

Scope

In food polycyclic aromatic hydrocarbons (PAH) emanate primarily from processing practices like heating, drying, smoking, roasting or charcoal grilling. They are combustion products and are most likely adsorbed onto smoke particles settling on all kinds of surfaces and thus can also be found in rivers and groundwater [1]. The Drinking Water Directive (98/83/EC) [2] sets the maximum level for benzo[a]pyrene (BaP) at 0.010 µg/L, and for the sum of benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[g,h,i]perylene (BgP) and indeno[1,2,3-cd]pyrene (IcP) at 0.10 µg/L. To determinate these limit values in the ultra trace level, enrichment techniques like stir-bar sorptive extraction (SBSE) are necessary. In 2006 a review [3] about the current legislative situation of PAH analysis in the European Union was published, which emphasized the **needs for further investigations and analytical research** for new EU legislation of food and environment.

Results and discussion

The SBSE workflow (Fig. 1) enabled a **faster** sample throughput than liquid/liquid extraction according to ISO 7981-1:2005.

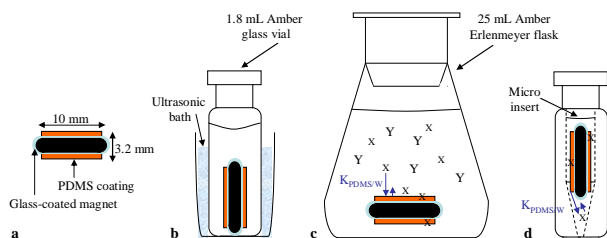


Fig. 1: SBSE and its workflow (a) layers of the twister with 0.5 mm polydimethylsiloxane (PDMS) coating (Gerstel), (b) cleaning of the twister with first isopropyl acetate-methanol 3:2 (v/v) and then acetonitrile, both for 10 min in a vial placed in an ultrasonic bath followed by 3 min N₂-drying, (c) extraction process of 10 mL water sample, and (d) liquid micro desorption in a 300 µL micro-insert filled with 150 µL acetonitrile.

The optimized chromatographic system included HPTLC plates silica gel 60, impregnated with a solution of 1.7 % caffeine in acetonitrile, using isopropyl acetate - acetonitrile 7:3 (v/v) as mobile phase. After documentation of the plate images with DigiStore 2, **digital detection** and quantification with VideoScan, was compared to quantification after conventional scanning by TLC Scanner 3 (all from CAMAG). A comparable quality of the calibration curve (Table 1) was obtained by both methods.

Table 1: Conventional scanning versus digital detection

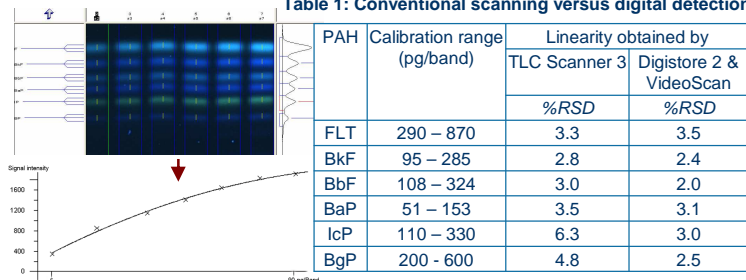


Fig. 2: Calibration curve obtained by a digital evaluation by DigiStore 2/VideoScan

PAH **recoveries** using the same twister were between 87–100% ± 0.4 - 6 % (n = 3) depending on the PAH, and using 3 different twistors between 77 – 103 % ± 1 – 5 %. The **repeatabilities** (%RSD, n = 3, 10 – 58 ng/L depending on the PAH) using the same twister were between 0.4 and 6.3 % and using 3 different twistors between 0.8 and 7.0 %. The **LOQ** in matrix was established to be between 84 and 520 pg/band depending on the PAH and between 80 and 435 pg/band for standards. Extracting a 10 mL-sample, LOQs in the range of 8 and 52 ng/L were determined. Starting with a standard level around the LOQ, satisfying coefficients of correlation $r \geq 0.9920$ and standard deviation (%RSD) ≤ 6.3 % were obtained (Fig. 3).

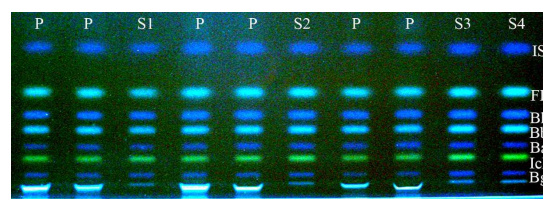


Fig. 3: Digital documentation at UV 366 nm of the analysis of PAH in drinking water: different drinking water samples (P, spiked with PAH) and standards (S) between 0.1 and 0.9 ng/band depending on the PAH (IS: control standard)

The cleaning of the twistors by thermal desorption using the tube conditioner (Gerstel) was compared with drying at room temperature, both using nitrogen gas. The results indicated, that the use of **thermal cleaning** was not justified.

The usage of three commercially available, inexpensive **silicone tube** pieces (Table 2) put on magnetic stir bars as a kind of PDMS coating substitute was also investigated for PAH analysis.

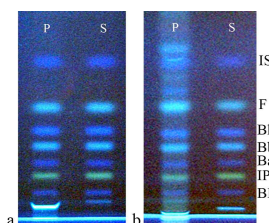


Table 2: Comparison of three silicone tubes

Recoveries (%) for	BgP	IcP	BaP	BbF	BkF	FLT
Tube 1 No. 14244	28	33	31	39	35	104
Tube 2 No. 14248	44	40	39	34	32	105
Tube 3 No. 28731	59	61	71	76	75	105

Fig. 4: Comparison of the extraction of a spiked ultrapure water sample (P) related to a standard track (S) by (a) a commercially available twister and (b) hand-made stir bar (silicon tubes from Reichelt Chemietechnik, Heidelberg)

Even a copious cleaning procedure was not sufficient for proper cleaning of the silicone tubes, which arose in the higher background noise (Fig. 4). The usage of the twistors was much more comfortable and the manufacturer guaranteed their purity.

Conclusion

In comparison to hitherto existing methods, the HPTLC/FLD method for determination of PAH in drinking water [4] is a **low-cost, rapid and minimized alternative**. The avoidance of chlorine-free solvents for cleaning of the twister, plate impregnation and the mobile phase allowed a more environmentally friendly analytical system. This method was reliable for control of the limit levels for BaP and the sum of BkF, BbF, IcP and BgP. It was possible to extract and analyze **30 water samples** within an 8-hour shift.

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- [1] L. Sarrazin et al., J Liq Chromatogr Rel Technol 29 (2006) 69-85
- [2] European Commission. Directive 98/83/EC, Off J Eur Comm L330 (1998) 32-54
- [3] T. Wenzl et al., Trends in Anal Chem 7 (2006) 716-725
- [4] G. Morlock, S. Kopacz, J Liq Chromatogr Rel Technol, in press