma atomic emission spectrometry (ICP-AES) [5], voltammetric techniques [6], atomic fluorescence spectrometry (AFS) [7] and neutron activation analysis [8] have been developed for the determination of mercury. However, cold vapor atomic absorption spectrometry (CV-AAS) is widely accepted technique for the determination of mercury due to its simplicity, high sensitivity and relative freedom from interferences [9–11]. CV-AAS is not straightforwardly applicable to some environmental, clinical,

or biological samples when a low amount of analyte is available or the sample matrix is complex. To meet these requirements, a reliable preconcentration step is essential for quantitative separation and enrichment of mercury ions from a real sample.

Since real samples have some characteristics such as complicated composition, various interfering species and very low concentration of analyte, they can only be analyzed after a complicated pre-treatment. Thus, sample pre-treatment is a key step in 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. Various separation–preconcentration techniques including solvent extraction [12], electro-deposition [13], coprecipitation [14], cloud point extraction [15], membrane filtration [16] and solid phase extraction [17–19] had been used in analytical studies. Among them, solid phase extraction is still of more interest on account of its simplicity, higher preconcentration factor, rapid phase separation, and time and cost saving [20,21].

Triazene compounds, characterized by having a diazoamino group ($-\text{N}=\text{N}-\text{N}-$), have been studied for over 130 years concerning their interesting structural and anticancer properties. In inorganic chemistry point of view, the synthesis and crystal structures of some new triazene–mercury complexes were reported [22]. Recently, it was also found that, the newly synthesized triazene ligands are interestingly applicable for the determination of

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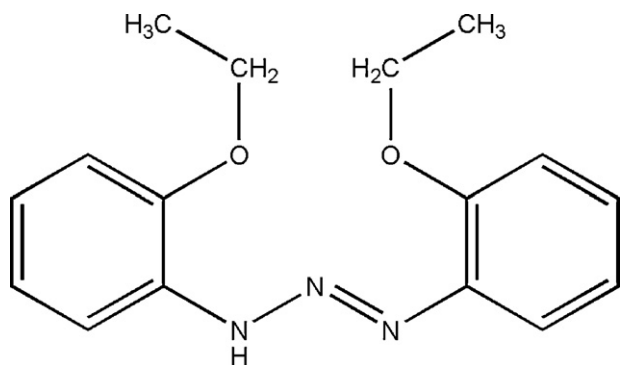


Fig. 1. Chemical structure of 1,3-di(2-ethoxyphenyl) triazene (EPT).

silver ions by solid phase extraction [23] and Hg(II) by an optical sensor [24].

In this paper, for the first time, we reported on the application of the newly synthesized 1,3-bis(2-ethoxyphenyl)triazen ligand (EPT) as a disk modifier in solid phase extraction of mercury. To detect the pre-concentrated mercury level, cold vapor atomic absorption spectroscopy was used. The complex formation of EPT and different metal ions (including Hg(II)) was also studied and evaluated by “Stability Quotients from Absorbance Data program” (SQUAD). The data further showed that a highly efficient preconcentration and determination of ultra-trace amounts of Hg(II) ions both in synthetic and real water samples were achievable by the modified disk and CV-AAS technique.

2. Experimental

2.1. Instruments

A Varian AA220 atomic absorption spectrometer (equipped with VGA77) was used for all absorption measurements. A mercury hollow cathode lamp was used as light source. The operation condition of the instrument was adjusted according to the manufacturer instruction (lamp current 4.0 mA, absorbance wavelength at 253.7 nm, spectral bandwidth at 0.5 nm). HP spectrophotometer (Agilent 8453) equipped with a thermostated bath (Huber polystat CC1) was used for electronic absorption spectra recording. The pH adjustment was done by a Metrohm digital pH meter, model 632 equipped with a combined glass-calomel electrode. Extraction was performed with a Empore high performance extraction membrane disk (47 mm diameter \times 0.5 mm thickness), containing octadecyl-bonded silica (8 μ m particles, 6 nm pore size) from 3 M company. The disk was used in conjunction with a standard Millipore 47 mm filtration apparatus.

2.2. 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 any purification. A 1000 mg L⁻¹ stock solution of Hg(II) was prepared by dissolving 0.1349 g HgCl₂ in 5 mL concentrate nitric acid and diluting to 100 mL with deionized water. Working solutions were prepared daily from the stock solution by successive dilution with water. A solution of 1.5% (w/v) sodium tetrahydroborate was prepared by dissolving NaBH₄ powder in water and adding 0.5% (w/v) NaOH to stabilize the solution. A buffer solution was prepared by adding 0.2 M NaOH to the appropriate volume of 0.2 M acetic acid and adjusting the pH to 3.5 by a pH meter. 1,3-Bis(2-ethoxyphenyl)triazen (EPT) (Fig. 1) was synthesized and purified according to the reported procedure [25]. All

glassware was kept in 10% nitric acid while not in use and washed three times with double distilled water before use.

2.3. 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 7.5 mg EPT was dissolved in 15 mL methanol 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 filtrated 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 triazene 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.

2.4. Sample pretreatment

After collecting water samples from Persian Gulf in glass bottles, samples were acidified by 5 mL of nitric acid. Then, they were filtered through a filter paper (Whatman No. 40) before use and kept at 4 °C while not in use. 200 mL of the filtered sample was transferred to a round-bottom flask, 7.5 mL of H₂SO₄ (98%), 2.5 mL of HNO₃ (70%), 8.0 mL of K₂S₂O₈ (5%) and 15 mL of KMnO₄ (5%) were added and refluxed at 80 °C for 2 h [26,27]. The resulting solution was cooled down to the room temperature, neutralized with sodium hydroxide and diluted to 1000 mL in a volumetric flask, then used for the preconcentration procedure.

2.5. Recommended procedure

The pH of 500 mL sample solution was adjusted to 3.5 by adding an appropriate volume of acetate buffer solution. This solution was passed through the modified membrane disk at a flow rate of 50 mL min⁻¹ 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 M HClO₄ at a flow rate of 3 mL min⁻¹. The final solution was directly measured by CV-AAS.

3. Results and discussion

3.1. Complex study

In order to determine the stoichiometry and stability of the resulting EPT complex with mercury ion in an acetonitrile solution, the spectra of a series of solutions containing a constant concentration of the ligand (5.0×10^{-5} M) at 25 °C and varying amounts of the metal ion were obtained and the results are shown in Fig. 2. As it can be seen, the complexation was accompanied by decreasing in the absorption band of the EPT at 375 nm, and producing a new absorption band at about 268 nm. The obtained mole ratio plot (absorbance versus [Hg²⁺]/[EPT]) at wavelength of 375 nm for EPT is shown in the inset Fig. 2. As shown the absorbance–mole ratio plot revealed a level off at ([Hg²⁺]/[EPT]) molar ratio of 1, emphasizing the formation of 1:1 (metal to ligand) complex in solution. The complexation of EPT with a number of metal ions was also investigated. Table 1 shows the formation constants of the resulting 1:1 complexes. As it can be seen, EPT forms the most stable complex with

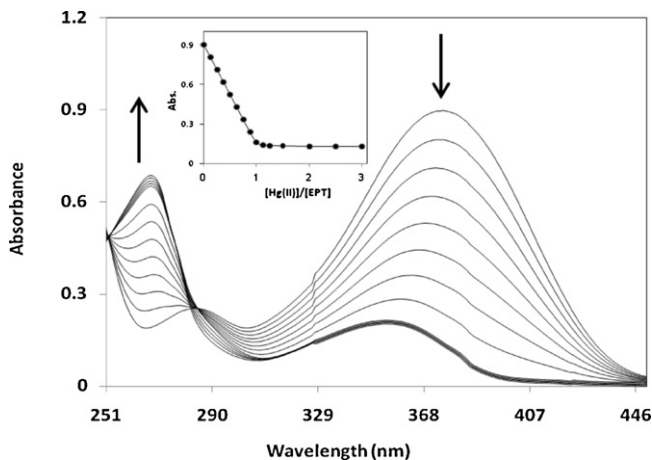


Fig. 2. Electronic absorption spectra of ligand (EPT) upon addition of Hg(II) ion. Inset: corresponding mole ratio plot at 375 nm.

Table 1
Formation constants of different metal–EPT complexes in acetonitrile.

Metal	Log K_f
Hg(II)	7.37 ± 0.03
Ag(I)	4.92 ± 0.02
Cu(II)	4.15 ± 0.02
Pb(II)	3.55 ± 0.03
Zn(II)	2.40 ± 0.03
Cd(II)	3.21 ± 0.02
Al(III)	2.32 ± 0.02
Ni(II)	3.06 ± 0.04
Co(II)	2.25 ± 0.04
Mn(II)	2.08 ± 0.02
Sr(II)	2.03 ± 0.04
Fe(III)	2.28 ± 0.03

Hg(II) ion. Then, it was expected that EPT could act as a selective solid phase absorbent and disk modifier in Hg(II) separation. The formation constants of the resulting EPT–metal complexes were evaluated by “Stability Quotients from Absorbance Data” computer program, SQUAD [28]. To study the complexation, the temperature of the cell holder was maintained at 25 ± 0.1 °C.

3.2. Effect of pH

The effect of pH on the preconcentration of 0.5 µg L⁻¹ of mercury ions was investigated. The pH was adjusted by either diluted nitric acid or sodium hydroxide. Fig. 3 shows that the sorption of mercury

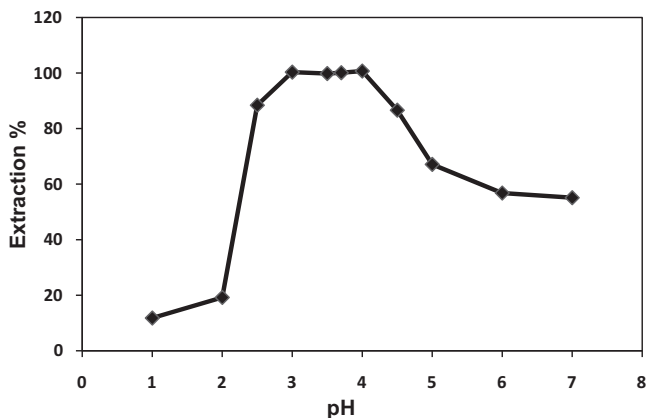


Fig. 3. Effect of sample pH on the preconcentration of 500 mL of sample solution containing 250 ng Hg(II).

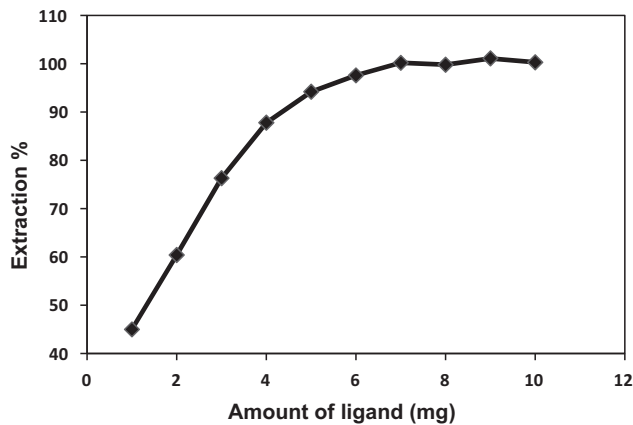


Fig. 4. Effect of the amount of the EPT ligand on the preconcentration of 500 mL sample solution containing 250 ng Hg(II).

ions increases up to pH 3.0 and remains constant in the pH range of 3–4. In highly acidic media, pH lower than 3.0, nitrogen atoms of EPT are likely protonated. Thus, these donors do not have any pairs available to form a complex with mercury ions. On the other hand, at pH values higher than 4.0, the percentage of Hg(II) extraction decreases. This phenomenon can be attributed to the possibility of mercury (II) hydroxide formation. Finally, pH 3.5 was selected as an optimum value for the further study. To maintain the optimized pH, acetate buffer solution pH 3.5 was used.

3.3. Effect of amount of ligand

The effect of different amounts of EPT on the modification of octadecyl silica membrane disk was studied. A quantitative extraction of Hg(II) ions was achieved in the presence of EPT in the range of 1–10 mg using 500 mL solution containing 0.25 µg mercury ions. The results indicated the important role of the ligand to retain and extract metal ions. As shown in Fig. 4, the most efficient amount of EPT for the complete extraction of mercury ions was observable at no less than 6 mg, while the use of lower amounts of ligand resulted in a considerable decrease in the extraction of the analyte. Therefore, to obtain maximum accuracy, all studies were carried out with 7.5 mg of the ligand.

3.4. Choice of eluent

In order to choose a proper eluent for the retained mercury ions, after the extraction of 0.25 µg of mercury ions from 500 mL sample solution by the modified disks, the mercury ions were stripped with 5 mL of various stripping agents and the results are summarized in Table 2. The results of this study revealed that, among different stripping agents being examined, 1.5 M perchloric acid solution provided a quantitative elution of mercury from the modified disk (see Table 3).

Table 2
Recovery of 0.5 µg L⁻¹ Hg(II) from modified disc using different stripping solutions.

Stripping solution	Recovery (%)
NH ₃ (0.1 mol L ⁻¹)	12.7
HCl (0.1 mol L ⁻¹)	40.4
HNO ₃ (0.1 mol L ⁻¹)	18.2
HClO ₄ (0.1 mol L ⁻¹)	80.3
HClO ₄ (1.0 mol L ⁻¹)	97.3
HClO ₄ (1.5 mol L ⁻¹)	100.2

Table 3Comparison of the different methods performance for determination of Hg²⁺ ions.

Method	Linear range ($\mu\text{g L}^{-1}$)	Detection limit (ng L^{-1})	Enrichment factor	Precision Concentration (RSD%)	Reference
SPE-CV-AAS	0.040–2.40	20	100	2.0 (1.9%)	[29]
CPE-HPLC-ICP-MS	0.05–10	4	42	N/A	[30]
CPE	5.0–80.0	830	33.3	5 (0.27%)	[31]
SPE-CV-AAS	0.02–1.20	12	333	1.00 (1.2%)	[27]
CPE-ICP-OES	0.25–100	56.3	18.7	10 (3.6%)	[32]
SPE-CV-AAS	N/A	5	150	N/A	[33]
SPE-CV-AAS	N/A	3.8	500	2.5 (3.1%)	[34]
SPE-CV-AAS	0.020–1.90	10.6	380	1.0 (1.1%)	Present work

SPE: solid phase extraction; CV-AAS: cold vapor atomic absorption spectroscopy; CPE: cloud point extraction; HPLC: high performance liquid chromatography; ICP-MS: Inductivity coupled plasma-mass spectroscopy; OES: optical emission spectrometry; N/A: not available.

3.5. 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 $0.5 \mu\text{g L}^{-1}$ of Hg(II) in the range of 5–100 mL min⁻¹ was investigated. The results showed that Hg(II) can quantitatively be retained on the disk (>95%) with flow rates in the range of 5–85 mL min⁻¹. Thus, to achieve a higher speed of operation, a sample rate of 50 mL min⁻¹ was selected as an optimum value. The effect of the eluent flow rate was also studied in the range of 1–10 mL min⁻¹ and it was found that the recovery remained constant at the flow rates up to 6 mL min⁻¹. Then, to achieve maximum control of stripping step, a flow rate of 3 mL min⁻¹ was selected for the eluent.

3.6. Breakthrough volume

The breakthrough volume refers to the maximum sample volume that 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 $0.5 \mu\text{g}$ mercury in 250, 500, 1000, 1500, 1800, 1900 and 2000 mL water and the recommended procedure was conducted under optimal experimental conditions. The extraction was found to be quantitative in all cases up to 1900 mL of sample. Thus, the breakthrough volume for the method should be greater than 1900 mL. Consequently, by considering the final elution volume of 5.0 mL and the breakthrough volume of 1900 mL, an enrichment factor of 380 was easily achievable.

3.7. Capacity of the modified disk

In order to determine the maximum amount of Hg(II) ions retained on the modified disk, 500 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 $742 \pm 18 \mu\text{g}$ mercury per 7.5 mg ligand.

4. Analytical performance

4.1. Limit of detection

The detection limit of mercury (II) ions based on three times the standard deviations of the blank ($k=3$, $N=10$) was 10.6 ng L^{-1} in a sample volume of 500 mL.

4.2. Linear calibration curve

The linear calibration curve was obtained in the range of $0.02\text{--}1.9 \mu\text{g L}^{-1}$ of Hg(II) in 500 mL of the initial solution. The linear equation was $A=0.2287C+0.0105$, with $r^2=0.9990$ ($n=8$) where A and C are absorbance and concentration of mercury in $\mu\text{g L}^{-1}$, respectively. The relative standard deviations (RSD) for the determination of 500 mL of 0.1 and $1.0 \mu\text{g L}^{-1}$ of Hg(II) were 2.9 and 1.1% ($n=8$), respectively. The improvement factor (defined as the slope of calibration curve after preconcentration divided by the slope before preconcentration) was obtained 74.

4.3. Effect of diverse ions

In order to investigate the selective separation and determination of Hg²⁺ ion from its binary mixtures with diverse ion, an aliquot of aqueous solutions (500 mL) containing $0.25 \mu\text{g Hg}^{2+}$ 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 4. These data show 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.

4.4. Analysis of synthetic sample

In order to assess the applicability of the proposed method to real samples with different matrices containing varying amounts of a variety of diverse ions, it was applied to the separation and recovery of different amounts of Hg²⁺ ions from 500 mL solutions of a series of synthetic samples. The synthetic samples contained: Na⁺ 100, K⁺ 12, F⁻ 1.5, Fe²⁺ 0.2, Cu²⁺ 2.0, NO₃⁻ 50, Ca²⁺ 20 (values

Table 4
Effect of diverse ions on the preconcentration of $0.5 \mu\text{g L}^{-1}$ of Hg(II).

Diverse ion	Concentration (mg L^{-1})	Recovery (%)
Na ⁺	100	100.8
K ⁺	100	99.1
Ca ²⁺	100	99.7
Mg ²⁺	100	100.4
Pb ²⁺	5	97.2
Cu ²⁺	5	100.6
Zn ²⁺	5	99.0
Fe ²⁺	5	100.5
Co ²⁺	5	100.7
Ag ⁺	5	96.1
Cd ²⁺	5	97.8
NO ₃ ⁻	100	99.8
SO ₄ ²⁻	100	99.3
Cl ⁻	5	98.9
CN ⁻	5	97.6
F ⁻	5	100.3

Table 5

Determination of Hg(II) ions in 500 mL synthetic water samples using recommended procedure.

Sample number	Hg ²⁺ added (ng)	Found (ng)	RSD (n = 3, %)	Recovery (%)
1	25	24.3	3.9	97.2
2	50	50.3	3.2	100.6
3	100	98.6	3.3	98.6
4	200	194.9	2.9	97.5

Table 6

Determination of Hg(II) ions in 500 mL of real samples after applying recommended procedure.

Sample	Hg ²⁺ added (ng L ⁻¹)	Found (ng L ⁻¹)	RSD (n = 3, %)	Recovery (%)
Kashmar ^a mineral water	–	47.8	4.6	–
	100	146.2	3.3	98.4
	200	241.7	3.2	97.0
Sanandaj ^a mineral water	–	107.2	3.4	–
	100	209.4	2.8	102.2
	200	304.7	3.0	98.8
Persian Gulf sea water ^b	–	961	3.8	–
	100	1058	3.9	97.0
	200	1164	2.8	101.5

^a The reason of choosing water samples from Kashmar and Sanandaj cities was that they are polluted to mercury.

^b After pretreatment (Section 2.4).

are concentration in mg L⁻¹ and confirming the maximum admissible concentration for drinking water according to the European committee for environmental legislation). The results are summarized in Table 5 and show that the mercury recovery is quantitative in each sample.

4.5. Analysis of real samples

The proposed method was applied to the determination of Hg²⁺ ions in three water samples (the results are given in Table 6). The first two water samples were tested without any pretreatment due to the low chloride concentration (less than 40 mg L⁻¹). After pretreatment (Section 2.4) of sea water sample, this method is able to determine Hg(II) ions even in high chloride content water samples (Persian Gulf with 36.6 g L⁻¹ salinity). The results are given in Table 6 indicating that the modified disk is able to determine Hg²⁺ ions in water samples even in sub-ppb levels with a high level of accuracy and reliability.

5. Conclusion

The developed preconcentration–separation procedure offered a facile and highly selective determination of mercury ions in real water samples. 1,3-Bis(2-ethoxyphenyl)triazene (EPT) was used as a modifier for the octadecyl silica disk in solid phase extraction of the mercury ions. The results showed that the retention of other cations by the modified disk is negligible. The highly selective and sensitive recovery of mercury ions in a complicated matrix (sea water) originate from the high affinity of EPT ligand to form a complex compound with Hg(II). The preconcentration factor derived from the presented procedure was as high as 380. In addition, the modified disk contributed to a fast, reproducible (RSD 1.1%) and reliable mercury extraction in a wide linear dynamic range.

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