Simplified gas-chromatographic procedures for the determination of C1-C7 Hydrocarbons in urban atmospheres

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Simple procedures for the determination of C_1-C_7 Hydrocarbons in air are described. C_2-C_7 hydrocarbons are collected on a carbon molecular sieve trap and desorbed directly into a porous layer open-tubular column by means of a programmed temperature injector. Methane is determined by direct injection.

Measurements of the concentrations of volatile organic compounds (VOC) in air are required both as indicators of air quality[1] and as input for models of atmospheric chemistry[2]. A number of on-line collection and analysis systems have been described in which air is drawn through a sorbent trap[3] from which analytes are desorbed by rapid heating; carbon molecular sieves are especially effective[4]. Analysis of C_2-C_7 VOC generally requires focusing in a cooled trap before introduction into a capillary gas chromatography column. Devices involving focusing with cooling by liquid nitrogen or carbon dioxide[5, 6] and the Peltier effect[7] have been described.

Here we show how intermediate focusing is made unnecessary if the C_2-C_7 hydrocarbons in air are trapped on a carbon molecular sieve sorbent tube and desorbed by means of a simple programmed temperature injector (PTV) into a porous layer open-tubular (PLOT) column. Such columns are suitable for volatile hydrocarbons analysis, but have been shown[8] to induce dehydrochlorination of certain halo carbons. Analysis for methane in air is carried out with the same apparatus by direct injection.

Experimental

Air samples

Methane determinations were carried out on air sampled into a Tedlar bag by pumping with a personal air sampler (Supelco PAS-3000). C_2-C_7 hydrocarbons were adsorbed from 120 cm^3 air by passing through 28 mg of Carbosieve S-III (Supelco) packed in a glass tube (8.1 x 0.11 cm).

Gas chromatography

The gas chromatograph was a Fisons (MFC 800) fitted with an Optic 400 (Ai Cambridge), programmed temperature vaporization injector, and flame ionization detector. The column was a PLOT column Al_2O_3/Na_2SO_4 , length 50 m, I.D. 0.53 mm, film thickness 10 µm (Chrompack). The carrier gas was helium.

Analyses

Analyses for methane were made by direct injection of 1 cm^3 samples air with a 1 cm^3 gastight syringe (SGE) into the injection port liner of the cold PTV. The column was held at room temperature.

C_2-C_7 hydrocarbons were desorbed from the Carbosieve by using the packed tube as injection port liner and heating to 270°C at 16° C s^{-1}. The flow direction during desorption was reversed from that during sampling. The column temperature program was 30°C for 2 minutes, followed by 10°C per minute to 100°C, then 7°C per minute to 200°C.

Results and discussion

Chromatograms from repeated injections of 1 cm^3 of City Centre street air are shown in (Fig. 1). Clearly, the methane concentration is high enough for determination without pre concentration. A calibration curve (Fig. 2) was constructed by injecting 5-90 µl of 0.1% and 0.01% of methane in air. The curve allowed the

Methane concentration in air from a number of sites to be determined with RSDs of approximately 3.0% (Table 1).

Fig. 3 is the chromatogram of the C_2-C_7 hydrocarbons of urban air collected by adsorption on Carbosieve and demonstrates how the Optic injector permits a single desorption step before chromatography. The desorbed compounds are focused at the front of the column without cryo-cooling. Calibration curves (Figs. 4, 5) for known masses of ethane; ethene and n-heptane were constructed in two ways:

(a) direct injection of 1-9 µl using gas tight syringe from a gas mixture prepared by dilution of 1 ml of each gas in 3.5 l of air for ethane and ethene; direct injection of 1-9 µl from a gas mixture prepared by dilution of 2 µl of heptane in 2 l of air and,

(b) Desorption after injection onto the Carbosieve cartridge of the same samples. The similarity of peak areas for the same mass injected by the two methods confirms that the mass of Carbosieve is sufficiently large to avoid breakthrough during collection of C_2 hydrocarbons from urban air, but sufficiently small to avoid irreversible desorption of hydrocarbons up to C_7.

We conclude that gas chromatography on a PLOT column with a PTV injector allows the C_1- C_7 hydrocarbons of urban air to be simply determined. Methane may be determined by direct injection, and C_2-C_7 compounds by trapping on Carbosieve and desorption without a second cryogenic trapping step. Work is now in progress to automate these procedures.

Acknowledgements.

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Table 1 Methane content of air samples determined by direct injection

Source of air	Methane concentration ppm	Methane concentration ng mL^{-1}
Laboratory	6.13 ± 0.17[a]	4.01 ± 0.14
City centre street	5.07 ± 0.14[a]	3.32 ± 0.09
City centre park	4.78 ± 0.14[a]	3.13 ± 0.09

[a] Standard deviation from six injections

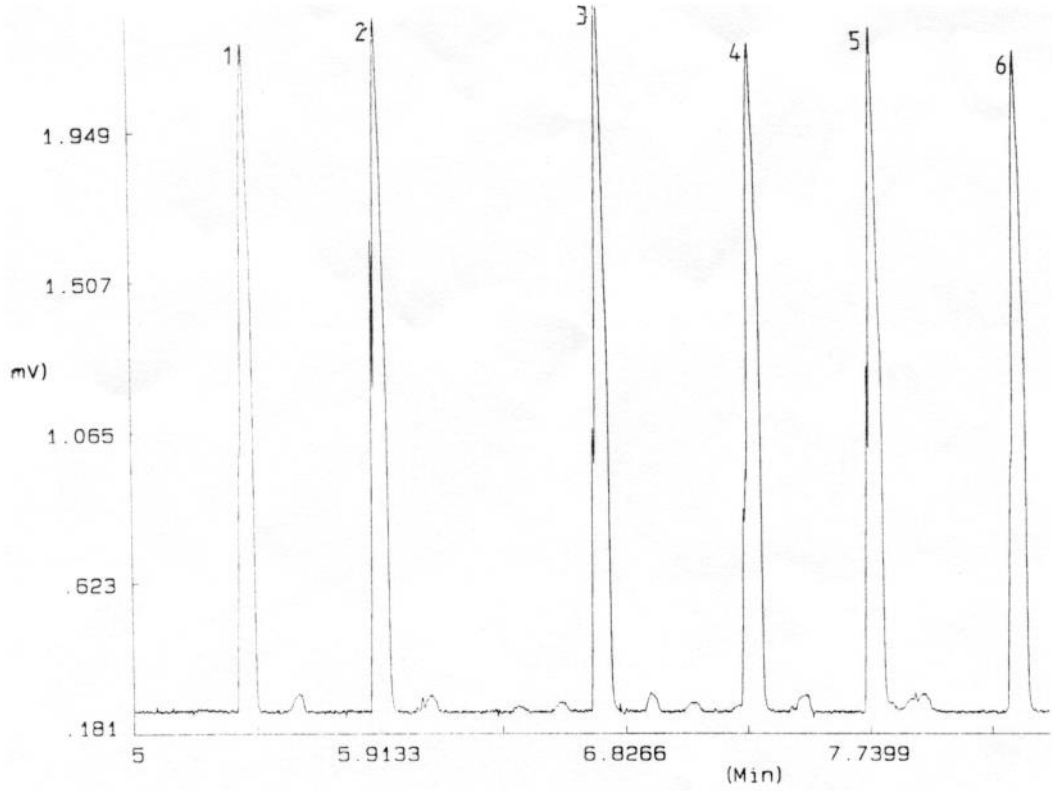

Fig. 1 multiple injections of 1 ml of city Centre Street air; shows methane peaks (1-6)

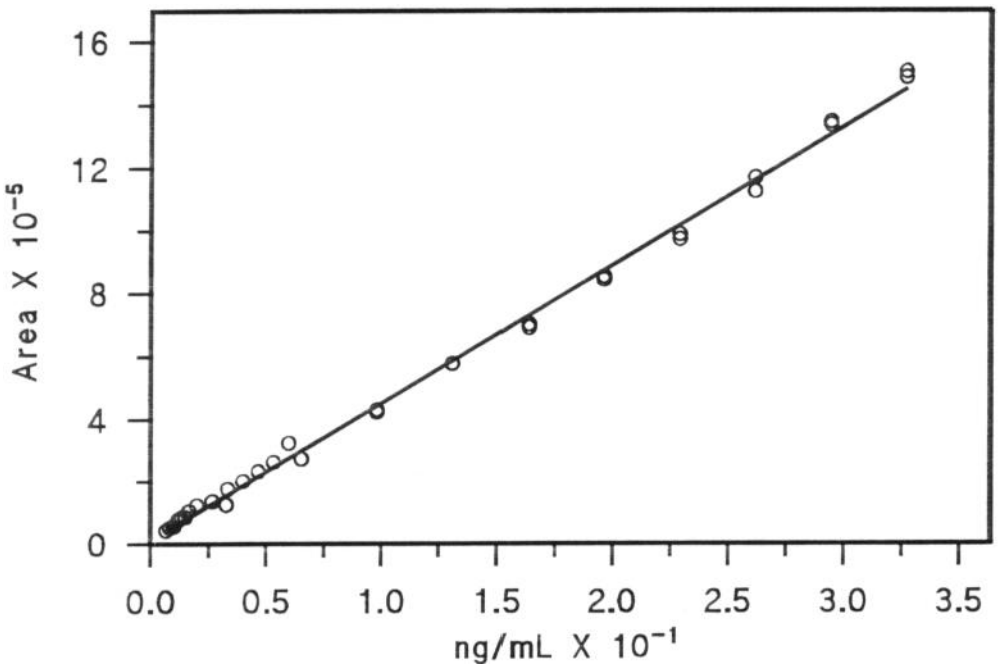

Fig. 2 Calibration curve for methane from injection of 5-90 µl of 0.1% and 0.01% of methane standard in air

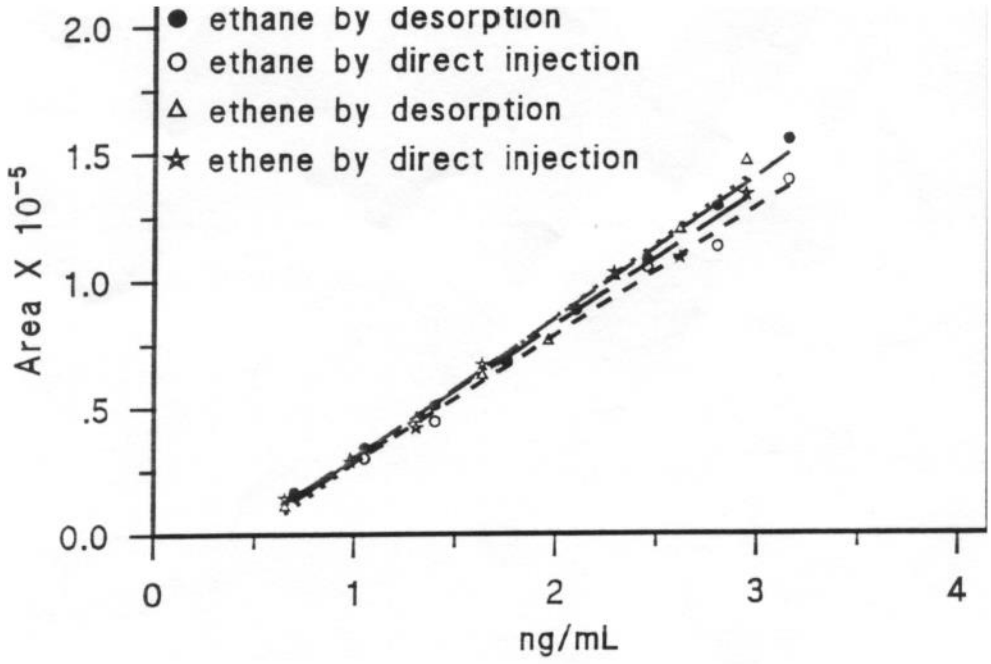

Fig. 4 Calibration curves for ethane and ethane

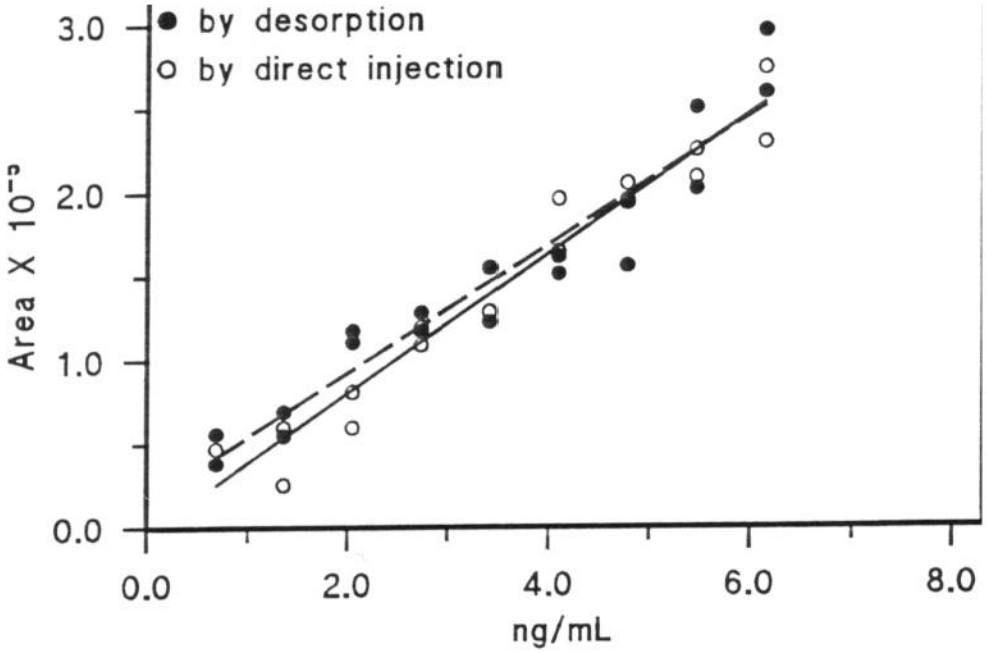

Fig. 5 Calibration curve for heptane

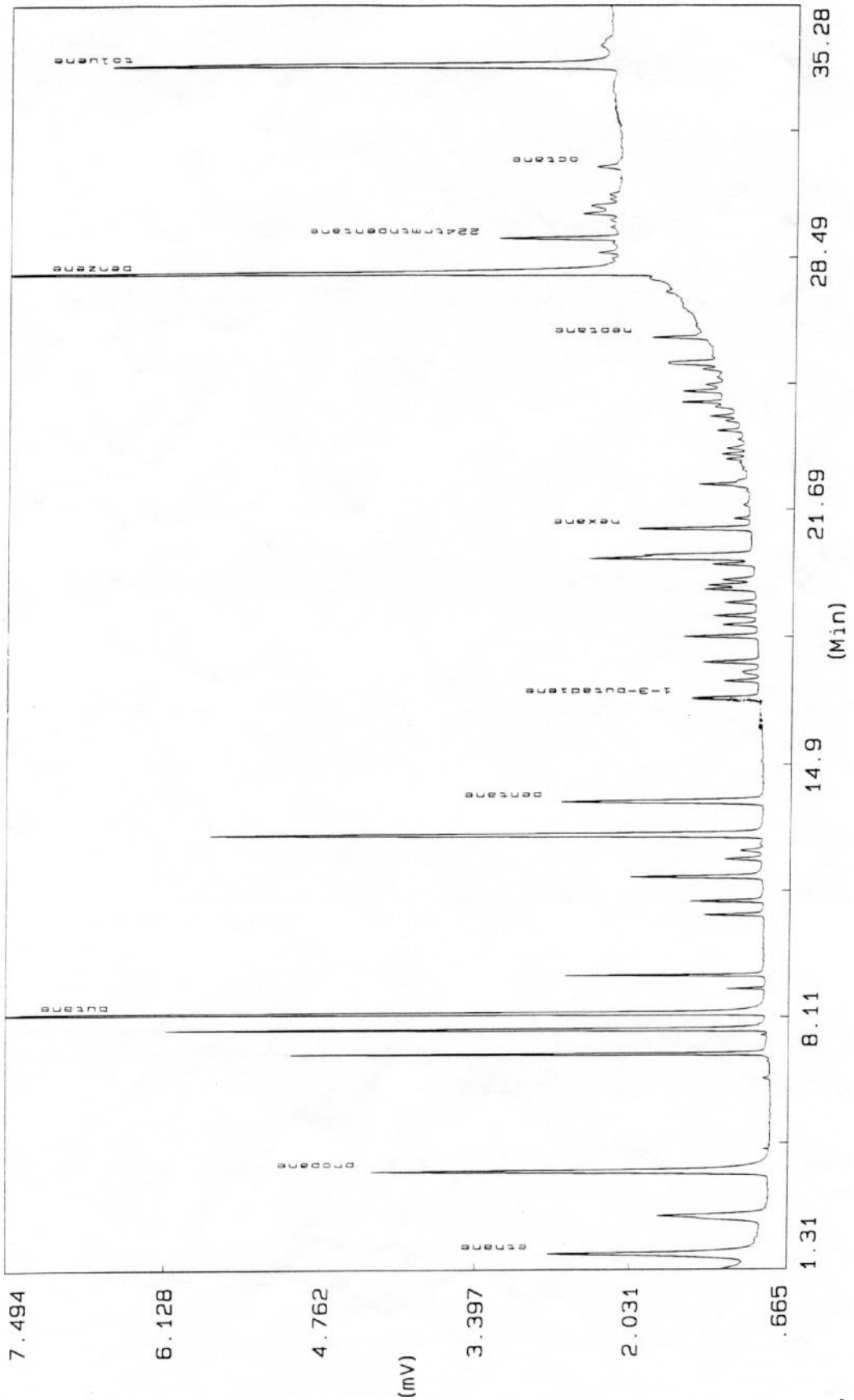

Fig 3 Chromatogram of 120 ml of urban air sample, on alumina PLOT column at 30°C for 2 minutes to 100°C at 10°C/min then to 200°C at 7°C/min for 20 minutes; carrier gas: 150 kPa.