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Analytical method development using functionalized polysulfone membranes for the determination of chlorinated hydrocarbons in water

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ABSTRACT

In this study, functionalized polysulfone membrane has been utilized as a sorbent for the extraction of chlorinated hydrocarbons (CHCs) in water samples. Two different functionalized polysulfones (i) phosphonic acid functionalized polysulfone (PPSU-A) with different forms (cross-linked and non cross-linked) membranes and (ii) phosphonic ester functionalized polysulfone (PPSU-E) with different forms (cross-linked and non cross-linked) were evaluated for the extraction of CHCs in water. A 10 ml of spiked water sample was extracted with 50 mg piece of the functionalized membrane. After extraction, the membrane was desorbed by organic solvent and the extract was analyzed by gas chromatography–mass spectrometry. Eight CHCs, 1,3,5-trichlorobenzene (1,3,5-TCB), 1,2,3-trichlorobenzene (1,2,3-TCB), 1,1,2,3,4,4-hexachloro-1,3-butadiene (HCBD), 1,2,4-trichloro-3-methylbenzene (TCMB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) were used as model compounds. Experimental parameters such as extraction time, desorption time, types of polymer membrane as well the nature of desorption solvent were optimized. Using optimum extraction conditions calibration curves were linear with coefficients of determination between 0.9954 and 0.9999 over wide range of concentrations (0.05–100 $\mu g\,l^{-1}$). The method detection limits (at a signal-to-noise ratio of 3) were in the range of 0.4–3.9 $ng\,l^{-1}$. The proposed method was evaluated for the determination of CHCs in drinking water samples.

1. Introduction

Chlorinated hydrocarbons (CHCs) or organochlorines are a variety of volatile and semi-volatile compounds including chlorobenzenes, chloroethanes, and chlorotoluenes which contain at least one chlorine atom covalently bonded to a carbon. Beginning from the early 1940s, many compounds of this nature have been designed for various reasons, the initial one being mainly the exploitation of their insecticidal potentials. CHCs have also been widely employed as solvents, heat transfer agents, deodorants, degreasers and intermediates in dye production [1,2]. Anthropogenically, these compounds enter the environment as a result of emissions, industrial effluents, and via inefficient waste disposals [3]. Consequently, they can now be found in the air, food, soil, surface, ground, and drinking water systems and sediments [4,5]. Many marine organisms can also harbor these pollutants [6]. Recently, CHCs were detected in high arctic common eiders [7], and in the breast adipose tissue of California women undergoing biopsy [8]. Different kinds of CHCs were also isolated from breast milk of residents of Hong Kong and other locations in China [9,10]. The daily dietary intake of organochlorine pesticides in the Danish population has been estimated at between 0.03 and 0.3 μg/day. Fish, meat and dairy products were recognized as the major contributors to these estimates [11].

Though some types of CHCs are natural components of human cells, bacteria and lichens, many others including the infamous dichlorodiphenyltrichloroethane (DDT) are well known toxins. Toxicity can be elicited in the form of pericardial and yolk sac edema, cardiovascular dysfunction, and skeletal deformities [12]. CHCs can also interfere with drug metabolism in the body [13], and may cause reproductive effects including spontaneous abortions [14].

Many types of these compounds can resist degradation by chemical or biological means, giving rise to their environmental persistence [15]. Hence, CHCs are increasingly becoming a major health concern, and this calls for correct and sensitive means of

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their determination. Gas chromatography (GC) is widely utilized in the quantitative determination of CHCs. After separation, the component analytes can be detected by means of different types of detectors. Both electron capture detector (ECD) [16] and flame ionization detector (FID) [17] can offer low limits of detection (LOD) for trace amounts of CHCs. However, GC coupled with mass spectrometric detection may provide for even better resolution and ease of identification of peaks [18].

CHCs are present at trace levels in the environmental samples, therefore, extraction and pre-concentration procedures are usually employed before the quantitative analysis. Traditional methods such as liquid–liquid extraction (LLE) and solid phase extraction (SPE) can be used [19], but they are time consuming and often involve the use of large sample or solvent volumes. These usually multi-step procedures can also lead to loss of analytes. To reduce the volume of waste solvents generated in laboratories, and to expedite analysis, alternative sample preps for these analytes are needed. This quest has led to the development of simpler sample preparation techniques that are also more environmentally friendly. In the last decade or so, many promising methods that can be suitable for the extraction of CHCs from different media have been developed. A liquid-phase microextraction (LPME) which minimizes solvent use has found applications in the analysis of pesticides including those of CHCs origin [20]. Different solvents are often tested for optimum extraction recovery and a mixture of chloroform and methanol has been found suitable for the extraction of these compounds [21]. A different method which extracts analytes based on sorption is the solventless technique called solid phase microextraction (SPME); it uses polymeric coating on fibers to extract and pre-concentrate analytes [22]. However, SPME fibers are expensive and have limited sorptive phase [23]. To overcome these limitations, many researchers are now experimenting with various types of materials as substitute sorbents for application in the extraction of analytes of diverse polarities. Lu et al. [24] have employed chitosan beads and porous crab shell as sorbents for the removal of seventeen CHCs from water. Recently, we have introduced a functionalized polymer coated microextraction technique for routine environmental monitoring [25].

The selectivity and sorption ability of certain sorptive membrane is usually improved through attachment of functional groups via chemical reactions [26]. For example, the hydrophobic nature of neat polysulfone (PSU), an engineering polymer possessing high thermal and mechanical stability, can be changed into more hydrophilic one by grafting the PSU backbone with a variety of polar functional groups that generate various functionalized membranes suitable for different applications, such as polyelectrolyte membranes for fuel cell applications [27], nanofiltration membranes with enhanced antifouling properties [28], sorbing carrier for isolation of adherent polyaromatic hydrocarbons degrading bacteria [29] or as a membrane for separation of certain hydrocarbons such as olefins and paraffins [30]. The use of polyimide [31] and polystyrene [32] that were functionalized with phosphonic ester groups has resulted in improved separation of aromatic compounds (π electron donors) due to the high affinity of phosphonic ester groups (π electron acceptors) toward these compounds. Hence, it can be suggested that phosphonic acid/ester functionalized polymers can be used as candidates for extraction and removal of aromatic chlorinated hydrocarbons from water samples.

Recently, phosphonated PSUs were introduced with high phosphonic acid functionality to the PSU by two steps procedure, chloromethylation of PSU backbone followed by phosphonation utilizing Michaels–Arbuzov reaction [33]. Then phosphonated PSU in their ester forms (PPSU-E) were quantitatively hydrolyzed into the corresponding acid forms (PPSU-A) by refluxing in hydrochloric acid.

In the present study, we introduced the first example of utilizing phosphonated PSU membranes in their acid and ester forms as sorption matrices for micro solid-phase extraction (μ-SPE) of CHCs from water.

2. Materials and methods

2.1. Reagents and materials

Spectrometric grade xylene (Fluka Chemie AG, Switzerland), acetone (Lab-Scan Analytical Sciences), n-hexane (J.T. Baker Chemical Co, USA), and toluene (HiperSolv, BDH, Australia) were used in this study. Methanol (HPLC-grade) was purchased from Sigma–Aldrich (St. Louis, MO). Certified alkaline buffer solutions were supplied by Fischer Chemical Ltd (St. Louis, MO). Acidic buffer solutions were prepared from anhydrous sodium acetate (BDH Chemicals Ltd, VWR, USA) and glacial acetic acid (Winlab Ltd, Leicestershire, UK). Sodium hydroxide (NaOH) solution prepared from NaOH pellets (Riedel-de-Haen, AG, Switzerland) was used for pH adjustment. CHC mixed standards were purchased from Supelco (Bellefonte, PA). 10 μg ml^{-1} working standard was prepared in acetone. Ultra pure water was prepared using Nanopure water purification (Barnstead, Dubuque, IA, USA) system.

Four different membranes were considered for investigation as potential polymeric matrices for the extraction of CHCs. These membranes can be categorized into two groups; the first group contains the phosphonic acid functionalized PSU and the second group includes the phosphonic ester functionalized ones. Both groups have one cross-linked PSU and a non-cross-linked one, to enable the evaluation of the effect of crosslinking on membrane/polymer performance.

These analytes can be classified into four groups based on the number of chlorine atoms in their structures: trichlorinated, tetrachlorinated, pentachlorinated and hexachlorinated CHCs. With the exception of HCBD, which is a conjugated alkene, all other CHCs are aromatic.

2.2. Instrumentation

The eight CHCs were separated on gas chromatography-mass spectrometric (GC–MS) 6890N system (Agilent) equipped with autosampler 7683B series and a 6890B injector. It was operated through a Chemstation which contained an NIST 98.L and wiley7n.l libraries. An Agilent 19091Z-213 column of 30 m $\times$ 0.32 mm dimensions and a film thickness of 1 μm HP-1 methyl siloxane stationary phase were used. High purity helium flowing at a rate of 2 ml min^{-1} was the carrier gas. The column temperature was initially set at 50 °C, and then increased to 250 °C at the rate of 10 °C min^{-1}. It was held at the 250 °C for 2 min and then ramped to the final temperature of 300 °C at a linear rate of 20 °C min^{-1}. This was maintained until the end of the run time of 25.50 min. The injector (splitless), interface and detector temperatures were all set at 250 °C. Total Ion Current (TIC) in SCAN mode for ions of masses between 50 and 550 was used for acquisition, and Selective Ion Monitoring (SIM) mode was used for quantification of 1,3,5-TCB, 1,2,3-TCB, HCBD, TCMB, 1,2,3,4-TeCB, 1,2,4,5-TeCB, PeCB and HCB with m/z of 180, 182, 260, 194, 216, 214, 250 and 284, respectively.

2.3. Water sample collection

Three brands of bottled water, all produced in Saudi Arabia, were used; NOVA, with source from Nuffoud Al-Wasse'e, SHIFA with source in Al-Hasa and AFNAN with source in Riyadh. They were purchased from a local store. Tap water samples were collected in glass bottles from Riyadh, Khafji and Rastanura, different locations

in Saudi Arabia. They were wrapped with paper and stored at 4 °C before use. All the samples were extracted in the laboratory without any pretreatment performed.

2.4. Extraction with functionalized PSU membranes

All extractions were performed in the laboratory according to the following procedure: 10 ml ultrapure water was placed in a 30-ml vial and spiked with 20 $\mu g\,l^{-1}$ of CHC mixture and 50 mg piece of the functionalized membrane was placed. The sample vial was agitated at 1200 rpm. After extraction for 50 min, the membrane was removed and dabbed dry with lint-free tissue to remove water. The membrane was then placed in a vial, followed by the addition of 200 μl methanol for solvent desorption. The analytes were desorbed via ultrasonication for 5 min. Finally, 2 μl of extract was injected in to the GC–MS for analysis. After each extraction, the membrane was cleaned and conditioned with acetone (ultrasonicated for 10 min) to avoid any carry over. After conditioning, blank extraction performed and no carryover was observed, the membrane was reused after each extraction. The membrane could be re-used for at least ten times without compromising its performance.

3. Results and discussion

3.1. Effect of extraction and desorption times

Extraction was performed at different times between 10 and 50 min. As an index of extraction efficacy, the peak area of analyte was observed after each extraction time considered. Within this range, 50 min appeared to be the best time. It would probably require much longer time for all the analytes to attain optimum extraction. Therefore, to avoid excessively long experiment duration, all further experiments were performed using 50 min as the agitation (extraction) time. Similarly, analytes were desorbed in solvent via ultrasonication and desorption duration was studied from 5 to 20 min. Generally, 5 min appeared to be suitable for the ultrasonic desorption of most the analytes. However, >5 min desorption, there is no additional increments in peak areas were observed. This short desorption time contributes to the speed of sample preparation step and was, therefore, selected for use in subsequent experiments.

3.2. Effect of polymeric matrix

The interaction of the eight analytes with the two groups of phosphonated PSU was investigated as shown in Fig. 1.

For all the CHCs, it was found that the response was much higher in the case of phosphonic acid functionalized PSU (PPSU-As) than in case of phosphonic ester functionalized PSU (PPSU-Es). This might be attributed to the enhanced π electron acceptor property in case of presence of acid functionality which can form a type of hydrogen bonding with the π electron donor aromatic rings. In addition, the higher hydrophilicity of the phosphonic acid functionalized PSUs compared to their ester counterparts, can allow better extraction ability of the hydrophilic CHC analytes as might be inferred from the selection of polar desorption solvent (*vide infra*). Fig. 1 shows the peak areas obtained for the analytes after 50 min extraction at pH 7 using different functionalized materials as sorbents followed by desorption in xylene for 5 min. This result indicates that, generally, the conjugated hexachlorinated 1,3-butadiene was much less sorbed compared to the aromatic ones, and the non-cross-linked membranes were better sorbents than the cross-linked ones under these experimental conditions. Therefore, PPSU-A 0.75 which displayed the best response for most of the analytes was selected as the sorbent material in subsequent experiments.

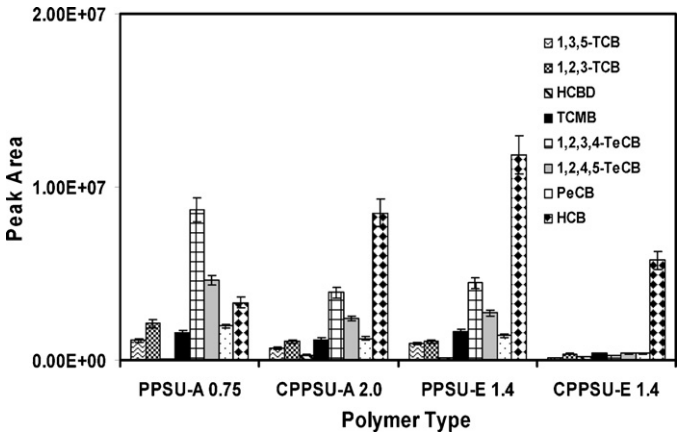

Fig. 1. Effect of phosphonated polysulfone polymer/membrane types on peak areas of CHCs using xylene as solvent, at experimental conditions of pH 7, 50 min extraction and 5 min desorption. 0.75, 1.4 and 2.0 in the sorbent names correspond to 75%, 140% and 200% degrees of phosphonation, respectively; 'A' and 'E' stand for acid and ester functionalities while 'C' indicates the presence of cross-links.

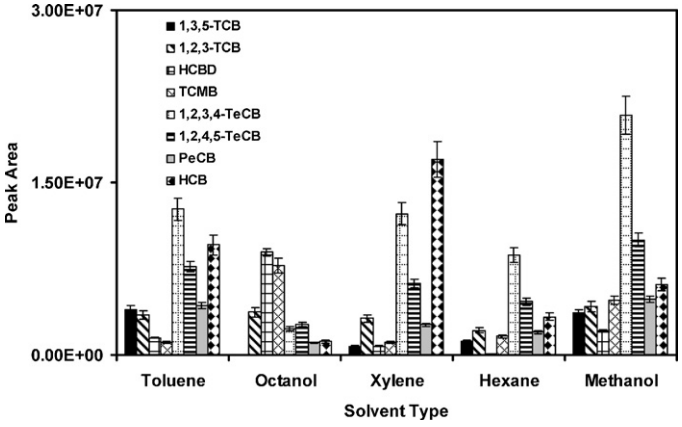

Fig. 2. Effect of solvent types on peak areas of CHCs at experimental conditions of pH 7, 50 min extraction, and 5 min desorption, with PPSU-A 0.75 as sorbent.

3.3. Choice of desorption solvent

In order to have better extraction efficiency, different solvents were tested as shown in Fig. 2.

All membranes/polymers were insoluble in the tested solvents. Non polar solvents like hexane, toluene and xylene showed weak ability to desorb the analytes from the phosphonic acid functionalized membranes/polymers due to the large difference in the hydrophilic character of the solvent-polymer system. Similar observation was found in the case of using long chain alcohol such as 1-octanol.

However, methanol which has a similar geometric structure to water was found to provide the best interaction and desorption of the analytes from the functionalized membranes/polymers due to its higher hydrophilic and polar characters compared to other solvents. In addition, methanol can have interaction through hydrogen bonding [34] with phosphonic acid functionalized PSUs as well as the chlorinated benzenes which make it possible to pull out the organic chlorinated hydrocarbons from the polymeric matrix.

Table 1
Calibration parameters, LODs and LOQs for the chlorinated hydrocarbons.

Analytes	Slope ± SD[a] (×10^{-5})	Intercept ± SD (×10^{-4})	r^2 [b]	LOD[c] (ng l^{-1})	LOQ[d] (ng l^{-1})
1,3,5-TCB	2.25 ± 0.098	5.67 ± 0.694	0.9998	1.8	6.0
1,2,3-TCB	2.07 ± 0.023	8.07 ± 1.062	0.9975	1.9	6.3
HCBD	1.02 ± 0.004	0.55 ± 0.327	0.9997	3.9	13.0
TCMB	2.55 ± 0.021	−0.18 ± 0.329	0.9995	1.6	5.3
1,2,3,4-TeCB	10.00 ± 0.077	4.46 ± 15.862	0.9981	0.4	1.3
1,2,4,5-TeCB	4.09 ± 0.025	66.19 ± 6.069	0.9954	1.0	3.3
PeCB	2.53 ± 0.015	1.85 ± 1.948	0.9998	1.6	5.3
HCB	3.21 ± 0.030	−0.47 ± 0.769	0.9999	1.3	4.3

[a] SD, standard deviation for three replicates.
[b] Coefficient of determination for 6 standards (0.05–100 μg l^{-1}).
[c] Estimated from S/N = 3.
[d] Estimated from S/N = 10.

Table 2
Enrichment factor, relative recovery and reproducibility of the method.

Analytes	Enrichment factor[a]	RR (%)[b] (5 μg l^{-1} spiked)	%RSD (n = 3)
1,3,5-TCB	25	84.9	8.8
1,2,3-TCB	336	86.8	10.9
HCBD	80	102.4	3.5
TCMB	268	79.3	8.1
1,2,3,4-TeCB	382	88.5	7.7
1,2,4,5-TeCB	43	110.1	6.3
PeCB	36	79.0	6.2
HCB	1008	72.9	9.2

[a] Calculated by taking the ratio of peak area for the extract of spiked water sample to that of un-extracted sample.
[b] Relative recovery: recovery of spiked tap water sample relative to that of spiked ultra pure water.

Consequent to this observation, methanol was chosen for application in further experiments.

3.4. Effect of pH

As presented in Fig. 3, effect of different sample pH (2, 4, 7, 9 and 12) values on the extraction procedure was also tested. While some analytes performed relatively better at pH other than neutral (pH = 7), the overall effect seems to favor the neutral pH at which the functionality of the native polymer/membrane for sorption toward the analytes, in general, was optimal. This effect mimics the natural setting in which bio-concentration of chlorinated hydrocarbon insecticides was optimal at pH 7 [35]. This may be due to enhanced sorption of the analytes from water to the surface of bacterial membrane containing phosphate groups in membrane phospholipids. Considering this result, ultrapure water (pH = 7) was used for spiking in subsequent extraction procedures for method optimization.

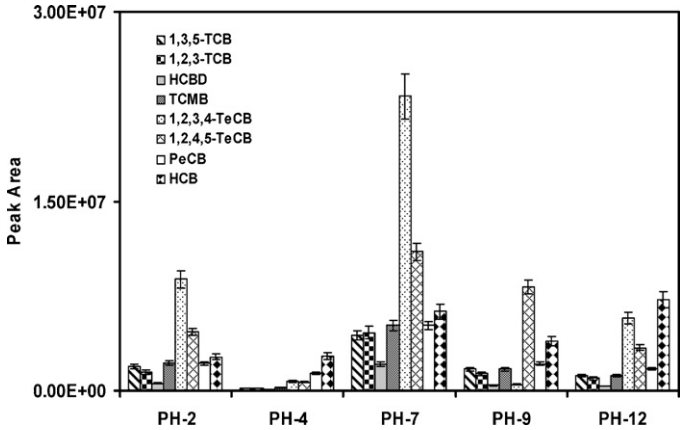

Fig. 3. Effect of pH variation on the peak areas of CHCs at experimental conditions of 50 min extraction and 5 min desorption, with PPSU-A 0.75 as sorbent and methanol as solvent.

4. Method appraisal

To evaluate the performance of this method, 50 mg piece of the functionalized polymer/membrane was used for the extraction of CHCs from ultrapure water spiked with different concentrations of the analytes. Good linearity was established over wide range of concentrations (0.05–100 μg l^{-1}) as signified by the coefficients of determination (r^2) between 0.9954 and 0.9999 for the eight analytes under investigation (Table 1).

LODs for the different compounds were calculated based on the signal-to-noise (S/N) ratio of 3. The tetrachlorinated hydrocarbons showed lower values compared to other analytes. However, the general LODs calculated in ng l^{-1} (0.4–3.9) and the estimated limits of quantitation (LOQ) of 1.3–13.0 ng l^{-1} indicate high sensitivity and suitability of the method for the quantitative determination of all the analytes in water matrix. The extraction method high enrichment factor (25-1008) (Table 2, Fig. 4) has contributed to this sensitivity.

The developed μ-SPE method compared favorably with documented ones in the literature, including head-space (HS)-SDME-GC–MS [36], SPE-GC–MS [37], LLE-GC-ECD [38], and LPME-GC–MS [39], SPME-GC-ECD [40], ionic-liquid (IL)-HS-SDME-thermal desorption (TD)-GC–MS [41], SPME-GC–MS [42], microwave (MW)-HS-SDME-HPLC [43], dispersive liquid–liquid microextractin (DLLME)-GC-ECD [44] and headspace sorptive extraction (HSSE)-GC–MS [45] based on sample volume, extraction time, LOD and %RSD as presented in Table 3.

These results stress the rapidity of this method and its suitability for application as a viable and reproducible means of determining CHCs in water. Furthermore, the method was applied to the analysis of CHCs in real water samples from six sources: three bottled water samples and three tap water samples. CHCs were detected in all water samples. One of the samples (tap water) was spiked with 5 μg l^{-1} of CHCs and recoveries were calculated using external calibration. Recoveries were between 73 and 110% and %RSDs were calculated between 3.5 and 10.9%. The quantities of CHCs detected and quantified within the method LODs are presented in Table 4.

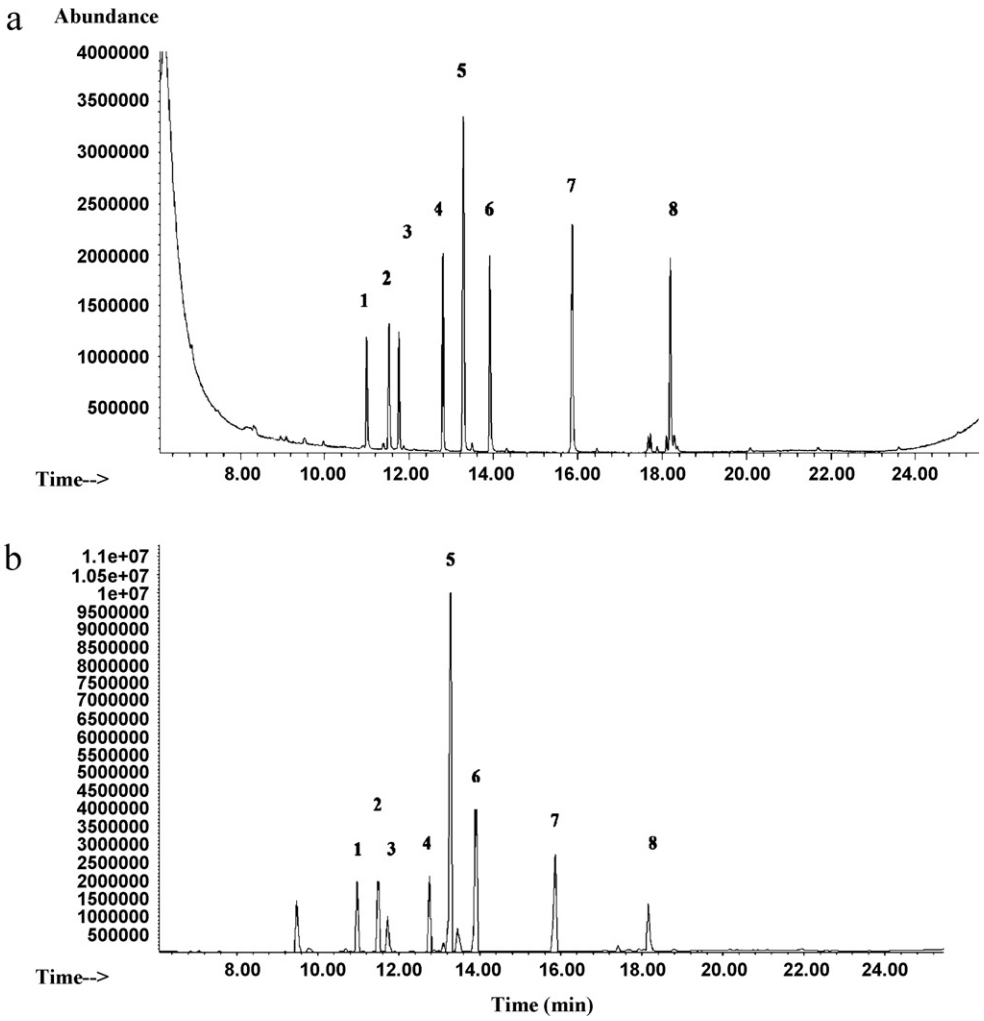

Fig. 4. Chromatograms of (a) 10 μg ml^{-1} of analyte mixed standards, and (b) spiked 100 μg l^{-1} water sample extract after peak identification: (1) 1,3,5-TCB, (2) 1,2,3-TCB, (3) HCBD, (4) TCMB, (5) 1,2,3,4-TeCB, (6) 1,2,4,5-TeCB, (7) PeCB, and (8) HCB.

Table 3
Method performance as compared with literature results.

Method	Sample volume (ml)	Extraction time (min)	LOD (ng l^{-1})	%RSD	Reference
HS-SDME-GC–MS	10	5	3–31	2.1–13.2	[36]
SPE-GC–MS	200	≅50	10–45	1.6–13.3	[37]
LLE-GC-ECD	4000	>240	0.01–500	10	[38]
LPME-GC–MS	4	3.5	20–50	1.6–17.9	[39]
SPME-GC-ECD	5	15	0.32–2.25	2.1–4.9	[40]
IL-HS-SDME-TD-GC–MS	10	37	1–4	2–17	[41]
SPME-GC–MS	10	30	0.004–0.02	2.7–4.9	[42]
MW-HS-SDME-HPLC	30	20	16–39	1.7–12	[43]
DLLME-GC-ECD	5	≤1	0.5–50	0.52–6	[44]
HSSE-GC–MS	50	60	2–120	5–10	[45]
μ-SPE-GC–MS	10	50	0.4–3.9	3.5–10.9	This work

Table 4
Organochlorines in bottled and tap water sources of Saudi Arabia.

Analytes	Concentration (μg l^{-1})[a,b]					
	SHIFA	NOVA	AFNAN	Khafji	Riyadh	Rastanura
1,3,5-TCB	0.16 ± 0.01	0.34 ± 0.03	0.09 ± 0.01	0.18 ± 0.02	0.45 ± 0.04	0.11 ± 0.01
1,2,3-TCB	ND[c]	ND	ND	ND	ND	ND
HCBD	0.59 ± 0.02	0.46 ± 0.02	0.63 ± 0.02	0.81 ± 0.03	0.53 ± 0.02	0.70 ± 0.03
TCMB	0.20 ± 0.02	0.31 ± 0.03	0.47 ± 0.04	1.07 ± 0.09	0.92 ± 0.07	0.30 ± 0.02
1,2,3,4-TeCB	ND	ND	ND	ND	0.05 ± 0.01	ND
1,2,4,5-TeCB	ND	ND	ND	ND	ND	ND
PeCB	0.89 ± 0.05	1.55 ± 0.1	1.66 ± 0.1	2.10 ± 0.13	2.01 ± 0.14	2.19 ± 0.13
HCB	0.99 ± 0.09	1.33 ± 0.12	1.49 ± 0.14	2.17 ± 0.2	1.74 ± 0.16	2.19 ± 0.2

[a] Mean ± SD for three determinations.
[b] SHIFA, NOVA and AFNAN are bottled water sources while Khafji, Riyadh and Rastanura are tap water sources.
[c] Not detected.

The highest value for the bottled water was obtained in the AFNAN sample. This was followed by NOVA, and the lowest value was in SHIFA, with source from Al-Hasa, an area in the Eastern Province of Saudi Arabia which harbors the world's largest oasis. Mixing and dilution phenomena might have contributed to its low levels of CHCs. For the tap water analysis, the sample from Khafji, an area between Saudi Arabia and Kuwait where an immense hydrocarbon activity has been going on for the last three decades or so, has the highest percentage of the detected CHCs. The Riyadh tap water has slightly lower concentration than that of Rastanura. On the other hand, the penta- and hexachlorinated hydrocarbons, commonly used in agriculture as pesticide and for seed dressing, respectively, account for more than 70% of the detected CHCs. While the values obtained for tap water analysis, within the error of determination, may be slightly above the current $1\,\mu g\,l^{-1}$ maximum contaminant level (MCL) for HCB [46], none of the TCBs came close to the $70\,\mu g\,l^{-1}$ stipulated for 1,2,4-trichlorobenzene.

5. Conclusions

In this investigation, we have developed a simple and efficient μ-SPE method for the analysis of CHCs in water matrix using novel phosphonic acid/ester functionalized polysulfone membranes as sorbents. The membranes provided good sorption ability for the aromatic CHCs due to enhanced hydrophilicity and π electron donor–acceptor interactions between the polymeric matrix and the aromatic analytes.

Various factors governing extraction have been studied. Results obtained indicate the optimized conditions as 50 min extraction time, 5 min desorption time and the use of methanol as desorption solvent. Enhanced extraction recoveries were obtained at neutral pH. The polymeric membrane that showed the best result was PPSU-A 0.75, due to non cross-linked backbone and the presence of phosphonic acid functionality.

The method response was found to be linear within wide range ($0.05–100\,\mu g\,l^{-1}$) of analyte concentrations as signified by the r^2 values, and its very low LOQ values have allowed quantitation of analytes in real samples at sub part-per-billion levels. These performances and all other appraisal indices such as LOD, relative recovery and %RSD indicate the suitable applicability of the present method in the analysis of real water samples.

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