

## **Simplified gas-chromatographic procedures for the determination of C<sub>1</sub>-C<sub>7</sub> Hydrocarbons in urban atmospheres**

**A.M. Denha\*, K.D. Bartle, and M.J. Pilling**

School of Chemistry, University of Leeds, Leeds, LS2 9JT

**Simple procedures for the determination of C<sub>1</sub>-C<sub>7</sub> Hydrocarbons in air are described. C<sub>2</sub>-C<sub>7</sub> 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<sup>1</sup> and as input for models of atmospheric chemistry<sup>2</sup>. A number of on-line collection and analysis systems have been described in which air is drawn through a sorbent trap<sup>3</sup> from which analytes are desorbed by rapid heating; carbon molecular sieves are especially effective<sup>4</sup>. Analysis of C<sub>2</sub>-C<sub>7</sub> 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<sup>5, 6</sup> and the Peltier effect<sup>7</sup> have been described.

Here we show how intermediate focusing is made unnecessary if the C<sub>2</sub>-C<sub>7</sub> 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<sup>8</sup> 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<sub>2</sub>-C<sub>7</sub> hydrocarbons were adsorbed from 120 cm<sup>3</sup> 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<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub>, 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<sup>3</sup> samples air with a 1 cm<sup>3</sup> gastight syringe (SGE) into the injection port liner of the cold PTV. The column was held at room temperature.

C<sub>2</sub>-C<sub>7</sub> hydrocarbons were desorbed from the Carbosieve by using the packed tube as injection port liner and heating to 270°C at 16° C s<sup>-1</sup>. 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<sup>3</sup> 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

**ATAS GL INTERNATIONAL B.V.**

De Sleutel 9, 5652 AS, Eindhoven, The Netherlands

Tel. +31 (0)40 254 95 31 Fax. +31 (0)40 254 97 79

E-mail: [info@atasgl.com](mailto:info@atasgl.com) Internet: [www.atasgl.com](http://www.atasgl.com)

Web shop: [www.atasgl.com/shop](http://www.atasgl.com/shop)

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<sub>2</sub>-C<sub>7</sub> 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<sub>2</sub> hydrocarbons from urban air, but sufficiently small to avoid irreversible desorption of hydrocarbons up to C<sub>7</sub>.

We conclude that gas chromatography on a PLOT column with a PTV injector allows the C<sub>1</sub>- C<sub>7</sub> hydrocarbons of urban air to be simply determined. Methane may be determined by direct injection, and C<sub>2</sub>-C<sub>7</sub> compounds by trapping on Carbosieve and desorption without a second cryogenic trapping step. Work is now in progress to automate these procedures.

#### Acknowledgements.

We thank DOE for financial support of this work and Dr Ray Perkins of Ai Cambridge for helpful advice.

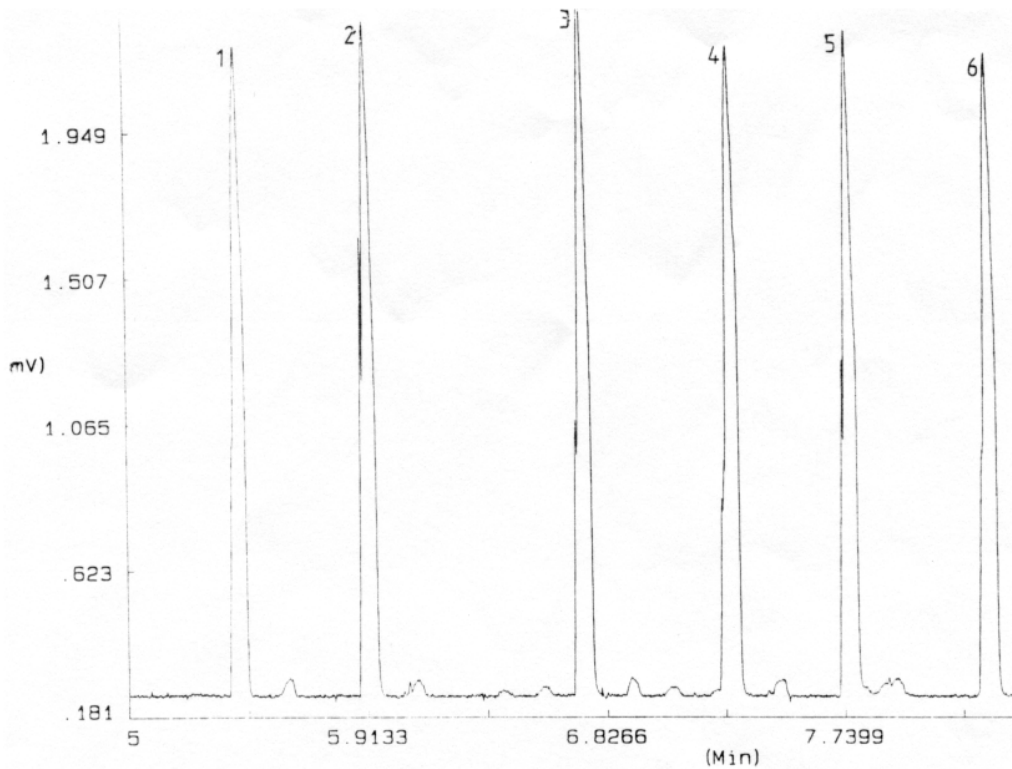
#### References

- 1 Sweet, C. W., and Vermette, S. J., Environ. Sci. Technol., 1992, 26, 165
- 2 Harley, R. A., and Cass, G. R., Environ. Sci. Technol, 1994, 28, 88
- 3 Frank, W., and Frank, H., Chromatographia, 1990,29, 571
- 4 O'Doherty, S. J., Simmonds, P. G., and Nickless G., J. of Chromatography, 1993,630, 264
- 5 Mattinen, Maija-Liisa and Ojala, Maria, 14th International Symposium on Capillary Chromatography, Baltimore, Maryland, May 25-29, 1992 (USA) p.307-314
- 6 Cicciooli, P., Cecinato, A., Brancaloni, E., Frattoni, M., and Liberti, A., J. High Resolution Chromatography, 1992, 15, 75
- 7 Woolfenden, E. A., Broadway, G. M., Higham, P., and Seeley, I., Proceeding of the International Conference on Volatile Organic Compounds in the Environment held in London, 27-28 Oct, (1993) p.321-329
- 8 Sturrock, G. A., Simmonds, P. G., and Nickless, G., J. of Chromatography, 1993, 648, 423

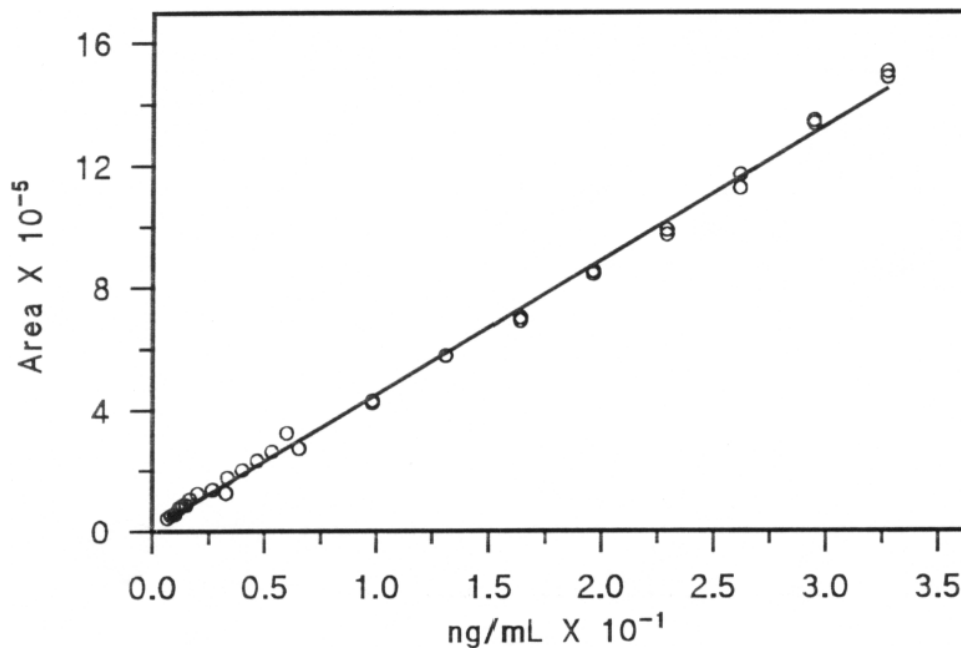
Table 1 Methane content of air samples determined by direct injection

Source of air	Methane concentration	
	ppm	ng mL <sup>-1</sup>
Laboratory	6.13 ± 0.17 <sup>a</sup>	4.01 ± 0.14
City centre street	5.07 ± 0.14 <sup>a</sup>	3.32 ± 0.09
City centre park	4.78 ± 0.14 <sup>a</sup>	3.13 ± 0.09

<sup>a</sup> Standard deviation from six injections

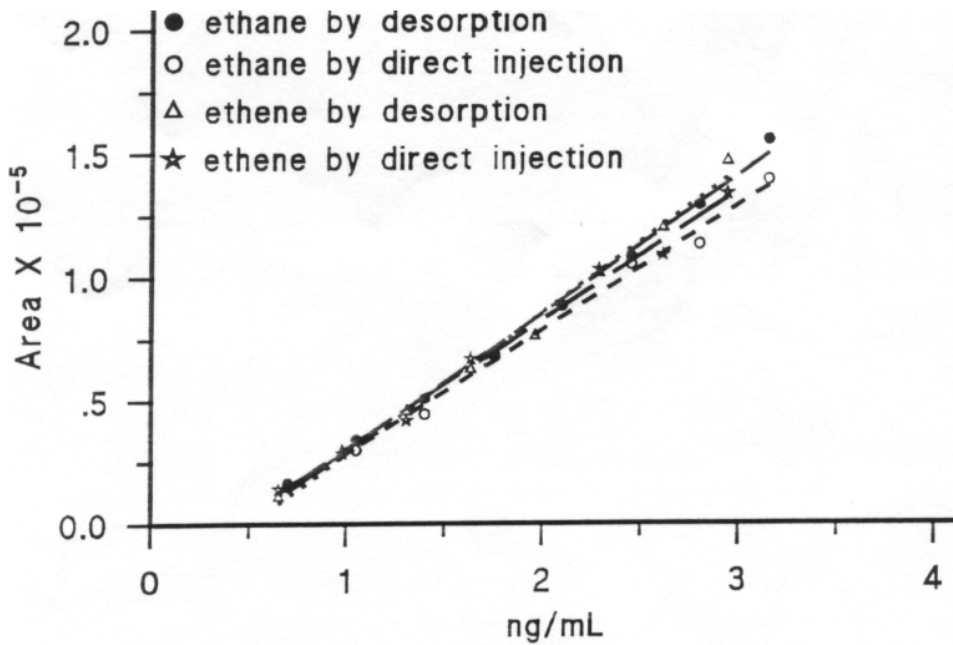


**Fig. 1** multiple injections of 1 ml of city Centre Street air; shows methane peaks (1-6)

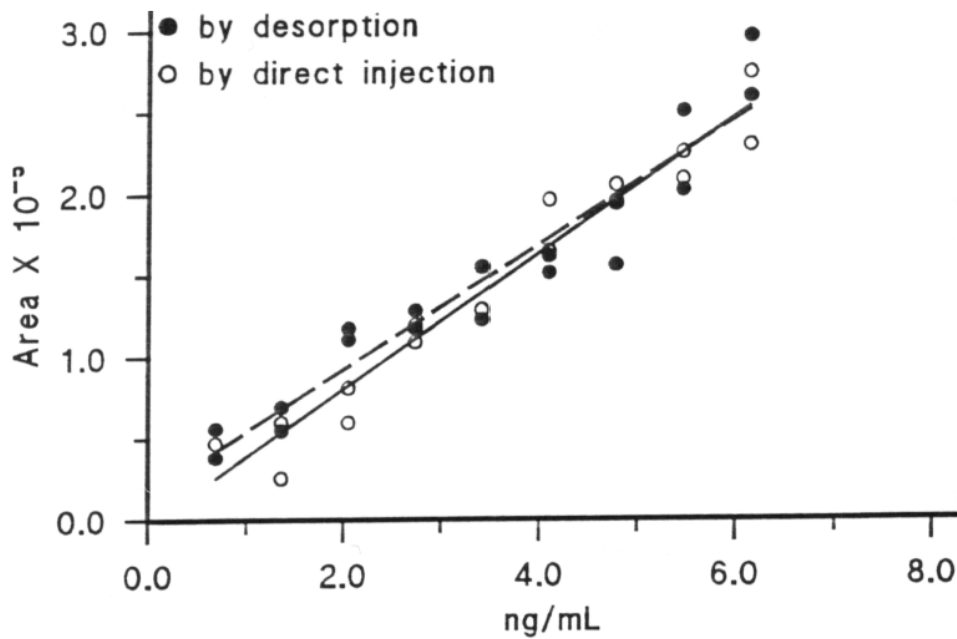


**Fig. 2** Calibration curve for methane from injection of 5-90  $\mu$ l of 0.1% and 0.01% of methane standard in air

**ATAS GL INTERNATIONAL B.V.**  
 De Sleutel 9, 5652 AS, Eindhoven, The Netherlands  
 Tel. +31 (0)40 254 95 31 Fax. +31 (0)40 254 97 79  
 E-mail: [info@atasgl.com](mailto:info@atasgl.com) Internet: [www.atasgl.com](http://www.atasgl.com)  
 Web shop: [www.atasgl.com/shop](http://www.atasgl.com/shop)



**Fig. 4 Calibration curves for ethane and ethene**



**Fig. 5 Calibration curve for heptane**

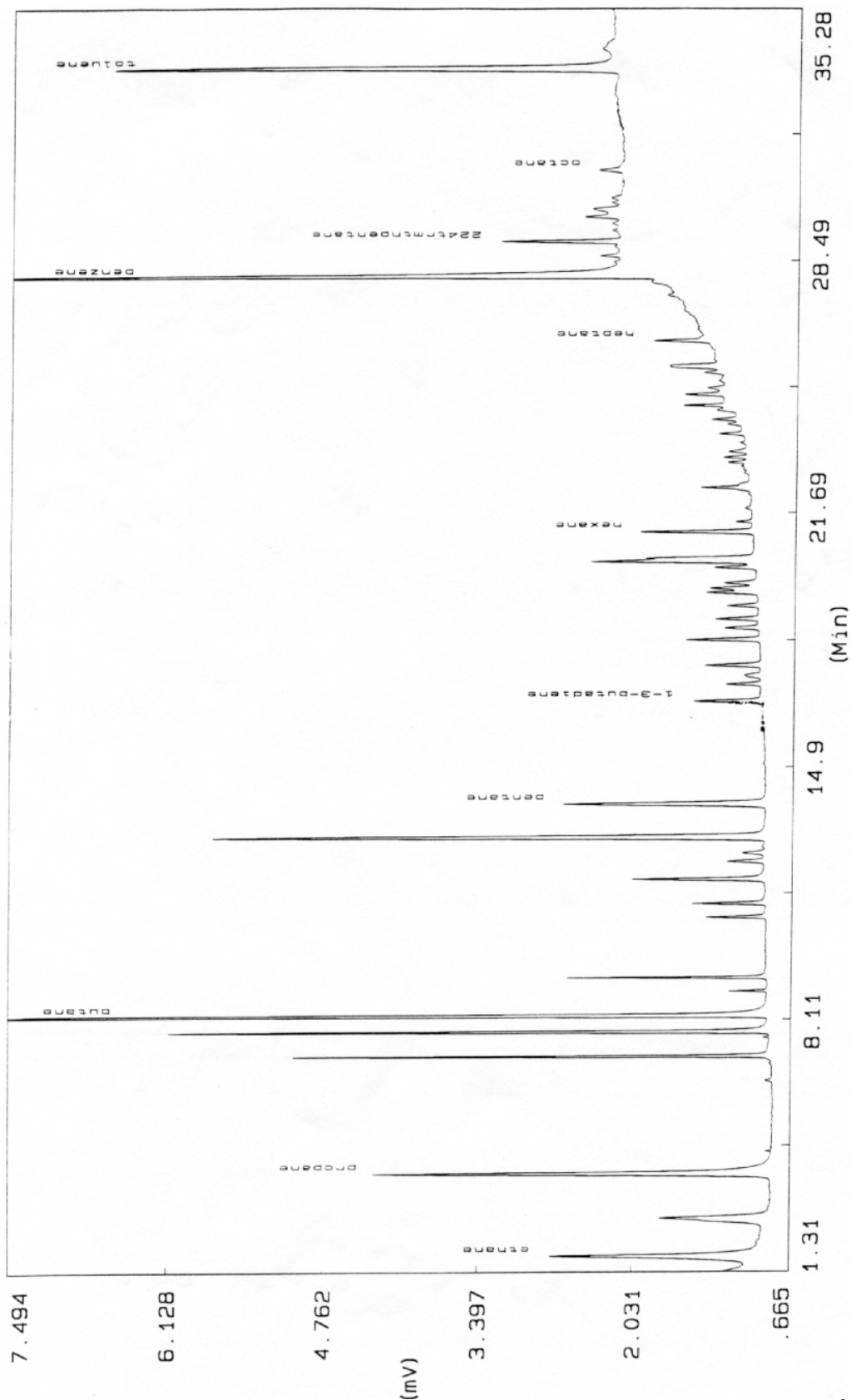


Fig 3 Chromatogram of 120 ml of urban air sample, on alumina PLOT column at 30°C for 2 minutes to 100°C at 10°C/min then to 200°C at 7°C/min for 20 minutes; carrier gas: 150 kPa.

**ATAS GL INTERNATIONAL B.V.**  
 De Sleutel 9, 5652 AS, Eindhoven, The Netherlands  
 Tel. +31 (0)40 254 95 31 Fax. +31 (0)40 254 97 79  
 E-mail: [info@atasgl.com](mailto:info@atasgl.com) Internet: [www.atasgl.com](http://www.atasgl.com)  
 Web shop: [www.atasgl.com/shop](http://www.atasgl.com/shop)