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Solid phase extraction–preconcentration and high performance liquid chromatographic determination of 2-mercapto-(benzothiazole, benzoxazole and benzimidazole) using copper oxide nanoparticles

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ABSTRACT

This study introduces a novel method of solid phase extraction (SPE), preconcentration and HPLC determination of 2-mercaptobenzimidazole (2MBI), 2-mercaptobenzoxazole (2MBO) and 2-mercaptobenzothiazole (2MBT) from an aqueous solution by a SPE cartridge loaded with copper oxide nanoparticles. Results demonstrated that copper oxide nanoparticles are quite efficient for extraction and preconcentration of trace amounts of these mercaptans at room temperature. The study also investigated the effects of parameters such as pH, buffer and its volume, electrolyte concentration, flow rate of the test solution, composition and volume of the desorbing solvent, accepted tolerable volume, amount of adsorbent, reusability of cartridges and evidence of some co-existing species on extraction and determination of the above mentioned mercaptans. The method showed good linearity for determination of these mercaptans in the range of 0.01–10 μg mL^{-1} with regression coefficients better than 0.9969. The limits of detection (LODs) evaluations were 0.0021, 0.0027 and 0.0019 μg mL^{-1} for 2MBT, 2MBO and 2MBI, respectively. The relative standard deviations (RSDs) for 0.2 μg mL^{-1} and 5 μg mL^{-1} of the measured mercaptans were below 3.04% and 4.23%, respectively. Ramin Power Plant (3000 MW, Ahvaz, Iran) cooling water containing some 2MBT (as corrosion inhibitor) was used as the real sample. Recovery tests with spiked levels of 2MBT, 2MBI and 2MBO were carried out and satisfied results were obtained.

1. Introduction

Discharge of untreated or inadequately treated industrial wastewater in the environment may cause serious disease and major health problems in many developing countries. Water polluted with toxic compounds incurs devastating impacts on all living creatures and may negatively affect water resources used for drinking, household consumption, recreation, fishing, transportation, agriculture and commerce. Therefore, wastewater requires effective treatment to remove at least the most toxic and hazardous pollutants in order to improve and purify water. The process will also make the water suitable for reuse or reproduce it as discharge and send it back to the environment. Maintaining overall acceptable water quality requires appropriate methods of water treatment.

Chemicals including 2-mercaptobenzothiazole (2MBT), 2-mercaptobenzoxazole (2MBO) and 2-mercaptobenzimidazole (2MBI) (Fig. 1) are in a class of high production volume chemicals that are employed in many different industrial processes. These compounds are used as corrosion inhibitor agent [1–3], antifungal drug in medical applications [4], coating agent of metallic surfaces [5] and predominately, as vulcanization accelerator in rubber industry [6–8]. Use of these chemical compounds is widespread and they are well known toxic and poorly biodegradable pollutants. Such chemicals are frequently released to the environment and could be found in effluent of wastewater treatment plants and surface waters. They are the most important volatile organic compounds contributing to the unpleasant stench in wastewater treatment plants [9,10].

Annual release of 2MBT into the environment has been estimated to be 1 million lb, according to the United States Environmental Protection Agency (US EPA) [11]. Toxicity and allergenicity of these chemicals, when released to the environment, is a cause for concern and needs effective management [11–15]. Some reports state that the use of 2MBT, 2MBO and 2MBI may induce tumors, cause allergic reactions and be toxic to aquatic organisms. Additionally, it has been demonstrated that 2MBT can inhibit the degradation of easily degradable organics; hence wastewater nitrification was inhibited at far lower concentrations of 2MBT [1]. High eco-toxic properties of 2MBT, 2MBO and 2MBI and their toxic threat to ecosystems and human health is the main concern for chemists to monitor the concentration of these compounds in water samples. Several methods have been cited in the literatures which are commonly used to analyze 2MBT, 2MBO and/or 2MBI and thiols in environmental samples. Among these are spectrophotometric and electrochemical methods used for analysis

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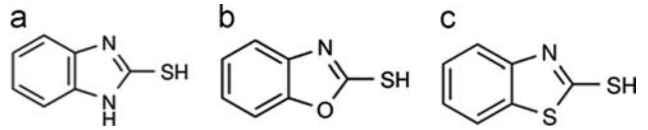

Fig. 1. Chemical structure of (a) 2MBI, (b) 2MBO and (c) 2MBT.

of mercaptans [16–20]. Methods for simultaneous determination of aromatic thiols [21–25] and aliphatic thiols [26,27] are mainly based on different chromatographic techniques [21–27]. However, to the best of our knowledge there have not been any reports hitherto on simultaneous solid-phase extraction and high performance liquid chromatography (HPLC) for determination of trace amounts of 2MBT, 2MBO and 2MBI in water solution samples.

We report herein for the first time, a new procedure for solid phase extraction that introduces highly efficient preconcentration of toxic sulfur containing compounds such as 2MBT, 2MBO and 2MBI from water samples by passing a contaminated water solution through a cartridge containing CuO nanoparticles (CONs). The proposed method demonstrated high potential ability of CuO nanoparticles to separate these hazardous compounds even at very low concentrations with a high level of efficiency on the one hand and monitoring the preconcentrated 2MBT, 2MBO and 2MBI by HPLC method after desorption by an efficient desorbing solvent on the other hand.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents were of analytical grade. Acetone (99.5% w/w), acetonitrile (HPLC grade), water (HPLC grade), 2MBI, 2MBT and 2MBO, phosphoric acid (85% m/m), methanol (99.9% m/m), ammonia solution (25% m/m) and acetic acid (99.9% m/m) were purchased from Merck (Darmstadt, Germany) and were used without further purification. Copper oxide nanoparticles (purity 99+%, specific surface area $>80\ \mathrm{m^2\,g^{-1}}$, average particle size <50 nm) were obtained from Neutrino (Tehran, Iran). A $2000\ \mu\mathrm{g\,mL^{-1}}$ mixture of CONs was prepared by an addition of 100 mL water to 0.200 g of nanoparticles. This mixture was prepared just prior to use. Stock solutions ($1000\ \mu\mathrm{g\,mL^{-1}}$) of 2MBI, 2MBT and 2MBO were prepared by dissolving 0.1 g of each mercaptan into 10 mL of acetone, which was then diluted to the mark with water in 100 mL volumetric flask. Other concentrations were prepared by successive dilution of stock solutions with water. Acetic acid solution (0.25% v/v) was prepared by dissolving 0.5 mL of concentrated acetic acid into 100 mL water, which was then diluted to the mark in 200 mL volumetric flask. The buffer solution was prepared by adjusting the pH of a phosphoric acid solution (0.1 M) to 6.5 using NaOH solution (0.1 M).

2.2. Apparatus

Chromatographic measurements were carried out using a Knauer (Germany) HPLC system consisting of a K-1001 pump and a k-2501 UV detector. Cellulose acetate filter (SCA grade, 0.2 μm, 25 mm, CHMLAB. Barcelona, Spain) was applied as the cartridge bed. A one stage vacuum pump (RS-4, REFCO, Switzerland) was used to control the flow rate of solutions and a pH-meter (827 pH lab, Metrohm®, Herisau, Switzerland) was also used to control the solution pH.

2.3. Chromatographic analysis procedure

A Eurosphere (C18, 250 mm × 4.6 mm) column with a mixture of acetic acid (0.25% V/V), acetonitrile and water at the ratio of 10:30:60, respectively, was used throughout as the mobile phase with a 20 μL injection loop. The temperature of the column oven was adjusted to a constant temperature (40 °C). Flow rate was increased linearly for the first 5 min after injection, from $1\ \mathrm{mL\,min^{-1}}$ up to $1.3\ \mathrm{mL\,min^{-1}}$ and then remained constant for up to 10 min. Under these conditions, retention times for 2MBI, 2MBO and 2MBT chromatographic peaks were 3.5, 6.7 and 9.2 min, respectively. Detection wavelength was set to 300 nm in the first 8 min of each chromatogram for the analysis of 2MBI and 2MBO and then was switched to 320 nm for determination of 2MBT.

2.4. General procedure

The CONs mixture ($2000\ \mu\mathrm{g\,mL^{-1}}$) was shaken vigorously and 7 mL of the mixture (equivalent to 14 mg CONs) was immediately transferred to a cartridge using a 10 mL syringe and passed through it leaving nanoparticles employing a positive pressure on the piston of the syringe to produce the copper oxide nanoparticles loaded cartridge (CONLC). Preconcentration was carried out using a 10 mL solution of 2MBI, 2MBT and 2MBO (each $1.5\ \mu\mathrm{g\,mL^{-1}}$) transferred to the previously prepared CONLC using a syringe and then letting to pass through the cartridge by applying a positive pressure on the piston of the syringe or by a vacuum pump providing a flow rate of $0.5\ \mathrm{mL\,min^{-1}}$. Any adsorbed mercaptans deposited on the nanoparticles were desorbed by washing the cartridge twice with 0.5 mL methanol. The washings were combined and 20 μL of the methanolic solution was injected to HPLC. Fig. 2 shows chromatograms of solution mixture of 2MBI, 2MBO and 2MBT ($8\ \mu\mathrm{g\,mL^{-1}}$ for each) in initial solution, remained mercaptans in the initial solution after removal by the CONs, and preconcentrated 2MBI, 2MBO and 2MBT after desorption by two 0.5 mL methanol as desorbing solvent.

Optimization of parameters affecting the preconcentration process was carried out using peak areas for each mercaptan obtained from corresponding chromatograms of the solutions.

3. Results and discussion

3.1. Mechanism of adsorption

The chemical reactions that occur between copper and thiols are well-known, and so are the reactions between copper oxide, CuO, and thiols as well as some proposed mechanisms which can be found in the literature [21]. It is well known that mercaptans

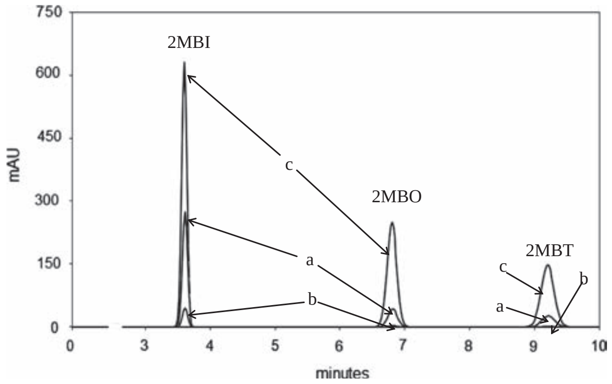

Fig. 2. Typical chromatograms of solution mixture of 2MBI, 2MBO and 2MBT ($8\ \mu\mathrm{g\,mL^{-1}}$ for each): (a) initial solution, (b) remained mercaptans in the initial solution after removal by the CONs, and (c) preconcentrated 2MBI, 2MBO and 2MBT after desorption by two successive 0.5 mL of methanol. [Conditions: initial volume of test solution: 10 mL; adsorbent: 14 mg CONs loaded on SPE cartridge; flow rate: $0.5\ \mathrm{mL\,min^{-1}}$].

form strong complexes on the surface of copper oxide. Chromatographic peak retention times for the mercaptans were identical before adsorption and after desorption (preconcentration) which confirmed the release of these mercaptans from the surface of nanoparticles (Fig. 2). The hydrophilic mercapto group (–SH) in the 2MBI, 2MBT and 2MBO molecules has a strong affinity for formation of a complex with copper, and these molecules anchor onto copper surfaces via a thiolate bond, while the hydrophobic benzene ring with different substituents constitutes an ultra thin protective monolayer [22]. The mechanism of this action is found to be chemisorption on the copper surface that follows Langmuir isotherm [23].

Moreover, it is well-known that thiols will self-assemble into strictly arranged monolayers (SAMs) onto the surface of metal coins, especially gold, silver, and copper [21]. These SAMs have widely been studied and are of great interest thanks to the unique properties manifested on the resulting surfaces.

3.2. Effect of the amount of copper oxide nanoparticles (CONs)

Effect of the amount of CONs on sorption and the preconcentration process was evaluated in the range of 8 to 24 mg of adsorbent. To this end, different amounts of nanoparticle mixture (2000 μg L^{-1}) were loaded onto the cartridge. The mercaptan solution was passed through the cartridge and corresponding chromatograms were obtained after desorption of analytes by 1 mL of methanol (two successive 0.5 mL). These results are shown in Fig. 3. Peak areas were decreased for CONs less than 12 mg due to lower adsorption of mercaptans and were also decreased above 20 mg of CONs which seems to be as a result of incomplete desorption of mercaptans from nanoparticle surfaces. Addition of 7 mL of the nanoparticle mixture (equivalent to 14 mg dry CONs) was chosen as the optimum value for further experiments.

3.3. Effect of pH

The pH of test solutions was adjusted by NaOH or HCl (0.1 M) to determine an optimum pH value. Processes of preconcentration and determination of the above mentioned mercaptans were performed within the pH range of 4 to 11. The results obtained from these tests are shown in Fig. 4. At low pH values (pH < 4) the CONs began to dissolve, thus resulting in a decrease in adsorption and preconcentration as well. However, at high pH values (pH 10 and pH 11) hydroxide ions seems to compete with mercaptans in terms of adsorption onto the surface of nanoparticles leading to a decrease in preconcentration affected by the adsorbent. Peak areas in the pH range of 5 to 8 were almost constant for each mercaptan; therefore, this range was chosen as the optimum pH range. Since pH of the non-buffered solutions of mercaptans was about 6, no pH adjustment was made in those solutions. Moreover, the effect of buffer (pH 6.5) was also investigated and the amount of added buffer was examined. Results showed that the amount of buffer volume up to 4 mL had no significant effect on peak areas or the preconcentration process.

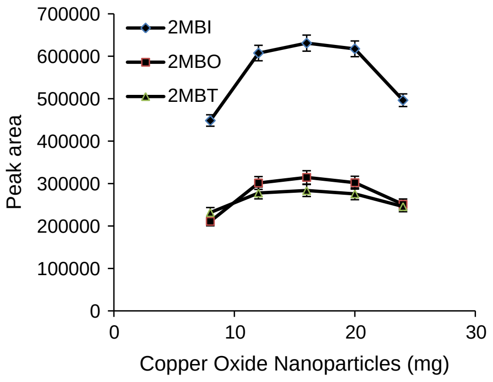

Fig. 3. Effect of the amount of copper oxide nanoparticles loaded on a cartridge. [Conditions: initial volume of test solution: 10 mL: flow rate: 0.5 mL min^{-1}; desorbing solvent: two successive 0.5 mL of methanol]. All experiments were done in triplicate; average results and standard deviations are shown.

3.4. Desorption of the mercaptans from CONs

In order to determine the best composition for a desorbing solvent, various solvents were tested either in pure forms or in mixed ratios of methanol, acetic acid, ammonia, sodium thiosulfate, thourea and ethylenediamine tetraacetic acid (EDTA). Desorbing solvents were selected by due attention to their potential for replace and release of the complexed mercaptans [28,29] on the surface of copper oxide nanoparticles (Fig. 5). The results obtained from these tests showed that washing the adsorbent with 0.3 mL of sodium thiosulfate 0.5 M (in order to compete with complexed mercaptans and to release them from the surface of CuO nanoparticles) and then desorbing the mercaptans using 1 mL methanol in two successive 0.5 mL volumes exhibited the best desorbing ability for adsorbed mercaptans [30].

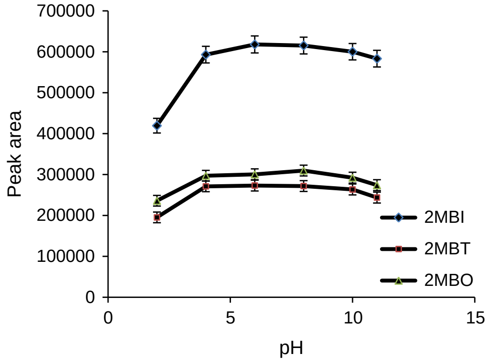

Fig. 4. Effect of pH on the chromatogram peak areas. [Conditions: initial volume of solution 10 mL, 14 mg CONs loaded on SPE cartridge, flow rate 0.5 mL min^{-1}, desorbing solvent: two successive 0.5 mL of methanol]. All experiments were done in triplicate; average results and standard deviations are shown.

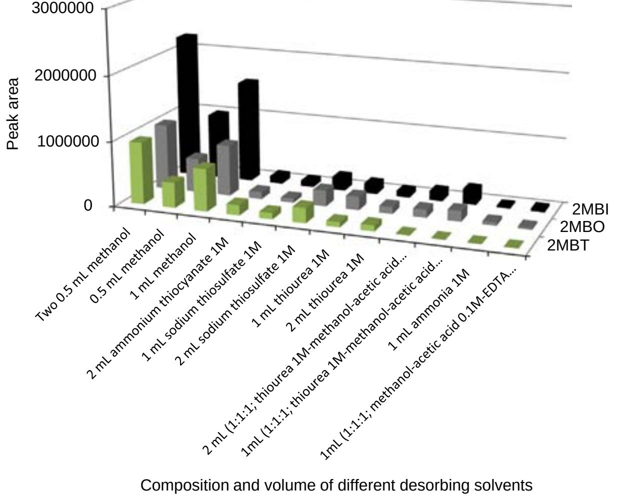

Fig. 5. Effect of composition and volume of the desorbing solution. [Conditions: initial volume of test solution: 10 mL; adsorbent: 14 mg CONs loaded on SPE cartridge; flow rate: 0.5 mL min^{-1}].

3.5. Effect of Ionic strength

The effect of ionic strength on adsorption and the preconcentration process was examined in different concentrations of KNO_3 as an electrolyte. Results showed that adsorption and the determination of the mercaptans were not affected by KNO_3 concentrations up to 0.1 M, but peak areas decreased slightly in more concentrated solutions. This implied that electrostatic attraction did not have a significant role in the adsorption step under these examination conditions.

3.6. Effect of co-existing species

The previously described optimum experimental conditions were used to study the effect of some ions, thiols and benzotriazole, on the determination process. To this end, preconcentration and determination of the mercaptans were performed in the presence of co-existing species. The maximum acceptable error was assumed $\pm 5\%$. The results obtained from these tests are shown in Table 1. The table shows that although most ions and benzotriazole do not affect the system, Ag^+ and Hg^{2+} may interfere at 10 times the concentration with the mercaptans. This is because of high tendency of these two ions to form stable complexes with those mercaptans [31,32].

3.7. Effect of the sample volume

The effect of the initial volume of the sample on adsorption and the preconcentration process was investigated using a series of solutions containing fixed amounts of 2MBI, 2MBO and 2MBT (15 μg of each) in different volumes of solution. Results (Fig. 6) showed that initial volume of samples had no effect on preconcentration and determination up to 200 mL. Considering the volume of the final desorbing solution, which was 1 mL methanol, a preconcentration factor of about 200 may be achieved.

Table 1
Effect of co-existing species on the chromatogram peak areas [Conditions: initial volume of test solution: 10 mL; adsorbent: 14 mg CONs loaded on SPE cartridge; flow rate: 0.5 mL min^{-1}; desorbing solvent: two successive 0.5 mL of methanol]. The presented data were averages taken from three replicated analysis.

Species[a]	Tolerance ratio $[C_{species}]/[C_{mercaptans}]$
Cd^{2+}, Co^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+},	100
Cu^{2+}, Bi^{3+}, benzotriazole	100
K^+, NO_3^-, SO_4^{2-}, Na^+, PO_4^{3-}, Cl^-	1000
thiosalicylic acid, thiophenol, cysteine	50
Ag^+, Hg^{2+}	10

[a] All cations were prepared from nitrate salts and anions were prepared from sodium or potassium salts.

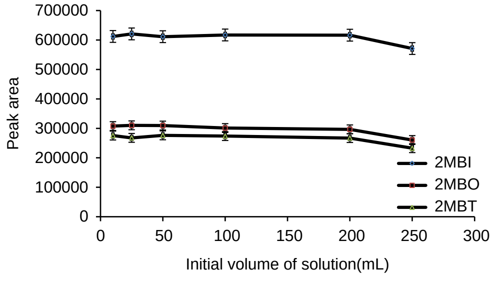

Fig. 6. Effect of solution initial volume on the chromatogram peak areas. [Conditions: 14 mg CONs loaded on SPE cartridge, flow rate 0.5 mL min^{-1}, desorbed by two successive 0.5 mL of methanol]. All experiments were done in triplicate; average results and standard deviations are shown.

3.8. Reusability of the cartridge bed

Due to the fact that cellulose acetate filters act as a suitable bed for CONs, their potential for reusability was examined in several successive preconcentration processes. The cartridge was backwashed thoroughly by methanol after each mercaptan desorbing cycle. Results obtained from these tests (Fig. 7) showed that these filters can be reused effectively for three times without incurring any considerable loss in their adsorption efficiency (> 95%).

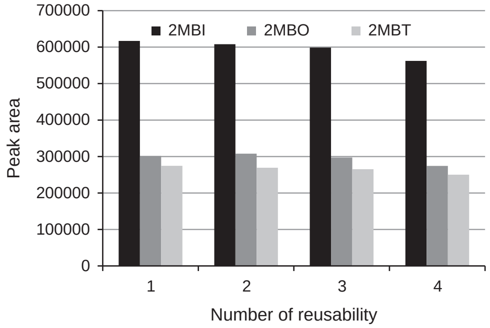

Fig. 7. Effect of reusing of cartridges on the chromatogram peak areas. [Conditions: initial volume of solution 10 mL, 14 mg CONs loaded on SPE cartridge after the backwashing process, flow rate 0.5 mL min^{-1}, desorbed by two successive 0.5 mL portions of methanol].

Table 2
Calibration curve characteristics [Conditions: initial volume of test solution: 10 mL; adsorbent: 14 mg CONs loaded on SPE cartridge; flow rate: 0.5 mL min^{-1}; desorbing solvent: two successive 0.5 mL of methanol].

Compound	Concentration range (μg mL^{-1})	Calibration equation	Regression coefficient	RSD%	LOD, LOQ (μg mL^{-1})
2MBI	0.01–0.5	$y=250747x+8056$	0.9969	(0.2) 3.0	0.0019, 0.0076
2MBI	0.5–10.0	$y=457811x-74234$	0.9989	(5) 4.2	–
2MBO	0.01–0.5	$y=138294x+2608$	0.9989	(0.2) 2.4	0.0027, 0.0092
2MBO	0.5–10.0	$y=235461x-48281$	0.9989	(5) 3.4	–
2MBT	0.01–1.0	$y=146283x+3160$	0.9996	(0.2) 2.7	0.0021, 0.0069
2MBT	1.0–10.0	$y=196520x-23632$	0.9970	(5) 3.1	–

Table 3
Real sample analysis (Ramin Power Plant cooling water, 2000MW) with spiking levels of: 0, 50,100, and 200 ng mL^{-1} of 2MBI, 2MBO and 2MBT. [Conditions: adsorbent: 14 mg CONs loaded on SPE cartridge; flow rate: 0.5 mL min^{-1}; desorbing solvent: two successive 0.5 mL portions of methanol].

Compound	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
2MBI	0	–	–
2MBI	50	51	102
2MBI	100	96	96
2MBI	200	206	103
2MBO	0	–	–
2MBO	50	48	96
2MBO	100	101	101
2MBO	200	194	97
2MBT	0	110.3	–
2MBT	50	162	104
2MBT	100	213	103
2MBT	200	305	97

Table 4
Comparison of the proposed method with some reported methods for determination of some aromatic mercaptans.

Method (analytes)	RSD (%)	LOD/LOQ (μg L^{-1})	Recovery (%)	pH	Ref.
SWV[a] (2MBT, 2MBO)	2.3	LOD = 140, 800	89–114	8	[16]
SBSE GC-MS[b] (BT)[g]	9.8	LOD = 0.256	–	2.0	[24]
SPE LC/MS[c] (BT, 2MBT, etc.)	25	LOQ = 0.2	60–105	–	[25]
LLE LC[d](BT, 2MBT, MTBT[h], etc.)	–	LOD = 5	≥90	8.5	[21]
IE-S[e] (2TCMBT[i])	3.34	LOQ = 2800	99–101	10	[20]
HPLC-ED[f] (2MBT)	13	LOQ = 4.1	93–96	–	[23]
This work; (2MBT, 2MBO, 2MBI)	4.23	LOD = 2.7, LOQ = 9.2	96–104	5–8	–

[a] Square wave voltammetry.
[b] Stir bar sorptive extraction/gas chromatography–mass spectrometry.
[c] Solid phase extraction liquid chromatography–mass spectrometry.
[d] Liquid–liquid extraction/liquid chromatographic.
[e] Indirect extraction-spectrophotometry.
[f] High performance liquid chromatography-electrochemical detection.
[g] Benzothiazole.
[h] 2-Methylthiobenzothiazole.
[i] 2-(Thiocyanomethylthio)benzothiazole.

3.9. *Analytical figures of merit*

Calibration curves were obtained in the concentration range of 0.01–10 μg mL^{-1} of 2MBI, 2MBO and 2MBT with good correlation coefficients ($R > 0.996$). Results are shown in Table 2. HPLC peak area and concentration (μg mL^{-1}) are indicated by y and x, respectively, for each mercaptan. The relative standard deviation ($n = 10$) for 0.2 μg mL^{-1} and 5 μg mL^{-1} solutions of 2MBI, 2MBO and 2MBT were calculated as to be less than 3.0% and 4.2%, respectively. LODs (signal/noise = 3) and LOQs (signal/noise = 10) of the method were lower than 0.0027 μg mL^{-1} and 0.0092 μg mL^{-1}, respectively. The enrichment factor of the method was calculated to be up to 200 depending on the initial volume of the solution.

3.10. *Analysis of the Ramin PowerPlant water sample*

To determine the capability of the proposed method for the analysis of 2MBI, 2MBO and 2MBT in real sample, cooling water of the Ramin power plant was tested and spiked. The spiked levels were 0, 50, 100 and 200 ng mL^{-1} of each mercaptan. The spiked solutions were successfully determined in water samples and the results are summarized in Table 3. Excellent recoveries indicated that the matrix of cooling water samples did not interfere with analysis of the mercaptans.

4. Conclusions

A simple and new method for simultaneous adsorption and preconcentration of 2MBI, 2MBT and 2MBO in aqueous solutions was successfully developed using a cartridge prepared by loading CONs. The proposed method offers the advantage of using cartridge as a bed for nanoparticles which can be reused for further preconcentration processes on the one hand and the process also uses only a small amount of adsorbent for analysis (14 mg of CONs) on the other hand. The new presented method of mercaptans determination is effective in a wide range of pH values. Furthermore, the procedure is clean, offers high preconcentration factors and is effective in a relatively short preconcentration time. It also has better or comparable LOD and/or LOQ, RSD, applicable pH range and recovery values compared with a variety of other methods reported in the literature for the determination of some related compounds (Table 4).

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