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Nordic laboratory intercomparison of supercritical fluid extraction for the determination of total petroleum hydrocarbon, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in soil

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Abstract

Two developed supercritical fluid extraction (SFE) methods [one for the determination of total petroleum hydrocarbon (TPH) and polychlorinated biphenyls (PCBs), and one for polycyclic aromatic hydrocarbons (PAHs) and creosote components in soil] were evaluated in a Nordic laboratory intercomparison study with 11 participating laboratories. The interlaboratory comparison showed that excellent recoveries can be obtained with SFE for PAHs and PCBs compared to the solvent extraction. For the TPH, the recoveries were significantly higher than those achieved with solvent extraction. The accuracy, expressed as the relative standard deviation, was higher than expected (generally 8–25% for PAHs, 6–20% for PCBs and less than 18% for TPH with a few very high values, especially for PCBs), but not different from the other intercomparison studies. Difference between liquid- and solid-phase collection in SFE was found to be significant only for more volatile PAH components such as naphthalene and fluorene. For PCBs and TPH, there were some variation in the results obtained with the two trapping methods. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

An increased awareness of the environment and its pollution has also created a demand for more efficient, accurate and reliable analytical tools to obtain information of our endangered planet. Sample pretreatment, including extraction, is usually the most error-prone, laborious and time-consuming step of an

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analytical determination. Unfortunately, it is only in the last decade that serious work has been done on new extraction techniques. Especially in the field of environmental analysis, traditional solvent extraction techniques like Soxhlet are being challenged by alternative techniques like supercritical fluid extraction (SFE), microwave assisted extraction (MAE) and pressurized liquid extraction (PLE) [1–6].

Supercritical fluid extraction has been used for the determination of organic pollutants in environmental solids with variable success for more than 10 years [1–3,7–12]. In addition, SFE has been shown to produce equivalent or better results compared to other extraction techniques like Soxhlet, sonication and accelerated solvent extraction [13–22]. These SFE methods have been working well in particular studies and in individual laboratories. However, only a few interlaboratory comparison studies on SFE for environmental matrices have been published [23,24].

Lopez-Avila et al. [23] conducted a mini-round-robin study on SFE of polycyclic aromatic hydrocarbons (PAHs) in soil samples. However, there was only three participating laboratories and samples were extracted only in triplicates. SFE recoveries were calculated as relative to sonication results, since the actual PAH concentrations were not known. Interlaboratory precisions (RSDs) for concentration levels below 1 mg/kg gave values ranging from 19 to 80%. Above 1 mg/kg, RSDs were 27% or better.

Good accuracy and precision was achieved in the study of Bøwadt et al. for polychlorinated biphenyls (PCBs) in soil [24]. In this study SFE was independently compared to Soxhlet in the soil certification process. Results obtained with SFE (only three laboratories) were excellent and comparable to those obtained with Soxhlet (21 laboratories). One reason for the good results was most likely that all participating laboratories were specialized in congener-specific PCB analysis.

Two official Nordic SFE methods were developed to replace the traditional solvent extraction procedures:

(1) Extraction of PAHs and creosote from soil using SFE.

(2) Extraction of total petroleum hydrocarbon (TPH) and PCBs from soil using SFE.

In this study, these methods were evaluated in an interlaboratory comparison study between 11 labo-

raries, where each participating laboratory extracted two soil samples with both SFE methods.

2. Experimental

2.1. Preparation of materials for the laboratory intercomparison

The two samples used for the laboratory intercomparison study originate from the same polluted soil collected by a company handling contaminated soil. The soil was known to contain PAHs and TPH. Before use, the soil was dried moderately, ground using an ATOX 3.5 mill (from F.L. Smidth, Denmark), so that more than 99% of the sample had a particle size less than $<90 \mu\text{m}$, and homogenised in the same procedure. The sample was treated with gamma-radiation to reduce the number of viable microorganisms that might degrade the contaminants. This together with the low content of water, less than 5%, ensured that the sample was stable [25].

Two subsamples of 15.0 kg were taken and mixed, respectively, with 2.2 and 22 g of CRM 481 [Community Bureau of Reference (BCR) Brussels, Belgium] which is heavily contaminated with PCBs [24]. As a consequence, two samples A (low level) and B (high level) were obtained with different concentrations of PCBs, but identical for PAHs, creosote and TPH.

For comparison, solvent extraction values of the samples were determined by DHI using the Nordic Guideline methods for PCBs and TPH [26]. For PAHs the values were known from another project that tested the extraction efficiency for PAHs and where several extraction techniques were used [25]. PCBs were assumed not to be present at relevant levels in the soil samples, before mixing with the certified material (CRM 481).

The internal standard solution contained 5.13 mg/ml eicocene (C20:1), 0.114 mg/ml *b,b'*-binaphthyl, 0.103 mg/ml 3,6-dimethylphenanthrene, 1.03 $\mu\text{g/ml}$ PCB 169 and 5.33 $\mu\text{g/ml}$ PCB 35. A glass vial with this solution was supplied to each laboratory with the samples. Additionally, electrolytic grade copper powder (99.5%, ca. 0.04 mm, extra pure from Riedel-de Häen, Seelze, Germany) and glass fiber

filters (GF/B diameter 15.0 cm, from Whatman, Kent, UK) were provided with the samples.

2.2. Intercomparison setup

For each method there were two different samples to be extracted in six replicates plus one blank. This gave a total of 28 extractions per laboratory. The extraction procedure is written below and also the extraction sequence was given to the laboratories.

2.2.1. Extraction procedure

(1) Ensure that the extraction cells are cleaned thoroughly to avoid contamination.

(2) For each of the extractions mix the 5.0 g of the sample with 2 g of electrolytic grade copper powder and 5–10 g of anhydrous Na₂SO₄ or an equivalent amount of SFE-support, e.g., Hydromatrix in order to fill the extraction cell.

(3) Cut out a piece of glass fiber filter that closely fits the extraction cell and place one at the bottom of the extraction cell. Fill the extraction cell with the sample prepared in (2). Add a glass fiber filter to the

top of the sample. Add modifier, if specified in the method.

(4) Extract the sample by use of the specified method (Table 1). Follow the extraction sequence by extracting the low level sample A first with methods 2 and 1, after which the same should be done for the high level sample B. Extract a blank as the last sample for each method.

(5) Transfer the extracts to the supplied glass vials, whereby rinsing the collection vial with a small amount of solvent. Combine the fractions if using solid-phase trapping with the HP instrument. Mark the sample with sample type, extraction number and method. Add 200 µl of internal standard using, e.g., a micropipette or syringe.

2.3. Supercritical fluid extraction conditions

Conditions for the SFE methods employed in the laboratory intercomparison study were obtained after testing various selected methods generally used in the field. ISCO SFX 3560 instruments were used for the creosote and PAH method development and

Table 1
SFE methods 1 and 2 for the interlaboratory comparison study

SFE parameter	Method 1 for TPH and PCBs		Method 2 for creosote and PAHs	
	Solid phase trapping	Liquid phase trapping	Solid phase trapping	Liquid phase trapping
Extraction pressure	355 bar	355 bar	350 bar	350 bar
Extraction temperature	100 °C	100 °C	150 °C	150 °C
Density	0.72 g/ml	0.72 g/ml	0.55 g/ml	0.55 g/ml
Modifier	–	–	1 ml acetone	1 ml acetone
Static extraction time	5 min	5 min	5 min	5 min
Dynamic extraction time	30 min	30 min	30 min	30 min
Flow rate	1 ml/min	1 ml/min	1.5 ml/min	1.5 ml/min
Temperature restrictor (nozzle)	45 °C	80 °C	60 °C	80 °C
Temperature trap	40 °C	–	56 °C	–
Adsorbent	Florisil	–	ODS (C ₁₈)	–
Solvent for elution	1.4 ml heptane, 3×14 ml acetone ^a	–	Acetone, 4×1.4 ml ^a	–
Solvent for collection	–	10 ml acetone	–	10 ml acetone
Temperature, collection	–	10 °C	–	10 °C
Pressure, collection ^b	–	30 p.s.i.	–	30 p.s.i.
Post-extraction solvent rinse ^c	–	1 ml acetone	–	1 ml acetone
Sample size	5 g	5 g	5 g	5 g

1 p.s.i.=6894.76 Pa.

^a Valid only for the HP 7680 instrument, all others use a total of 6 ml elution solvent.

^b Valid only for the SFE instrument from ISCO with pressurized collection.

^c On the new ISCO SFX 3560, that uses a needle valve type restrictor, the tube after the restrictor must be rinsed.

ISCO 3560 and HP 7680T were used for the TPH and PCB method development. Various soil, sediment and clay materials with known amounts of studied compounds were used in the method development. Samples used were either certified reference materials or intensively analysed with different techniques and by various laboratories. Generally, two to three different concentration levels were used in the test samples [27].

Results obtained with SFE were compared with those gained by conventional solvent extraction techniques [25,26]. After the testing phase, four methods remained and they were compressed to two [27]. This was possible, because the methods for creosote and PAHs as well as for TPH and PCBs were similar and with small compromises, two methods resulted (Table 1).

2.3.1. Preparing the extracts for the analysis

The volume of each extract was adjusted to 10 ml with acetone and split into two fractions for the analysis. Sample fractions were analysed by four laboratories each analysing one specific compound type: University of Helsinki (PAHs), DHI (PCBs), ITM (creosote) and SINTEF (TPH).

2.4. Analysis of PAHs

Each extract from the interlaboratory comparison was analysed with gas chromatography–mass spectrometry (GC–MS) using selected ion monitoring (SIM). HP Model 5890 GC and HP 5989 A MS instruments were employed. All samples (1 μ l) were injected on-column using a HP Model 7673 autosampler. A deactivated retention gap (2.5 m \times 0.53 mm I.D.) was used in front of the 40 m long HP-5 column of 0.25 mm I.D. and 0.25 μ m film thickness. The GC oven was programmed from 40 °C (2 min) to 150 °C at 8 °C/min and from 150 °C (5 min) to 300 °C (10 min) at 3 °C/min. The GC–MS interface, ion source and quadrupole analyser temperatures were 300, 250 and 120 °C, respectively. A PAH standard solution containing 17 components (Z-014G-R; AccuStandard, New Haven, CT, USA) was used for calibration. Molecular ions of the PAHs and six level calibration (0.1–6 μ g/g) were used for quantitation.

2.5. Analysis of creosote

The volume (5 ml) of each extract from the interlaboratory comparison was reduced with nitrogen to 1 ml. The extracts were analysed with a Varian STAR 3400 GC system, with a flame ionization detection (FID) system. All samples were injected splitless (1 μ l) with an autosampler into a 30 m long DB-5 column of 0.25 mm I.D. and 0.25 μ m film thickness. Injector and detector temperatures were 275 and 300 °C, respectively. The GC oven was programmed from 70 °C (1 min) to 300 °C (5 min) at 5 °C/min. The creosote standard solution used for calibration and quantification was SRM 2260 (23 compounds) from NIST (National Institute of Standards and Technology). This mixture contained only PAHs, some methylated PAHs and biphenyl. More polar creosote specific compounds, like *o*-cresol, *p*-cresol, dibenzofuran, dibenzothiophene and carbazole that were determined in the method development phase, were not detected in the samples from the interlaboratory comparison.

2.6. Analysis of PCBs

The analysis was performed by dual column GC–electron-capture detection (ECD) as described elsewhere [24,30].

2.7. Analysis of total petroleum hydrocarbon

The volume of each TPH extract from the interlaboratory comparison was reduced with nitrogen to 1 ml. The extracts were analysed with a HP Model 5880 GC system with an FID system. All samples were injected splitless (1 μ l) with an autosampler, HP 7673A, into a 12.5 m \times 0.20 mm I.D. (0.33 μ m film thickness) fused-silica column, crosslinked with dimethylsilicon (HP-ultra 1, Agilent Technologies). Injector and detector temperatures were 280 and 350 °C, respectively. The GC oven was programmed from 50 °C (3 min) to 350 °C (10 min) at 20 °C/min. Quantification was carried out using the added eicosene as internal standard.

2.8. Statistical data evaluation

The data processing and subsequent outlier-test

was performed in accordance with ISO 5725 part 2 [28]. The proficiency test was conducted using a uniform-level design. Results, which the laboratories (upon inspection of the preliminary report) identified as having technical problems, were excluded manually from the data set. Cochran's test was applied to identify duplicates with an unusually high standard deviation, followed by Grubbs' test to identify duplicates with a deviating average compared to the data set from all laboratories. Outliers according to these tests were excluded from statistical data treatment, whereas stragglers were retained.

2.8.1. General quality of analyses

The general quality of analyses was calculated from an analysis of variance of each sample pair data. From this analysis the variance between laboratories (S_L^2), between samples and residual variance were calculated. Repeatability variance, S_r^2 , and reproducibility variance, S_R^2 , were calculated from $S_R^2 = S_L^2 + S_r^2$.

Relative standard deviation within the laboratories, RSD(r), and the total relative standard deviation, RSD(R), were calculated as follows: $RSD(r) = (S_r \cdot 100) / \mu$ and $RSD(R) = (S_R \cdot 100) / \mu$, where μ is an assigned value (weighted average). In addition to average and median values, figures such as S_r , S_R , S_L , RSD(r) and RSD(R) are given in Tables 2 and 3.

2.8.2. Method evaluation

An analysis of variance (ANOVA) was conducted within every level regarding the effects of methods

as well as laboratories. Method evaluation included a two-way nested random effects model implementation, including tests of between-laboratory variability within every method. A parallel analysis based on ranks was implemented to account for lacks of homogeneous variances, along the lines given in Conover and Iman [29]. A test for homogeneity of variance was conducted using Lehmann's test.

3. Results and discussion

3.1. Laboratory intercomparison

Tables 2 and 3 shows the results obtained in the laboratory intercomparison study. Average and median values together with general relative standard deviation within the laboratories, RSD(r), and the total relative standard deviation, RSD(R), are given for selected PAHs, PCBs and for TPH.

3.1.1. Polycyclic aromatic hydrocarbons and creosote

The results obtained for selected PAHs (sample A) in the interlaboratory comparison study are given in Table 2. For a group of the PAHs with a content of 0.5 mg/kg or higher the relative standard deviations RSD(r) and RSD(R) are in the range of 15% or even lower. This group contains phenanthrene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene and benzo[*k*]fluoranthene. Some of the heavier PAHs, benzo[*a*]pyrene, indeno[1,2,3-*cd*]-

Table 2
Results of selected PAHs for sample A and general analytical quality (number of laboratories is 7–8) [30]

Compound	Obtained results						
	Average	Median	S_r	S_R	S_L	RSD(r)	RSD(R)
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(%)	(%)
Acenaphthylene	0.08	0.09	0.01	0.02	0.02	14	26
Fluorene	0.10	0.11	0.01	0.02	0.02	12	21
Phenanthrene	1.28	1.38	0.19	0.20	0.07	15	16
Anthracene	0.18	0.20	0.03	0.04	0.02	18	20
Fluoranthene	1.68	1.74	0.12	0.13	0.06	7	8
Pyrene	1.26	1.29	0.08	0.13	0.10	6	10
Benzo[<i>a</i>]anthracene	0.60	0.65	0.09	0.09	0.03	14	15
Chrysene	0.69	0.74	0.11	0.12	0.02	17	17
Benzo[<i>a</i>]pyrene	0.56	0.61	0.10	0.12	0.07	17	22
Dibenzo[<i>a,h</i>]anthracene	0.20	0.21	0.05	0.06	0.03	27	30
Benzo[<i>g,h,i</i>]perylene	0.61	0.61	0.14	0.15	0.04	24	24

Table 3
Results of selected PCBs and TPH, and general analytical quality (number of laboratories is 6–9) [30]

Compound	Sample	Obtained results					
		Average ($\mu\text{g}/\text{kg}$)	S_r ($\mu\text{g}/\text{kg}$)	S_R ($\mu\text{g}/\text{kg}$)	S_L ($\mu\text{g}/\text{kg}$)	RSD(r) (%)	RSD(R) (%)
PCB 28	A	1.3	0.1	0.4	0.4	11	29
	B	1.5	0.2	0.3	0.2	14	21
PCB 52	A	0.8	0.08	0.09	0.04	9.7	11
	B	3.5	0.1	0.3	0.2	3.9	7.3
PCB 101	A	4.6	0.3	0.4	0.2	7.2	8.9
	B	30.3	1.0	3.2	3.1	3.3	11
PCB 118	A	2.6	0.2	0.3	0.2	7.9	11
	B	13.5	0.7	1.2	1.0	5.1	9.0
PCB 138	A	14.1	1.0	1.3	0.9	6.7	9.3
	B	85.8	2.9	9.9	9.5	3.4	12
PCB 153	A	21.7	1.6	2.2	1.5	7.2	9.9
	B	126	4.3	17.2	16.6	3.4	14
PCB 180	A	23.2	1.4	2.1	1.6	6.1	9.1
	B	141	5.4	17.0	16.1	3.8	12
TPH	A	336 ^a	16 ^a	21 ^a	13 ^a	4.8	6.1

^a Values given in mg/kg.

pyrene and benzo[*g,h,i*]perylene, showed a somewhat higher relative standard deviation, around 20%.

Normally, the relative standard deviation within the individual laboratories is less than between the laboratories. This is also the case with the results obtained for PAHs (Table 2). For the phenanthrene, fluoranthene, pyrene, Benzo[*a*]anthracene and chrysene there are actually two sets of results, as these compounds are included in the determination of both PAH and creosote (data not shown). The general results expressed as average value after exclusion of outliers showed that the results were in agreement. When individual extracts were compared it was clear that in some cases there was a high random error. On the other hand, the results also indicated that the deviation was related to the extracts and not to the determination.

In addition, excellent agreement was achieved for the PAHs between A (Table 2) and B (data not shown) samples, in which the concentrations were the same (see Experimental). This indicates very good extraction performance between and within the laboratories as well as good analytical determinations. Unfortunately, the content of the

heteroaromatic compounds, like carbazole, dibenzothiophen, dibenzofuran and biphenyl, specific for creosote, were not present in the samples at relevant levels. Therefore, conclusions on the SFE method suitability for these compounds cannot be made.

3.1.2. Polychlorinated biphenyls and total petroleum hydrocarbon

The results obtained in the interlaboratory comparison for selected PCBs and for TPH are given in Table 3. These results for the PCBs are as expected, when SFE with GC–ECD determination is used, as normally, SFE analyses for PCB in soil samples yield excellent recoveries. For PCBs, the relative standard deviations within the laboratories [RSD(r)] are clearly higher for the low level sample A than for the values obtained at higher concentration level. On a contrary, the total relative standard deviations [RSD(R)] are for many congeners higher with high level samples. Generally, the quality of analytical determination for PCBs was very good and most of the interferences caused by coeluting compounds has been resolved by using a dual column GC system [except for PCBs 31, 105 and 156, where higher than

50% RSD(R) values were obtained with low level sample].

For the TPH determination, the B sample showed relatively high variation on the results between the laboratories [RSD(R)=18%] and within the laboratories [RSD(r)=12%] compared to the A sample (Table 3). This is likely caused by the high number of statistical outliers for the B sample (only for TPH) and thereby lower number of analytical results included in the final dataset. However, since the sample matrix was about the same, the basic reason for the high number of statistical outliers with the B sample remained unclear.

3.2. Comparison of SFE with solvent extraction

In Tables 4 and 5, the results from the SFE laboratory comparison study for PAHs, PCBs and TPH are compared with the values obtained with solvent extraction. SFE weighted averages for instruments using different trapping techniques (liquid trap or solid-phase trap) are also listed.

3.2.1. Polycyclic aromatic hydrocarbons and creosote

For the major part of the PAH components the SFE results are very close to the values from solvent

extraction (Table 4). This has never been seen before for SFE methods. Normally, the heavier PAH components show poor extraction efficiency compared to the traditional methods. Some components, such as acenaphthylene and dibenzo(a,h)anthracene, show a deviating recovery percent. These components are in the sample at low concentrations and an evaluation of the differences shows that the differences in mg/kg are rather small. For phenanthrene the difference is surprisingly high. The results from the SFE method are in accordance with the values achieved with solvent extraction, when the uncertainties of both results are included.

When creosote measurement results for PAHs (not shown) are compared with the solvent extraction values, there is again agreement between the two sets of data when the uncertainty is included. For creosote with this SFE method (and also due to the lower analytical sensitivity) only high-level components were determined. In general, the recoveries were higher than 100% with the SFE method and the large difference for phenanthrene noticed, was less for this set of results. This difference can be explained by the different analytical performance at the two analysing laboratories.

When comparing the performance of the two different SFE trapping technique, the results are

Table 4
Comparison of SFE (average of A and B sample) with solvent extraction for PAHs [30]

Compound	Solvent extraction, average (mg/kg) (n=6)	SFE			Comparison, recovery (%)
		Average liquid trap (mg/kg) (n=60)	Average solid-phase trap (mg/kg) (n=36)	Assigned value (μ) for SFE* (mg/kg)	
Naphthalene	0.12±0.04	0.16±0.06	0.03±0.02	0.11	92
Acenaphthylene	0.14±0.03	0.09±0.02	0.08±0.02	0.08	57
Fluorene	0.09±0.01	0.11±0.02	0.09±0.02	0.10	111
Phenanthrene	0.89±0.09	1.39±0.23	1.20±0.15	1.24	139
Anthracene	0.18±0.01	0.19±0.04	0.18±0.03	0.18	100
Fluoranthene	1.56±0.04	1.70±0.14	1.59±0.12	1.63	104
Pyrene	1.21±0.10	1.28±0.12	1.20±0.11	1.23	102
Benzo[a]anthracene	0.57±0.01	0.66±0.09	0.58±0.09	0.59	104
Chrysene	0.65±0.04	0.75±0.12	0.65±0.09	0.67	103
Benzo[b+k]fluoranthene	1.42±0.11	1.57±0.14	1.33±0.13	1.46	103
Benzo[a]pyrene	0.58±0.05	0.63±0.11	0.49±0.13	0.56	97
Indeno[1,2,3-cd]pyrene	0.62±0.06	0.74±0.18	0.56±0.17	0.65	105
Dibenzo[a,h]anthracene	0.12±0.01	0.21±0.06	0.16±0.04	0.18	150
Benzo[g,h,i]perylene	0.56±0.05	0.63±0.14	0.47±0.15	0.56	100

*Weighted average.

Table 5
Comparison of SFE with solvent extraction for PCBs and TPH (sample A) [30]

Low level (sample A) compound	Solvent extraction		SFE			Comparison	
	Nordic guideline ($\mu\text{g}/\text{kg}$) ($n=6$)	Soxhlet ($\mu\text{g}/\text{kg}$) ($n=6$)	Average liquid trap ($\mu\text{g}/\text{kg}$) ($n=35-36$)	Average solid-phase trap ($\mu\text{g}/\text{kg}$) ($n=17$)	Assigned value (μ) for SFE* ($\mu\text{g}/\text{kg}$)	SFE contra NG (%)	SFE contra Soxhlet (%)
PCB 28	0.7 \pm 0.0	1.1 \pm 0.1	1.1 \pm 0.5	1.5 \pm 0.4	1.3	186	118
PCB 52	0.7 \pm 0.1	0.7 \pm 0.1	0.8 \pm 0.1	0.8 \pm 0.1	0.8	114	114
PCB 101	6.8 \pm 0.4	5.1 \pm 0.5	4.6 \pm 0.4	4.6 \pm 0.4	4.6	68	90
PCB 118	1.8 \pm 0.1	1.6 \pm 0.1	2.6 \pm 0.3	2.5 \pm 0.2	2.6	144	163
PCB 128	1.7 \pm 0.1	1.4 \pm 0.1	3.6 \pm 2.0	2.3 \pm 0.5	2.4	141	171
PCB 138	17.4 \pm 0.9	14.8 \pm 1.0	14.2 \pm 1.3	14.1 \pm 1.3	14.1	81	95
PCB 153	25.3 \pm 1.5	21.3 \pm 1.5	22.0 \pm 2.2	21.6 \pm 1.9	21.7	86	102
PCB 156	1.4 \pm 0.1	1.3 \pm 0.1	3.4 \pm 1.4	3.8 \pm 1.5	2.8	200	215
PCB 170	9.1 \pm 0.7	7.6 \pm 0.4	8.9 \pm 2.1	7.4 \pm 0.4	8.0	88	105
PCB 180	22.2 \pm 1.4	20.2 \pm 1.0	24.2 \pm 2.5	23.2 \pm 2.0	23.2	105	115
TPH ^a	245 \pm 4		337 \pm 19	335 \pm 38	336	137	

*Weighted average.

^a Values given in mg/kg.

logical. The most volatile compound naphthalene is partly lost with solid-phase trapping. For the other compounds, the recovery is slightly lower with the solid-phase trap than with the liquid trap. This is likely due to the higher cleanliness of the solid-phase trapping extracts [2,21] and thereby less interfering compounds. Alternatively, this could be due to a small loss of analytes in the trapping or elution process of the solid-phase collection. Use of modifier in the extraction can affect the trapping efficiency as well. In general, both type of SFE instruments were working very well.

3.2.2. Polychlorinated biphenyls and total petroleum hydrocarbon

With certain PCB congeners there were large deviations from the values determined with solvent extraction (Table 5). This lack of agreement with the values for some of the congeners can be explained with the low concentration in the samples. At a higher concentration level there is a fine agreement with the values obtained with traditional solvent extractions. This can easily be seen from the average recovery values vs. Nordic guideline and Soxhlet. SFE average recoveries were for sample B (high

level) 99 \pm 23% and 97 \pm 20%, and for sample A (low level) 126 \pm 46 and 135 \pm 43, respectively.

For PCBs the two trapping methods in SFE were working equally well. Due to the lower volatility of the lightest PCBs, compared to naphthalene, solid-phase trap was working very well for all the analytes. It seems that there is a similar trend for PCBs as for PAHs, that the solid-phase trap gives slightly lower values (with some exceptions). Generally, good results were achieved for PCBs with SFE compared to Nordic Guideline method or Soxhlet method, which gave slightly lower values than the NG method.

For the TPH the recovery with SFE was higher than that obtained by using the existing Nordic Guideline method. There is no obvious explanation for the high recovery with the SFE analysis of TPH other than, that the extraction efficiency with the Nordic guideline method on this sample was insufficient.

4. Conclusions

The results from this interlaboratory comparison showed that it is possible to use SFE methods for the

extraction of organic contaminants from soil samples. It is also possible to obtain reliable results where the trueness, expressed as recovery relative to solvent extraction, is excellent for PAHs and PCBs and acceptable for TPH. The accuracy expressed as the relative standard deviation was higher than expected, especially for PAHs, but not different from other inter-comparisons for organic contaminants in solid samples.

For PAHs (and creosote), the difference between the two SFE trapping methods was assumed to be significant only for volatile components such as naphthalene and for fluorene. This was actually the case, since in both samples (A and B) the statistics showed “not homogeneous” results (see Section 2.8.2) for naphthalene and fluorene. For the rest of the components, there are no significant differences in any of the samples.

For PCBs, there were more test results showing a variance, that cannot be assumed to be homogeneous. In general, the solid-phase trapping gave the lowest standard deviations. In the same extracts, the content of TPH were measured and there the results were the opposite, the liquid trapping gave the lowest standard deviations.

It is not clear whether the increased standard deviation is related to the extraction procedure or to the following determination. Most likely, it is a combination of both effects. In principle, low standard deviations should be possible to obtain when the extractions are made following a standard procedure with standardised instruments and all the extracts are analysed at the same laboratory. In practice, it turned out impossible to fully achieve this objective. A reduction of the random error, however, is work that has to be given further effort.

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