IDENTIFICATION OF ORGANIC POLLUTANTS IN CITY ATMOSPHERES

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SUMMARY

A suitable gas chromatographic analytical technique is described for the characterization of organic components in air samples from traffic dense areas. The method employs a Chromosorb 102 cold trap to collect and con- centrate samples and a 30 metre SCOT DC 550 Silicone column for separating the components. Chromatograms yielding about 150 peaks have been obtained which are superior to those reported in the literature.

Tentative identification could be made or paraffinic, cycloparaffinic, olefinic, acetylenic and aromatic hydrocarbons in the C_1 to C_{13} range, using a standard addition method.

INTRODUCTION

Analytical studies reported so far in the field of atmospheric pollution have been concerned either with the determination of individual pollutants or with specific groups of pollutants. It was felt that there was scope for the development of analytical methods whereby a broader spectrum of organic substances present in city atmospheres could be analysed. Such methods, in time, would be invaluable to detect potentially harmful pollu- tants.

For the present study it was decided to concentrate first on traffic dense areas since

(i) the man in the street is daily subjected to pollution from the exhaust fumes of cars

(ii) a complex spectrum of pollutants will be found in these areas and once a suitable method has been developed, it could also

be more readily adapted for identification of pollutants in other types of environments.

The purpose of this paper is to report the progress which has been made in developing a suitable gas chromatographic method for the identifica- tion of organic air pollutants. Several cold trap and gas chromatographic column combinations have been evaluated and the results obtained are re- ported. Also described is a useful "Mylar" plastic bag sampler whereby large air samples can be collected and stored for several days without sample decomposition occurring.

Sample collection

Initial work by the Air Pollution Research Group indicated the need for a sampler whereby large air samples could be collected, eliminating any possible contamination from the air sampling pump and in which samples could be kept for several days without decomposition. Such a sampler would enable multiple analysis of the same sample, using different analy- tical techniques such as gas chromatography and gas chromatography combined with physical-chemical methods; a feature which is essential for charac- terization of sample components in complex mixtures such as those from traffic dense areas.

A "Mylar" plastic bag air sampler has been designed which fulfills these requirements. This sampler consists of a 100 litre "Mylar" bag enclosed in a plastic drum fitted with an airtight transparent lid through which an inlet tube attached to the "Mylar" bag extends to ambient air. The "Mylar" bag is filled by developing a vacuum around the bag by the use of a high capacity air pump and the inlet tube closed when the bag is inflated to its full capacity, an operation which usually takes about 10 minutes. This sampler is light in weight, yet rigid and can be easily transported on a small truck.

"Mylar" plastic film* was selected because of its known inertness to a large range of organic substances. Tests carried out in this laboratory with traffic area samples stored in "Mylar" bags showed no change in sample composition after one week's storage at 22°C.

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* "Mylar" is a trade name for a polyester film made from polyethelene terephthalate.

Sample concentration

Because of the relatively low concentrations (parts per million to parts per billion range) in which organic pollutants occur in city atmospheres, large air volumes are required to yield sufficient sample quantities for gas chromatographic analysis. Inefficient separation will result if too large air volumes are introduced directly into the gas chromatograph. Consequently techniques to concentrate samples during their collection have been investigated.

A relatively simple sample concentration method has been developed. Samples are collected either directly from the atmosphere or from the "Mylar" bag sampler on a cold trap consisting of a short packed gas chromatographic column held at -80°C (coolant: dry ice-ethanol) using an air sampling pump to draw air through the system. The cold trap still being held at -80°C is subsequently coupled to the gas chromatographic column and the collected components are desorbed by back-flushing and heating the cold trap using an oil bath held at 90°C or 160°C depending upon the type of the cold trap packing material.

The problem of simultaneous collection of atmospheric moisture in the cold trap has been overcome by judicious selection of the cold trap packing material. The use of dehydrating agents has been avoided to eliminate the possibility of sample losses due to adsorption.

Analysis of traffic area samples

The gas chromatograph used in the course of this investigation is a Beckman model GC-4 equipped with a low temperature accessory allowing temperature programming from sub-ambient temperatures, a duel flow controller to maintain carrier flow constant during the temperature programming and a gas switching valve to reverse the carrier gas flow through the cold trap (back flushed) prior to sample desorption onto the gas chromatographic column. High purity helium (99,995%) was used throughout as the carrier gas.

It was anticipated that high efficiency gas chromatographic columns would be required for the analysis for traffic area samples because of their very complex nature. Consequently a large number of packed and SCOT capillary

columns with stationary phases of different polarities were evaluated in combination with different cold traps (see Table 1). Actual atmospheric samples from traffic dense areas were used to find optimum operating conditions. Support coated open tubular (SCOT) capillary columns were selected because they bridge the gap between the more conventionally used capillary and packed columns; whilst retaining the separating power of capillary columns they have an increased sample capacity.

The best analytical separation was achieved with a Chromosorb 102 cold trap combined with a 30 metre SCOT DC 550 Silicone capillary column (see Table 1). The chromatograms obtained with this system yielded about 150 peaks and are superior to those separations reported so far in the literature. Moreover, daily analysis of the same sample gave reproducible chromatograms (compare Figs. 1 and 2).

An attempt was made to identify the chromatographic peaks shown in Fig. 1 using a spiking, or standard addition method. This was accomplished with a dynamic flow system whereby air samples could be spiked with standard hydrocarbon mixtures during their collection on the cold trap. Those chromatographic peaks which exhibited increased heights were then regarded as those most likely to be the same as the added standards (see Fig.). The advantage of this spiking technique as opposed to the more conventional method of separate analysis of standard mixtures is that it is not affected by variations in analytical conditions which may occur during an analysis.

Fifty of the hundred and fifty chromatographic peaks displayed in Fig. 1 could be identified tentatively as paraffinic, cycloparaffinic, olefinic, acetylenic and aromatic hydrocarbons in the C_1 to C_{13} range. Several of the chromatographic peaks appear to be associated with more than one compound and this further demonstrates the complex nature of traffic area samples.

Combination of gas chromatography with physical-chemical methods

In view of the complex nature of traffic dense area samples as demonstrated above, it was thought expedient to combine the present gas chromatographic method with physical-chemical methods to substantiate the tentative identification obtained with the spiking method.

Work is under way to

(i) evaluate different chemical subtractors. These are inserted as short pre-columns between the cold trap and the gas chromatographic column and will serve to subtract selectively, certain hydrocarbon classes

(ii) develop a suitable on-line gas chromatographic infra-red spectrometric technique. The results obtained with these investigations will be reported in due course.

Table I – Analysis of traffic area samples on different cold traps and gas chromatographic columns

Sample size ml	Cold trap — Type and dimensions	Cold trap — Operating conditions	Gas chromatographic column — Type	Gas chromatographic column — Operating conditions	Number of peaks in chromatogram
10 / 25	SE-30 packed		SE-30 packed	a, b	17,18 / 33
10 / 25			SE-30 packed	c, d	35,37,38 / 34
10 / 25	Carbowax/SE-30 58 cm × 1,00 mm id. 21 cm 10% Carbowax 1540 on Chromport A (60/80 mesh) 37 cm 10% SE-30 on Chromport A (80/100 mesh)		Squalane(i) SCOT	i	15 / 61,62
25			DC 550(i) SCOT	j	83
10 / 25			DC 550(i) SCOT	g, h	16 / 57
25			DC 550(i) SCOT		80
10 / 25			DC 550(ii) SCOT	k, l	92 / 98
10 / 29			Carbowax(i) SCOT	g, h, m	12 / 22,26 / 33
10 / 29	Al₂O₃/SE-30 58 cm × 1,00 mm id. 21 cm 10% SE-30 on Chromport A (80/100 mesh) 37 cm 10% NaOH on Al₂O₃ (80/90 mesh)		SE-30 packed	a, c, d	19 / 30,36,36 / 39,40
10 / 29			Squalane(i) SCOT	g, h	19 / 53
10 / 29			DC 550(i) SCOT	g, h	17 / 52
10 / 29			Carbowax(i) SCOT	g, h	12 / 18

Table I (continued)

Sample size ml	Cold trap — Type and dimensions	Cold trap — Operating conditions	Gas chromatographic column — Type	Gas chromatographic column — Operating conditions	Number of peaks in chromatogram
10 74	Porapak Q(50/80 mesh) 58 cm x 1,00 mm id.	x	SE-30 packed	a	7,8
				b	33
				c	42
		y		c	43,46
				d	60
10 74		x	Squalane(i) SCOT	g	9
				h	29
10 74		x	DC 550(i) SCOT	g	6
				h	45
10 74		x	Carbowax(i) SCOT	g	8
		y		h	26
500	Chromosorb 102 (80/100 mesh) 16 cm x 2,15 mm id.	y	Squalane(i) SCOT	c	39,45
				e	63
				f	66
			SE-30 packed	h	75,79
				i	110
			DC 550(i) SCOT	k	124
				l	140,150
10 74		x	DC 550(ii) SCOT	h	83
10 74		y	Carbowax(i) SCOT	h	30,40
				m	32

Cold trap operating conditions

x : freeze-out temperature, −80°C; desorption temperature, 90°C;

y : freeze-out temperature, −80°C; desorption temperature, 160°

Gas chromatographic column dimensions

SE-30 column, 3 m x 2,15 mm id.
Support-coated open tubular (SCOT) columns,
(i) 15 m x 0,5 mm id.
(ii) 30 m x 0,5 mm id.

The following packed Durapak type columns were also evaluated but no better separation could be obtained:

Carbowax 400 (non polar), 100 cm x 2,15 mm id., OPN (medium polar), 100 cm x 2.15 mm id., and n-octane (polar) 150 cm x 2,15 mm id.

Table I (continued)

Gas chromatographic column operating conditions

a : 58°C; carrier gas (He) 25 ml/min.

b : 40° to 110°C programmed at 7°C/min for 10 mins; carrier gas (He), 25 ml/min.

c : −10° to 80°C programmed at 9°C/min for 10 mins; carrier gas (He), 25 ml/min.

d : −10° to 80°C programmed at 5°C/min for 10 mins and at 10°C/min for 5 mins; carrier gas (He), 25 ml/min.

e : −10° to 110°C programmed at 6°C/min for 10 mins and at 11°C/min for 5 mins; carrier gas (He), 25 ml/min.

f : −10° to 150°C programmed at 5,3°C/min for 30 mins; carrier gas (He), 25 ml/min.

g : 50°C; carrier gas (He), 5,5 ml/min.

h : −10° to 80°C programmed at 9°C/min for 10 mins; carrier gas (He), 5,5 ml/min.

i : −10° to 80°C programmed at 3°C/min for 30 mins; carrier gas (He), 5,5 ml/min.

j : −10° to 85°C programmed at 2,4°C/min for 40 mins; carrier gas (He), 5,5 ml/min.

k : −10° to 85°C programmed at 4,8°C/min for 20 mins; carrier gas (He), 5,5 ml/min.

l : −10° to 85°C programmed at 3,2°C/min for 30 mins; carrier gas (He), 5,5 ml/min.

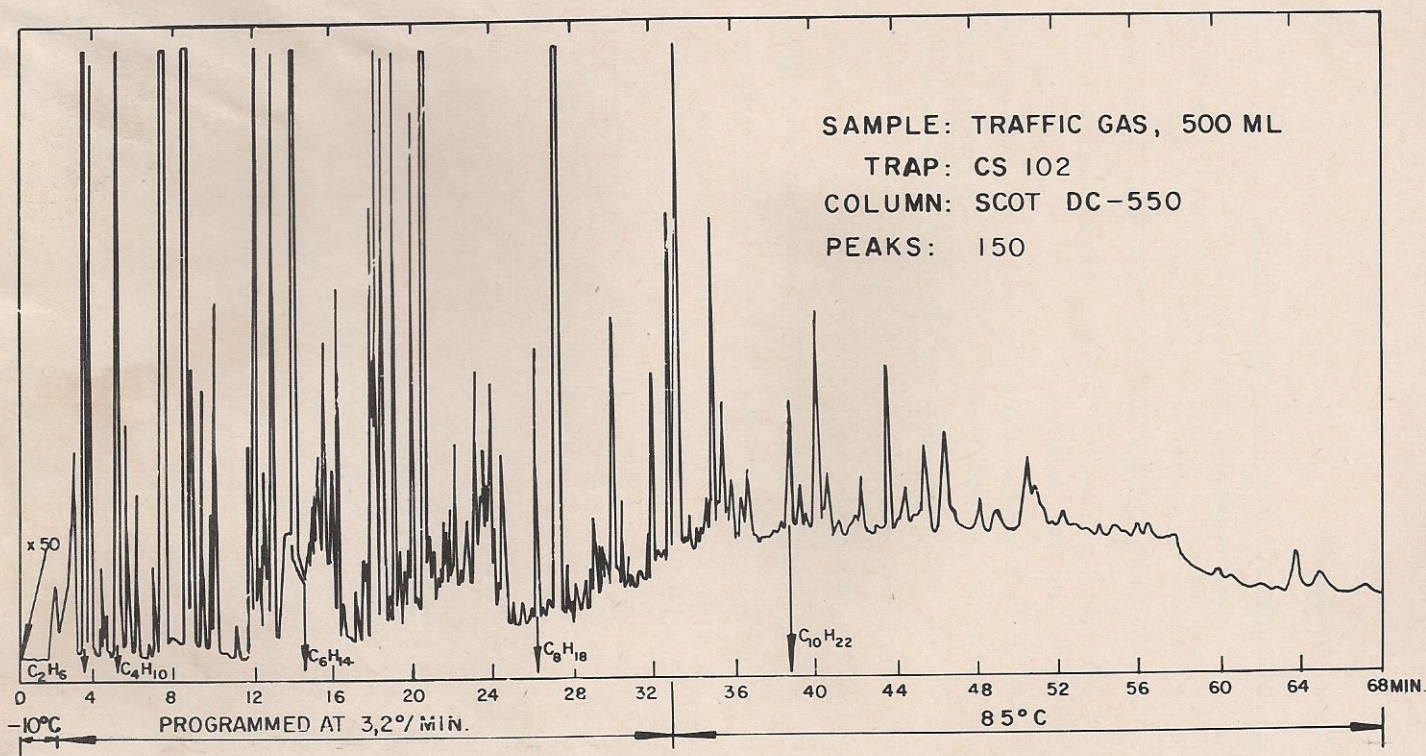m : 25° to 85°C programmed at 6°C/min for 10 mins; carrier gas (He), 5,5 ml/min.

FIGURE 1. Analysis of an air sample from a traffic dense area in Pretoria
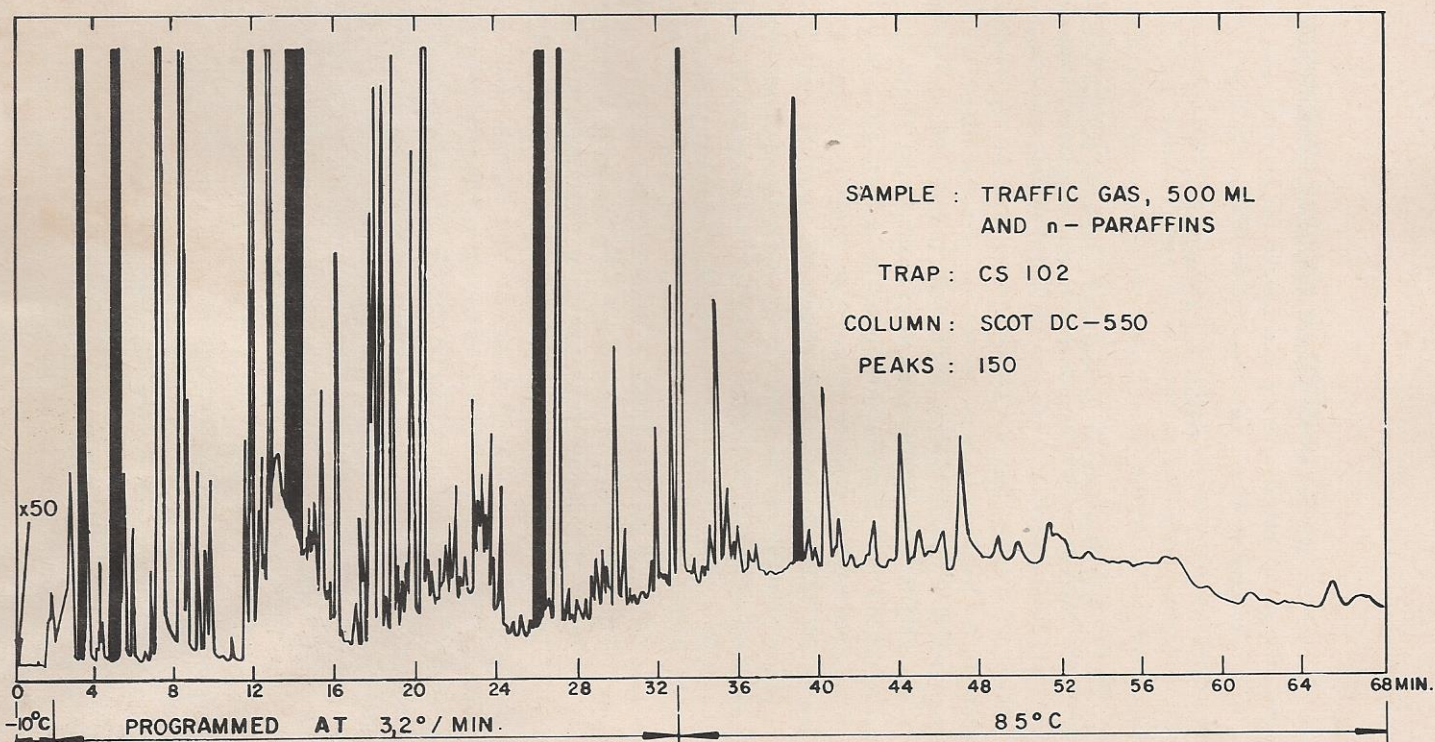

FIGURE 2. Identification of traffic gas components using the spiking techniques.
Peaks which exhibit increased heights are darkened.