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On-line coupling of subcritical water extraction with high-performance liquid chromatography via solid-phase trapping

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Abstract

Although ambient water is very polar and cannot dissolve many organic species, water at elevated temperatures behaves like a polar organic solvent. Thus, subcritical water has been proven to be an effective extraction fluid for several classes of organic compounds. While solvent trapping was used to collect the extracted analytes in most of previous subcritical water extractions, sorbent trapping has also been developed for subcritical water extraction. In this study, an on-line system for subcritical water extraction and high-performance liquid chromatography (HPLC) was built and tested. A sorbent trap was used as the interface between subcritical water extraction and HPLC. Several shut-off valves have been utilized to switch the system from one mode to another (e.g., from the extraction mode to HPLC mode). The coupling technique of subcritical water extraction and HPLC eliminates the liquid–liquid extraction used in solvent trapping subcritical water extraction and provides higher sensitivity. Compared to the off-line system reported in an earlier work, the operation of this on-line system is even easier. Some peak broadening occurred after the coupling the water extraction with HPLC for the analytes studied. The performance of this on-line system was evaluated by the extraction and determination of caffeine, nitrotoluenes, polychlorinated biphenyls, chlorophenols and anilines.

Keywords: Solid-phase trapping; Extraction methods; Caffeine; Chlorophenols; Chloroanilines; Nitrotoluenes; Polychlorinated biphenyls; Subcritical water

1. Introduction

Water is a very polar solvent. Therefore, many organic species either cannot be dissolved or have poor solubilities in water. However, temperature has a tremendous effect on organic solubility in water. It has been clearly demonstrated that organic solubility is dramatically increased at higher temperatures. Sanders [1] reported that the solubility of benzo[*e*]pyrene, one of the polycyclic aromatic hydrocarbons (PAHs), is enhanced 25 million times by raising the temperature from ambient to 350°C. Miller and co-workers [2,3] determined the solubility of several pesticides and PAHs and found out that solubility increases of four- to five-orders of magnitude can be reached by heating water from ambient to 200–250°C. Yang et al. [4] reported the solubility of toluene in water at elevated temperatures, while

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Mathis and Yang investigated the solubility behavior of benzene, ethylbenzene and *m*-xylene in water at different temperatures [5]. Even though benzene and alkylbenzenes are more water-soluble compounds compared to PAHs, solubilities of these species are still enhanced up to ca. 40 times by increasing the temperature from 25 to 200°C [4,5].

In the last few years, subcritical water (also called as high-temperature water, superheated water, pressurized hot water, or hot liquid water by different investigators) has received increasing attention as an alternative extraction fluid [6–21]. Hawthorne et al. reported the extraction of phenols, *n*-alkanes and PAHs from sand using solvent trapping followed by gas chromatography (GC) analysis [6]. A potentially selective extraction was mentioned in this work. Later, Yang et al. reported class-selective extractions of polar analytes, PAHs and *n*-alkanes from sludge samples at different temperatures and pressures [7]. While polar analytes like phenols were already quantitatively extracted at 100°C and 50 bar, nonpolar PAHs and *n*-alkanes still remained in the sludge sample. When the extraction temperature was raised to 250°C at 50 bar, the PAHs were effectively removed from the matrix. However, the *n*-alkanes were not quantitatively extracted until a superheated steam condition (250°C and 5 bar) was reached [7]. The extraction of polychlorinated biphenyls (PCBs) from soil samples were also investigated [8–10]. The extraction recoveries of PCBs were increased by raising the water temperature. At temperatures at or higher than 250°C, all of the tested PCBs congeners from mono- to nonechlorobiphenyls were effectively removed from the soil matrices. The extraction of herbicides from soil by subcritical water was reported by Crescenzi et al. [11]. Subcritical water extraction (SBWE) was also used for soil characterizations [12]. Even though the majority of subcritical water extraction has been focused on organic pollutants, selenium was also extracted from soil using subcritical water and detected by atomic fluorescence [13].

The subcritical water extraction of non-environmental solids has also been reported. Pawlowski and Poole extracted thiabendazole and carbendazim from foods using subcritical water [14]. Yang et al. reported subcritical water extraction of selected analytes from different sorbents including: Florisil, Aluminum, silica-bonded C_{18} and XAD-2 resins [15]. Jimenz-Carmona and de Castro monitored subcritical water extraction kinetics of fluorescent analytes [16]. Decontamination of toxic organics and wastes has also been investigated under subcritical water conditions [17,18].

Organic solvents (e.g., methylene chloride) were used to collect the extracted analytes in most of the previous SBWE processes. Thus, a methylene chloride–water extraction has to be performed before the GC analysis. Another drawback of this solvent trapping technique is that the sensitivity is limited. Since only 1–2 μl of a 3–5-ml sample is used for GC analysis, trace analytes may not be detected.

The liquid–liquid extraction used in previous subcritical water extraction with solvent trapping can be eliminated by some coupling techniques. For example, Hageman et al. [19] and Hawthorne et al. [10] performed static subcritical water extraction of soils using a closed extraction cell without a delivery pump. Solid-phase microextraction was used after the static subcritical water extraction. Daimon et al. [20] reported the coupling of dynamic subcritical water extraction with solid-phase microextraction. Chromatographic analysis was employed after solid-phase microextraction in all three works [10,19,20]. While these coupling techniques do not require the post liquid–liquid extraction step, the quantitation is rather difficult. Young et al. performed subcritical water extraction, then an aliquot of the water extractant was injected into a liquid chromatography (LC) system using ambient water as the mobile phase for separation [21]. The drawback of this method is that only a very small fraction (10–20 μl) of the water extractant was collected during the extraction process and then analyzed, therefore, no quantitative extraction data can be obtained.

Very recently, SBWE was coupled to high-performance liquid chromatography (HPLC) via a solid trapping interface in an off-line arrangement [22]. This new coupling technique eliminates the liquid–liquid extraction after subcritical water extraction and provides better sensitivity compared to the solvent trapping method employed in previous subcritical water extractions. In this study, subcritical water extraction has been directly coupled to HPLC in an on-line arrangement. A HPLC guard column packed with silica-bonded C_{18} served as the interface

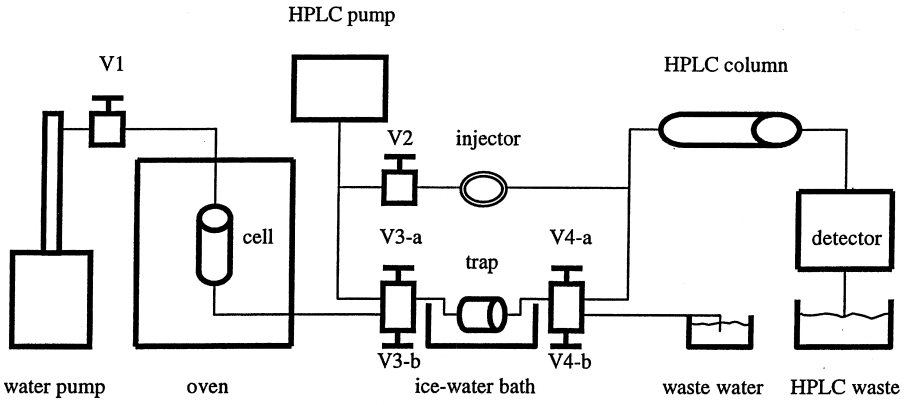

Fig. 1. Block diagram of the on-line coupling system of subcritical water extraction with high-performance liquid chromatography.

between subcritical water extraction and HPLC. During the water extraction, the extracted analytes are collected in the sorbent trap. Then, the collected analytes are introduced into a LC column for separation. Subcritical water extraction and HPLC analysis can be performed simultaneously using this on-line system. The extraction mode and HPLC mode can be conveniently switched by using shut-off valves as shown in Fig. 1. The operation of the on-line coupling system is simpler and easier than the off-line coupling system reported in previous work [22]. Several classes of compounds including caffeine, chlorinated phenols and anilines, nitrotoluenes and PCBs have been extracted and analyzed using this on-line coupling technique.

2. Experimental

2.1. Analytes and solvents

Caffeine was obtained from Eastman Kodak (Rochester, NY, USA). Nitrotoluenes and chlorinated phenols and anilines were purchased from Aldrich (Milwaukee, WI, USA). PCBs were provided by AuccuStandard (New Haven, CT, USA). HPLC-grade methanol (Fisher Scientific, Fair Lawn, NJ, USA) and deionized water (18 MΩ, laboratory prepared) were used as the mobile phase for HPLC. A sample size of 10 μl was used for both SBWE and HPLC calibration.

2.2. On-line coupling system and its operation

Fig. 1 shows the block diagram of the laboratory-made on-line coupling system of SBWE–HPLC. The subcritical water extraction part is consisted of an ISCO 260 D syringe pump (ISCO, Lincoln, NE, USA), a Fisher Isotemp oven, and Keystone SFE (supercritical fluid extraction) vessels (50×4.6 mm I.D. or 150×9 mm, Keystone Scientific, Bellefonte, PA, USA). The HPLC part includes a Hewlett-Packard high-pressure pump (series 1050, Hewlett-Packard, Avondale, PA, USA), a six-port Valco injector fitted with a 10-μl sample loop, a separation column (ODS, 5 μm, 250×4.6 mm I.D., DuPont, Wilmington, DE, USA), and a UV detector (Perkin-Elmer, Norwalk, CT, USA). The subcritical water extraction and HPLC systems are coupled via a solid trap (a HPLC guard column packed with silica-bonded C_{18}, 20×4 mm I.D., Keystone Scientific), two two-way shut-off valves (V1 and V2, HIP Model 15-11AF1, High Pressure Equipment, Erie, PA, USA), and two three-way shut-off valves (V3 and V4, HIP Model 15-15AF1). V3-a and V4-a are closed during subcritical water extraction so that the extracted analytes can be collected in the solid trap. HPLC calibration can also be performed by opening V2 while subcritical water extraction is in process. Therefore, both subcritical water extraction and HPLC calibration can be performed simultaneously. After the water extraction, V2, V3-b and V4-b are closed and V3-a and V4-a are opened. Thus, the trapped analytes are

eluted by the mobile phase and injected into the HPLC column for separation and quantitation.

Deionized water was purged by helium and then filled into the ISCO pump serving as the extraction fluid. Ottawa sand (Fisher) was precleaned using methylene chloride followed by acetone, then dried in an oven at 100°C for an hour. Either the precleaned sand or clean Kleenex paper (for the extraction of caffeine) was packed into SFE vessels. Approximately 1.2 g sand was loaded into the smaller extraction cell (50×4.6 mm), while the bigger cell (150×9 mm) held ca. 17 g sand. For the extraction of caffeine, clean Kleenex paper was fully loaded into the smaller extraction vessel. The analytes were spiked onto the sand or Kleenex paper for recovery studies. The inlet of the loaded extraction cell was connected to the ISCO 260 D syringe pump using a 1-m preheating coil and placed inside the Fisher Isotemp oven. The outlet of the cell was then connected to V3. The solid trap was located between V3 and V4, and placed inside an ice-water bath during the subcritical water extraction. Before the extraction, the system was pressurized to 15 atm by the ISCO syringe pump with V3-b opened and V4-b closed to check possible leaks of the system (1 atm=101 325 Pa). After checking leaks, the oven was heated to the desired temperature with V3-b and V4-b opened, while the ISCO pump was operated at a constant flow-rate of 0.1 ml/min. After the extraction temperature was reached, the pump was set at 0.6 ml/min in constant flow-rate mode, and subcritical water extractions were performed. The pressure of the system was determined by the solid trap and the flow-rate used. V4-b was adjusted to obtain ca. 50 atm for the system. The extracted analytes were separated from the sample matrix and collected in the solid trap.

After the SBWE extraction, V2, V3-b and V4-b were closed and V3-a and V4-a opened. Thus, the HPLC mobile phase eluted the collected analytes from the trap and injected them into the analytical column. The analytes were then separated by the column and detected by the UV detector at the wavelength of 254 nm. A mixture of methanol and water was used as the HPLC mobile phase. Both methanol and water were degassed using helium. The flow-rate was 0.9 ml/min for analyses unless otherwise noted. Isocratic elutions were used for caffeine (methanol–water, 40:60), chlorophenols (methanol–water, 60:40), nitrotoluenes (methanol–water, 30:70), and PCBs (methanol–water, 90:10). A solvent gradient was used for the separation of chloroanilines. The initial methanol concentration was 40%, followed by an increase of 2% methanol per minute with a final methanol concentration of 90%.

3. Results and discussion

3.1. Chlorophenols

Chlorophenols were extracted at 100°C using 5 ml of water. Fig. 2 shows the chromatograms of phenol and mono-, di- and trichlorophenols. The left chromatogram was obtained from HPLC calibration mode (no subcritical water extraction), while the right chromatogram was achieved by the SBWE–HPLC coupling mode (after subcritical water extraction). These chromatograms show that there was only some peak broadening occurred after coupling subcritical water extraction to HPLC. The peak width of chlorophenols before and after the coupling is summarized in Table 1. We can see that the peak broadening ranges from 15 to 30%.

Different extraction vessels were used for phenols study. First, a smaller extraction vessel (50×4.6 mm I.D.) was used. The concentration ranges from 8 to 11 ppm for this experiment. As shown in Table 2, all of the target analytes were quantitatively extracted under the conditions used. The recovery ranged from 95 to 102% with a typical relative standard deviation (RSD) of 10%. Then, a bigger extraction cell (150×9 mm I.D.) and lower concentrations (120–125 ppb) were investigated. Despite the low concentrations, all of the chlorophenols were effectively removed from the contaminated sand with favorable recoveries (89–108%), as shown in Table 2. The chromatograms with low chlorophenol concentrations are shown in Fig. 2. Please note that the phenol peak disappeared after the SBWE. This was resulted by the extremely high solubility of phenol in ambient water, so that the collected phenol in the sorbent trap was eluted from the trapping column by low-temperature water during the SBWE process. Based on the peak areas for the peaks in these chromatograms

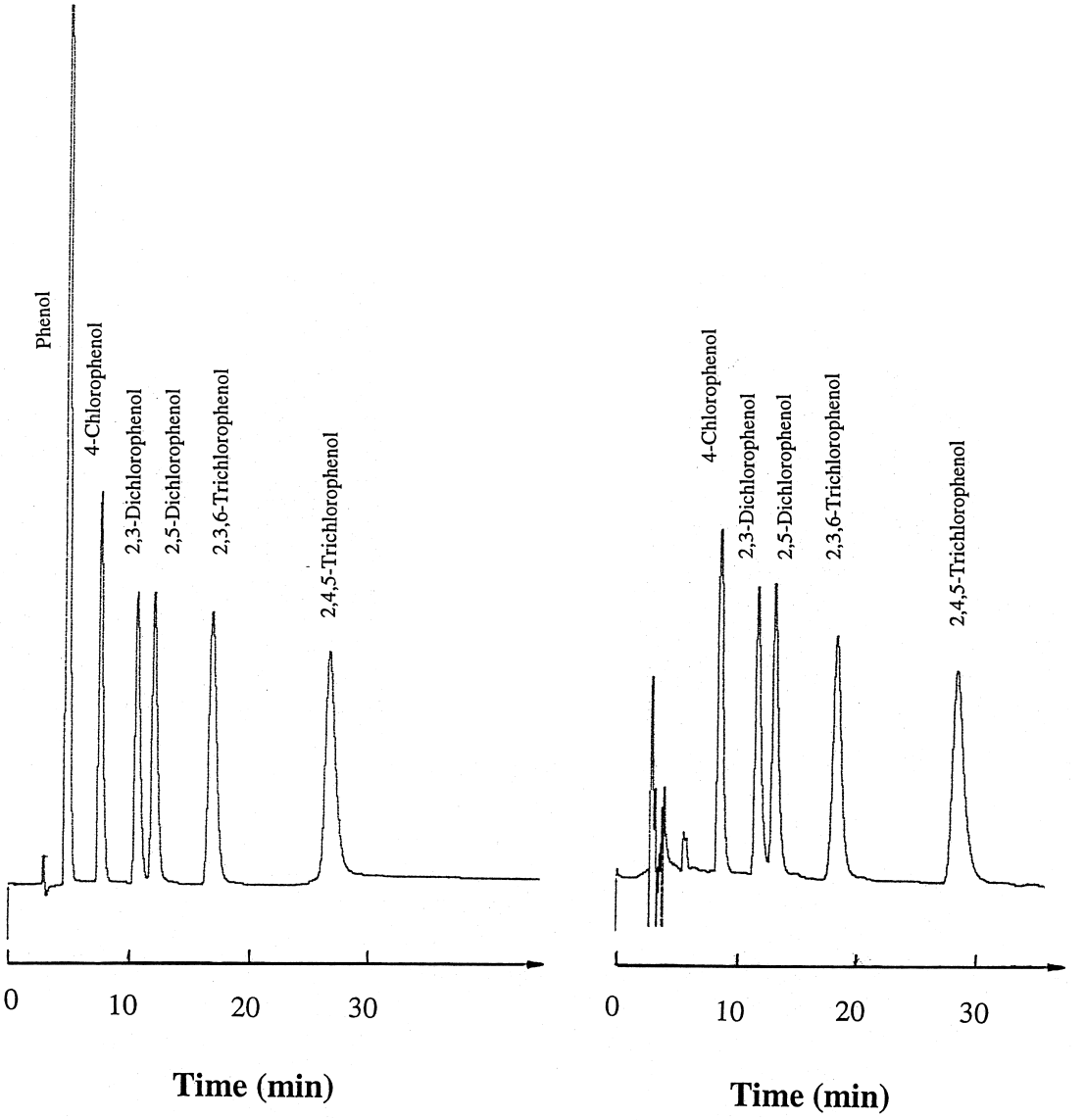

Fig. 2. Chromatograms of chlorophenols obtained by HPLC calibration mode (left) and the coupling mode after subcritical water extraction (right).

in Fig. 2, the detection limit of chlorophenols is estimated to be at the lower ppb and the upper ppt levels for this on-line coupling technique.

3.2. Chloro- and methylanilines

Table 3 shows the recoveries of five chloroanilines and methylanilines obtained at 100°C and using 5 ml of water. For extractions of sand containing 16–23 ppm anilines, the recovery ranged from 96 to 108%. Extractions of anilines with lower concentrations (120–170 ppb) were also performed and the recoveries were 94–104%. The RSD was generally less than 10% in both cases. The chromatograms of anilines with lower concentration are shown in Fig. 3. Like phenol, aniline was already eluted from the

Table 1
Comparison of peak width before and after the coupling of SBWE–HPLC

Analyte	HPLC calibration		SBWE–HPLC coupling		% Broadening
	Width (min)	RSD (%)[a]	Width (min)	RSD (%)[b]	
4-Chlorophenol	0.385	5	0.443	6	15
2,3-Dichlorophenol	0.469	5	0.610	3	30
2,4-Dichlorophenol	0.518	4	0.672	5	30
2,4,5-Trichlorophenol	0.734	13	0.939	5	28
2,3,6-Trichlorophenol	0.975	7	1.20	10	23
3-Chloroaniline	0.384	15	0.469	10	22
2,6-Dimethylaniline	0.458	12	0.565	15	24
2,3-Dichloroaniline	0.337	23	0.407	24	21
2,4-Dichloroaniline	0.347	15	0.416	21	20
2,4,6-Trichloroaniline	0.298	12	0.343	22	15

[a] Based on triplicate HPLC runs.
[b] Based on triplicate SBWE–HPLC runs.

Table 2
Recoveries of chlorophenols at 100°C and using 5 ml of water

	Concentration (μg/g)[a]	% Recovery (RSD, %)[b]	Concentration (μg/g)[c]	% Recovery (RSD, %)[b]
4-Chlorophenol	0.15	89 (3)	11	95 (8)
2,3-Dichlorophenol	0.14	103 (10)	9	100 (7)
2,4-Dichlorophenol	0.12	101 (14)	9	100 (6)
2,4,5-Trichlorophenol	0.12	108 (12)	8	99 (8)
2,3,6-Trichlorophenol	0.12	100 (9)	9	102 (11)

[a] Extraction cell: 150×9 mm.
[b] Based on triplicate extractions and HPLC analyses.
[c] Extraction cell: 50×4.6 mm.

sorbent by low-temperature water during subcritical water extraction. Therefore, aniline peak was not found in the chromatogram after SBWE. By comparing the peaks in the HPLC calibration mode (Fig. 3, left) and in the coupling mode (Fig. 3, right), one can see that there is some peak broadening for anilines after the on-line coupling of subcritical water to HPLC. As summarized in Table 1, the peak broadening for anilines ranges from 15 to 24%. When the concentration of anilines was further

Table 3
Recoveries of chloro- and methylanilines at 100°C and using 5 ml of water

	Concentration (μg/g)[a]	% Recovery (RSD, %)[b]	Concentration (μg/g)[c]	% Recovery (RSD, %)[b]
3-Chloroaniline	0.15	101 (1)	21	104 (2)
2,6-Dimethylaniline	0.12	104 (10)	16	96 (8)
2,3-Dichloroaniline	0.17	100 (7)	23	108 (7)
2,4-Dichloroaniline	0.12	100 (7)	17	108 (4)
2,4,6-Trichloroaniline	0.12	94 (4)	17	102 (6)

[a] Extraction cell: 150×9 mm.
[b] Based on triplicate extractions and HPLC analyses.
[c] Extraction cell: 50×4.6 mm.

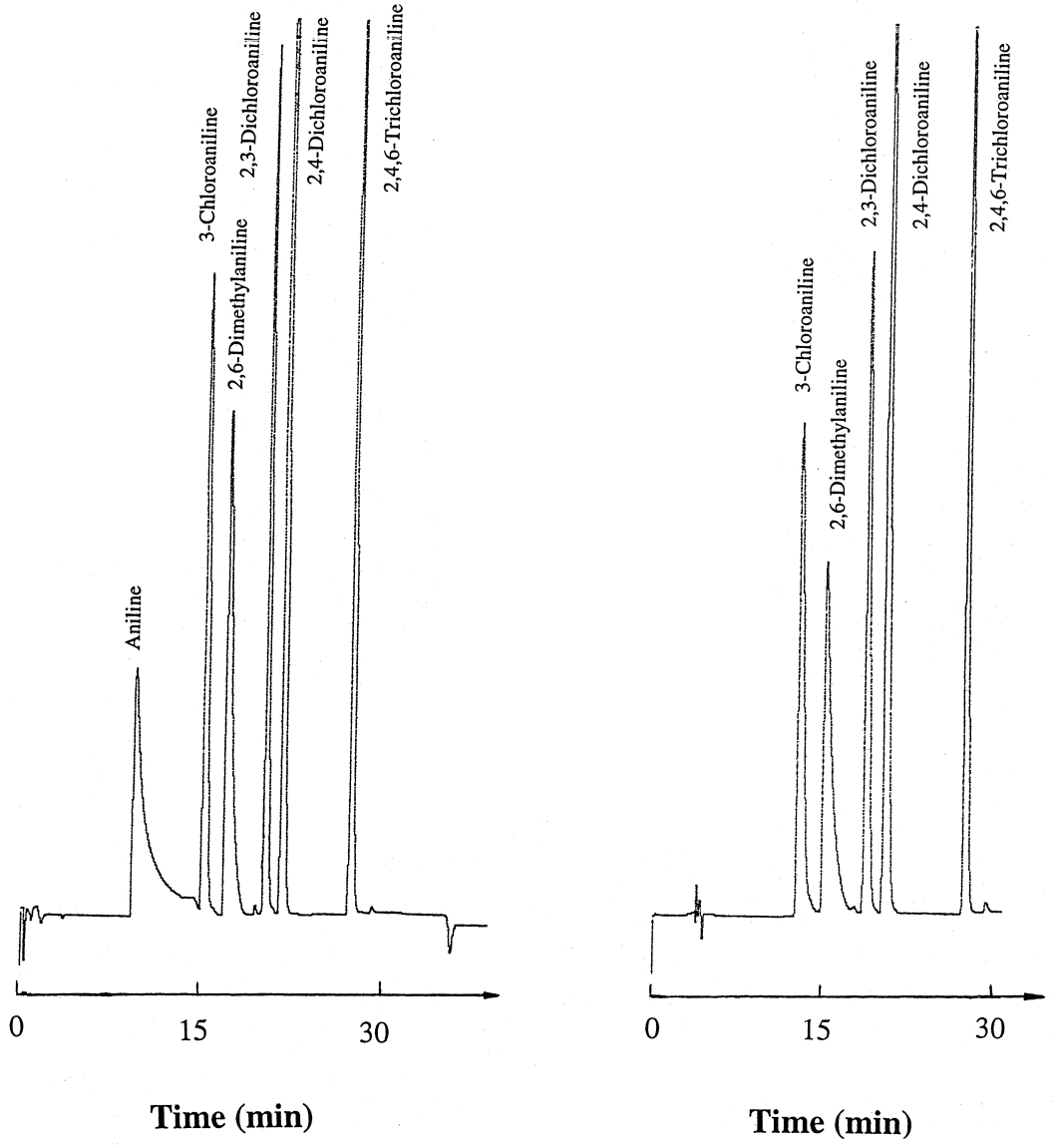

Fig. 3. Chromatograms of chloro- and methylanilines obtained by HPLC calibration mode (left) and the coupling mode after subcritical water extraction (right).

reduced to 1.2–1.7 ppb, the recovery was still higher than 80%.

3.3. Caffeine

The SFE vessel (50×4.6 mm I.D.) was filled with clean Kleenex paper. Then, 10 μl of caffeine solution (1000 ppm in methanol) was spiked onto the paper. Subcritical water extractions were performed at 100°C with 5 ml of water. The peak shape of caffeine obtained after SBWE was similar to that of HPLC calibration (without SBWE), which demonstrates that the on-line coupling system worked well.

Table 4
Recoveries of nitrotoluenes at different temperatures

	Concentration (μg/g)[a]	% Recovery (RSD, %)[b]	
		150°C	200°C
2-Nitrotoluene	2	76 (2)	88 (10)
3-Nitrotoluene	2	73 (3)	95 (11)
4-Nitrotoluene	2	79 (3)	108 (0)
2,6-Dinitrotoluene	2	81 (3)	94 (4)
2-Amino-4,6-dinitrotoluene	2	76 (5)	87 (17)
4-Amino-2,6-dinitrotoluene	2	75 (6)	94 (20)
Tetryl	2	77 (2)	88 (5)

[a] Extraction cell: 50×4.6 mm.
[b] Based on triplicate extractions and HPLC analyses.

Based on triplicate analyses, the recovery of caffeine was 110% with a RSD of 8%.

3.4. Nitrotoluenes

The extraction and analysis of seven nitrotoluenes was performed to evaluate the on-line system. The analytes were initially extracted at 150°C with 5 ml of water. The concentration is 2 ppm for each analyte. As shown in Table 4, the extraction efficiency is not very high since the recovery ranges from 73 to 81%. Based on previous work [22], the extraction efficiency can be improved by increasing the water volume or the extraction temperature. We then raised the extraction temperature to 200°C, and the recoveries were increased to 87–108%. The RSD was less than 20%.

3.5. Polychlorinated biphenyls

PCBs were previously extracted by subcritical water at different temperatures [8–10]. In this work, six PCBs up to heptachlorobiphenyl were initially extracted at 200°C using 10 ml of water. Since PCBs are more hydrophobic and have poorer solubility than the analytes in other classes described above, not every tested PCB congener was efficiently extracted at 200°C. As shown in Table 5, while quantitative recoveries were reached for the less chlorinated PCBs (e.g., mono-, tri- and tetrachlorobiphenyls), the recoveries for PCBs with more chlorines (e.g., penta-, hexa- and heptachlorobiphenyls) were only 68% or lower. However, the recoveries of the penta-, hexa- and heptachlorobiphenyls were improved to 87% or greater when water temperature was increased to 250°C even

Table 5
Recoveries of polychlorinated biphenyls at different temperatures

	200°C				250°C
	Concentration (μg/g)[a]	% Recovery (RSD, %)[b]	Concentration (μg/g)[c]	% Recovery (RSD, %)[b]	% Recovery (RSD, %)[b]
2-Chlorobiphenyl	12	104 (19)	0.08	110 (4)	102 (12)
2,2′,5-Trichlorobiphenyl	33	95 (8)	0.24	92 (3)	90 (13)
2,2′,5,5′-Tetrachlorobiphenyl	15	96 (13)	0.11	92 (3)	100 (23)
2,2′,4,5,5′-Pentachlorobiphenyl	18	65 (20)	0.13	68 (13)	95 (30)
2,2′,4,4′,5,5′-Hexachlorobiphenyl	15	61 (20)	0.11	63 (6)	87 (35)
2,2′,3,4,4′,5,5′-Heptachlorobiphenyl	9	54 (27)	0.07	61 (24)	90 (23)

[a] Extraction cell: 50×4.6 mm.
[b] Based on triplicate extractions and HPLC analyses.
[c] Extraction cell: 150×9 mm.

though the same volume of water (10 ml) was used for the extraction. Please note that the concentration of each individual PCB congener ranges from 80 to 240 ppb for the extractions at 250°C. Although the chromatograms are not shown, there was only some peak broadening observed after the coupling of water extraction to HPLC.

The temperature effect observed for extractions of nitrotoluenes and PCBs was mainly resulted by the decreased polarity of water at higher temperatures. As noted in previous works [6–8,15,22], the dielectric constant of water is dramatically reduced by raising water temperature. Therefore, water behaves more like an organic solvent at elevated temperatures. The decreased polarity of water at higher temperatures makes it possible to dissolve more organic species so that the solubility is enhanced [1–5]. Since the extraction efficiency is highly dependent upon the solubility in the extraction fluid, better recovery is obtained at higher temperatures for analytes that have poor solubility in ambient water.

While the above-mentioned results strongly demonstrate the success of the on-line coupling technique, there are still some improvements need to be done in the future. For example, the inlet frit of the solid trap needs to be cleaned after a few extractions. Since the frits used in this work are permanently mounted to the trap column by the manufacturer, replaceable frits are preferred.

4. Conclusions

An on-line coupling system of SBWE with HPLC was constructed via a solid trap and several shut-off valves. Several classes of organic compounds including chlorophenols, chloro- and methylanilines, caffeine, nitrotoluenes and PCBs were extracted and analyzed by this on-line system. The peak shapes obtained after the coupling of SBWE–HPLC are similar to those of HPLC calibration for all of the five classes studied. Therefore, only some peak broadening occurred using this on-line coupling technique. Quantitative recoveries of phenols, anilines and caffeine were achieved at 100°C, demonstrating that water is an effective extraction fluid for these analytes at relatively low temperatures. However, efficient extractions of nitrotoluenes and PCBs required higher temperatures. The recoveries of nitrotoluenes were not quantitative until 200°C, while all of the six PCBs tested were effectively removed from the sand at 250°C. This on-line coupling technique eliminates the organic solvent–water extraction required for solvent trapping subcritical water extraction, and provides higher sensitivity. Compared to the off-line coupling of SBWE–HPLC reported previously, this on-line system is more convenient to operate.

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