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Monitoring polycyclic aromatic hydrocarbons in waste gases

Anne Höner, Michael Arnold, Norbert Hüsers, Wolfgang Kleiböhmer*

Institut für Chemo- und Biosensorik, Lehrstuhl für Analytische Chemie, Westfälische Wilhelms-Universität, Mendelstr. 7, D-48149 Münster, Germany

Abstract

A fast off-line monitoring system based on supercritical fluid extraction (SFE) and supercritical fluid chromatography (SFC) is introduced that allows the quantification of polycyclic aromatic hydrocarbons (PAHs) in the crude gas of fuel-oil-stoked industrial boiler plants. In this paper we present a comparison of our recently developed monitoring system with a standard method of a reference laboratory. Samples were taken according to VDI-3873 (dilution method) on polyurethane foam (PUF) plugs. The PUF plugs were extracted with toluene-modified carbon dioxide within 60 min. The extracts were analysed using packed column SFC with fluorescence detection.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) form a large class of organic compounds, which is of great environmental concern. Polynuclear aromatics are toxic and many of them are known to be carcinogenic and/or mutagenic [1]. They are produced through incomplete combustion of organic matter and therefore may be present in any kind of waste gas. This leads to the necessity of monitoring PAH-emissions of various combustion plants in order to avoid pollution of the environment.

PAHs occur both in the vapour phase and adsorbed on particulate matter. The analytical process, especially the sampling method, has to take this into account. Existing methods use for example paraffined fibre glass filters for collection of all compounds [2]. An alternative is deposition of particulate phase PAHs on fibre glass filters with subsequent collection of vapour phase PAHs using solid adsorbents, for example polyurethane foam.

The extraction of the analytes usually is accomplished with organic solvents, in most cases using a Soxhlet extractor. One of the drawbacks of liquid extractions is the large amount of harmful organic solvents which have to be used. Another problem is the relatively high extraction time, which may exceed 24 h. Following the liquid extraction, several time-consuming clean-up steps have to be performed. The separation and quantification is usually accomplished with high-performance liquid chromatography (HPLC). This method requires organic solvents as well and the total run time, including an equilibration step, is about 60 min. An alternative for HPLC is gas chromatography with flame ionisation detection (FID). The drawback of this method, especially for real-world samples, is mainly the missing selectivity of FID.

In recent years a lot of effort was put into the development of solvent reduced analytical techniques [3,4]. Ideal substitutes for harmful organic solvents are non-toxic and inflammable

* Corresponding author.

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supercritical fluids like carbon dioxide. Conventional liquid extraction methods can be replaced by supercritical fluid extraction (SFE). SFE allows one to separate the components from the matrix and to concentrate and clean them simultaneously [5,6]. Hawthorne et al. [7] and Wright et al. [8] already used supercritical fluids for the extraction of polyurethane foams. Supercritical fluid chromatography (SFC) is an attractive alternative for many HPLC applications [9]. For the analysis of PAHs it was already used by Sandra et al. [10] and Wenclawiak and Hees [11]. Furthermore the combination of both SFE and SFC may allow on-site extraction and analysis.

For these reasons the aim of the present work is the development of a fast and solvent-free PAH monitoring system based on SFE and SFC methods. In a further stage of development this monitoring system should allow on-site measurements and thus quasi-continuous emission monitoring of combustion plants.

In this paper we present a comparison of our recently developed monitoring system with a standard method of a reference laboratory.

2. Experimental

2.1. SFE–SFC monitoring system

Sampling system

The sampling procedure of the new monitoring system is similar to that described in guideline VDI 3873 [2]. This method relates both to gaseous and to particle-attached PAHs, which are quantitatively collected on a silicone-bonded fibre glass filter impregnated with paraffin oil. For the collection of lower-volatility PAHs a solid adsorbent can be linked downstream. The sample gas is diluted with air and cooled to temperatures below 50°C. For the experiments described herein the sampling device was modified. A disk of fibre glass filters (5 cm diameter, Schleicher und Schuell, Germany) and three polyurethane foam (PUF) plugs (5 cm diameter, K. Ziemer, Germany) were used instead of paraffin-impregnated fibre glass filters. The polyurethane foam plugs were precleaned using SFE. The total sample volume was about 1.4 m^3 (see Table 1).

Supercritical fluid extraction

The extractions were carried out using a Dionex SFE system (SFE-703) equipped with a Dionex SFE-703M modifier module. Extraction cells (10 ml) (Keystone Scientific) and Dionex linear restrictors (wafer restrictors, flow-rates ca. 1200 ml/min of gaseous CO_2) were used. The optimised extraction conditions were as follows: extraction fluid CO_2–10% toluene, pressure 40 MPa, oven temperature 130°C, restrictor temperature 150°C. For analyte collection a modified dual chamber trapping vial (solid–liquid collection) with an integrated clean-up system (ICUS) was used [5,6]. This clean-up system consists of

Table 1
Operating conditions for crude gas sampling (date 29.06.1994)

	Sample No.		
	1	2	3
Sampling time from:	14:00	15:15	16:30
to:	15:00	16:15	17:30
Crude gas temperature (K)	462	464	465
Sample volume ($V_{p0,T0}$) (m^3)	4.56	4.10	4.50
Temperature at the PU-foam (°C)	42	42	42
Sample volume ($V_{p0,T0}$)[a] (m^3)	1.42	1.45	1.37
Temperature at the PUF[a] (°C)	40	40	39

[a] Sampling for the SFE–SFC monitoring system.

silica gel and *n*-hexane. For all supercritical fluid extractions no further clean-up was performed. The solvent was evaporated under a gentle stream of nitrogen. For the preliminary investigations acetonitrile was added to the sample prior to HPLC analysis. In the comparison studies methanol–water (90:10) instead of acetonitrile was used.

HPLC analysis

For HPLC analysis a HP Series 1050 liquid chromatograph (Hewlett Packard) with autosampler, quaternary pump, degasser, HP 1046A programmable fluorescence detector and HP ChemStation for 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 with a flow-rate of 0.5 ml/min. For identification the retention times were compared and for quantification an external calibration with the SRM 1647c standard in acetonitrile (Promochem, Germany) was performed.

SFC system

The SFC experiments were performed using a Dionex series 600-D system. A multiple-wavelength detector Model UVIS-206 and a fluorescence detector Model FLUOR LC304, both from Linear Instruments, were connected in series. The injection system consisted of two Valco injection valves, one of them equipped with a 20-μl external sample loop, which is described in detail elsewhere [12]. The SFC column was packed with Envisil (Dr. Molnar, Berlin, Germany) by Grom, Herrenberg (Envisil, C_{18}, 200 × 1 mm I.D., 5 μm, 300 Å). Connections between column and detector cells were made of fused-silica capillaries, 50 μm I.D. Data acquisition was done using Linear Instruments UVIS 206 PC Software (version 2.1) and Dionex AI-450 SFC chromatography software (version 3.32). SFC-grade carbon dioxide was purchased from Air Products (Hattingen, Germany). The test mixture (Polyaromatic Hydrocarbons Mixture) was obtained from Sigma-Aldrich and methanol for HPLC was purchased from Baker.

For UV detection a commercially available flow cell (volume 250 nl) was employed. The flow cell for fluorescence detection was built in-house. It is made of a short piece of fused-silica tubing (320 μm I.D.), from which a small section (ca. 6 mm) of polyimide coating was removed. Into one end a fused-silica capillary of 50 μm I.D., which is connected to the UV detector, was inserted. For pressure restriction a fused-silica capillary of 25 μm I.D. (total length ca. 70 cm) was placed at the other end. The resulting cell volume is approximately 500 nl. The mounting of the detector cell is made of aluminium and resembles the commercially available mounting of the HPLC cell. It is possible to cool the cell mounting using a circulating pump. An additional device allows adjustment of the detector cell in the focal path.

All SFC experiments were carried out using pure carbon dioxide as the mobile phase. The separations were performed employing a density gradient at 80°C as follows: 3 min at 0.15 g/ml, programmed to 0.35 g/ml at 1 g ml^{-1} min^{-1}, then programmed to 0.78 g/ml at 0.015 g ml^{-1} min^{-1}, then held at 0.78 g/ml for 8 min.

2.2. Standardised method

Sampling system

The sampling procedure for the reference measurements is following guideline VDI 3873 "Measurement of PAHs in stationary industrial plants — dilution method — gas chromatographic determination" [2] with minor modifications. Fibre glass filters and polyurethane foam plugs (25 cm diameter) took the place of paraffined fibre glass filters. The total sample volume was about 4.5 m^3 (see Table 1).

Sample preparation and analysis

For validation studies the entire filters and PUF plugs were extracted with toluene under reflux. After extraction a clean-up procedure was performed and for separation and quantification gas chromatography with FID was used [2].

3. Results and discussion

3.1. Development of a SFE method for PAH extraction from polyurethane foam

In a first step the optimum extraction conditions had to be determined. In this case (SFE of adsorbents) spike experiments were assumed to give extraction conditions that are transferable to real-world samples. An aliquot of 100 μl of a PAH solution in toluene (200 ng of each component) was spiked on the PUF plugs. After evaporation of the solvent the PUF plug was placed in the extraction cell. The cell was then connected to the SFE system in such a way that the PAHs had to be carried through the whole extraction cell and with this through the whole length of the PUF plug. The following extraction parameters were optimised: modifier and modifier concentration, fluid flow, pressure and oven temperature. In Table 2 the SFE recoveries using the optimised extraction conditions (CO_2 modified with 10% toluene, pressure 40 MPa, oven temperature 130°C, restrictor temperature 150°C, flow ca. 1200 ml/min) are shown. The total extraction time was 60 min. After an extraction time of half an hour the trapping vials were replaced and the extraction was continued for another 30 min. Each vial was analysed separately by HPLC with fluorescence detection. The lower mass PAHs are extracted within 30 min. For the other substances 60 min are necessary for quantitative recoveries.

During the development of a new SFE method it is very important to test the extraction conditions using real-world samples. Therefore three samples were taken in the crude gas of a sawdust-stoked boiler. Because a simultaneous sampling was not possible, the samples were taken successively. The sampling filters and PUF plugs were analysed in our laboratory. In order to compare the extraction results of the SFE method with conventional techniques, one of the samples was extracted using a Soxhlet apparatus. With the integrated clean-up system (ICUS) a further clean-up process in SFE becomes un-

Table 2
Percent recoveries of spiked PUF samples

	Recovery (%)	
	1st extraction	2nd extraction
Naphthalene	102	n.d.
Acenaphthene	91	n.d.
Fluorene	93	n.d.
Phenanthrene	98	n.d.
Anthracene	102	n.d.
Fluoranthene	105	n.d.
Pyrene	107	n.d.
Benz[*a*]anthracene	105	n.d.
Chrysene	100	n.d.
Benzo[*b*]fluoranthene	102	n.d.
Benzo[*k*]fluoranthene	100	1
Benzo[*a*]pyrene	101	4
Dibenz[*a,h*]anthracene	99	6
Benzo[*ghi*]perylene	94	11
Indeno[1,2,3-*cd*]pyrene	100	8
Anthanthrene	79	11
Coronene	80	20

Spiking level ΣPAHs 5.2 μg; extraction conditions CO_2–10% toluene, 40 MPa, 130°C oven temperature, 150°C restrictor temperature, 1200 ml/min flow of gaseous CO_2, 60 min total extraction time (2 × 30 min); chromatographic analysis was performed by HPLC (for detailed description see Section 2); number of replicate extractions $n = 3$ (standard deviations < 10%).

necessary. However, a clean-up had to be performed for the Soxhlet extract. The separation and quantification of the components were performed using HPLC and fluorescence detection. The extraction results are given in Table 3.

Table 3 shows that there are no significant differences between the two supercritical fluid extractions as well as between these and the Soxhlet extraction, in particular when it is taken into account that the sampling had to be performed successively. The experiments show that SFE is a promising alternative for conventional liquid extraction. SFE gives similar results in shorter analysis time and without further clean-up.

3.2. Supercritical fluid chromatography

One aim of this work was to develop a sensitive and efficient alternative for HPLC using packed column SFC.

Injection

To overcome the limitations caused by the relatively low injection volumes of conventional techniques we used a home-made solid-phase injector. With this system it is possible to inject 20 μl without any loss of chromatographic resolution. In Table 4 the detection limits of four PAHs obtained with direct injection (0.5 μl) are compared to those obtained using the new solid-phase injector.

Table 4
Comparison of detection limits (in units of concentration) of direct injection (0.5 μl) versus injection via solid-phase sample loop (20 μl), signal-to-noise ratio 3

Compound	Direct injection (ng/μl)	Solid-phase sample loop (ng/μl)
Fluorene	6	0.3
Fluoranthene	15	0.4
Chrysene	3.5	0.1
Benzo[*a*]pyrene	8	0.2

Separation

For the SFC separation of the priority PAHs we used a polymeric C_{18} column. With this column it is possible to separate 15 out of 16

Table 3
Extraction results of three real-world samples; comparison of Soxhlet and supercritical fluid extraction

	SFE1 (μg/m^3)	SFE2 (μg/m^3)	Soxhlet (μg/m^3)
Naphthalene	89.0	92.4	39.5
Acenaphthene	18.0	12.0	8.0
Fluorene	11.0	10.0	8.1
Phenanthrene	55.0	52.0	50.2
Anthracene	28.0	22.5	18.2
Fluoranthene	17.0	22.0	24.3
Pyrene	16.0	25.0	28.0
Benz[*a*]anthracene	2.8	5.6	5.9
Chrysene	2.3	4.0	6.3
Benzo[*b*]fluoranthene	3.9	6.1	6.1
Benzo[*k*]fluoranthene	1.1	1.2	1.6
Benzo[*a*]pyrene	1.9	2.4	2.6
Dibenz[*a,h*]anthracene	[a]	[a]	[a]
Benzo[*ghi*]perylene	1.9	2.0	2.2
Indeno[1,2,3-*cd*]pyrene	2.1	2.2	2.4
Anthanthrene	0.4	0.5	0.6
Coronene	0.7	0.9	1.1

[a] Not detected.

EPA-PAHs within 35 min. As far as we know this is the first separation of the 15 fluorescent EPA-PAHs using single-column SFC with pure carbon dioxide. These experiments demonstrate that it is possible to obtain satisfying SFC separations provided a suitable packing material is employed (Fig. 1).

Detection

To overcome the problems related to low selectivity in UV detection, the aim of this work was to use fluorescence detection in SFC. A commercially available fluorescence detector equipped with a home-made high-pressure flow cell assembly was employed. Although the fluorescence detector cell assembly is still in the stage of development, similar limits of detection and a significantly higher selectivity compared to UV-detection are obtained.

Our next aim is to combine the above-described extraction and separation steps based on supercritical carbon dioxide in order to form a PAH monitoring system. Therefore the suitability of the single components in the present state of development has to be tested.

3.3. Suitability test

In the following experiments the results obtained with the described off-line SFE–SFC monitoring system were compared with those of a reference method. The reference measurements were carried out by the RWTÜV Essen, an accredited institute for official emission control in Germany. During three successive sampling intervals, two samples were taken simultaneously in the crude gas of a fuel-oil-stoked industrial boiler plant. The sampling for both methods differed in size of the PUF plugs and waste gas volume. All relevant values are listed in Table 1.

One sample of every sampling interval was analysed by the reference laboratory (RWTÜV). Liquid extraction was accomplished using a Soxhlet apparatus (toluene). Following several clean-up steps, the analysis was performed using GC–FID. The results for the three sampling intervals are given in Table 5.

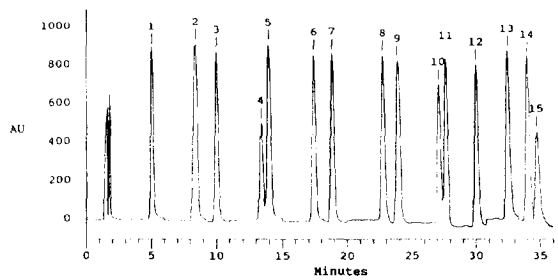

Fig. 1. SFC chromatogram using a polymeric C_{18} stationary phase. Mobile phase: carbon dioxide; oven temperature 80°C; density 3 min at 0.15 g/ml, programmed to 0.35 g/ml at 1 g ml^{-1} min^{-1}, then programmed to 0.78 g/ml at 0.015 g ml^{-1} min^{-1}, then held at 0.78 g/ml for 8 min. UV detection, wavelengths are given in brackets: 1 = naphthalene (212 nm); 2 = acenaphthylene/acenaphthene (220 nm); 3 = fluorene (208 nm); 4 = phenanthrene (240 nm); 5 = anthracene (240 nm); 6 = fluoranthene (230 nm); 7 = pyrene (232 nm); 8 = benz[*a*]anthracene (270); 9 = chrysene (240 nm); 10 = benzo[*b*]fluoranthene (240 nm); 11 = benzo[*k*]fluoranthene (240 nm); 12 = benzo[*a*]pyrene (258 nm); 13 = dibenz[*a,h*]anthracene (290 nm); 14 = indeno[1,2,3-*c,d*]-pyrene (244 nm); 15 = benzo[*ghi*]perylene (293 nm).

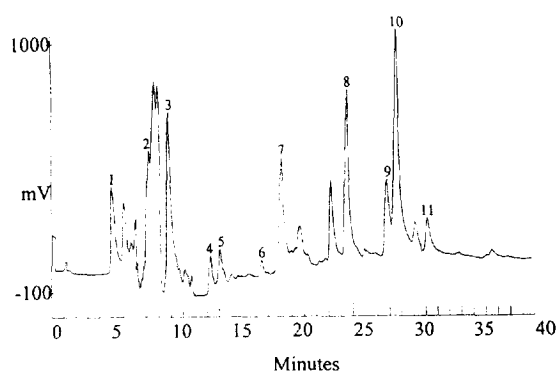

Fig. 2. SFC–fluorescence chromatogram. For chromatographic conditions see Fig. 1. Fluorescence wavelengths (excitation/emission) are given in brackets: 1 = naphthalene (210 nm/328 nm); 2 = acenaphthene (220 nm/338 nm); 3 = fluorene (200 nm/310 nm); 4 = phenanthrene (240 nm/372 nm); 5 = anthracene (240 nm/372 nm); 6 = fluoranthene (234 nm/432 nm); 7 = pyrene (236 nm/414 nm); 8 = chrysene (256 nm/380 nm); 9 = benzo[*b*]fluoranthene (240 nm/430 nm); 10 = benzo[*k*]fluoranthene (240 nm/430 nm); 11 = benzo[*a*]pyrene (252 nm/418 nm).

Table 5
Comparison of different analysis methods; for detailed description see text

Compound	Sample 1			Sample 2			Sample 3		
	RWTÜV (ng/m^3)	SFE–SFC (ng/m^3)	SFE–HPLC (ng/m^3)	RWTÜV (ng/m^3)	SFE–SFC (ng/m^3)	SFE–HPLC (ng/m^3)	RWTÜV (ng/m^3)	SFE–SFC (ng/m^3)	SFE–HPLC (ng/m^3)
Naphthalene	1754	n.d.	54470	2625	6750	10340	3067	n.d.	27940
Acenaphthene	10088	710	1750	8831	800	820	6444	820	1170
Fluorene	2083	1030	1220	2076	900	960	1689	840	810
Phenanthrene	1820	1010	1360	1766	790	1060	1511	740	990
Anthracene	n.d.[a]	230	230	n.d.	140	130	n.d.	80	50
Fluoranthene	175	320	340	47.7	70	230	44.4	[b]	200
Pyrene	88	430	490	14.3	340	410	67	350	370
Benz[*a*]anthracene	n.d.	n.d.	440	n.d.	n.d.	200	n.d.	n.d.	240
Chrysene	66	210	300	35.8	50	80	44.4	30	60
Benzo[*b*]fluoranthene	55	260	260	23.9	90	60	22.2	70	30
Benzo[*k*]fluoranthene	21.9	110	90	16.7	50	20	17.8	50	10
Benzo[*a*]pyrene	32.9	90	70	23.9	40	20	22.2	60	10

[a] n.d. = not determined, because of peak overlapping.
[b] – Not detected.

The smaller PUF plugs of the three sampling intervals were extracted with the described SFE method. In order to check the SFC results all extracts were analysed using both HPLC and SFC. Figs. 2 and 3 show the corresponding SFC and HPLC chromatograms of sample 1. The chromatograms and Table 5 show that the waste gas consists mainly of two- and three-ring PAHs. The agreement between SFC and HPLC results indicates that SFC using fluorescence detection may be a competitive way to analyse PAHs.

The results of the SFE–SFC monitoring system differ from those of the reference laboratory (Table 5). For naphthalene, acenaphthene, fluorene and phenanthrene the RWTÜV obtained higher concentrations than we did. For all other components the concentrations were lower. This fact is assumed to be caused mainly by differences in the sampling technique (gas volume and PUF size) and not by the extraction method. To verify this a comparison of both sampling techniques is under present investigation.

However, Table 5 illustrates that the PAH concentration pattern obtained with both methods correlates well. Thus the SFE–SFC method can now be used as a fast monitoring system for PAHs.

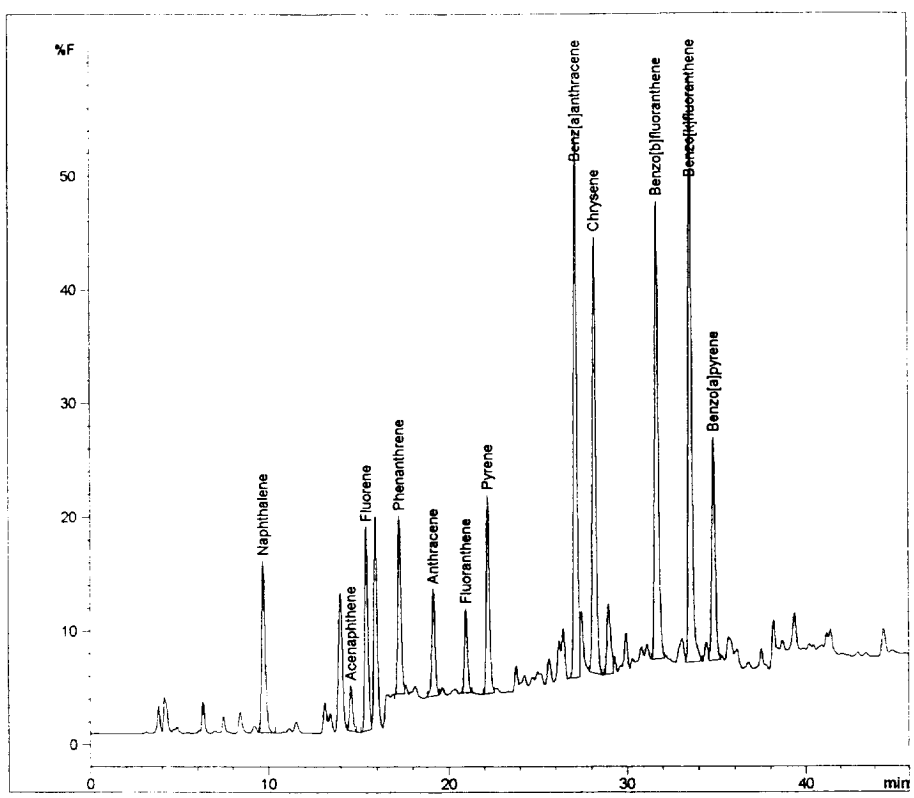

Fig. 3. HPLC–fluorescence chromatogram. Chromatographic conditions: flow-rate 0.5 ml/min, mobile phase acetonitrile–water (50:50, v:v), initially for 6 min, then programmed to 99:1 (v:v) in 29 min. Fluorescence wavelengths (excitation/emission) are given in brackets: naphthalene, acenaphthene (210 nm/320 nm); phenanthrene, anthracene (248 nm/384 nm); fluorene, pyrene (236 nm/430 nm); benz[*a*]anthracene, chrysene (270 nm/390 nm); benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene (250 nm/440 nm); dibenz[*a,h*]anthracene, benzo[*ghi*]perylene (296 nm/405 nm); indeno[1,2,3-*c,d*]pyrene (245 nm/480 nm).

4. Conclusions

The aim of this work was to simplify the measurement of PAHs in exhaust gas emissions. Conventional methods are time-consuming and use relatively large quantities of potentially harmful organic solvents. The new off-line SFE–SFC system reduces both the analysis time and the amount of solvents. The latter aspect is of high importance with respect to the fact that a solvent-free method may be used in a mobile lab for on-site analysis. Fast on-site measurements for quasi-continuous monitoring of emission sources are important tools for the reduction of emissions.

The SFE–SFC system was compared with a standard method. The results of this comparison show that the PAH concentration patterns obtained with both methods correlate very well. However, there are some differences in the absolute concentration values. It is assumed that these are caused mainly by differences in the sampling techniques.

In conclusion these first results of the recently developed method show that methods using supercritical fluids are powerful technologies. Using SFE and SFC it is possible to reduce the quantity of toxic organic solvents and to shorten and simplify sample preparation. In a further step it may be possible to construct a fully automated monitoring system not attainable with classical methods.

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