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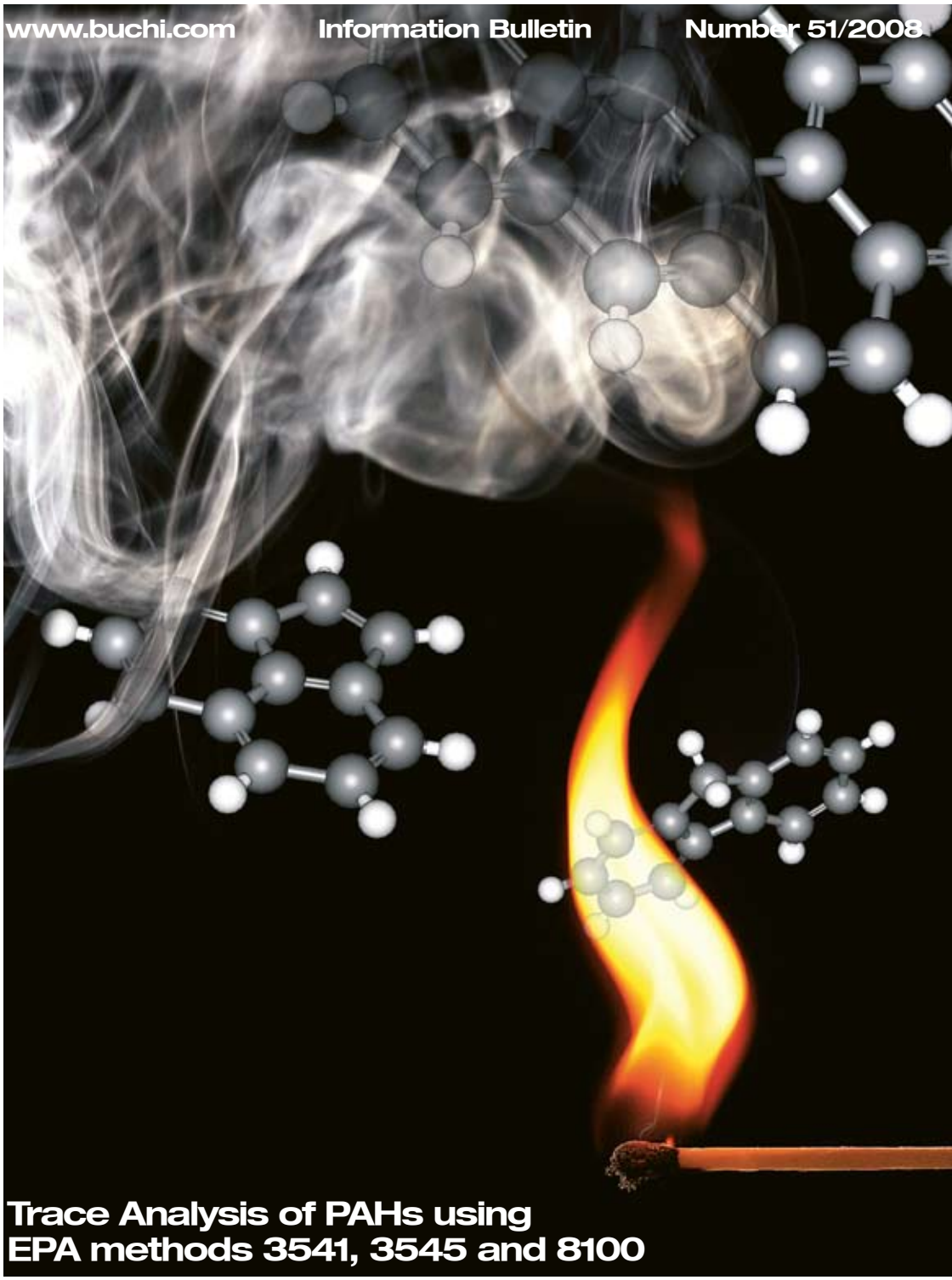

Trace Analysis of PAHs using EPA methods 3541, 3545 and 8100

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Trace Analysis of PAHs: Evaluation of two Extraction Methods (EPA3541 and EPA3545) and Optimization of subsequent Concentration

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The Extraction System B-811 and the Syncore Analyst parallel concentrator as well as the Pressurized Solvent Extractor were evaluated for the pretreatment of samples containing PAHs. Recoveries of extraction and subsequent concentration using acetone + n-hexane (1+1) were 70-95% for 2 ring and 90-100% for the less volatile 3-5 ring PAHs. A good precision (95% confidence level) of less than 6%, naphtalene excluded (12%), was found. No significant difference was observed between the two extraction methods.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants primarily formed by incomplete combustion and incineration. PAHs adsorb strongly to small carbonaceous particles but are also present in the vapor phase. Therefore, they can undergo long range transport. Typical concentrations are in the sub-ppb to ppm range. PAHs also bioaccumulate in food webs and are partially mutagenic and carcinogenic. Therefore, PAH analysis is requested by regulatory bodies. The US Environmental Protection Agency (EPA) introduced a priority pollutant list of 16 PAHs (EPA610) in 1982. For solid and hazardous waste testing, the EPA approved method reference is SW-846.

The analyses of PAHs contamination at the trace level includes sample extraction and extract concentration. Both automated Soxhlet extraction (EPA3541) and pressurized solvent extraction (EPA3545) are approved extraction techniques (EPA3500) for solid samples. The extract volume is reduced to 1 ml for maximum sensitivity (EPA8100).

2-3 ring PAHs can be lost by evaporation and the heavy volatile PAHs due to adsorption to glass walls. Therefore, concentration and extraction procedures as well as cleaning of the glass equipment are crucial factors to be optimized. Cross contamination between samples of high and low concentrations is one of the critical points in trace analysis. This is particularly valid for simultaneous sample concentration. Reasons can be sample transfer by vapor phase or contaminated glass surfaces. Therefore, frequent analyses of blanks are mandatory check procedures.

Fig. 1: Extraction System B-811 from Buchi for automatic Soxhlet extraction of 4 samples.

Fig. 2: SpeedExtractor E-916, the successor of the fastPSE system from Applied Separations

Experimental

Instrumentation

Automated Soxhlet extraction was performed with the Extraction System B-811 (Buchi), pressurized solvent extraction with the PSE system (Applied Separations) and subsequent concentration was carried out with the parallel evaporator Syncore Analyst (Buchi) holding 12 positions. The locally cooled appendix of the sample vessel prevents evaporation to dryness. Vacuum was generated by the Vacuum Pump V-700 (Buchi). A pressure profile was optimized and programmed with the Vacuum Controller V-855 (Buchi) and the condenser was cooled with ethanol+water (40+60) using the Recirculating Chiller B-740/8 (Buchi).

Solvents, Chemicals and Standards

n-Hexane and acetone of SupraSolv® quality were from Merck AG. Isooctane and cyclohexane for residue analyses were obtained from Fluka AG. The PAHs refrerence solution was obtained from Accustandard and contained each of the 16 EPA-PAHs (see table 1) at concentrations of 2 mg/ml in dichloromethane/benzene (1+1). The two quantification standards 3,6-dimethylphenanthrene (98.5%) and 2,2'-binaphthylene (99.5%) were purchased from Dr. Ehrenstorfer GmbH. A stock solution was prepared containing 2 mg/ml of each quantification standard (QS or internal standard) in toluene. A solution of 2 mg/ml 2-fluorobiphenyl in cyclohexane was obtained from Dr. Ehrenstorfer GmbH was used as recovery standard (RS or surrogate). Calibration solutions were prepared by dilution of stock solutions with isooctane. The reference material ERM-CC013a (PAHs in soil) was obtained from BAM, Germany.

Cleaning

Glass equipment. PAHs can be adsorbed on glass surfaces contaminated by organic impurities. Therefore, proper glass cleaning is necessary to obtain good recoveries and precision. All glass equipment was soaked over night in purified water added 2% of Deconex 20NS (Borer Chemie).

Then, it was rinsed twice with both hot tap water followed by purified water and afterwards heated in an oven (Fusing Toplader F75, Nabertherm) at 450 °C.

PSE equipment. The vessels were filled with sand and extracted with acetone+*n*-hexane (1+1) prior to use using method 3 (see below). Frits and the lower frit holders were ultrasonicated in acetone+*n*-hexane (1+1) for 15 min.

Soxhlet extraction conditions

Method 1 using n-hexane. Step 1 (extraction): Heating level 10, 2 h (20 cycles). Step 2 (rinse): Not used. Step 3 (dry): Heating level 10, 3 min. Cooling temperature: 5 °C.

Method 2 using acetone+n-hexane (1+1). Step 1 (extraction): Heating level 8, 2 h (20 cycles). Step 2 (rinse): Not used. Step 3 (dry): Heating level 8, 5 min. Cooling temperature: 5 °C.

PSE extraction conditions

Method 3. Oven temperature: 100 °C. Pressure: 110 bar (1600 psi). Static time: 10 min. Solvent flush time: 1 min. Gas flush time: 2 min. Total extraction time approx. 23 min.

Concentration conditions

Method 4, optimized concentration of n-hexane. Speed of orbital movement: 170 rpm. Heating block temp.: 50 °C. Cooling water temp.: 5 °C. Flushback module temp.: 5 °C. Pressure profile: From 700 to 320 mbar in 4 min, from 320 to 240 mbar in 5 min, from 240 to 180 mbar in 30 min, hold at 180 mbar for 10 min, then slowly aerated from 180 to 1000 mbar in 10 min. Total time: 59 min.

Method 5, not optimized concentration of n-hexane. Speed of orbital movement 300 rpm. Heating block temp.: 50 °C. Cooling water temp.: 18 °C. Pressure: 180 mbar. Total time: 60 min.

Method 6, optimized concentration of acetone+n-hexane (1+1). Speed of orbital movement: 170 rpm. Heating block temp.: 50 °C. Cooling water temp.: 5 °C. Flushback module temp.: 5 °C. Pressure profile: 900 to 500 mbar in 10 min, 500 to 180 mbar in 10 min, hold at 180 mbar for 20 min, then slowly aerated from 180 to 1000 mbar in 10 min. Total time: 60 min.

Method 7, optimized concentration of cyclohexane. Speed of orbital movement: 170 rpm. Heating block temp.: 50 °C. Cooling water temp.: 5 °C. Flushback module temp.: 5 °C. Pressure profile: 700 to 320 mbar in 5 min, 320 to 200 mbar in 5 min, 200 to 140 mbar in 30 min, hold at 140 mbar for 10 min, then slowly aerated from 140 to 1000 mbar in 10 min. Total time: 60 min.

Fig. 3: Parallel evaporation system to a predefined volume: Syncore Analyst R-12 from Buchi for 12 samples equipped with Flushback module and a condenser.

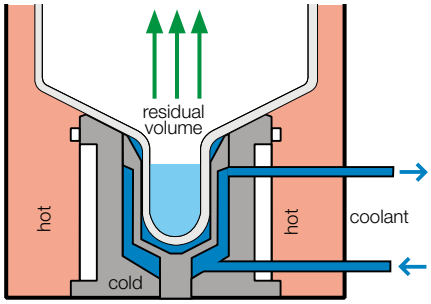

Fig. 4: Syncore Analyst with the locally cooled appendix of the sample vessel preventing evaporation to dryness.

Fig. 5: Buchi Vacuum Pump V-700 with Vacuum Controller V-855 and post-pump condenser.

Fig. 6: Gradient mode of the Buchi Vacuum Controller V-855.

Clean-up

Method 8. The high concentration of oil in the reference material ERM-CC013a made a clean-up after extraction necessary. A solvent transfer to cyclohexane was carried out by adding 10 ml of cyclohexane and concentrating the extract to approx. 10 ml again. The PAHs were extracted with a solution of 90+10 dimethylformamide(DMF)+water (1 x 5 ml and 2 x 3 ml). 10 ml of water were added to the collected DMF-phase and the PAHs back-extracted with cyclohexane (1 x 5 ml, 3 x 3 ml). The united cyclohexane extracts was concentrated to 1.5 ml using method 7. Recoveries after cleanup were approximately 60% due to the high load of oil.

Analysis

All analyses were carried out according to the EPA method 8100 employing gas chromatography combined with flame ionization detection (GC/FID 6890, Agilent) and an EPC split/splitless injection. Injections of 1 µl were performed by hot needle injection. A capillary of 15 m length and 0.25 mm ID (0.1 µm film of DB-5ms) was obtained from J&W Scientific. The temperature of the injector was 280 °C and of the detector 300 °C. Hydrogen was used as carrier gas at a flow rate of 38 cm/s (1.2 ml/min). The temperature profile was: 40 °C for 2 min, then to 150 °C at 40 °C/min, then with 30 °C/min to 300 °C (isothermal for 5 min). Figure 8 shows an example of the separation. Linear calibration curves were obtained for each of the 16 EPA

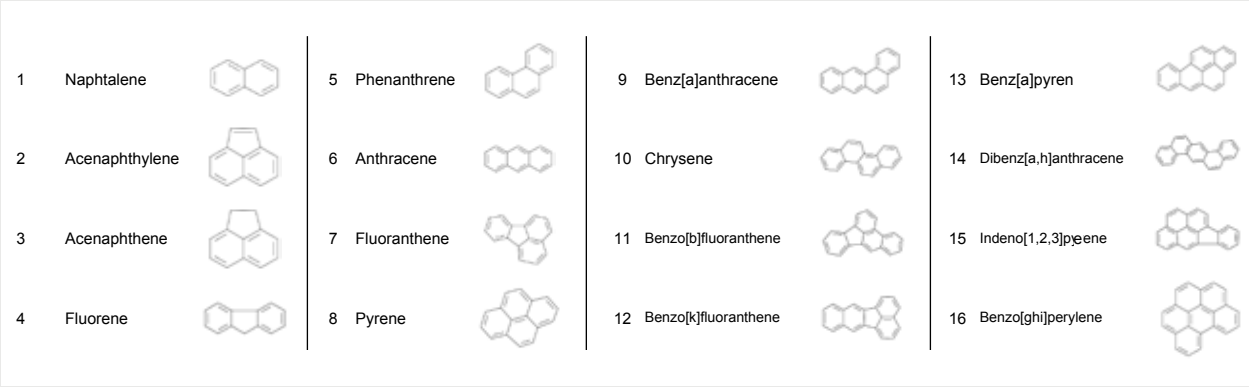

Fig. 7: Chemical structure of the 16 EPA PAHs

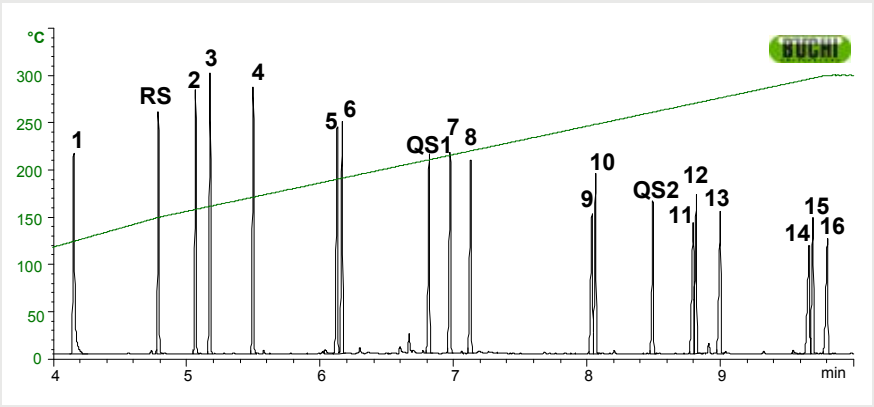

Fig. 8: Separation of the 16 EPA PAHs by GC-FID.

PAHs within 2-40 µg/ml. Detection limits established on the signal-to-noise ratio 3:1 varied between 0.02-0.17 µg/ml (Syncore Analyst), 0.02-0.33 µg/ml (PSE) and 0.03-0.60 µg/ml (B-811) and quantification limits between 0.02-0.2 mg/kg for a sample weight of 10 g. PAHs 1-8 were quantified with 3,6-dimethylphenanthrene (QS1) and PAHs 9-16 with 2,2'-binaphthylene (QS2).

Precision was defined as twice the standard deviation to obtain approximately the 95% confidence interval. Precision of the quality control standard was better (1-3%) than for the whole procedure including extraction and extract concentration.

Results

Syncore Analyst

20 ml of *n*-hexane, 10 µl of both the PAHs standard solution and the recovery standard stock solution were added to a Syncore Analyst vessel of 200 ml with a 1 ml appendix and concentrated on a 12 position rack. A sequence consisted of 3 samples and one blank in each row (4 in total). Samples were concentrated to a final volume of 1.5±0.2 ml (method 4) or to 0.5±0.2 ml (method 5). 10 µl of the quantification standard solution were added before injection.

Figure 9 and table 1 summaries the recoveries for eight parallels. A good recovery (95-100%) and precision (3%) was obtained for the less volatile 3-5 ring PAHs independently from the applied parameters. Lower recoveries were found for the more volatile 2-ring PAHs. However, recoveries were significantly higher for the optimized concentration procedure (method 4, 90-100%) compared to method 5 (80-95%). Furthermore, precision was better. Optimization of vacuum gradient, Flushback effect as well as a low cooling temperature and the speed of orbital movement improved the recoveries of the 2 ring PAHs by 10%. The use of isooctane as keeper did not further improve recoveries.

Extraction System B-811

A glass sample tube with frit (Buchi) covered with a formed wet strengthened round filter made from cellulose (Whatmann, No.91, 150 mm) was used for Soxhlet extraction.

10 g of pre-extracted soil were weighed into the thimble, spiked with 10 µl of both the PAH and the recovery standard stock solution. The top of the sample was not covered. Extraction was carried out with method 2 and 100 ml of acetone+*n*-hexane (1+1). Step 2 (rinse) was not used, since it is followed by step 2A (evaporating of the extract nearly to dryness) leading to losses of the most volatile PAHs. Step 3 concentrated the extracts to 15-25 ml (see details before).

Extracts were transferred to the Syncore Analyst vessels with a 1 ml appendix with a Pasteur pipette. The glass walls of the B-811 beaker were rinsed twice with 5 ml of *n*-hexane. Concentration (method 6) was performed under vacuum to approximately 1.5 ml. 10 µl of the quantification standard were added before injection.

Figure 9 and table 1 show the recoveries and precision for the automated Soxhlet extraction and concentration of the spiked soil

samples (n=11). Good recoveries (80–100%) and precisions (2-6%) were obtained. The lower precision found for naphthalene (83±12%) can be partly explained by the signal distortion caused by the acetone fraction in the extract. Extraction of spiked soil with *n*-hexane resulted in similar recoveries but a considerably better precision (86±6% for naphthalene, n=4).
The checked blanks determined after the extraction of 5 g soil spiked with 80 µg of each PAH did not contain any measurable PAHs quantities. This allows a reuse of the unit without any further cleaning step, which saves time and minimizes use of solvent.

PSE
10 g of pre-extracted soil were filled into a 11 ml extraction vessel and spiked with 10 µl of both the PAH and recovery standard stock solution and extracted with method 3 and acetone+*n*-hexane (1+1). Four positions were occupied by samples and two by blanks in order to determine cross contamination.
The obtained extracts (15-20 ml) were transferred to Syncore Analyst vessels with a 1 ml appendix. The glass walls of the PSE vials were rinsed twice with 5 ml of *n*-hexane and concentrated under vacuum to approximately 1.5 ml (method 6). 10 µl of the quantification standard were added before injection.

Figure 9 and table 1 show the recoveries and precision for the pressurized extraction and concentration of the spiked soil samples (n=12). Recoveries (80-100%) and precision (2-5%) were comparable to Soxhlet extraction. Also here the precision was poorer for naphthalene (81±10%) due to the acetone effect. *n*-Hexane alone was not suitable for extraction due to poor recovery of the high boiling PAHs (50–90%). Nevertheless, precision improved also here for naphthalene (86±3%, n=4). No cross contamination was detectable. Blanks were equal to the detection limits even when increasing the quantity to 80 µg of each PAH in two samples.
However, a second extraction of three samples (5 g soil spiked with 80 µg of each PAH) contained traces of PAHs of about 2%, which indicates an incomplete extraction. Therefore, a second cycle should be performed achieving a complete extraction.

Check with reference material

Extraction System B-811 5 g of the reference material ERM-CC013a and 10 µl of the recovery standard stock solution were extracted with method 2 and 100 ml of acetone+ *n*-hexane (1+1). While EPA method 3541 refers to a hot extraction, we have demonstrated a Soxhlet extraction in the proposed time (2 hours). A hot extraction can be performed as well with the flexibility of our Extraction System B-811 and would reduce the extraction time.

PSE 5g of the reference material were filled in between two sand beds of 2-3 g into a pre-extracted 11 ml vial. 10 µl of the recovery standard stock solution were added. The quartz sand of 0.3-0.9 mm size (Carlo) was extracted prior to use. Extraction was performed using method 3 and acetone + *n*-hexane (1+1).
A clean-up (method 8) was performed for both extraction methods after extraction and before concentration (method 7).

The results summarized in table 2 clearly show the applicability and comparability of both extraction methods. The PSE system gave slightly higher yields.

A second Soxhlet extraction was free of PAHs, corresponding to detection limits of 0.04-0.2%. However, about 5% of the certified levels were present in the repeated PSE extraction. This means that a second static cycle is necessary for a complete extraction. Though the values shown in table 2 resulted from 1 cycle.

Conclusions

High recoveries and good precision were found for the PAHs sample preparation. The results are better than described in the EPA method 8270.

Soxhlet extraction and PSE are able to extract the 16 EPA-PAHs nearly exhaustive and with good precision. Recoveries and precision are similar for both methods. However, the influence of solvent is more critical for PSE and should be carefully optimized. A second static cycle can be necessary for a complete extraction.

The results were obtained with the fastPSE system, but comparable results are archieveable with the SpeedExtractor E-916, too [1].

Loss of the most volatile PAHs during extract concentration could be nearly completely reduced by the combined application of a vacuum controller, a Flushback module, low cooling temperature and low speed of orbital movement.

Acknowledgments

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References

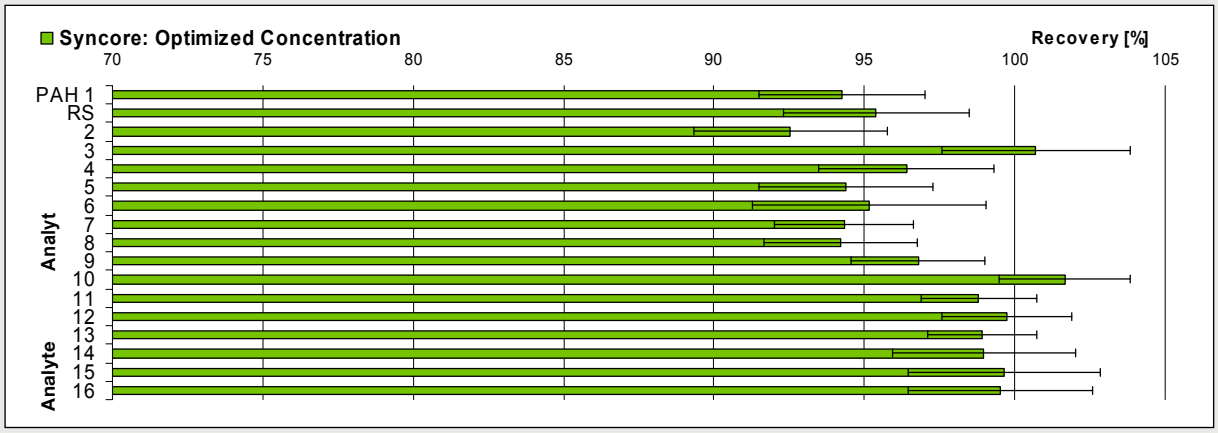
[1] Application Note 008/2009: Extraction of Sediment using the SpeedExtractor E-916 for the Determination of PAHs

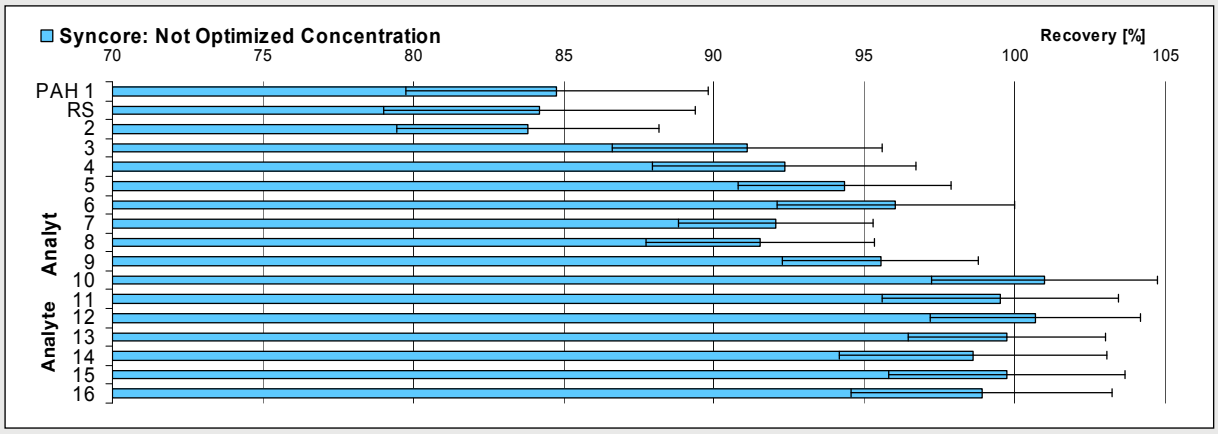
Compound		CAS-No.	Recovery and Precision (95% confidence) [%]				
			Automated Soxhlet **EPA3541/8270** values published in EPA8270	Concentration **Syncore** Optimized Method 4	Concentration **Syncore** Not optimized Method 5	Automated Soxhlet EPA3541/8100 **B-811** Method 2+6	Pressurized solvent Extraction EPA3545/8100 **PSE** Method 3+6
			n = 3	n = 8		n = 11	n = 12
1	Naphthalene	91-20-3	26.2±15	94 ± 3	85 ± 5	83 ± 12	81 ± 10
RS	2-Fluorobiphenyl	-	-	95 ± 3	84 ± 5	90 ± 6	89 ± 5
2	Acenaphthylene	208-96-8	71.6 ± 5.7	93 ± 3	84 ± 4	86 ± 4	89 ± 4
3	Acenaphthene	83-32-9	79.2 ± 4	101 ± 3	91 ± 4	91 ± 5	93 ± 4
4	Fluorene	86-73-7	82.1 ± 3.4	96 ± 3	92 ± 4	93 ± 5	94 ± 3
5	Phenanthrene	85-01-8	83.9 ± 5.4	94 ± 3	94 ± 4	94 ± 3	94 ± 2
6	Anthracene	120-12-7	96.3 ± 3 .9	95 ± 4	96 ± 4	93 ± 2	94 ± 2
7	Fluoranthene	206-44-0	87.7 ± 6.9	94 ± 2	92 ± 3	95 ± 2	95 ± 2
8	Pyrene	129-00-0	102 ± 0.8	94 ± 3	92 ± 4	95 ± 2	95 ± 2
9	Benz[a]anthracene	56-55-3	73.4 ± 3.8	97 ± 2	96 ± 3	96 ± 3	94 ± 3
10	Chrysene	218-01-9	76.2 ± 4.4	102 ± 2	101 ± 4	100 ± 3	98 ± 3
11	Benzo[b]fluoranthene	205-99-2	82.7 ± 5.0	99 ± 2	100 ± 4	98 ± 3	96 ± 3
12	Benzo[k]fluoranthene	207-08-9	71.7 ± 4.1	100 ± 2	101 ± 3	99 ± 3	99 ± 2
13	Benzo[a]pyrene	50-32-8	71.7 ± 4.1	99 ± 2	100 ± 3	97 ± 3	97 ± 2
14	Dibenz[a,h]anthracene	53-70-3	66.7 ± 6.3	99 ± 3	99 ± 4	98 ± 5	97 ± 4
15	Indeno[1,2,3]pyrene	193-39-5	72.2 ± 4.3	100 ± 3	100 ± 4	98 ± 4	97 ± 3
16	Benzo[ghi]perylene	191-24-2	63.9 ± 8.0	100 ± 3	99 ± 4	98 ± 3	97 ± 2

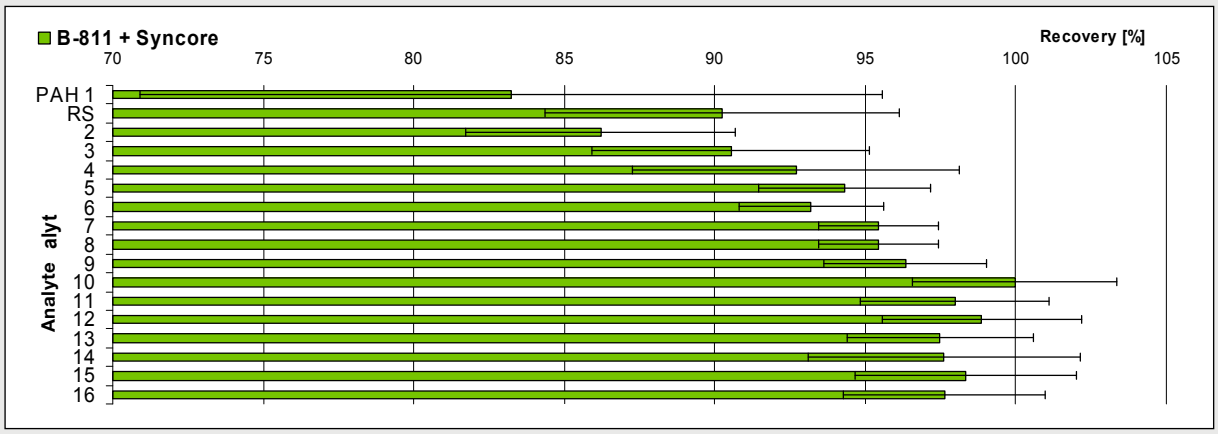
Tab. 1: Comparison of recovery and precision for different extraction procedures of PAHs in spiked soil samples.

Compound		CAS-No.	Concentration and SD [mg/kg]		
			Certified Value	Automated Soxhlet EPA3541/8100 B-811 (2 h, 20 Cycles) n=3	Pressurized solvent Extraction EPA3545/8100 PSE (10 min, 1Cycle) n=3
1	Naphthalene	91-20-3	2.4 ± 0.5	2.0 ± 0.1	2.1 ± 0.1
4	Fluorene	86-73-7	1.14 ± 0.11	1.1 ± 0.1	1.2 ± 0.1
5	Phenanthrene	85-01-8	12.0 ± 0.6	11.5 ± 0.3	12.1 ± 0.2
6	Anthracene	120-12-7	1.41 ± 0.22	1.3 ± 0.1	1.4 ± 0.1
7	Fluoranthene	206-44-0	12.9 ± 0.7	12.0 ± 0.4	12.5 ± 0.3
8	Pyrene	129-00-0	9.6 ± 0.3	9.5 ± 0.2	9.7 ± 0.1
9	Benz[a]anthracene	56-55-3	5.6 ± 0.5	5.4 ± 0.2	5.7 ± 0.2
10	Chrysene	218-01-9	5.3 ± 0.8	5.5 ± 0.2	6.2 ± 0.2
13	Benzo[a]pyrene	50-32-8	4.9 ± 0.7	5.1 ± 0.4	5.3 ± 0.3
16	Benzo[ghi]perylene	191-24-2	4.6 ± 0.5	4.7 ± 0.4	4.8 ± 0.3

Tab. 2: Certified values and Buchi results for reference material ERM-CC013a (PAHs in Soil).







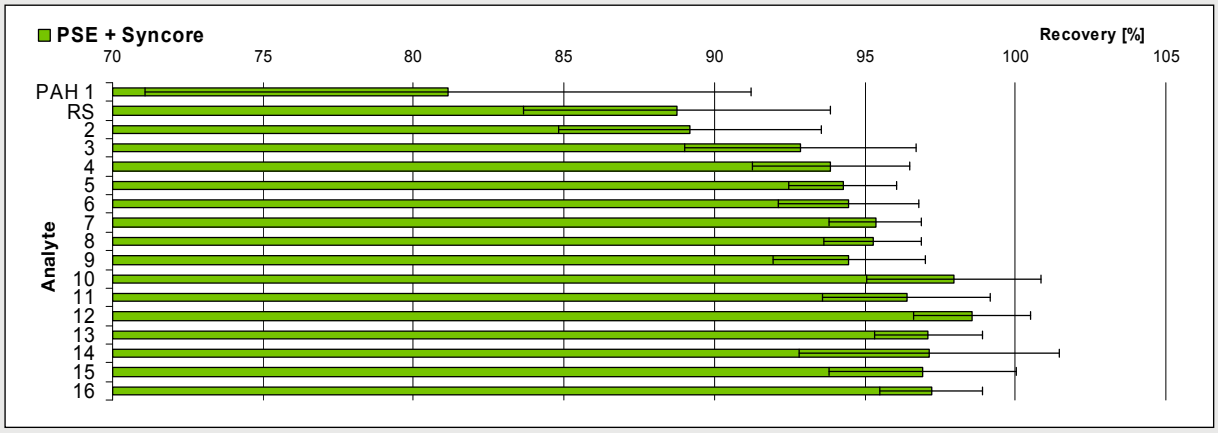


Fig. 9: Comparison of recovery and precision of the different systems applied for concentration and extraction.

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