Studies on trapping efficiencies of various collection devices for off-line supercritical fluid extraction

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Abstract

Analyte collection in supercritical fluid extraction can be difficult, especially for relatively volatile substances. Losses of polycyclic aromatic hydrocarbons (PAHs) of up to 30% are observed with different liquid collection devices. A solid–liquid trap can minimize these trapping problems. Silica gel and two different octadecylsilanes were tested as solid sorbents. Good recoveries were found with pure carbon dioxide as the extraction fluid. Higher flow-rates did not increase analyte losses. The analytes were trapped on the solid surface. The use of modified carbon dioxide was also no problem. The analytes were eluted from the solid matrix after extraction by the modifier in the liquid phase. In the extraction of PAHs from real samples, further clean-up may be unnecessary when silica gel is used as a solid trapping material.

1. Introduction

Supercritical fluid extraction (SFE) is a modern alternative to Soxhlet extraction. The advantages of this extraction method are the shorter extraction times and smaller amounts of organic solvents required. The acceptance of SFE by the regulatory authorities has already started, as was demonstrated when the US Environmental Protection Agency (EPA) approved the first SFE method as a replacement for the conventional Soxhlet extraction of total petroleum hydrocarbons [1].

Generally there are two important steps in supercritical fluid extraction. First, the extraction parameters have to be correctly chosen to overcome solute–matrix interactions and to transport the analytes properly out of the extraction cell. The second step is the trapping of the analytes

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after the extraction process. Inefficient trapping leads to inaccurate results with low reproducibility. Hence the first step in developing any SFE method should be the testing of quantitatively efficient collection methods and, if necessary, the development of a new collection device [2].

In the case of "off-line" supercritical fluid extraction several trapping techniques are possible, e.g., solvent traps [3–5], solid-phase traps [6,7] and cryogenically cooled traps [8]. Collection will occur after depressurizing the compressed fluid. The resulting flow-rates of the expanded gas may reach 1000 ml/min and more. In this case, it is obvious that the trapping of the analytes, especially of volatile substances, can be difficult.

For collection using a liquid trap, the efficiency depends on the solubility of the analyte in the collection solvent, the flow-rates and the temperature of the solvent. Langenfeld et al. [3] investigated the collection efficiencies of differ-

ent solvents for semi-volatile pollutants [e.g., polycyclic aromatic hydrocarbons (PAHs)]. They used 2–10 ml of liquid solvent and a flow-rate of 500 ml/min. They found a dependence of the extraction results on the volatility of the analytes: the more volatile the substances, the poorer were the recoveries. Different solvents gave different collection efficiencies. Methylene chloride was the solvent with the best trapping efficiency. Acetone gave recoveries similar to those with methylene chloride. Methanol and n-hexane gave the highest losses. Cooling methylene chloride to 5°C increased the collection efficiency for the investigated PAHs.

In another study, the influence of flow-rate on solvent collection was investigated [9]. Higher flow-rates are problematic for solvent collection. Losses during the extraction process are possible. Even the restrictor temperature has an influence on the trapping efficiencies.

Solid-phase traps are an alternative for analyte trapping. Several traps have been investigated, e.g., μBondapack C_{18} for PCBs [10] and or phenyl-, octyl-, diol-, cyano- and amino-bonded silica for a polar test mixture containing acetophenone, N,N-dimethylaniline, n-decanoic acid, 2-naphthol and tetracosane [6]. After the extraction the analytes have to be eluted from the sorbent with an organic solvent. For solid traps, flow-rates of up to ca. 2000 ml/min of expanded fluid are usual [6]. The use of modified carbon dioxide, which generally in SFE is necessary to increase the extraction results, is difficult for solid traps. The organic solvents used as modifiers may elute the collected analytes from the solid sorbents during the extraction. Mulcahey and Taylor [7] investigated the effect of methanol as modifier on stainless steel and on octadecylsilane traps for the polar test mixture mentioned above. Here the trap temperature and the amount of modifier are very important for minimizing analyte losses.

The aim of this investigation was to determine the collection efficiencies for PAHs of a combined solid–liquid trap. Our first results with the solid–liquid trap have been published elsewhere [11,12]. The extraction results with different solvent traps and the solid–liquid trap were compared. Silica gel and octadecylsilane solid phases (ODS) were used. The extractions were performed with pure carbon dioxide and modified CO_2. The influence of the flow-rate of the expanded fluid on the recoveries was also investigated.

2. Experimental

2.1. Chemicals

Acetonitrile (HPLC grade) was obtained from Baker (Gross Gerau, Germany). Acetone, n-hexane, methylene chloride and toluene, which were of purity for residual analysis, were obtained from Merck (Darmstadt, Germany). Carbon dioxide (purity 4.5) was purchased from Westfalen AG (Münster, Germany).

Silica gel (40 μm) (Baker) was heated at 105°C for 1 h and cooled to room temperature before adding 10% (w/w) of water. After shaking for 1 h, the matrix was ready to use. ODS-modified silica (Chromabond) was obtained from Macherey–Nagel (Düren, Germany).

2.2. Supercritical fluid extraction

All extractions were carried out using a Dionex SFE-system (SFE-703). For extraction with modified carbon dioxide the system was equipped with a Dionex SFE-703M module. The extraction cells (3.5 ml, 5 cm × 9.4 mm I.D.) (Keystone Scientific) were filled with silanized glass-fibre wadding (Macherey–Nagel) and 1 g of ODS. A solution of sixteen EPA PAHs in benzene–methylene chloride (2000 μg/ml)(Sigma and Aldrich) was diluted in toluene (2 μg/ml). A 100-μl volume of this solution (total 3.2 μg of PAHs) was spiked on ODS. The extractions were performed in a dynamic mode at 40 MPa, oven temperature 90°C and restrictor temperature 150°C for 30 min with pure CO_2 or with CO_2 modified with 5% toluene. These parameters were selected because the same conditions were used for real sample extractions [11]. All extractions were performed in triplicate.

Two different linear restrictors (A and B) from Dionex (restrictor wafer, 250 and 1200 ml/min) were used. Restrictor A gave a flow-rate of ca. 300 ml/min and restrictor B ca. 1200 ml/min under the selected extraction conditions.

For analyte collection a dual-chamber trapping vial (Fig. 1a) [4] with 10 or 15 ml of different organic solvents was used. In case of the solid–liquid trap, the transfer tube was modified (Fig. 1b). The tube was filled with 0.3 g of silica gel or ODS material. A new transfer tube from Dionex with a disc of C_{18} material (octadecyl-modified glass-fiber matrix), fixed at the bottom end of the tube, was also tested. In the solid–liquid trap 10 ml of *n*-hexane were used as organic solvent. The collection vial with the trapping device was cooled to ca. 5°C.

After extraction with the modified dual-chamber trapping vial, the collected analytes were eluted from the solid traps. For silica gel 4 ml of toluene–light petroleum (1:2, v/v) and for ODS material 4 ml of methylene chloride were used. The Dionex solid trap was eluted with 3 ml of *n*-hexane.

To minimize evaporation losses, 50 μl of diethyl phthalate were added to each extract prior to evaporation of the solvent under a gentle stream of nitrogen. A 950-μl volume of acetonitrile was added and the extracts were analysed by HPLC.

2.3. HPLC analysis

For HPLC analysis an HP Series 1050 liquid chromatograph (Hewlett-Packard) equipped with an autosampler, quaternary pump, degasser, HP 1046A programmable fluorescence detector and HP ChemStation for data acquisition and data analysis was used. The PAHs were separated on a Bakerbond PAH 16-Plus column (250 × 3 mm I.D.) with a 20 mm precolumn at a column temperature of 30°C. Acetonitrile and water were used as the mobile phase at a flow-rate of 0.5 ml/min. The composition gradient of the mobile phase started with 50% acetonitrile and 50% water for 6 min, then the acetonitrile content was increased to 99% in 29 min with a linear gradient. This content was held constant for 10 min until the end of the analysis. For equilibration, the initial conditions were maintained for 15 min. For detection, the following excitation (Ex) and emission (Em) wavelength programme was used; naphthalene and acenaphthene (Ex 210 nm, Em 320 nm), phenanthrene and anthracene (Ex 248 nm, Em 384 nm), fluorene and pyrene (Ex 236 nm, Em 430 nm),
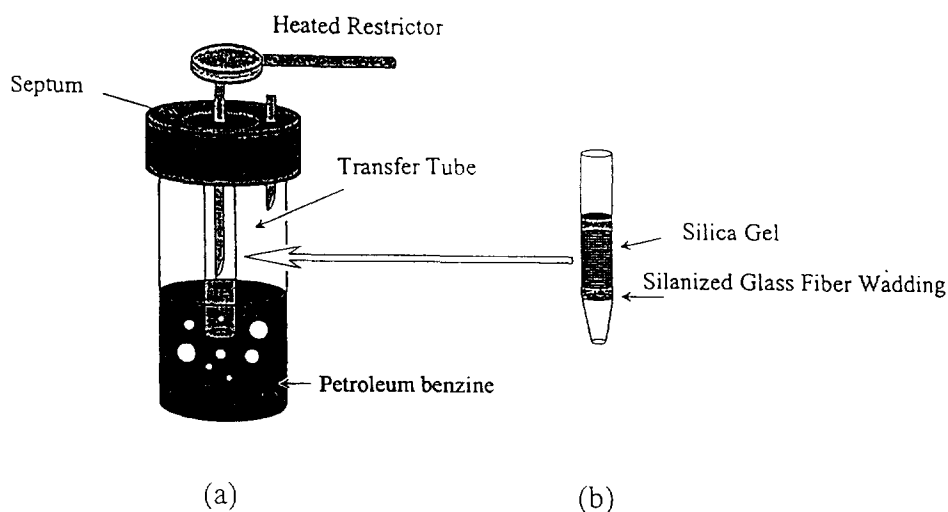

Fig. 1. (a) Dual-chamber trapping vial; (b) modified transfer tube.

benz[a]anthracene and chrysene (Ex 270 nm, Em 390 nm), benzo[b]fluoranthene, benzo[k]-fluoranthene and benzo[a]pyrene (Ex 250 nm, Em 440 nm), dibenz[a,h]anthracene and ben-zo[ghi]perylene (Ex 296 nm, Em 405 nm) and indeno[123-cd]pyrene (Ex 245 nm, Em 480 nm). For identification the retention times were compared and for quantification an external calibration with SRM 1647c solution in acetonitrile (Promochem, Wesel, Germany) was performed.

3. Results and discussion

The extraction yields in SFE depend on the solubility of the analytes in the supercritical fluid, the flow-rate, the extraction time, the interaction between analytes and the matrix and the trapping efficiency of the collection device. The aim of this investigation was to test several collection devices. Therefore, the PAH solution was spiked on ODS material. It is known that the interaction between PAHs and ODS material is low so that the selected extraction parameters, 90°C and 40 MPa, are sufficient to remove the analytes from the matrix and to sweep them out of the extraction cell.

3.1. Solvent collection

Influence of solvents

The trapping efficiencies of solvent collection in SFE depend on several parameters, such as the geometry of the trapping device, the solubility of the analytes in the solvent, the restrictor temperature, the solvent temperature and the flow-rate of the expanded fluid.

First the collection efficiencies of different organic solvents for PAHs were compared. The results with the dual-chamber trapping vial, restrictor A (flow-rate 300 ml/min) and different organic solvents (n-hexane, methylene chloride, acetone) are given in Table 1. The best results were found with acetone as collection solvent. Excluding the anomalous anthracene and ben-zo[a]pyrene, the recoveries of the low- to high-molecular-mass PAHs varied from 95% to 83% with standard deviations of 3.5 and 1.0%. The recoveries for methylene chloride were slightly lower (Table 1). The results for anthracene and benzo[a]pyrene with methylene chloride and acetone indicate that there may be a systematic error. n-Hexane gave recoveries of ca. 90% for the analytes with high volatility and ca. 70% for analytes with low volatility (Table 1). It was

Table 1
Recoveries (with standard deviations; $n = 3$) for PAHs of different liquid traps and of the purge studies with collection solvent n-hexane and flow-rates of gaseous CO_2 of 300 and 1200 ml/min

No.	Compound	n-Hexane		Methylene chloride 300 ml/min	Acetone 300 ml/min	Purge studies	
		300 ml/min	1200 ml/min			300 ml/min	1200 ml/min
1	Naphthalene	78.0 ± 3.3	72.2 ± 6.8	78.1 ± 7.2	83.1 ± 3.4	92.0 ± 5.4	96.0 ± 4.2
2	Acenaphthene	88.4 ± 6.6	76.1 ± 7.8	80.0 ± 3.4	89.4 ± 2.2	95.4 ± 1.8	96.4 ± 0.6
3	Fluorene	89.5 ± 7.5	76.0 ± 8.1	78.1 ± 1.5	90.0 ± 1.6	97.4 ± 1.2	97.7 ± 0.5
4	Phenanthrene	92.4 ± 8.8	84.9 ± 9.1	82.9 ± 1.0	95.3 ± 1.0	100.7 ± 0.2	111.1 ± 1.5
5	Anthracene	85.9 ± 2.7	70.0 ± 8.0	69.1 ± 2.4	80.0 ± 3.6	104.2 ± 1.9	102.6 ± 0.9
6	Fluoranthene	86.7 ± 11.2	81.5 ± 10.1	83.1 ± 4.2	90.6 ± 1.7	97.3 ± 0.5	112.0 ± 1.8
7	Pyrene	88.6 ± 11.6	78.7 ± 10.1	85.2 ± 4.1	91.5 ± 1.7	99.8 ± 0.3	107.8 ± 1.2
8	Benz[a]anthracene	78.0 ± 14.8	68.4 ± 8.9	77.2 ± 5.4	82.2 ± 0.7	100.4 ± 0.4	100.0 ± 0.3
9	Chrysene	78.9 ± 17.3	66.6 ± 8.1	80.3 ± 5.9	84.7 ± 1.1	98.8 ± 0.3	99.3 ± 0.3
10	Benzo[b]fluoranthene	73.2 ± 18.3	68.2 ± 10.5	78.1 ± 3.1	83.2 ± 1.3	97.9 ± 0.6	100.4 ± 0.5
11	Benzo[k]fluoranthene	75.1 ± 18.4	67.6 ± 7.7	78.9 ± 3.9	83.3 ± 0.9	97.8 ± 0.5	99.7 ± 0.5
12	Benzo[a]pyrene	70.7 ± 7.9	58.9 ± 9.1	66.7 ± 5.6	74.0 ± 3.4	106.3 ± 3.1	105.5 ± 1.6
13	Dibenz[a,h]anthracene	72.0 ± 19.4	70.3 ± 8.4	78.6 ± 3.5	83.9 ± 1.1	98.4 ± 0.4	100.0 ± 0.5
14	Benzo[ghi]perylene	70.5 ± 18.4	72.4 ± 11.7	79.4 ± 2.8	84.8 ± 2.0	98.3 ± 0.8	100.2 ± 0.6
15	Indeno[1,2,3-cd]pyrene	69.1 ± 18.7	75.7 ± 9.4	77.7 ± 2.7	83.1 ± 1.8	97.9 ± 1.2	99.7 ± 0.6

expected that the collection efficiencies of analytes with lower volatility would be better because of their higher molecular mass. This agrees with the results of Langenfeld et al. [3]. In contrast, with methylene chloride and acetone we observed a slight decrease in collection efficiencies from the less to the more volatile analytes. We have no reasonable explanation for this effect.

Langenfeld et al. [3] achieved quantitative recoveries with methylene chloride by keeping the solvent vial at 5°C (flow-rate ca. 500 ml/min).

Thompson et al. [5] reported recoveries for naphthalene of >90% with acetone and n-hexane and 83% with methylene chloride. They used the same dual-chamber trapping vial as we did but with different extraction parameters.

These three examples show the difficulties in trapping analytes in SFE with liquid solvents. It can be concluded that the collection parameters have to be optimized for each extraction problem.

Influence of flow-rates

The influence of higher flow-rates was investigated with restrictor B, which gives flow-rates of about 1200 ml/min (Table 1). n-Hexane was used as the collection solvent. For higher molecular mass analytes the recoveries were similar to those with restrictor A (Table 1), but for the more volatile substances the recoveries were lower. An influence of the flow-rate on the recoveries is obvious for the volatile substances, but surprisingly the recoveries for the more volatile analytes are better than those for the lower less volatile compounds. Although the flow-rate had been increased fourfold, the influence of this parameter on the recoveries was very low.

Losses of analytes while trapping with liquid solvents depend on either insufficient collection or the analytes being purged from the solvent with the gas flow. The purge losses of analytes from the collection solvent were tested by spiking the standard solution into the collection solvent, here n-hexane, and performing the

normal extraction procedure. The extraction was performed with restrictors A and B to investigate the influence of different flow-rates. The recoveries were about 100% for both restrictors (Table 1). Analytes collected in the organic solvent were not purged from the solvent by the expanded fluid. This leads to the conclusion that poor recoveries are due to insufficient collection capacities of the trapping system.

3.2. The solid–liquid trap

ODS and silica gel–liquid trap

To increase the trapping efficiency of the dual-chamber vial, different solid–liquid traps were investigated. The transfer tube was filled with silica gel or ODS material (Fig. 1b). In Fig. 2 the recoveries with the silica gel–n-hexane trap, the ODS–n-hexane trap and the n-hexane solvent trap are compared. The collection efficiency of the solid–liquid trap is clearly better than that of the liquid trap. The recoveries increased by 10–30% for each analyte and reached more than 90%. Silica gel and ODS material showed no difference in adsorbing the analytes during extraction. Separate analyses of the organic solvent and the solid traps (silica gel and ODS material) after the extraction with pure carbon dioxide showed no PAHs in the organic solvent. After the extraction, the analytes were trapped on the solid matrix, while the expanded gas flowed through the solid phase. After the extraction the collected substances have to be eluted with a few millilitres of an appropriate organic solvent.

The same experiment was carried out with CO_2 modified with 5% of toluene. Again, the organic solvent and the solid matrix were analysed individually (Fig. 3). In this case the analytes were found in the organic solvent. This shows that the substances were eluted by the organic modifier. Eluation of the analytes after the extraction with an organic solvent may no longer be necessary.

In contrast to the solid trap, the extraction with modified carbon dioxide did not reduce the collection efficiencies. When the new solid–liquid
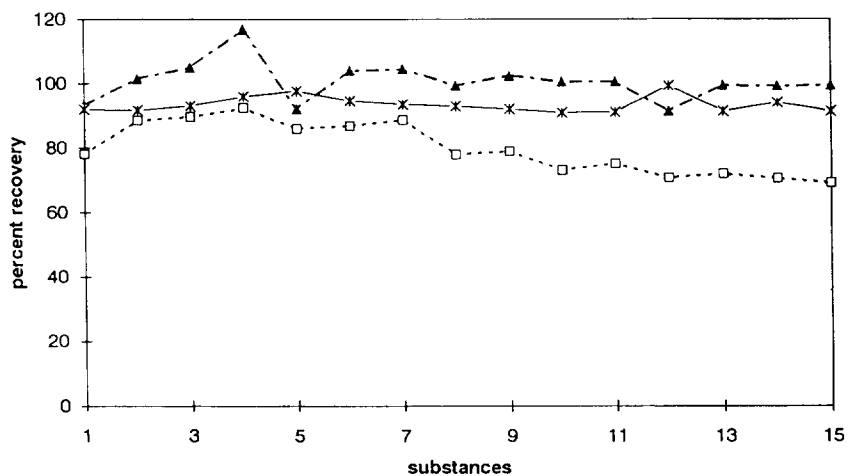
Fig. 2. Comparison of solid–liquid and liquid traps. Flow-rate of gaseous CO_2, 300 ml/min. $\square$ = n-hexane; $\blacktriangle$ = silica gel–n-hexane; $*$ = ODS = n-hexane. For substance identification, see Table 1.

trapping device was used, the eluted analytes were collected in the liquid.

Influence of flow-rates

The solid–liquid trap was tested with restrictor B (flow-rate 1200 ml/min). Silica gel was used as solid sorbent. The results are given in Table 2. In

contrast to the liquid trap, there was no influence of the flow-rate on the recovery. All analytes were collected with good recoveries.

Dionex transfer tube

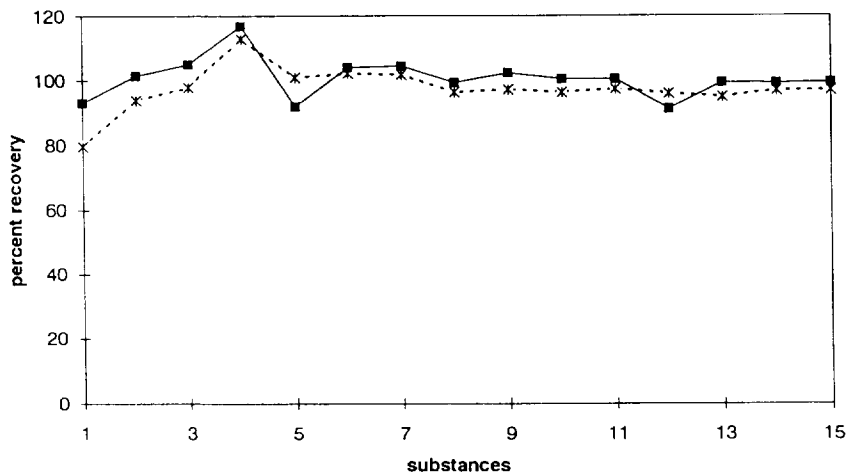Extractions with restrictors A and B were performed with the C_{18} transfer tube. This solid–

Fig. 3. Collection efficiencies with the silica gel–n-hexane trap for ($\blacksquare$) carbon dioxide and ($*$) carbon dioxide modified with 5% of toluene. Flow-rate of gaseous CO_2, 300 ml/min. For substance identification, see Table 1.

Table 2
Collection efficiencies (recoveries with standard deviations: $n = 3$) for PAHs with different solid–liquid traps and flow-rates of gaseous CO_2 of 300 and 1200 ml/min

No.	Compound	Silica gel–n-hexane		ODS–n-hexane 300 ml/min	Dionex tubes–n-hexane	
		300 ml/min	1200 ml/min		300 ml/min	1200 ml/min
1	Naphthalene	93.2 ± 9.8	89.2 ± 24.0	91.8 ± 2.5	82.9 ± 10.0	95.1 ± 5.7
2	Acenaphthen	101.5 ± 8.5	89.9 ± 8.0	91.6 ± 0.1	86.8 ± 5.8	98.6 ± 0.8
3	Fluorene	105.0 ± 8.1	87.3 ± 6.6	93.0 ± 0.1	89.1 ± 6.5	98.7 ± 0.6
4	Phenanthrene	116.9 ± 6.6	94.8 ± 6.2	95.9 ± 1.3	92.4 ± 5.5	112.8 ± 0.7
5	Anthracene	92.0 ± 6.2	90.7 ± 6.9	97.6 ± 1.4	89.6 ± 4.2	95.4 ± 2.0
6	Fluoranthene	104.0 ± 5.5	99.7 ± 6.0	94.6 ± 1.8	97.8 ± 2.5	113.9 ± 0.8
7	Pyrene	104.5 ± 8.6	116.1 ± 11.0	93.4 ± 4.3	93.6 ± 2.2	110.1 ± 0.7
8	Benz[a]anthracene	99.4 ± 5.6	98.2 ± 2.6	92.8 ± 2.0	93.1 ± 1.4	99.0 ± 0.3
9	Chrysene	102.4 ± 5.8	96.0 ± 3.3	92.0 ± 1.4	93.6 ± 1.4	96.3 ± 0.2
10	Benzo[b]fluoranthene	100.5 ± 4.9	97.0 ± 3.0	90.8 ± 1.8	96.4 ± 0.8	99.1 ± 0.0
11	Benzo[k]fluoranthene	100.5 ± 4.9	95.0 ± 3.0	91.0 ± 1.8	94.8 ± 3.1	97.4 ± 0.5
12	Benzo[a]pyrene	91.3 ± 5.5	90.7 ± 4.7	99.3 ± 3.7	94.6 ± 8.1	85.8 ± 1.6
13	Dibenz[a,h]anthracene	99.4 ± 4.7	96.3 ± 4.9	91.2 ± 2.2	92.8 ± 5.6	98.0 ± 2.7
14	Benzo[ghi]perylene	99.2 ± 4.9	99.7 ± 4.9	94.0 ± 2.2	91.8 ± 4.8	102.0 ± 0.1
15	Indeno[1,2,3-cd]pyrene	99.4 ± 4.6	98.9 ± 4.5	91.2 ± 2.6	99.0 ± 7.4	107.9 ± 0.9

liquid trap gave the same results as the other two traps tested (Table 2). The collection efficiencies were much better than with the liquid trap and there was also no dependence on the flow-rate.

4. Conclusions

Combined solid–liquid traps clearly show advantages over liquid or solid traps. The recoveries were increased by ca. 20% by using the solid–liquid traps. There were no losses of the less volatile analytes, and we found no dependence on the flow-rate of the extraction fluid. Variations of the extraction parameters seem not to influence the trapping efficiencies. The use of modified carbon dioxide caused no problems, because the analytes that were trapped on the solid surface were washed out by the organic solvent and collected in the liquid phase. As can be seen, the solid–liquid trap is easy to handle and usable under different extraction conditions.

Our experiments have shown that the use of silica gel as a solid trap in real sample extraction minimizes the clean-up procedures. In many

instances an additional clean-up is no longer necessary because it is integrated in the extraction process.

Acknowledgements

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