

A New Method for Determination of Polychlorinated Biphenyls (PCBs) in Water Samples by Switchable Hydrophilicity Solvent Based Homogenous Liquid-Liquid Microextraction Combined with GC-MS

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Abstract

Herein, a simple, rapid, and efficient method based on pH assisted homogenous liquid-liquid microextraction was combined with gas chromatography- mass spectrometry (GC-MS) to do trace analysis of polychlorinated biphenyls (PCBs) in water samples. Triethylamine (TEA) was used as a switchable hydrophilicity solvent which can be miscible/immiscible with aqueous sample by varying the pH of the sample solution. In this regard, the effects of various parameters were explored on the extraction performance of PCBs. Detection limits, quantification limits and linear dynamic ranges were equal to 0.15 $\mu\text{g L}^{-1}$, 0.5 $\mu\text{g L}^{-1}$ and 0.5-150 $\mu\text{g L}^{-1}$ respectively. The RSDs% ($n = 3$) were in the range of 5.2-6.4 and 5.6-7.2 for intra-day and inter-day assays, respectively. Ultimately, the method was employed for determination of PCBs in water samples.

Keywords

Polychlorinated Biphenyls; Switchable Hydrophilicity Solvent; Homogenous Liquid-Liquid Microextraction; GC-MS Analysis.

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) consisted of 209 possible congeners are regarded as a typical group of compounds, causing great harm to human health and environment because of their carcinogenicity, toxicity, lipophilicity and biomagnification in the food chain [1]. Before PCBs were banned in the 1970s, they had been widely applied as insulating fluids (heat carriers and coolants) in electric equipment and additives in plastics, paint, sealants and carbonless copy paper, due to their excellent chemical, thermal stability and non-inflammability properties [2,3]. Though PCBs have been banned, they can still exist in trace levels within soil and water due to their resistance to environmental degradation in addition to their hydrophobic nature [4].

Hence, developing a rapid, facile and efficient approach is urgent for environmental risk and impact assessment of PCBs residues in water [5]. There are detection systems for PCBs such as immunoassays and gas chromatography (GC)-based systems while the latter provides superior detection limits especially through coupling with mass spectrometry (MS) or through electron capture detection (ECD) [4]. Trace amounts monitoring of PCBs in complex water samples has some difficulties including matrix effect and

low concentrations of the analytes; therefore, final chromatographic determination requires some prior selective enrichment and preconcentration procedures [6].

For PCBs analysis, numerous classical extraction techniques have been utilized such as soxhlet extraction [7], solid-phase extraction (SPE) [8,9], supercritical fluid extraction [10], pressurized fluid extraction [11] and liquid-liquid extraction (LLE) [12]. However, over the last two decades, the trend has been shifting from conventional SPE and LLE sample preparation methods toward miniaturization methods which are faster, cost effective, efficient, green, comparatively simple and facile to perform [13]. Some of these methods include vortex assisted liquid-liquid microextraction (VALLME) [14], solid-phase microextraction (SPME) [6,15-17], magnetic solid phase extraction (MSPE) [18], hollow-fiber liquid-phase microextraction (HF-LPME) [19,20], dispersive liquid-liquid microextraction (DLLME) [21], microwave-assisted extraction (MAE) [22], ultrasonic extraction (USE) [23] and stir bar sorptive extraction (SBSE) [24].

Homogeneous liquid-liquid microextraction (HLLME) as a one of the favorable methods has been developed in a green chemistry point of

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view, for improvement of analytical characteristics of conventional microextraction methods. HLLME is an efficient extraction method in which the infinitely large contact surface between the extractant and the aqueous sample is achieved providing the complete solubilisation of the extractant in the aqueous phase [25].

Switchable hydrophilicity solvents (SHSs) are a class of new generation solvents that can be modified abruptly regarding to their reversible physical characteristic changes [26–28]. Reversible behavior of these solvents is an attractive reason for using them as ideal acceptor phases in HLLME. In recently introduced switchable hydrophilicity solvent based HLLME procedures, non-ionic solvents change to an ionic form under the presence of carbon dioxide; thereafter, it reverts back to its non-ionic form by removing the gas from the solution [29–32]. In this regard, pH adjustment has been introduced by our team as a facile manner for controlling water miscibility of switchable hydrophilicity solvents with the aim of HLLME [33].

Herein, an efficient, rapid, sensitive and facile method relying on pH assisted switchable hydrophilicity solvent based HLLME was combined with GC-MS analysis for the determination of PCBs in water samples. Making use of acid solution instead of dry ice (CO₂), facile manner, simple equipments, and high speed of analysis are the most important advantages of the suggested method compared to preceding methods.

In this method, triethylamine (TEA) served as a switchable hydrophilicity solvent which can be miscible/immiscible easily by varying pH of the aqueous solution.

2. EXPERIMENTAL

2.1. Reagents and solutions

All chemicals were of analytical grade and were used without further purifications. A certified reference material of PCBs (10 mg L⁻¹ of each PCB, purity 99.99%) was provided from ULTRA Scientific (North Kingstown, USA).

Triethylamine (TEA), sodium hydroxide, methanol and hydrochloric acid were purchased from Merck Company (Darmstadt, Germany). The aqueous solutions were prepared in deionized water (Milli-Q system, Millipore, USA). Working solutions of PCBs were prepared by dilution of PCBs stock solution in methanol. The standard and working solutions were stored in a dark place at 4 °C.

2.2. Instrumentation

Quantitative analysis of the selected PCBs was carried out on a Varian CP-3800 gas chromatograph equipped with a SATURN 2000 mass spectrometric detector based on an ion trap analyzer and an electron multiplier detector with a split/splitless injector with split ratio of 1:5 operated at 260 °C. Data acquisition and system control were performed with Varian workstation toolbar software (Ms Workstation version 6.6). A silica capillary column (VF-5ms, 30.0 m × 250 μm × 0.25 μm; Varian, California, USA) and helium at a flow rate of 1 mL min⁻¹ as the carrier gas were used for chromatographic separations. The column temperature program was as follows: 2 min at 150 °C, ramped at 12 °C min⁻¹ up to 280 °C, and kept at 280 °C for 3 min. One microliter of the standards/ extracts was introduced to the chromatographic systems by manual injection using a 10 μL syringe (SGE, Trajan Scientific, Australia). Acquiring the mass spectra of each analyte was performed in full scan mode with a mass range from 40 up to 550 m/z, and quantitative analysis was performed in the selected-ion monitoring (SIM) mode, recording the selected m/z fragments as shown in Table 1. The electron impact (EI) ionization mode at 70 eV was used to operate the mass spectrometer and the temperature of the transfer line was 180 °C.

The temperature adjustment of the extraction medium at fixed levels was achieved with a water bath, heated by a Heidolph heater-stirrer (Germany) and pH measurements were carried out by a digital pH-meter (Ion Analyzer 827, Metrohm).

Table 1. Retention times and ions selected for MS analysis of selected PCBs.

PCB	Structures	Retention time (min)	selected Ions (m/z)
PCB-28	2,4,4'-Trichlorobiphenyl	8.46	150, 256, 258
PCB-52	2,2',5,5'-Tetrachlorobiphenyl	8.98	220, 257, 290, 292
PCB-101	2,2',4,5,5'-Pentachlorobiphenyl	10.39	254, 324, 326
PCB-118	2,3',4,4',5'-Pentachlorobiphenyl	11.42	324, 326, 328
PCB-153	2,2',4,4',5,5'-Hexachlorobiphenyl	11.71	292, 358, 360
PCB-138	2,2',3,4,4',5'-Hexachlorobiphenyl	12.45	292, 358, 360
PCB-180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	13.18	326, 390, 394

2.3. Switchable hydrophilicity solvent based Homogeneous liquid-liquid microextraction (SHS-HLLME) procedure

The extraction procedure consisted of different steps. First, 2 mL of the sample solution containing $50 \mu\text{g L}^{-1}$ of PCBs was placed in a test tube and then 100 μL TEA as the extraction solvent was added which formed two immiscible phases. Subsequently, 100 μL of HCl solution (6 mol L^{-1}) was transferred to the test tube, and then it was shaken manually for 10 s until a homogeneous phase formed. Thereafter, 1 mL of NaOH solution (10 mol L^{-1}) was added and a cloudy solution was appeared immediately indicating a rapid extraction of PCBs into the fine droplets of TEA phase. After 20 s, the separation of the TEA and water phase was completed without centrifugation. Finally, the TEA phase was collected on the surface of the water phase and 1 μL was injected into GC-MS manually.

2.4. Sample preparation

Different water samples were investigated including drinking water and tap water. The drinking water samples were purchased from local store and tap water samples were collected in glass bottle from the University of Zabol (Zabol, Iran). These samples were centrifuged immediately after sampling to remove any suspended particular matter. Then, the procedure described in section 2.3 was applied to 2 mL of each water sample.

3. RESULT AND DISCUSSION

3.1. Optimization of Switchable hydrophilicity solvent based Homogeneous liquid-liquid microextraction (SHS-HLLME) procedure

Effects of several variables such as SHS volume, pH, temperature, time and salt amount on the SHS-HLLME of PCBs were investigated. The one-factor-at-a-time approach was conducted to study and optimize the affecting variables for subsequent analysis of PCBs in real water samples.

3.2. Selection of extraction solvent and its volume

The solvent used in the extraction procedure of SHS-HLLME should fulfill some requirements such as high affinity for the analytes, low water solubility, low density in comparison with water and forming a single phase with water at a defined pH value. In general, amines with SHS features show logarithm of the octanol/water partition coefficient ($\log K_{ow}$) between 1.2 and 2.5 and the corresponding pK_{aH} above 9.5 [34]. Triethylamine (TEA) with $\log K_{ow}$ of 1.65 and pK_{aH} 10.75 can be a relatively non-polar extraction solvent. So, considering these features

and the low price and availability, TEA was selected as an acceptor phase.

In addition, for selecting the sample solution volume, extraction solvent (TEA) volume, and acid and base volumes, different experiments with variable amounts of these parameters were done. Based on the results (not shown) and our practical experiences, the sample volume was fixed at 2 mL. Additionally, to study the effect of extraction solvent volume, different volumes of TEA were tested within the range of 100–400 μL in a constant volume of sample solution (2 mL). The results indicated (Fig. 1) that by increasing the volume of TEA slight decrease in the peak area of PCBs is observable. This was probably due to the dilution effect on the enrichment factors of PCBs. Therefore, 100 μL of TEA was chosen as the optimal volume for subsequent tests. Also, it should be mentioned that the volumes lower than 100 μL were not tested because of the partial solubilization of TEA in water and practical limitations in collecting the TEA phase. Also, higher TEA volumes than 400 μL were not tested to avoid the generation of more organic waste and so diluting of extracting solvent and decrease of enrichment factor.

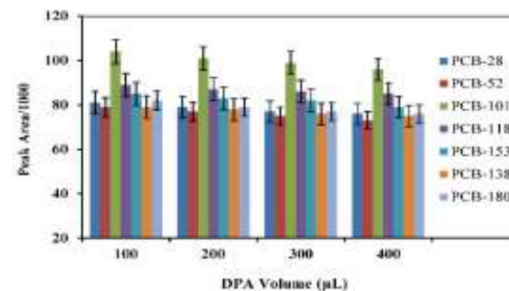


Fig. 1. The Effect of TEA volume on SHS-HLLME of PCBs.

3.3. Effect of pH

The pH of sample solution determines the dominant form of ionizable analytes in aqueous solution which plays an important role in many of the microextraction techniques. In this regard, the pH of sample was varied in the range of 3–10. Upon varying the pH value, the results showed no considerable changes in the extraction performance. This can be described by the fact that concentrated NaOH was utilized as a phase separating agent in the final step. Therefore, further experiments were performed at natural pH for the simplicity of the work.

3.4. Effect of temperature

The diffusion coefficient of the most analytes increases with temperature, although very high extraction temperatures may decrease the extraction proficiency due to solvent evaporation

and also increasing the organic solvent solubility in the sample solution [35]. Herein, the effect of temperature on the extractability of PCBs was investigated in the range of 20-60 °C and the results showed that the temperature has not any considerable effect on the peak area of PCBs. Accordingly; the experiments were performed at ambient temperature.

3.5. Effect of extraction time

Extraction time is an important parameter that may have a key role in microextraction methods. The extraction time was set as the time range between the addition of HCl and just before starting to collect the extractant from the top of the solution. It is necessary to note that the minimum time required for this process is 2.0 min. In this regard, to reveal the effect of extraction time, the time was varied in the range of 2.0-10.0 min. The results showed that extraction time has no noticeable effect on the SHS-HLLME efficiency.

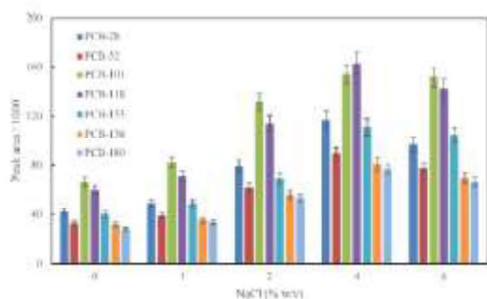


Fig. 2. The Effect of salt addition on SHS-HLLME of PCBs.

This owes to the fact that in acidic solutions, TEA and water are completely miscible and form a homogenous solution with infinitely large contact surface area. The time-independent nature of SHS-HLLME is an advantage of this method that makes it a fast extraction method. Accordingly, 2.0 min was selected as the optimum time for further studies.

3.6. Effect of NaCl addition

The effect of salt addition to the solution on the SHS-HLLME performance was evaluated by using various concentrations of NaCl in the range of 0-6% (w/v). Addition of salt to the sample solution can increase the ionic strength and alter the diffusion rate of PCBs from the aqueous solution to TEA. Results (Fig. 2) displayed that the extraction efficiencies of PCBs were increased by increasing the NaCl concentration up to 4% (w/v), regarding to the salting out effect based on decreasing the solubility of target analytes in water and increasing their tendency to the organic solvent. At the higher percentages of NaCl, the peak area of PCBs was not changed significantly; hence 4% w/v NaCl was selected for further studies.

3.7. Analytical performance of SHS-HLLME/GC-MS

Under the optimized experimental conditions, quantitative parameters of the SHS-HLLME/GC-MS method, including the limits of detection (LODs), limits of quantification (LOQs), linearity, coefficients of determination (r^2), enrichment factors (EFs), and extraction recoveries (ER%) were determined (Table 2). Good linearity with R^2 values of > 0.9973 was achieved for all the analytes. LODs and LOQs were calculated at 3 and 10 S/N (signal-to-noise), respectively. The intraday and interday repeatability of the method (as RSD %) were obtained by performing three replicate experiments at the concentration level of $50 \mu\text{g L}^{-1}$. The intraday and interday RSDs of the proposed SHS-HLLME method were $\leq 6.4\%$ and $\leq 7.2\%$, respectively. Also, the ER percentages were in the range of 76.01- 80.10 %. Enrichment factors for this method were obtained in the range from 47.21 to 49.75.

Table 2. Analytical performances of the proposed method for the quantification of selected PCBs.

PCB	Linear range (μgL^{-1})	R^2	LOD (μgL^{-1})	LOQ (μgL^{-1})	EF ^a	ER ^b (%)	RSD ^c (%)	RSD ^d (%)
PCB-28	0.5-150	0.9994	0.15	0.5	48.82	78.74	6.2	7.2
PCB-52	0.5-150	0.9991	0.15	0.5	47.36	76.26	5.4	6.5
PCB-101	0.5-150	0.9994	0.15	0.5	49.75	80.10	5.2	6.4
PCB-118	0.5-150	0.9973	0.15	0.5	49.41	79.55	5.9	5.6
PCB-153	0.5-150	0.9997	0.15	0.5	48.60	78.25	6.1	7.2
PCB-138	0.5-150	0.9977	0.15	0.5	47.21	76.01	6.4	5.7
PCB-180	0.5-150	0.9993	0.15	0.5	47.55	76.56	5.2	6.3

^a Enrichment factor, ^b extraction recovery, ^c intraday and ^d interday RSDs were calculated for $50 \mu\text{g L}^{-1}$

Table 3. Determination of selected PCBs in water samples.

	Drinking water			Tap water		
	Spiked (μgL^{-1})	Founded (μgL^{-1})	Recovery (RSD, n=3)	Spiked (μgL^{-1})	Founded (μgL^{-1})	Recovery (RSD, n=3)
PCB-28	10	9.74	97.4 (7.3)	50	48.73	97.5 (6.5)
PCB-52	10	9.98	99.8 (6.9)	50	49.22	98.4 (5.9)
PCB-101	10	10.12	101.2 (7.1)	50	50.8	101.6 (5.2)
PCB-118	10	9.63	96.3 (7.5)	50	50.12	100.2 (6.4)
PCB-153	10	10.26	102.6 (7.1)	50	49.81	99.6 (6.1)
PCB-138	10	9.84	98.4 (6.7)	50	51.14	102.3 (6.4)
PCB-180	10	9.76	97.6 (6.9)	50	47.93	95.9 (6.2)

3.8. Analysis of real samples

Finally, for checking the applicability of SHS-HLLME/GC-MS method, diverse types of water samples including tap water and drinking water were examined under the optimal conditions. The results of the determination and recovery studies with three replicates for these samples are demonstrated in Table 3. As can be seen, the relative recoveries were in the range of 95.9–102.6% with RSDs less than 7.5%. Therefore, the results confirmed that the applied method is sensitive, accurate and repeatable for determining trace amounts of PCBs in various water samples. Figure 3 displays typical GC-MS chromatograms of blank (non-spiked) and spiked drinking water samples after the extraction under the opted conditions.

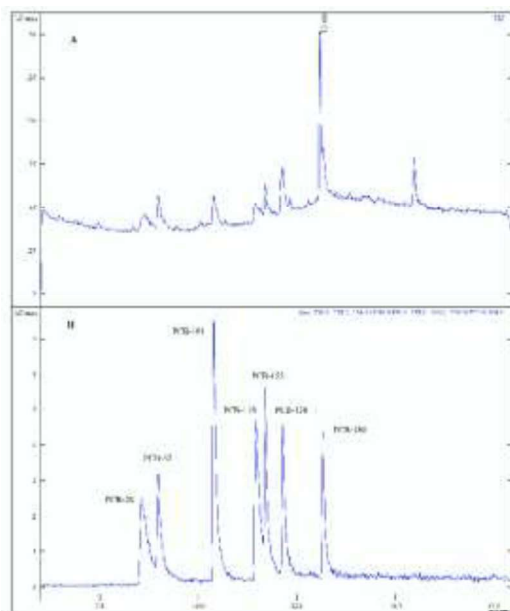


Fig. 3. (A) Total ion current (TIC) and (B) selected ion monitoring (SIM) chromatograms of PCBs ($50 \mu\text{g L}^{-1}$) after SHS-HLLME from tap water sample.

4. CONCLUSION

In the current study, for the first time, a facile, highly sensitive and efficient method named pH-assisted switchable hydrophilicity solvent based

homogenous liquid-liquid microextraction in combination with GC-MS analysis was developed for the preconcentration and determination of PCBs in aqueous samples. Triethylamine was used as a switchable solvent which can be miscible/immiscible by varying the pH of the aqueous solution using HCl and NaOH solutions. The new method showed acceptable analytical characteristics such as wide linear dynamic ranges and low LOD values along with good precisions. Besides, the mentioned method is simple, fast, selective, efficient and cost effective. Regarding to the consumption of few microliters of organic solvent, SHS-HLLME provides a green extraction method.

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اندازه گیری پلی کلروبی فنیل ها در نمونه های آبی به روش میکرواستخراج فاز مایع بر پایه حلال های دارای آبدوستی قابل تغییر جفت شده با کروماتوگرافی گازی-اسپکترومتری جرمی

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چکیده

در اینجا یک روش ساده، سریع و کارآمد بر پایه میکرواستخراج مایع-مایع همگن یاری شده با pH ترکیب شده با کروماتوگرافی گازی-طیف سنجی جرمی (GC-MS) برای تعیین مقادیر ناچیز پلی کلروبی فنیل ها شده (PCBs) در نمونه های آبی، بکار گرفته شده است. تری اتیل آمین (TEA) بعنوان یک حلال دارای آب دوستی قابل تغییر استفاده شده که می تواند با تغییر pH محلول نمونه، قابل اختلاط یا غیرقابل اختلاط با نمونه های آبی باشد. در این بررسی، اثرات پارامترهای مختلف در کارایی استخراج PCB ها بررسی شده است. حدود تشخیص، حدود اندازه گیری کمی و محدوده خطی دینامیکی به ترتیب برابرند با ۰.۱۵، ۰.۵ و ۱۵۰-۰.۵ میکروگرم بر لیتر و همچنین درصد RSD% (n=3) در محدوده های ۶.۴-۵.۲ و ۷.۲-۵.۶ برای سنجش در یک روز و روزهای مختلف بدست آمد. در نهایت، این روش برای تعیین PCB ها در نمونه های آبی به کار گرفته شد.

واژه های کلیدی

پلی کلروبی فنیل ها؛ حلال دارای آبدوستی قابل تغییر؛ میکرواستخراج مایع-مایع همگن؛ آنالیز کروماتوگرافی گازی-اسپکترومتری جرمی.