

# Extraction of polychlorinated biphenyls with water under subcritical conditions

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## Abstract

Supercritical fluid extraction is a fast and efficient method to extract all manner of organic compounds from a wide variety of solid sample matrices. Due to the marked change in its polarity with temperature, water is an interesting alternative to carbon dioxide as the extraction fluid. By merely adjusting the temperature, selectivity can be achieved for inorganic or organic compounds and for polar or non-polar organic compounds. Many organic compounds are sufficiently soluble to be extracted under subcritical conditions and, in this way, instrumental and other problems, such as the high corrosiveness of supercritical water, can be avoided. Instrumentation for sub- and supercritical water extraction was developed and modified in several ways with the aim of simplifying the procedure while maintaining good recoveries. Good recoveries of polychlorinated biphenyls (PCBs) spiked into sea sand and of native PCBs in a real soil sample were achieved with liquid collection. Relative to Soxhlet extraction, recoveries were higher or similar when solid-phase and liquid collection were combined. With a solid-phase trap packed with Tenax, the recovery was usually more than 85% for spiked PCBs. © 1997 Elsevier Science B.V.

*Keywords:* Subcritical fluid extraction; Polychlorinated biphenyls

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## 1. Introduction

Carbon dioxide has been the usual extraction fluid in the supercritical fluid extraction (SFE) of organic compounds from solid sample matrices. Although water has a high critical temperature (374.2°C) and supercritical water is more corrosive than normal water, it is an interesting choice for the extraction fluid because of its unique properties, which are dramatically altered by a change in temperature, especially near the critical temperature [1,2]. Water is also inexpensive and an environmentally friendly fluid.

Because of the high polarity of water at ambient temperature (dielectric constant,  $\epsilon=80$ ), many low

polarity organic compounds dissolve in it poorly. At 250°C, the value of the dielectric constant is about 1/3rd of that at room temperature, and polyaromatic hydrocarbons (PAHs) and other compounds of low polarity can be quantitatively extracted within a very short time [3]. Above the critical temperature, the dielectric constant of water may be as low as 2.5, resulting in the disappearance of the hydrogen bonding capability. This may explain the drop in solubility of inorganic compounds, which are precipitated at temperatures above 450°C. Under these conditions, water loses the ability to dissociate salts, resulting in a less ionic environment and a decrease in electrochemical processes, such as corrosion. On the other hand, water may become an ionic fluid at densities higher than 1.8 g/ml at high supercritical temperatures [4] and an opposite net effect will then

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result. That this change to ionic fluid actually occurs is supported by the increase in the specific conductance  $\sigma$  ( $\text{ohm}^{-1} \text{cm}^{-1}$ ) and the ionization product  $K_w$  ( $\text{mol}^2 \text{kg}^{-2}$ ) of pure water as a function of both temperature and pressure [2].

Under supercritical conditions, water is a strong solvent for all kinds of organic compounds; even wood can be dissolved. However, these conditions will also result in very dirty extracts and, in analyses with chromatographic techniques, this is not desirable. In addition, high temperatures put demands on the instrumentation, which is the main reason why SFE with water has not been performed so frequently. Fortunately, many extractions can be performed at lower temperatures (subcritical water), where suitable adjustments to the temperature allow the selective extraction of polar (chlorinated phenols), low-polarity (PCBs and PAHs) and non-polar (alkanes) organic compounds [3]. In general, the selectivity and the range of applications should be wider with water than with carbon dioxide. One should also keep in mind that reforming activity (the reforming and breaking down of organic molecules) increases rapidly at temperatures higher than the critical temperature.

SFE instrumentation for sub- and supercritical water extraction was developed with the goal of simplifying the procedure through avoidance of liquid–liquid extraction. Recoveries achieved with and without solid-phase trapping were compared in test extractions of PCB compounds from soil and sea sand samples.

## 2. Experimental

### 2.1. Chemicals and samples

Florisil (60–100 mesh and 30–60 mesh), used for the trap in high temperature water extraction, was obtained from Fluka (Buchs, Switzerland). Other materials tested were XAD-4 (20–60 mesh, Ega-Chemie, Germany), XAD-7 (20–60 mesh, Aldrich-Chemie, UK) and Tenax GC (60–80 mesh, Chrom-pack, Netherlands). The water that was used for the extraction was distilled. HPLC grade *n*-heptane and iso-octane were purchased from Rathburn Chemicals

(Walkerburn, UK). Acetone was from Lab Scan (Dublin, Ireland).

PCB spiking solutions (a mixture of neat Aroclors 1016 and 1260, and PCB-W22 standard mixture) were prepared in iso-octane where the level of the total PCBs was about 30  $\mu\text{g}/\text{ml}$  (Aroclors) and the level of the individual congeners was ca. 0.5  $\mu\text{g}/\text{ml}$  (PCB-W22). With a syringe, 50  $\mu\text{l}$  of solution was added to acid-washed sea sand (Riedel-de Haën, Seelze, Germany) and was extracted with water. In the spiking study using the Aroclor mixture, the internal standard for gas chromatography was hexachlorobenzene (Aldrich, Gillingham, UK) and in later studies with PCB-W22, one of the three PCBs (35, 77 and 169) was used. The aroclors, the calibration standard mixture, PCB-W22, containing fifteen PCB congeners, and neat PCB congeners 35, 77 and 169 were all purchased from Accu Standard (New Haven, CT, USA). The soil sample was from Tauw Millieu, Deventer, Netherlands. Gas chromatography (GC) calibration for the soil sample was carried out with the standard mixture PCB-W22, which was diluted with iso-octane. PCBs 35, 77 and 169, which were used as internal standards, were dissolved in iso-octane to give concentrations of 2.5, 8.8 and 9.9  $\mu\text{g}/\text{ml}$ , respectively. A 50- $\mu\text{l}$  volume of this mixture was added to soil sample extracts (before liquid–liquid extraction and concentration steps, if performed) and standards prior to chromatographic analysis. The water content of the soil sample was determined by drying the subsample (2 g) for 42 h at 120°C.

### 2.2. Subcritical water extraction

The instrumentation for sub- and supercritical water extraction is presented in Fig. 1. The system consisted of a Varian 8500 HPLC pump (Varian, USA), to pressurize the water, a Fractovap Series 2150 gas chromatograph oven (Carlo Erba, Milan, Italy), to heat the 3 ml extraction vessel (Suprex, Pittsburgh, PA, USA) or the 2.2 ml high temperature extraction vessel (Keystone Scientific, Bellefonte, PA, USA), a 30-15HF4-HT high temperature three-way valve (High Pressure Equipment, Erie, PA, USA), a Jasco PU-980 HPLC pump for the elution solvent, a manually adjustable pressure restrictor (gift from Dr. Muneo Saito, Jasco, Japan), an HPLC

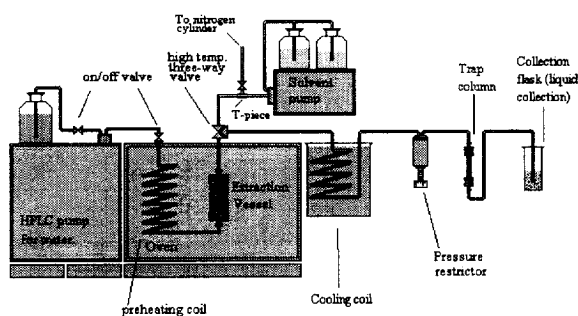


Fig. 1. Basic set-up for the sub- and supercritical water extraction instrument.

column (3 cm×4 mm I.D. or 7 cm×4 mm I.D.), for the solid phase trapping, and a 50-ml measuring flask for the collection flask (alternatively, with 5–10 ml of *n*-heptane used as a liquid trap). On/off valves were type 15-11AF1 from High Pressure Equipment. Approximately 3 m of 1/16 inch stainless steel tubing (I.D. 0.02 in.) was used for the preheating coil and ca. 1 m was used for the cooling coil. The same tubing was used for all the other connections between the different parts. At a later stage, the stainless steel Valco-type ferrules in the extraction vessel connections were replaced with double-ferruled Slipfree connectors (Keystone Scientific) in which Vespel ferrules were used as sealing ferrules. The following variations to the set-up depicted in Fig. 1 were tested:

(A) The outlet of the extraction vessel was directly connected to a 15 cm×40  $\mu$ m I.D. fused-silica restrictor (Composite Metal Services, Worcestershire, UK) via a 0.5-m 1/16 inch stainless steel capillary and 1/16 inch Swagelok union. The extract was collected in the 50 ml measuring flask, now containing 5–10 ml of *n*-heptane (liquid trap). After the extraction, the capillary from the vessel was eluted with *n*-heptane and the *n*-heptane extract was combined with the water extract.

(B) Same as in Fig. 1, but with no trap column. The extract was collected in the 50 ml measuring flask, now containing *n*-heptane.

(C) The three-way valve was disconnected and the capillary from the extraction vessel was connected to the cooling coil. No trap column was used. The extract was collected in the 50 ml measuring flask, now containing *n*-heptane. After each extraction, the

elution pump was connected to the system and the capillaries were rinsed with *n*-heptane.

(D) As in Fig. 1 but without the three-way valve and with the order of the trap column and the pressure restrictor reversed. After each extraction, the nitrogen line and the elution pump were connected to the 1/16-inch line leading out from the extraction vessel.

(E) As in Fig. 1 but the order of the trap column and the pressure restrictor was reversed.

PCBs were spiked onto the sea sand in the extraction vessel and the vessel was filled with the sand.

Real soil samples were placed in the extraction vessel, filling it completely (clean sea sand was added to the 0.5 g soil sample). Samples were swept by the water for 30 min at a flow-rate of ca. 1 ml/min, at the desired temperature and pressure. Small adjustments were made to the restrictor to keep the total volume at 30 ml over the 30-min period. During the extraction, the cooling coil was immersed in water that was at room temperature. After each extraction, the oven was cooled. Where the solid-phase trap was used, the trap and tubings were dried for 15 min with nitrogen before elution with *n*-heptane or other eluents (1 ml/min) into the GC vials. In spike recovery studies, a minimum of two vials (ca. 1.6 ml of eluent in each) were collected, and with soil samples, three vials were collected. When there was no trap column, only the liquid trap, the tubings were rinsed with *n*-heptane and the rinsing solution was combined with the water extract. When the measuring flask was used as the liquid trap for the water extract, 5 to 10 ml of *n*-heptane were added to the flask and the exit of the capillary was below the solvent level. Analytes were extracted from the water extract with several portions (5×2 ml) of clean *n*-heptane and these were concentrated under a flow of nitrogen to ca. 1.5 ml, for GC analysis. Between each extraction, the tubings and the trap column (if used) were cleaned by rinsing them with 10 ml of *n*-heptane, 10 ml of acetone and 10 ml of *n*-heptane. Finally, they were dried with nitrogen.

### 2.3. Gas chromatography

All samples were analysed with a Fisons 8160 gas

chromatograph (Fisons Instruments, Rodano, Italy) equipped with an electron capture detector and an AS 800 autosampler. On-column injection (2  $\mu$ l) was used. Helium was employed as the carrier gas at 170 kPa, resulting in a linear flow of 36 cm/s (80°C). Nitrogen provided the make-up gas (ca. 30 ml/min). A 2.5 m diphenyltetramethyldisilazane (DPTMDS)-deactivated retention gap with an I.D. of 0.53 mm (BGB Analytik, Rothenfluh, Switzerland) was used and this was connected to a 25-m BGB-5 column (0.2 mm I.D., with a film thickness of 0.15  $\mu$ m) with a glass pressfit connector. The oven was programmed from 80°C (2 min) to 170°C (7.5 min) at 10°C/min and to 270°C (10 min) at 3°C/min. The temperatures of the detector interface and the detector were held at 290 and 300°C, respectively. The column was changed later to a new 25-m BGB-5 column (0.25 mm I.D., with a film thickness of 0.25  $\mu$ m) and the column head pressure was decreased to provide a similar linear flow to that achieved with the smaller I.D. column that was used earlier.

### 3. Results and discussion

The Suprex 3 ml extraction vessel was modified for use at high temperature by replacing the PEEK seals at either end with similar seals made of copper. Stainless steel frits were fitted at the centre of the copper seal in the same way as in the original PEEK seals. The seals were first tested and worked well up to 400°C. Aluminium was tested as a seal material, but it was more easily damaged (oxidized) on the

surface, resulting in leakage of the high temperature water.

Since it had earlier been shown that PCBs can be quantitatively extracted with subcritical water [5], our first tests were made with set-up A, which included only a liquid trap (see Section 2). Recoveries of spiked PCBs from sea sand with water at 250 atm and 250°C, obtained with the silica restrictor, were reasonably good (see Table 1).

The capability of the cooling coil alone to trap the PCBs was briefly tested, but even cooling to +5°C was not sufficient to produce good recovery. Most of the analytes passed through the system. Our next step was to add a solid-phase trap to the system in the hope that this could replace the liquid trap. Florisil, of 60–100 mesh, was chosen as the trap material because it happened to be available at a large enough particle size at that time, not because of its suitability. Adding a 3-cm trap column with normal 2  $\mu$ m frits and packed with Florisil before the restrictor caused the adjustable restrictor to fail. Evidently, the trap was restricting the flow (and pressure) too much. Placing the trap after the restrictor instead (Fig. 1) allowed the flow to be adjusted via the restrictor, but the trap column was then easily blocked. This may explain the poorer repeatability with the set-up shown in Fig. 1 than with set-up B (see Table 1). Similar recoveries (ca. 20%) were obtained with the set-up in Fig. 1 at 350 atm and 250°C, but standard deviations were then even higher.

When only traces of PCBs were found in water passing through the trap, the reason for the bad

Table 1  
Recoveries of spiked PCBs from sea sand, extracted with water with different set-ups of the instrument ( $n=3$ )

| Compound             | Recovery (%) (SD)            |                                      |                              |
|----------------------|------------------------------|--------------------------------------|------------------------------|
|                      | Set-up A<br>(250 atm, 250°C) | Set-up in Fig. 1<br>(400 atm, 300°C) | Set-up B<br>(200 atm, 250°C) |
| PCB 101              | 88.6 (7)                     | 19.0 (7)                             | 20.7 (3)                     |
| PCB 149              | 78.4 (1)                     | 19.7 (10)                            | 23.0 (5)                     |
| PCB 153              | 80.3 (2)                     | 17.1 (8)                             | 22.4 (5)                     |
| PCB 138              | 100.9 (3)                    | 18.0 (9)                             | 25.4 (5)                     |
| PCB 128              | 61.4 (14)                    | 16.2 (8)                             | 17.8 (8)                     |
| PCB 156              | 100.0 (8)                    | 20.5 (10)                            | 34.9 (11)                    |
| PCB 180              | 119.9 (18)                   | 19.4 (11)                            | 53.4 (21)                    |
| PCB 170 <sup>a</sup> | 132.4 (18)                   | 162 (153)                            | 103 (24)                     |

<sup>a</sup> Some interference from the water, which co-eluted with PCB 170 in the BGB-5 column.

recovery with the system was sought. First the Florisil trap was removed and the water was collected directly into the measuring flask (set-up B in Table 1). The results were not much better, however, and further experiments were carried out without the trap and without the three-way valve (set-up C) at various pressures, at 250°C (see Table 2).

Recoveries were clearly improved when the three-way valve was removed, indicating that some dead volume and/or leaking in the valve or in the plumbing used to connect the elution pump and the nitrogen flow was responsible. The extraction pressure seemed to have no influence on the recovery of PCBs, as was noticed earlier for PAHs [3], but the repeatability was better at higher pressures.

With 10 µm frits and Florisil with a larger particle size (30–60 mesh) in the trap column (set-up D), several extractions, even with a real soil sample, were performed, with no blocking or pressure problems. The trap column could now be placed before the restrictor, without causing any problems, to adjust the flow with the restrictor. Results for the spiked sea sand and soil sample extractions obtained with the 30–60 mesh Florisil trap are given in Table 3. In the soil sample extractions, both the PCBs trapped in the Florisil and those escaping with water into the measuring flask were determined (Table 3).

The Florisil (30–60 mesh) trap was less efficient than the liquid trap: Relative to the liquid collection method, about 25–30% less PCBs were recovered from the spiked sand (see Tables 2 and 3) and, usually less than 50% of the PCBs recovered from the soil sample were recovered from the Florisil. This is not surprising since Florisil is usually classi-

fied as a normal-phase material (polar) and it probably retains considerable water, which changes the properties of the Florisil and reduces its trapping efficiency. Additionally, water elutes the analytes from the trap at low trap temperatures in the same way as modifiers with CO<sub>2</sub> do [6,7]. With Florisil of such a large size, we should have used a longer trap column, since water eluted only small amounts of the PCBs from the 60–100 mesh Florisil trap. However, except for PCB 101, where the value was lower, and PCB 118, where the value was similar, recoveries were higher for the water extraction (with Florisil and liquid trap combined) than those obtained by Soxhlet extraction. A proper comparison between the water and Soxhlet extractions cannot be made, however, since no information was received with the sample on how the Soxhlet extractions were done. Certified reference materials would have been required. Repeatability of the water extraction for the soil sample was quite good. Possible errors in quantitation might be due to the GC analysis, since only one column was used. With the use of at least two columns and/or mass spectrometry, errors due to compounds eluting with the same retention time as the analytes would be minimized.

Other adsorbent materials (XAD-4, XAD-7 and Tenax GC) were examined in addition to Florisil. These materials are more like reversed-phase sorbents (non-polar) and were used previously to trap organic compounds from water samples [8,9]. All have low affinity for water (XAD-7 being less hydrophobic than XAD-4), which is a factor of major importance in selecting the trapping material for water extraction. Before these sorbent materials

Table 2  
Water extraction of spiked PCBs from sea sand at different pressures using set-up C at 250°C

| Compound             | Recovery (%) (SD) |              |              |              |
|----------------------|-------------------|--------------|--------------|--------------|
|                      | 150 atm, n=7      | 200 atm, n=6 | 250 atm, n=3 | 300 atm, n=3 |
| PCB 101              | 73.9 (13)         | 70.3 (17)    | 76.1 (3)     | 73.8 (6)     |
| PCB 149              | 71.8 (15)         | 65.0 (18)    | 67.0 (6)     | 64.9 (5)     |
| PCB 153              | 67.2 (10)         | 66.3 (18)    | 69.0 (4)     | 68.2 (4)     |
| PCB 138              | 79.9 (15)         | 73.6 (22)    | 73.2 (3)     | 70.4 (5)     |
| PCB 128              | 72.5 (50)         | 57.6 (17)    | 58.6 (10)    | 58.1 (3)     |
| PCB 156              | 65.8 (8)          | 66.3 (16)    | 76.7 (5)     | 73.8 (5)     |
| PCB 180              | 107 (19)          | 108 (13)     | 119 (11)     | 125 (20)     |
| PCB 170 <sup>a</sup> | 157 (45)          | 234 (158)    | 142 (32)     | 212 (34)     |

<sup>a</sup> Some interference from the water, which co-eluted with PCB 170 in the BGB-5 column.

Table 3  
Water extraction of PCBs from spiked sea sand and from a real soil sample using set-up D at 200 atm, 250°C

| Compound             | Spiked sea sand<br>Recovery (%) (SD) | Soil sample with water content of 25.05% |                                |                           |
|----------------------|--------------------------------------|--|--------------------------------|---------------------------|
|                      |                                      | Total ng/g <sup>a</sup> (SD)             | Florisol trap <sup>c</sup> (%) | Soxhlet ng/g <sup>b</sup> |
| PCB 18               | —                                    | 44.8 (25)                                | 34.6                           | —                         |
| PCB 28 <sup>c</sup>  | —                                    | 78.4 (4.1)                               | 50.9                           | 17                        |
| PCB 20 <sup>d</sup>  | —                                    | 23.9 (11)                                | 66.8                           | —                         |
| PCB 52               | —                                    | 32.4 (13)                                | 29.2                           | 17                        |
| PCB 101 <sup>d</sup> | 31.9 (4)                             | 17.2 (2.8)                               | 40.3                           | 38                        |
| PCB 149 <sup>d</sup> | 43.9 (11)                            | 23.9 (12)                                | 52.1                           | —                         |
| PCB 118              | —                                    | 11.8 (3.2)                               | 21.5                           | 12                        |
| PCB 153              | 43.3 (12)                            | n.q.                                     | —                              | 25                        |
| PCB 105 <sup>d</sup> | —                                    | 24.5 (4.2)                               | 35.2                           | —                         |
| PCB 138 <sup>d</sup> | 46.4 (14)                            | 59.7 (12)                                | 11.6                           | 28                        |
| PCB 128              | 40.8 (12)                            | n.q.                                     | —                              | —                         |
| PCB 156              | 37.9 (15)                            | n.q.                                     | —                              | —                         |
| PCB 180              | 42.9 (11)                            | 120.2 (14)                               | 8.7                            | 14                        |
| PCB 170 <sup>d</sup> | 90.8 (62)                            | 115.6 (35)                               | 31.3                           | —                         |
| PCB 194              | —                                    | 16.4 (1.9)                               | 36.2                           | —                         |

<sup>a</sup> Values reported as ng/g dry matter,  $n=4$ .

<sup>b</sup> Soxhlet values (ng/g dry matter) received with the sample (determined by Tauw Millieu).

<sup>c</sup> Not fully resolved from PCB 31.

<sup>d</sup> Possible interference from PCB congeners eluting with the same retention time from the BGB-5 column: PCB 20+PDB 33+PCB 53, PCB 101+PCB 84, PCB 149+PCB 123, PCB 105+PCB 132, PCB 138+PCB 163+PCB 160, PCB 170+PCB 190.

<sup>e</sup> Percentage of the total amount trapped.

n.q.=not quantified.

were studied, the high temperature three-way valve was opened and laboratory-made PTFE seals were added on the two handle sides inside the valve body, to minimize the dead volume. It was clear that the valve had been leaking from the base of the handle extensions and this leak was partly responsible for the poor recoveries that were obtained earlier. The PTFE seals were expected to correct the problem. Because small leaks were also suspected in the extraction vessel, the copper seals on the vessel were

changed to PEEK seals. Tests showed that the PEEK seals were still reliable at 250°C.

Extractions were made with set-up B and, as can be seen from Table 4, the recoveries were excellent (92–98%, compared with ca. 20% in Table 1). The modified three-way valve was now functioning well and was, apparently, no longer responsible for variations in recovery. In contrast to other reports [10], the results also showed no discrimination or loss in recovery of PCBs with collection into hep-

Table 4  
Recovery of selected PCBs after water extraction at 250°C and 250 atm

| Compound | Recovery (%) (SD)                    |                                      |                                      |
|----------|--------------------------------------|--------------------------------------|--------------------------------------|
|          | Liquid collection<br>Set-up B, $n=6$ | XAD-4 trap (3 cm)<br>Set-up E, $n=4$ | XAD-7 trap (3 cm)<br>Set-up E, $n=4$ |
| PCB 101  | 92.3 (9)                             | 31.0 (13)                            | 28.6 (6)                             |
| PCB 138  | 98.6 (9)                             | 24.3 (11)                            | 23.5 (5)                             |
| PCB 180  | 98.1 (17)                            | 30.1 (24)                            | 27.2 (8)                             |
| PCB 194  | 97.2 (14)                            | 35.5 (29)                            | 29.6 (11)                            |

Table 5

Recovery of selected PCBs after water extraction at 250°C and 250 atm with a 7-cm XAD-4 trap and a 3-cm Tenax trap and different eluents

| Compound | Recovery (%) (SD)         |                                    |  |                           |  |
|----------|---------------------------|------------------------------------|--|---------------------------|--|
|          | 7 cm XAD-4 trap, Set-up E |                                    |  | 3 cm Tenax trap, Set-up E |  |
|          | Heptane, <i>n</i> =4      | 2% acetone in heptane, <i>n</i> =3 | 10% ethylacetate in heptane, <i>n</i> =2 | Heptane, <i>n</i> =6      | 10% ethylacetate in heptane, <i>n</i> =3 |
| PCB 101  | 39.1 (11)                 | 29.0 (18)                          | 57.4                                     | 83.3 (6)                  | 87.5 (6)                                 |
| PCB 138  | 43.8 (22)                 | 32.8 (12)                          | 52.7                                     | 85.6 (6)                  | 87.9 (5)                                 |
| PCB 180  | 45.1 (24)                 | 38.0 (11)                          | 54.8                                     | 84.7 (6)                  | 87.7 (2)                                 |
| PCB 194  | 46.4 (26)                 | 39.9 (13)                          | 54.8                                     | 81.1 (6)                  | 90.0 (3)                                 |

tane. Experiments done with methylene chloride as the trapping solvent gave results similar to those with obtained with heptane, showing that heptane is an equally good collection solvent. The advantage of heptane is that solvent exchange is not required when electron capture detection is used for detection.

The system with set-up E was used for further experiments. XAD-4 and XAD-7 were first tested with a 3-cm trapping column, but, as can be seen from Table 4, the recoveries were fairly poor. XAD-4 performed a little better than XAD-7, as might be expected due to the slightly lower polarity of XAD-4. PCBs were also detected in the water coming through the trap, however, so another experiment was carried out with XAD-4 and a 7-cm trap column. Also, in all subsequent experiments, Slipfree connectors with Vespel ferrules instead of metal ferrules (see Section 2) were used with the extraction vessel and the extraction vessel was changed to a seal-free high temperature vessel, to minimize possible leaks. Now the PCBs were trapped more efficiently, since fewer PCBs were detected in the water coming through the trap. As it turned out, the recovery was poor (see Table 5) due to the slow elution of the PCBs from XAD-4 material. Some 5–10% of the analytes could still be detected in the second and third sample bottles (more was not collected), showing that XAD-4 is not the material of choice for collecting the analytes and efficiently eluting them from the trap with a solvent volume that is small enough to give concentrated samples.

The third material, Tenax, proved to be almost ideal for the trapping of PCBs in water: Analytes were not eluted out with the water and could be eluted using only a small volume of solvent directly

into the GC sample vial. Table 5 shows the recoveries of selected PCBs with the Tenax trap. Through the avoidance of extract handling steps, Tenax provided better repeatability than solvent collection.

#### 4. Conclusions

Our purpose in introducing the solid-phase trap was to eliminate the liquid–liquid extraction and extract concentration steps after sub- and supercritical water extraction. Good recovery of the PCBs was achieved with the Tenax trap, in most cases being more than 85%. With subcritical water and the use of both solid-phase (Florisil) and liquid collection, PCBs were recovered with higher efficiency than in Soxhlet extraction.

Recovery and repeatability were improved by decreasing the dead volumes (especially in the three-way valve). Small, undetectable leaks during high temperature water extraction were a problem and more attention should be paid to sealing materials on all connections. Using a more inert material in the capillaries and extraction vessel would also help. Gas chromatographic analysis with more than one column (or with MS detection) would provide more reliable results.

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