

## Short Communication

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# Determination of polycyclic aromatic hydrocarbons from bitumen concrete roads in drainage water by microextraction, large-volume sampling and gas chromatography–mass spectrometry with selected ion monitoring

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### ABSTRACT

A method for the determination of ppt levels of polycyclic aromatic hydrocarbons in drinking and drainage water based on microextraction, large-volume injection of a toluene extract into a split–splitless injector and gas chromatography–mass spectrometry with selected ion monitoring is described. The elimination of solvent from the target analytes by controlling the temperature of the injector equipped with a liner packed with Chromosorb W coated with OV-1 was achieved.

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### INTRODUCTION

A possible contamination threat to ground water appeared when bitumen concrete was used as a road construction material. By mass, this type of concrete contains 1.5–2.0% of road tars; the basic compounds present in these tars, such as polycyclic aromatic hydrocarbons (PAHs) are partially soluble in water [1]. Therefore, all “eluates” from this material such as rain water and drainage water could be contaminated and could threaten ground water. Many PAHs are serious environmental contaminants because of

their carcinogenicity, mutagenicity and toxicity. The US EPA lists sixteen PAHs as “priority pollutants” of the environment. Under the standards adopted by the European Community (Netherlands), the reference concentration of PAHs (the *A* limit) in ground water for the most dangerous PAH, benzo[*a*]pyrene, is  $10 \text{ ng l}^{-1}$ , for fluoranthene and pyrene  $20 \text{ ng l}^{-1}$  and for phenanthrene and anthracene  $100 \text{ ng l}^{-1}$  [2].

For the analysis of such very dilute samples, preconcentration and selective pre separation are required in order to achieve the required sensitivity. For preconcentration and clean-up of environmental samples, microextraction has been widely utilized. The enrichment factors obtained, *i.e.*,  $10^2$ – $10^3$ , can be increased to  $10^5$  by further

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preconcentration of the extracts with the aid of large-volume sampling. The introduction of large-volume sampling in capillary gas chromatography (GC) is becoming increasingly important in various application areas [3], especially in the analysis of very dilute environmental samples [4].

The analysis of such extracts is greatly facilitated by using GC–mass spectrometry with selected ion monitoring (MS-SIM) owing to the reduced matrix interference for components of interest. Selective detection by MS-SIM results in improved detection limits and leads to more reliable analytical results.

The aim of this work was to study the applicability of the off-line coupling of microextraction of PAHs from water with large-volume sampling of extracts using a split–splitless injector for GC–MS-SIM analysis of ppt and sub-ppt concentrations of PAHs in drainage water from bitumen concrete roads and in drinking water respectively.

## EXPERIMENTAL

### Materials

The test blocks were made of either bitumen concrete or bitumen-free concrete. They were 138 mm high and 20 mm wide. The test blocks were extracted with 1500 ml of drinking water (the water to block surface area ratio was 10 ml of water to 1 cm<sup>2</sup> of surface area) during a 7-day period at 20 ± 2°C. A 1000-ml volume of each extract was used for PAH determination.

All solvents used were of analytical-reagent grade or of higher purity (Merck, Darmstadt, Germany). All individual PAHs used were of 99% minimum purity.

### Instrumentation

An HP 5890 Series II gas chromatograph was equipped with a split–splitless capillary inlet injector. Helium was used as the carrier gas. An HP 5971A mass-selective detector was used for detection with an ionization energy of 70 eV. Selected ion monitoring was used for the detection of selected PAH ions (*m/z* 154, 178, 202, 228, 252, 276, 300 and 302) [1]. The measured values and resulting characteristics were pro-

cessed by the computer which is part of the GC–MS system.

### GC analysis

A glass capillary column (20 m × 320 μm I.D.), coated with OV-1 and immobilized by γ-irradiation as the stationary phase with a film thickness of 0.4 μm, was used for the separation of PAHs. The separation was temperature programmed with an isothermal period at 80°C for 16 min, then increased at 15°C min<sup>-1</sup> to 300°C and an isothermal period at 300°C for 6 min.

### Microextraction of PAHs

A volume of 800 ml of water was extracted with 2 ml of toluene for 1 min with intensive shaking, followed by ultrasonic extraction for 10 min at ambient temperature (Tesla UG 160/320 TA). For the determination of PAHs in drinking water, 1 ml of the toluene extract layer [5] was then transferred into a glass separator and preconcentrated to 250 μl. For the analysis of the drainage water, the large extract volumes were introduced into the injector linear without any preconcentration. A model sample of PAHs in water was prepared from drinking water and 80 μl of PAH solution in methanol.

### Large-volume sampling

All injections were made with a 100-μl injection syringe (Hamilton). The injection port was rearranged with a splitless insert of 4 mm I.D. (Hewlett-Packard). The insert was packed like a short packed column with silanized Chromosorb W (60–80 mesh) coated with 4% (w/w) of OV-1 stationary phase immobilized by dicumyl peroxide. The length of the packing material was 5 cm. After the flash injection of 70 μl of sample (100 μl s<sup>-1</sup>), the solvent was purged out using a split with a purge flow of 60 ml min<sup>-1</sup> helium 80°C (*i.e.*, 30°C below the boiling point of toluene used as the solvent) for 2.8 min. After this split period, the system was turned to the splitless mode and the injection port was heated ballistically to 300°C for 5 min for thermal desorption of the analyte compounds. Because the head of the analytical capillary column was still at 80°C, thermally desorbed compounds condensed in it. After 16 min this preconcentration

period was stopped, the split was opened, the injection port was cooled to 80°C and the analysis was continued with the temperature programme of the capillary column.

### Quantification

Quantitative data were obtained on the basis of external calibration.

## RESULTS AND DISCUSSION

The reproducibilities of peak areas from seven replicate measurements for large-volume injection of 70  $\mu\text{l}$  of a standard PAH sample with corresponding concentrations of 1 and 10  $\text{ng l}^{-1}$  in water are given in Tables I and II. The average precision of peak-area measurement of PAHs for a 1  $\text{ng l}^{-1}$  concentration is 21.4% and for 10  $\text{ng l}^{-1}$  it is 11.6%; hence, according to expectation, the precision of peak-area measurements increases with increasing concentration of PAHs. The detection limits that were calculated on the basis of the average peak areas of PAHs for a concentration of 1  $\text{ng l}^{-1}$  and their standard deviations for the 99% confidence level are also given in Table I. It is clear from Table I that the detection limits of PAHs for large-volume injection are in the range 0.2–1  $\text{ng l}^{-1}$ .

TABLE I

REPRODUCIBILITY OF PEAK AREAS OF PAH STANDARDS AT A CONCENTRATION OF 1  $\text{ng l}^{-1}$  (ppt) PER COMPOUND

$X$  = average peak area measured from seven trials; S.D. = standard deviation; R.S.D. = relative standard deviation; MDL = method detection limit.

| PAH                             | $X$    | S.D.   | R.S.D. (%) | MDL (ppt) |
|---------------------------------|--------|--------|------------|-----------|
| Phenanthrene                    | 36 426 | 6798   | 18.7       | 0.7       |
| Anthracene                      | 38 615 | 10 250 | 26.5       | 0.9       |
| Fluoranthene                    | 40 043 | 8751   | 21.8       | 0.8       |
| Pyrene                          | 37 768 | 5812   | 15.3       | 0.6       |
| Benz[ <i>a</i> ]anthracene      | 22 315 | 6127   | 27.3       | 1.0       |
| Chryzene                        | 31 951 | 9385   | 29.4       | 1.1       |
| Benzo[ <i>b</i> ]fluoranthene   | 28 380 | 6254   | 22.0       | 0.8       |
| Benzo[ <i>k</i> ]fluoranthene   | 35 365 | 2287   | 6.5        | 0.2       |
| Benzo[ <i>e</i> ]pyrene         | 35 851 | 8432   | 25.0       | 0.9       |
| Benzo[ <i>a</i> ]pyrene         | 19 933 | 4527   | 22.7       | 0.8       |
| Perylene                        | 46 493 | 9815   | 21.1       | 0.8       |
| Indeno[1,2,3- <i>cd</i> ]pyrene | 25 720 | 5062   | 20.0       | 0.7       |

TABLE II

REPRODUCIBILITY OF PEAK AREAS OF PAH STANDARDS FOR A CONCENTRATION OF 10  $\text{ng l}^{-1}$  (ppt) PER COMPOUND

Abbreviations as in Table I.

| PAH                             | $X$     | SD     | R.S.D. (%) |
|---------------------------------|---------|--------|------------|
| Phenanthrene                    | 141 149 | 13 979 | 9.9        |
| Anthracene                      | 145 145 | 17 925 | 11.7       |
| Fluoranthene                    | 166 390 | 19 933 | 12.0       |
| Pyrene                          | 153 717 | 15 495 | 10.1       |
| Benz[ <i>a</i> ]anthracene      | 81 840  | 7739   | 9.5        |
| Chryzene                        | 119 259 | 11 013 | 9.2        |
| Benzo[ <i>b</i> ]fluoranthene   | 99 852  | 9707   | 9.7        |
| Benzo[ <i>k</i> ]fluoranthene   | 126 642 | 15 608 | 12.3       |
| Benzo[ <i>e</i> ]pyrene         | 114 262 | 11 627 | 10.2       |
| Benzo[ <i>a</i> ]pyrene         | 63 955  | 7924   | 12.3       |
| Perylen                         | 131 853 | 5961   | 19.7       |
| Indeno[1,2,3- <i>cd</i> ]pyrene | 97 284  | 11 972 | 12.3       |

The average PAH recoveries by liquid–liquid microextraction from water and large-volume sampling for three concentration levels, obtained from three measurements, are given in Table III. The recoveries of the compounds were calculated from the normalized peak areas for spiked samples of water and reference solutions using large-volume sampling (70  $\mu\text{l}$ ). The results show

TABLE III

## PAH RECOVERY BY LIQUID-LIQUID MICROEXTRACTION FROM WATER AND LARGE-VOLUME SAMPLING AT VARIOUS PAH CONCENTRATIONS

Average results for three measurements.

| PAH            | Concentration (ng l <sup>-1</sup> ) |            |              |            |              |            |
|----------------|-------------------------------------|------------|--------------|------------|--------------|------------|
|                | 10                                  |            | 50           |            | 100          |            |
|                | Recovery (%)                        | R.S.D. (%) | Recovery (%) | R.S.D. (%) | Recovery (%) | R.S.D. (%) |
| Phenanthrene   | 186                                 | 136        | 97.8         | 2.7        | 94.1         | 3.4        |
| Anthracene     | 170                                 | 66         | 77.8         | 3.2        | 77.8         | 9.6        |
| Fluoranthene   | 137                                 | 21         | 84.6         | 3.4        | 97.9         | 2.1        |
| Pyrene         | 130                                 | 25         | 83.9         | 3.4        | 97.1         | 0.9        |
| Chrysene       | 130                                 | 19         | 83.9         | 7.6        | 71.8         | 2.1        |
| Benzo[a]pyrene | 106                                 | 37         | 48.1         | 6.2        | 44.6         | 4.2        |
| Perylene       | 93                                  | 16         | 53.1         | 2.9        | 43.0         | 2.8        |

that relatively high recoveries and good reproducibilities for concentrations of 50 and 100 ng l<sup>-1</sup> of individual PAHs were achieved. The higher recoveries and higher R.S.D. values for lower concentrations (10 ng l<sup>-1</sup>) of PAHs (in comparison with those in Table II) may be caused by the presence of interfering compounds in the water analysed in the former instance and because the whole analytical procedure is included in the latter. The interference may in-

fluence the quantitative results of the GC-MS-SIM determination of PAHs at lower concentration levels.

The method was applied to the ultra-trace determination of PAHs in drinking water and in water extracts of bitumen concretes and bitumen-free concretes. The chromatogram of PAHs from a tar used for bitumen concrete test blocks is shown in Fig. 1, that of PAHs from drinking water used for leaching the concrete

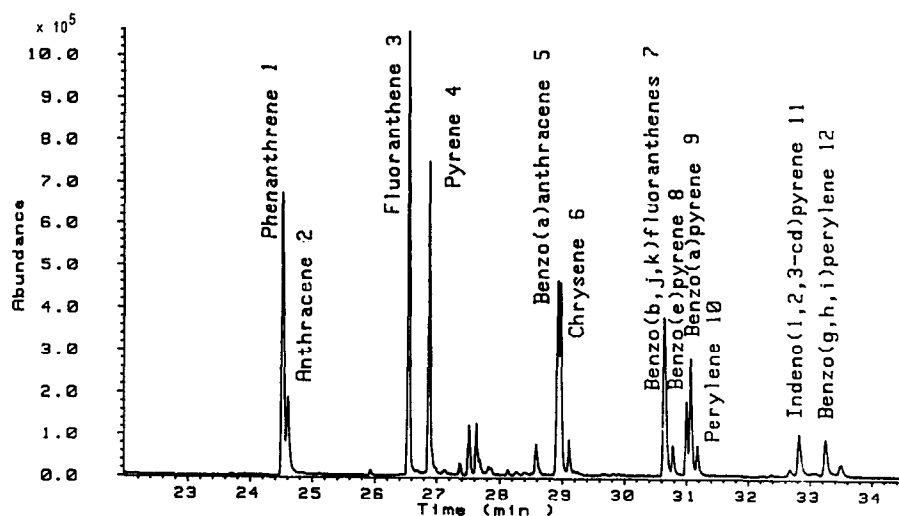


Fig. 1. Chromatogram of PAHs from tar obtained by GC-MS-SIM.

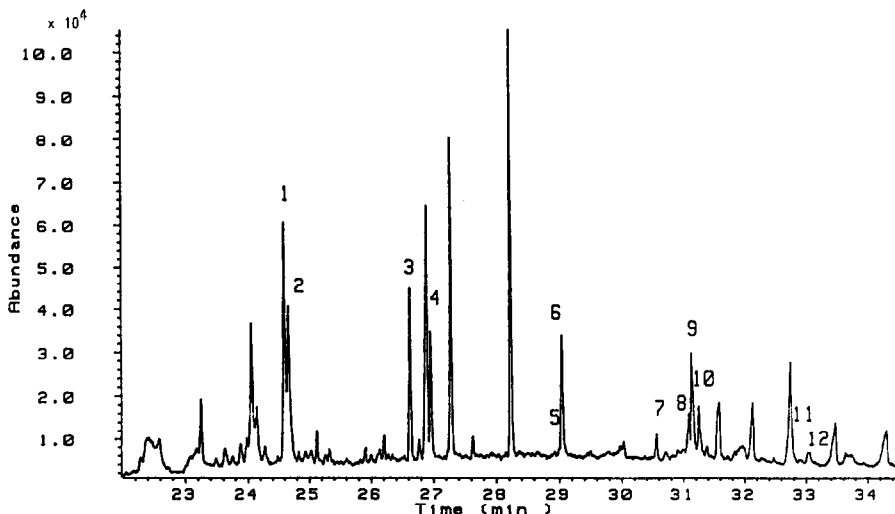


Fig. 2. Chromatogram of PAHs from drinking water obtained by GC-MS-SIM. Peak identifications as in Fig. 1.

test blocks in Fig. 2 and that of PAHs from the drainage water of bitumen concrete test blocks in Fig. 3. The results for the determination of PAHs in these samples by using the external standard method are given in Table IV. The concentration of PAHs in the drinking water sample are in the range  $0.7\text{--}3.5\text{ ng l}^{-1}$  (ppt) (and lower than these values in the case of co-elution PAHs with impurities) and in the drainage water in the range  $4\text{--}15\,000\text{ ng l}^{-1}$ . The latter results can be correlated with the characteristics of the water solubility of PAHs [1], which decreases

with increasing number of condensed rings in the PAH molecule. Nevertheless, the PAH isomers with a linear structure, *e.g.*, anthracene, are less soluble than those of an angular structure (phenanthrene). However, micelle formation by detergents and other soluble organic compounds can increase the solubility of PAHs [1]. The relatively high concentrations of PAHs determined in bitumen-free concrete probably resulted from contamination of the cement during the burning period in its manufacture (*e.g.*, burning of used tyres).

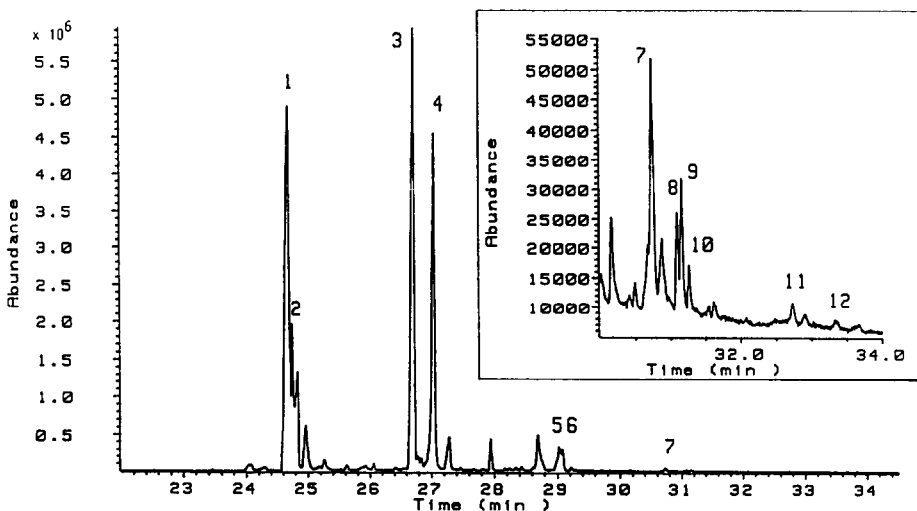


Fig. 3. Chromatogram of PAHs from drainage water obtained by GC-MS-SIM. Peak identifications as in Fig. 1.

TABLE IV  
PAH CONCENTRATIONS IN WATER SAMPLES AND THEIR SOLUBILITY IN WATER AT 25°C

| PAH                              | Concentration (ng l <sup>-1</sup> ) |                              |                         | Solubility in water (ng l <sup>-1</sup> ) |
|----------------------------------|-------------------------------------|------------------------------|-------------------------|---|
|                                  | Drinking water                      | Bitumen-free concrete eluate | Bitumen concrete eluate |   |
| Phenanthrene                     | 2.6                                 | 26.0                         | 13 600                  | 1 290 000                                 |
| Anthracene                       | 1.8                                 | 9.0                          | 4700                    | 73 000                                    |
| Fluoranthene                     | 3.5                                 | 326.0                        | 15 000                  | 260 000                                   |
| Pyrene                           | 2.5                                 | 888.0                        | 11 500                  | 135 000                                   |
| Benz[ <i>a</i> ]anthracene       | ND <sup>a</sup>                     | 68.0                         | 920                     | 14 000                                    |
| Chryzene                         | 3.0                                 | 64.0                         | 600                     | 2000                                      |
| Benzo[ <i>b,jk</i> ]fluoranthene | 0.7                                 | 25.0                         | 150                     | –   |
| Benzo[ <i>e</i> ]pyrene          | 1.5                                 | 10.0                         | 40                      | 3800                                      |
| Benzo[ <i>a</i> ]pyrene          | 3.2                                 | 16.0                         | 60                      | 400                                       |
| Perylene                         | 2.8                                 | 5.0                          | 17                      | 400                                       |
| Indeno[1,2,3- <i>cd</i> ]pyrene  | ND                                  | 2.0                          | 5                       | –   |
| Benzo[ <i>ghi</i> ]perylene      | ND                                  | 1.5                          | 4                       | 300                                       |

<sup>a</sup> ND = not determined.

The results obtained indicate that owing to the extremely high enrichment factors connected with the use of microextraction and large-volume sampling, and application of MS-SIM detection, the proposed method allows the determination of PAHs at ppt concentrations in drinking and contaminated waters.

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