

## Note

---

### Simple method for determination of polynuclear aromatic hydrocarbons in soil by clean-up on XAD-2

TORSTEN SPITZER\* and SHOZO KUWATSUKA

*Nagoya University, Faculty of Agriculture, Department of Soil Science, Furo-cho, Chikusa-ku, Nagoya 464 (Japan)*

(Received January 3rd, 1986)

The occurrence in the environment of polynuclear aromatic hydrocarbons (PAHs) with three to six condensed benzene rings has been confirmed by various investigations<sup>1-3</sup>. PAHs originating from combustion processes have also been found in airborne particulate matter<sup>4-6</sup>. Such particles finally settle on the ground, so PAHs that are not decomposed in the atmosphere are transferred into the soil. A great variety of PAHs can therefore be expected to be found in soil, originating either naturally (e.g. forest fires) or non-naturally (e.g. traffic or industry). In addition to these sources, perylene is believed to be generated naturally from plant material under reducing conditions<sup>7</sup>. PAHs in airborne particles normally occur at concentrations between 10 and 100 ppm<sup>8</sup>, and such relatively high concentrations facilitate their determination. In soil, however, individual PAHs are found at concentrations ranging from 1 to 100 ppb, which is four orders of magnitude lower, so their determination of PAHs requires extremely efficient clean-up. Since large sample numbers often have to be processed in order to compare PAH profiles from different sources, there is a need for a simple and efficient analytical procedure. Clean-up of PAHs on XAD-2 has proved valuable in analysis of airborne particles<sup>9</sup>, and this method has now been extended to soil samples.

#### EXPERIMENTAL

##### *Sample preparation*

A soil sample was taken from an urban area (Tomakomai, Hokkaido, Japan), in a park 50 m off a busy main road. The sampling depth was 0-5 cm. Grass and weeds were separated from the sample, and 20 g of the soil were filled into a glass-fibre extraction thimble (Schleicher & Schull, G.F.R.) and dried on silica gel in a desiccator at 37°C for 36 h.

##### *Extraction*

The sample was placed in a Soxhlet extraction apparatus and extracted with a mixture of ethanol (10 ml) and toluene (200 ml) for 4 h. The crude extracts were concentrated to 2 ml with a rotary evaporator.

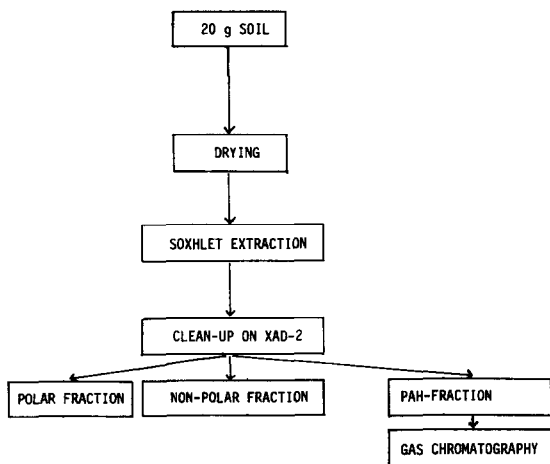


Fig. 1. Analytical procedure for determining PAHs in soil.

### *Clean-up*

Crude extracts (0.5 ml) were applied to the top of a column (1.2 cm I.D.) filled with XAD-2 to a height of 9 cm. Prior to analysis, the column was washed with 30 ml toluene and 25 ml ethanol. A toluene fraction was isolated according to the procedure outlined earlier<sup>9</sup>.

### *Recoveries*

A 20-g sample of pre-extracted soil was spiked with five PAHs at concentrations between 30 and 350 ppb. PAHs were then isolated by the procedure described in Fig. 1. The drying procedure, however, was prolonged to 8 days at 37°C, in order to investigate whether any loss of PAHs occurred by vaporization. PAHs were determined quantitatively by capillary gas chromatography (GC) using SE-54 as a stationary phase. A Hitachi 263 gas chromatograph adapted for capillary columns was used.

## RESULTS AND DISCUSSION

Sample preparation, extraction and clean-up are all critical steps in PAH determination in soil. Air-drying is a common practice in soil analysis, but it should not be carried out in PAH determination, unless particulate-free, purified air is being used. In this work samples were dried in a desiccator with silica gel as a drying agent. A temperature of 37°C was selected, at which the drying will be completed in a shorter time than at ambient temperature, and the drying was carried out for 36 h only. Since the whole drying process depends on the surface area and thus on the arrangement of the soil in the desiccator, the samples were put into beakers and the beakers were then placed in the desiccator, in order to achieve reproducible results. The samples will not be completely dry after 36 h, but small amounts of residual water will later be removed during extraction. However, soil often has a moisture content as high as 50% or more, and large amounts of water disturb the analysis if a separate aqueous phase is formed after extraction.

TABLE I  
RECOVERIES OF PAHs FROM SOIL

<i>Compound</i>	<i>Concentration (ppb)</i>	<i>Recovery (%)</i>
Pyrene	350	91
Benz( <i>a</i> )anthracene	159	93
Benzo( <i>k</i> )fluoranthene	30	100
Benzo( <i>e</i> )pyrene	135	100
Perylene	70	100

Losses of PAHs with four to six rings did not occur. Recoveries obtained after 8 days of drying at 37°C are listed in Table I.

Toluene is the most efficient solvent in PAH extraction, but its immiscibility with water is a disadvantage if the soil to be extracted contains residual moisture that may block the access of toluene to PAH adsorption sites. If this occurs, extraction can be improved by employing a mixture of ethanol and toluene. Ethanol boils first, and the material to be extracted will be wetted by ethanol, before toluene reaches its boiling point and distills into the extraction chamber. The toluene content will then rise gradually, and a quantitative recovery of PAHs will be assured. Toluene cannot extract large amounts of polar materials from samples, so toluene extracts contain limited amounts of coextractants other than PAHs, and clean-up is easy. Adversely, ethanol extracts additional polar materials, which might interfere with PAH clean-up. Clean-up on XAD-2 can cope with polar coextractants and provides a clean PAH mixture. The addition of ethanol to toluene in extraction has no detrimental effect on recoveries of PAHs with four to six rings, as indicated in Table I, where the recoveries listed are close to 100%.

Almost all interfering substances could be removed from crude extracts by clean-up on XAD-2, and the resultant PAH fractions could be submitted to capillary GC directly. If high concentrations of polychlorinated biphenyl (PCB) compounds are present in soil, interference with PAHs might occur after clean-up on XAD-2. However, such interference was not observed in the samples analysed until now. Approximately 70% of PCBs will be found in the pentane fraction, and about 30% will be coeluted with PAHs. Normally, total PCB concentration in soil is less than 10 ppb\*, so each PCB is less than 0.1 ppb (if there are 100 peaks of about the same height). No peaks resulting from PCBs were observed in the gas chromatograms of samples analysed in this work, with flame ionization detection (FID). Finally, the analytical procedure developed here was applied on a soil sample taken in a Japanese city (Tomakomai, Hokkaido, Japan). Concentrations of PAHs in this sample were in the range 5–50 ppb. Fig. 2 displays the FID gas chromatogram obtained from the PAH fraction of this sample. Pyrene (peak 3) slightly exceeds fluoranthene (peak 2). This ratio occasionally occurs, although the two compounds are normally present in roughly equivalent amounts. The other PAHs display a pattern similar to that of PAHs in airborne particulate matter. Benzo(*a*)pyrene occurs at a slightly lower con-

\* Throughout this article the American billion ( $10^9$ ) is meant.

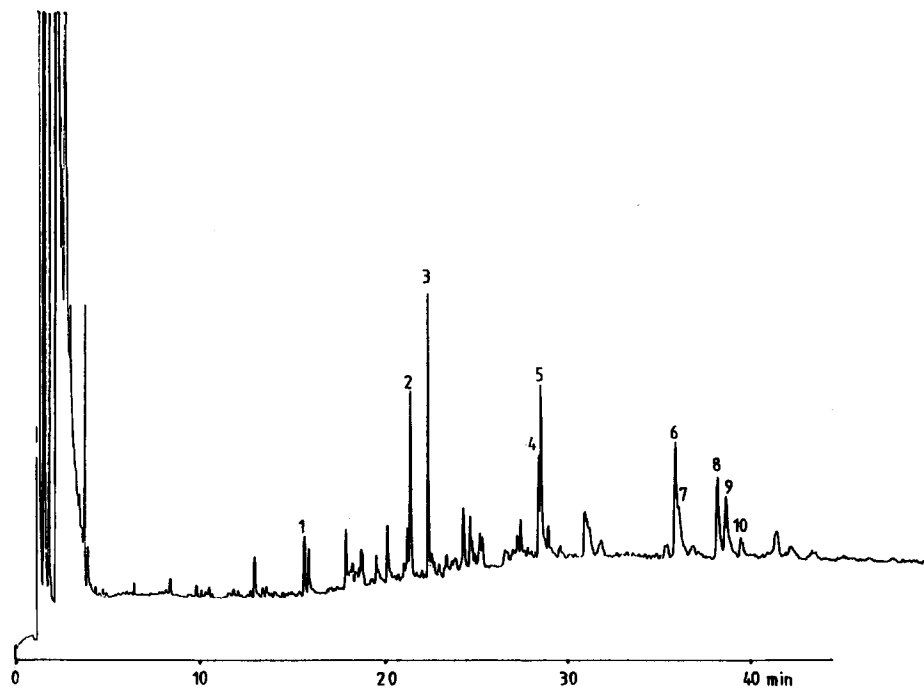


Fig. 2. Gas chromatogram of PAHs isolated from soil in Tomakomai, Hokkaido, Japan. Peaks: 1 = phenanthrene; 2 = fluoranthene; 3 = pyrene; 4 = benz(a)anthracene; 5 = chrysene; 6 = benzo(b+j)fluoranthene; 7 = benzo(k)fluoranthene; 8 = benzo(e)pyrene; 9 = benzo(a)pyrene; 10 = perylene. GC conditions: column, fused-silica coated with SE-54 (25 m); carrier gas, nitrogen; temperature programme, 110°C to 250°C at 5°C/min.

centration than benzo(e)pyrene, which is to be expected because benzo(a)pyrene decomposes faster than benzo(e)pyrene in the environment. It must be emphasized that the clean-up procedure employs simple and cheap equipment and chemicals, and takes only 30 min to complete.

#### CONCLUSION

Clean-up on XAD-2 rapidly separates PAHs from the toluene-ethanol extract of soil. The procedure can be used even if concentrations of PAHs in the soil are as low as several ppb.

#### REFERENCES

- 1 M. Heit, *Water, Air and Soil Pollution*, 24 (1985) 41-61.
- 2 M. Heit, Y. Tan, C. Klusek and J. C. Burke, *Water, Air and Soil Pollution*, 15 (1981) 441.
- 3 R. E. LaFlamme and R. A. Hites, *Geochim. Cosmochim. Acta*, 42 (1978) 289.
- 4 T. Spitzer and W. Dannecker, *Anal. Chem.*, 55 (1983) 2226.
- 5 J. König, W. Funcke, E. Balfanz, B. Grosch and F. Pott, *Atmos. Environ.*, 14 (1980) 609.
- 6 G. Grimmer, K. W. Naujack and D. Schneider, *J. Environ. Anal. Chem.*, 10 (1981) 265.
- 7 Z. Aizenshtat, *Geochim. Cosmochim. Acta*, 37 (1973) 559.
- 8 T. Spitzer, *Ph.D. Thesis*, University of Hamburg, Hamburg, 1982.
- 9 T. Spitzer, *J. Chromatogr.*, 237 (1982) 273.