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Note

Trace analysis of organic pollutants in air by polymer adsorption and dual flame ionization detection–electron-capture detection capillary gas chromatography

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Reported methods for the determination of volatile organic compounds in air at the low microgram per cubic metre concentration level include sample enrichment procedures followed by gas chromatography (GC) and/or mass spectrometry. Although developed only recently, the coupling of preconcentration techniques with capillary GC is well documented[1,2].

The methods described generally involve *in situ* adsorption of the volatiles on a suitable adsorbent (generally active charcoal[3,4] or porous polymers[5], the adsorbed compounds being later recovered by solvent elution[3,4,6] or thermal desorption[7]. The use of electrically heated desorbers needs particular care because the large injection volumes of the desorbed volatiles are not compatible with the injection volumes required for capillary GC work, implying the application of a special technique in order to avoid intolerable "broadening in time".

Split injection is able to restore the sharpness of the peak profiles but severely impairs the sensitivity of the method. The full performance of an electrically heated thermal desorption system can only be obtained with direct injection combined with a focusing technique, assuring "plug-type" injection of the whole desorbate. Such methods include trapping in thick stationary phase films[8] or cold trapping[9].

This paper reports the optimization of a commercially available thermal desorption and cold trap device in conjunction with capillary GC and dual flame ionization detection–electron-capture detection (FID–ECD) for the routine trace analysis of C_6–C_{20} air pollutants.

MATERIALS AND METHODS

Air sampling

The sampling was performed by adsorption and enrichment on polymer cartridges, according to a method described by Pellizari *et al.*[7]. The volatiles were trapped at a pumping rate of 23 l/h on two adsorbing cartridges assembled in series by means of 0.25 in. Swagelok® fittings. The cartridges were Pyrex tubes (15 cm × 6 mm O.D.), each filled with 90 mg of Tenax* T.A. 60–80 mesh (Chrompack).

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* Tenax is a porous polymer based on 2,6-diphenyl-*para*-phenylene oxide and manufactured by AKZO Research Laboratories.

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Immediately prior to use, the Tenax material was conditioned overnight at 250°C by purging with deoxygenated (Gas Clean^{tm} oxygen filter, Chrompack) nitrogen (Air Liquide, A52) at a flow-rate of 40 ml/min.

Analysis of the trapped volatiles

The adsorbed compounds were recovered and analysed by means of a Chrompack thermo-desorption and cold trap (TCT) unit coupled to a Hewlett-Packard 5880 gas chromatograph equipped with two terminals (level 3) and parallel flame ionization and electron-capture detectors. The carrier gas was hydrogen (Air Liquide, N57).

In the TCT system, the transfer of the trapped volatiles onto the capillary trap at −98°C (precooling time, 5 min) was performed by heating the desorption oven at 200°C for 5 min, while purging the Tenax cartridge with hydrogen at a flow-rate of 30 ml/min. The trap consisted of a persilylated fused-silica capillary (300 μm I.D.).

Injection of the whole desorbate into the analytical GC column (FSOT, CP-Sil 5, 50 m × 300 μ I.D., df = 1.2 μ from Chrompack) was performed by flash heating (15°C/sec) of the capillary trap to a maximum temperature of 200°C, which was held for 2 min. The heating of the trap and the temperature programme (from 40°C with an initial hold of 3 min to 250°C at 5°C/min) for the column were started simultaneously.

The column outlet was connected to an effluent splitter, ensuring a splitting ratio FID–ECD of 4:1, by means of deactivated fused-silica restricting lines. Make-up gas (nitrogen) was supplied to the splitter and to the electroncapture detector via the same auxiliary supply facility of the GC. The detection system temperature was 250°C.

RESULTS AND DISCUSSION

The chromatograms presented in Figs. 1 and 2 correspond to the analysis of a 70-l air sample (2°C, 60% relative humidity) collected on a tandem adsorbing cartridge in a rural environment near our Institute. The sharpness of the GC peak profiles shown in Fig. 1 demonstrates the ability of the desorbing system to perform "narrow band" injections. The chromatograms in Fig. 2 illustrate the sampling efficiency: they indicate that negligible sample loss occurred during the sampling.

The blank chromatograms obtained for the desorption of a preconditioned cartridge used for this analysis are shown in Fig. 3.

Qualitative and quantitative determination of specific compounds was performed by the TCT analysis of a calibrated mixture of pure compounds injected in a stream of nitrogen, flowing through a Tenax cartridge at a rate similar to that used for the air sampling. The chromatograms in Fig. 4 illustrate the analysis of such a mixture comprising compounds ranging from benzene to pentadecane in amounts of 3 ng per component.

The graph in Fig. 5 illustrates the overall linearity of the TCT system for C_9–C_{12} hydrocarbons. Good correlations were obtained between FID response and the amount of the analysed hydrocarbons in the 2–10 ng range. Compounds with higher vapour pressure were not reproducibly analysed, probably because of incomplete cold trapping. This observation is in agreement with previously published

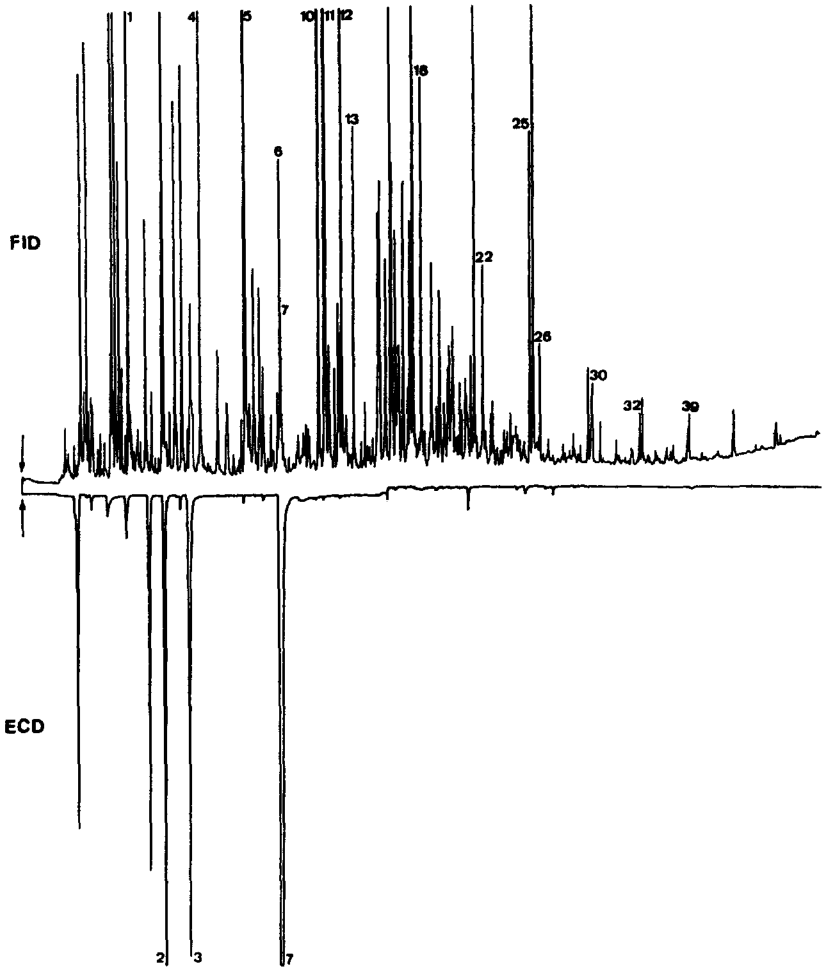

Fig. 1. Chromatogram of a 70-l air sample collected at Tervuren and analysed by TCT capillary GC. Desorption occurred to a 50-m fused-silica capillary column. Temperature programme: 40°C (initial hold, 3 min) to 250°C at 5°C/min. The peak numbers correspond to those presented in Fig. 4.

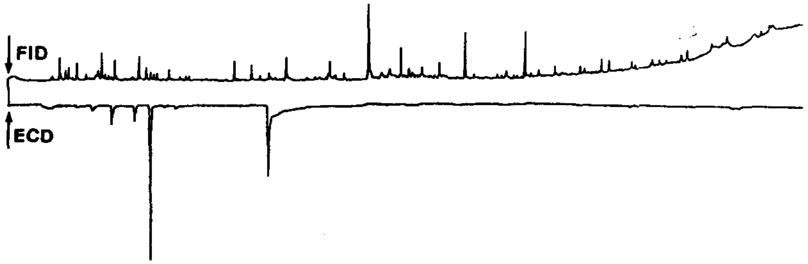

Fig. 2. Chromatogram corresponding to the desorption of the second adsorbing cartridge. The chromatographic conditions are the same as for Fig. 1.

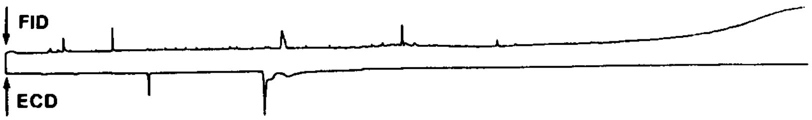

Fig. 3. Blank chromatogram obtained for the preconditioned cartridge. The chromatographic conditions are the same as for Fig. 1.

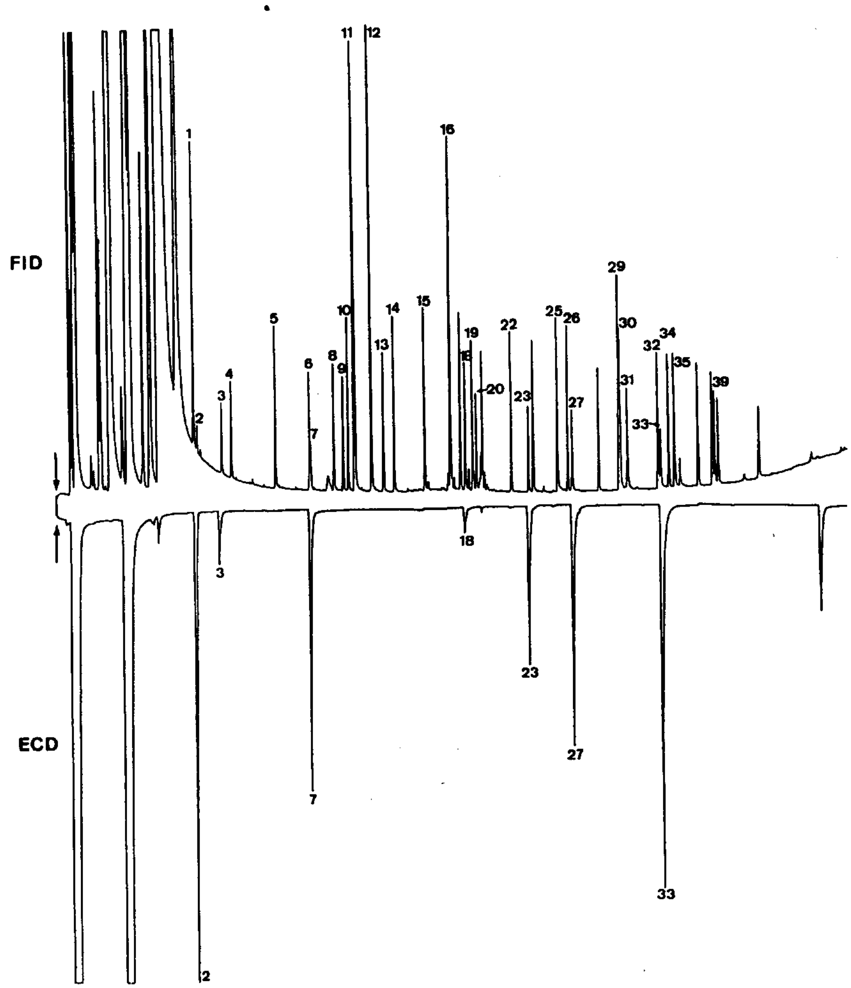

Fig. 4. Chromatogram of a calibrated mixture analysed by TCT capillary GC. The chromatographic conditions are the same as for Fig. 1. Peaks: 1 = benzene; 2 = carbon tetrachloride; 3 = trichloroethylene; 4 = *n*-heptane; 5 = toluene; 6 = *n*-octane; 7 = tetrachloroethylene; 8 = chlorobenzene; 9 = 1-chlorohexane; 10 = ethylbenzene; 11 = *m*-and *p*-xylene; 12 = *o*-xylene; 13 = *n*-nonane; 14 = isopropylbenzene; 15 = 1,3,5-trimethylbenzene; 16 = 1,2,3-trimethylbenzene and *n*-decane; 18 = 1,2-dichlorobenzene; 19, 20 = ethyltoluenes; 22 = *n*-undecane; 23 = 1,3,5-trichlorobenzene; 25 = naphthalene; 26 = *n*-docecane; 27 = 1,2,3-trichlorobenzene; 29 = 2-methylnaphthalene; 30 = *n*-tridecane; 31 = 1-methylnaphthalene; 32 = *n*-tetradecane; 33 = 1,2,3,4-tetrachlorobenzene; 34 = biphenyl; 35 = dimethylnaphthalene; 39 = *n*-pentadecane.

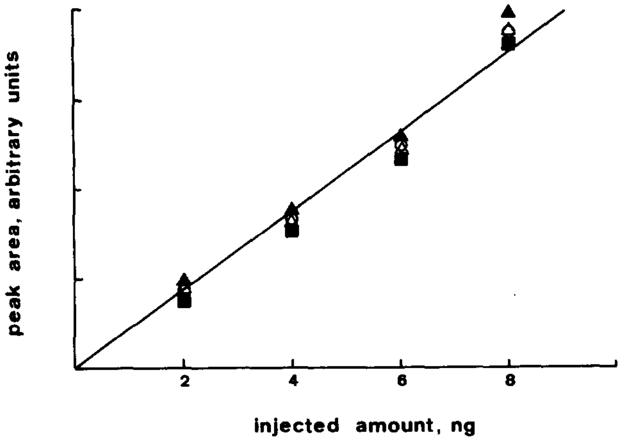

Fig. 5. Calibration graph for C_9–C_{12} hydrocarbons, analysed by the TCT capillary GC system. Key: ■, C_9; ▲, C_{10}; ○, C_{11}; △, C_{12}.

work[10], demonstrating that volatile compounds with boiling points below 70°C cannot be quantitatively recondensed by simple capillary cold trapping, even at liquid nitrogen temperature.

Owing to the very low water retention of Tenax[11], analysis of a 70-l air sample with a relative humidity up to 100% (no water condensation) was possible without freezing the cold trap during thermal desorption. However, when misty or rainy atmospheres were sampled, the amount of water retained on the cartridge was too high and blocking of the capillary occurred. A water-condensing system designed for flavour analysis[12] is under development for air sampling.

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