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CRITICAL EVALUATION OF SAMPLING AND GAS CHROMATOGRAPHIC ANALYSIS OF HALOCARBONS AND OTHER ORGANIC AIR POLLUTANTS

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SUMMARY

Problems connected with the analysis of ultra-trace amounts of halocarbons in air are discussed in terms of trapping procedures, interferences and chromatographic columns. A suitable column for the qualitative and quantitative analysis of C_1–C_2 halocarbons is described, and examples of applications are given. High-efficiency micropacked columns have been used for the analysis of hydrocarbons in the open atmosphere.

INTRODUCTION

The development of reliable techniques for the determination of pollution levels of organic compounds is of increasing concern. Among these methods, gas chromatography (GC) and ancillary techniques have attracted most attention, for obvious reasons. Further, owing to the strong emphasis in the recent years on environmental and health effects of anthropogenic organics, the need for accurate measurements of ultra-trace amounts of such compounds has increased. For example, carcinogenic compounds such as bis(chloromethyl) ether should be monitored at the parts per trillion (10^{12}) level, as its maximum acceptable concentration in industrial areas is 0.1 ppb (parts per 10^9)[1].

Halocarbons, whose effect on the stratospheric ozone layer is almost a certainty[2,3], should also be determined at the parts per trillion level. The complexity of the problem is increased as the quantitative analysis of specific halocarbons, such as Freon 21, to a high degree of accuracy is required. In fact, the hypothesis that this compound might be a reaction product of Freon 11 in the troposphere[4], makes its quantitative determination extremely important. Three major requirements should be satisfied in order to solve the above problems: (a) reliability of sampling and pre-analytical procedures; (b) overall sensitivity of the analytical system; (c) selective and efficient columns for correct peak identification.

This paper reports some attempts made recently to solve the problem of the sampling and GC analysis of organics in air.

EXPERIMENTAL

Carlo Erba Model 2501 and DANI 3600 gas chromatographs, both equipped with [63]Ni electron-capture detectors, were modified for injection of atmospheric samples from traps by the heating-stripping technique according to the scheme previously described[5]. Low-temperature trapping of halocarbons was effected with the system described elsewhere[6], the only difference being that in this instance no electric valves were used. The traps are immersed in dry-ice powder (ca. −93°).

The traps were made of glass tubing, 12 cm × 2 mm I.D., for room temperature sampling. For halocarbons analysis stainless-steel traps, 14 cm × 4 mm I.D., were used. These were filled with the adsorbent, with a stainless-steel net at each end to keep the packing in place and soldered to standard Swagelock-type fittings for connection to the carrier gas line.

For micropacked columns a double trap was used. The effluent from the sampling trap was transferred to a capillary trap placed on-line to the carrier gas line according to the scheme shown in Fig. 1. The capillary trap was cooled at the temperature of liquid nitrogen in a small Dewar cylinder, and the four-way valve was open in the injection position. Then the capillary trap was heated with a flash-heating system as described by Versino et al.[7]. The entire scheme is shown in Fig. 1.
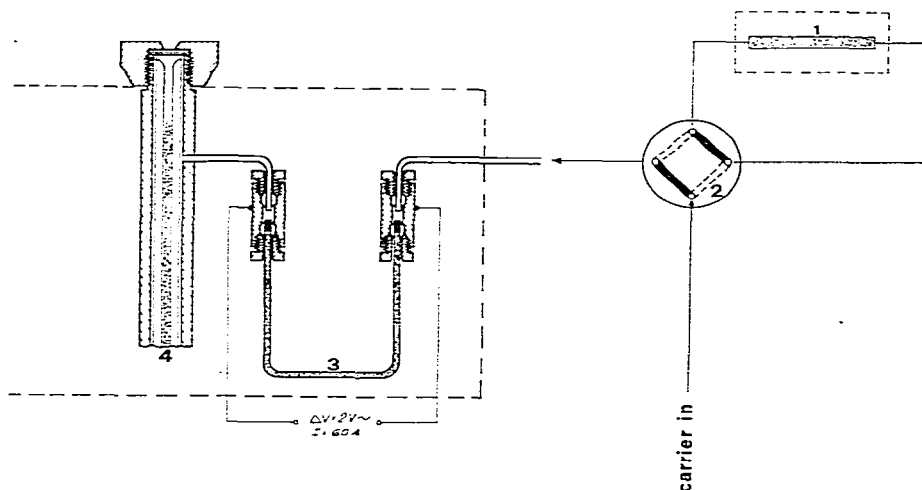

Fig. 1. Scheme of the double-trap injection system for micropacked columns. 1 = Sampling trap filled with Carbopack B (80–100 mesh); 2 = four-way valve in the heating position of the sampling trap; 3 = capillary trap filled with Carbopack C (80–100 mesh), frozen at liquid nitrogen temperature during injection from the sampling trap and flash heated for injection into the column; 4 = GC column head.

The micropacked columns were of the type described previously[8], but were made of glass tubing (6 mm O.D., 1 mm I.D.). Carbopack B, 80–100 mesh (Supelco, Bellefonte, Pa., U.S.A.) was also used as trapping material in the microtrap. The same adsorbent (60–80 mesh) was used as the packing material in the columns for halocarbons, coated with different amounts of SP1000 according to criteria that will be discussed later.

Carbopack C was used either for the packed or micropacked columns and coated 0.1% SP1000. Personal sampling pumps (Aircheck, from DKC, Pittsburg, Pa., U.S.A., Model 222-351) were used for low-volume sampling (1–3 l) and more powerful pumps for sampling of larger volumes. The sampling rates never exceeded 200 ml/min (S.T.P.).

Extra-pure (99.99%) nitrogen and helium (SIO, Milan, Italy) were used as carrier gases.

RESULTS AND DISCUSSION

Sampling techniques

Two sampling techniques were considered, both based on the capture of the organics from air by passing the latter through a tube containing an appropriate adsorbent. One, adopted by NIOSH for monitoring air pollutants in working areas, uses adsorption on active charcoal or other "strong" adsorbents, followed by dissolution of the compounds in a solvent (carbon disulphide in most instances) and GC analysis. The other is based on adsorption of the organics on "light" adsorbents such as Carbopack B[5], Tenax GC[6] and others[9,10], followed by thermal desorption and direct injection.

In the NIOSH method large volumes of air are sampled, so that by means of a personal pump the exposure of workers to air pollutants can be followed during 8 h of work. Such a long sampling time is also needed to collect enough sample to be analysed. Dissolution in a solvent implies considerable sample dilution, so that a single injection, which usually cannot exceed 10 μl, contains about one hundredth of the sample collected. On the other hand, sampling with a "light" adsorbent and direct injection of all of the sample collected allows a much higher sensitivity.

In Fig. 2 a comparison of the two methods is given. The two chromatograms are reported at the same sensitivity and refer to 5.5 l of air from our laboratory sampled through the active charcoal tube (A), and to 0.8 l of the same air, sampled simultaneously, using the thermal desorption method with a Carbopack B trap (B). Two disadvantages can be observed in chromatogram A in comparison with B: the solvent peak masks the acetone and other peaks with low retention times, and most peaks are undetected.

At least a four-fold volume is needed in order to obtain significant peaks using the charcoal method. This means that while pumping at the maximum acceptable rate (200 ml/min), one needs about 2 h for sampling. Although this is usually feasible when checking the average air quality in a working area, it is impossible to detect brief emissions during certain steps in plant processes. In our experience, this is a frequent necessity. As an example, we considered the problem of monitoring bis-(chloromethyl) ether during the first stages of a distillation step, which lasted not more than 15 min. In this instance we could not use the NIOSH method for the reasons mentioned above, whereas very clear chromatograms were obtained using Carbopack B and Tenax traps[1].

In conclusion, it appears that the thermal desorption procedure has several advantages over solvent extraction, namely: (1) higher sampling flexibility; (2) higher overall sensitivity; (3) more homogeneous behaviour to different substances; and (4) higher overall sensitivity. In spite of this, if the concentration of organics is high
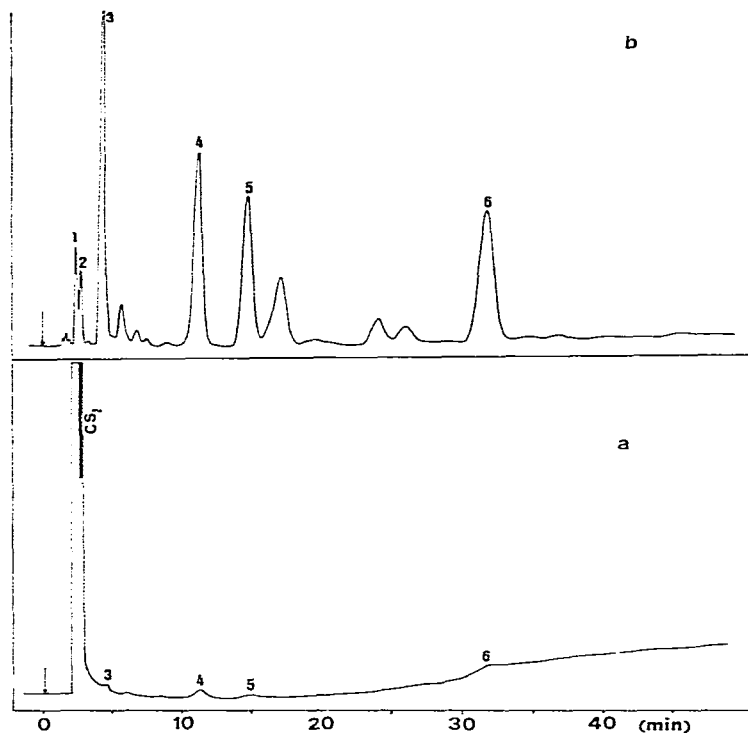
Fig. 2. Comparison of chromatograms obtained from laboratory air using different procedures: (a) 5.5 l trapped on active charcoal followed by solvent extraction with 1 ml of CS_2 (5.0 μl injected); (b) 0.8 l trapped on Carbopack B and directly injected with the heating stripping system. Column: glass, 2.0 m × 4 mm I.D., packed with Carbopack C + 0.1% SP1000. Temperature: initial, 100° for 5 min, then programmed at 5°/min to end. Peaks: 1 = acetone; 2 = CH_2Cl_2; 3 = n-C_5; 4 = benzene; 5 = n-C_6; 6 = toluene.

enough, or the sampling time can be as large as is required, there is a large advantage in using the NIOSH method, *viz.*, the possibility of repeating the same analysis many times.

As most halocarbons are volatile, the solvent extraction procedure cannot be used for them.

Analysis of halocarbons in air

The main problem we faced in halocarbon analysis was that of selecting a suitable column to obtain a complete separation of all of the compounds concerned, for the reasons stated above. In particular, the separation of Freon 21 from CH_3I is important in order to be able to quote the amount of the former in the atmosphere. The column chosen for this purpose consisted of Carbopack B (80–100 mesh) coated with 1.0% SP1000, with a polar acidic liquid phase, for two reasons, as follows. Firstly, we could use the outstanding selectivity of gas–liquid–solid chromatography, in which the driving force of the chromatographic process is molecular polarizability, which in several instances is independent of the vapour pressure. Secondly, the effects induced by using small amounts of a polar liquid phase do not influence the selectivity towards non-polar compounds such as halocarbons, as was shown in earlier work[11].

Further, by choosing the right amount of liquid phase, the separation factors can be adjusted to the particular analysis required.

Fig. 3 illustrates the analysis of halocarbons trapped from 30 l of air in a suburban zone. All of the main Freons and chlorinated solvents are detected and fairly well separated. However, the partial overlapping of the pairs Freon 21–CH$_3$I and CH$_2$Cl$_2$–Freon 114 may hinder the quantitative analysis of the two Freons when the relative amounts of the components are very different. The column used for this analysis was recently modified by coating Carbopack B with 0.5% SP1000 instead of 1.0%.
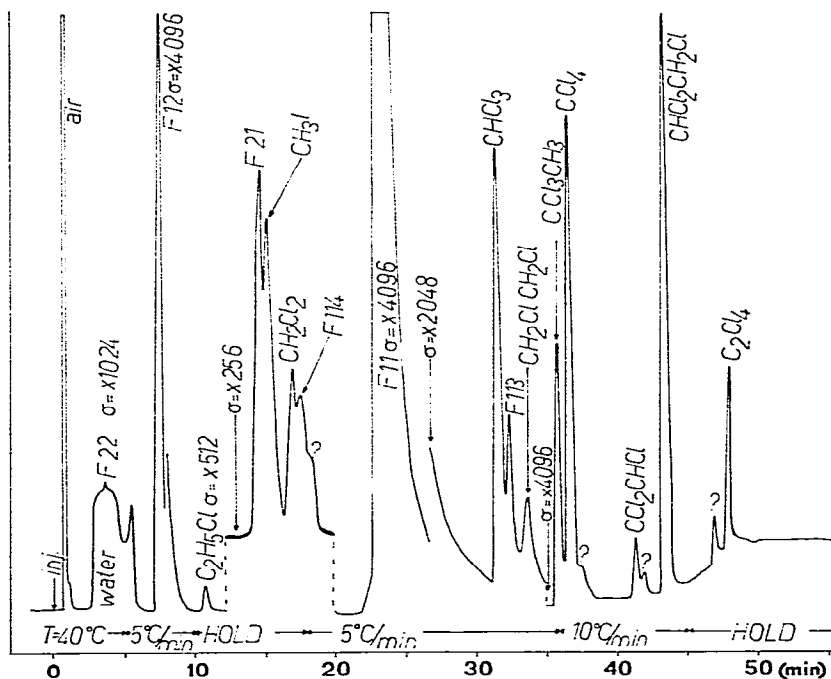

Fig. 3. Analysis of halocarbons in the atmosphere of a suburban area. Air trapped: 30 l. Column: stainless steel, 3 m × 2 mm I.D., packed with Carbopack B + 1.0% SP1000. Initial flow-rate, 40 ml/min; carrier gas, nitrogen; ΔP = 4.0 kg/cm^2; detector, ECD. (F = Freon).

On changing the temperature programme slightly, the chromatogram in Fig. 4 was obtained. All of the pairs are base-line separated, so that the compounds of interest can be quantitatively analysed.

Some problems still remain unsolved and need more study. The water peak covers both those of Freon 22 and CH$_3$Cl. However, with both of the columns used Freon 11, which gives the highest detector response, is well isolated from all other halocarbons, so that any interference is avoided. This is still a problem when gas–liquid chromatography is used[12].

Quantitative analysis of halocarbons

Some difficulties are encountered in the quantitative evaluation of halocarbons in the atmosphere, even when separation problems have been overcome. These are
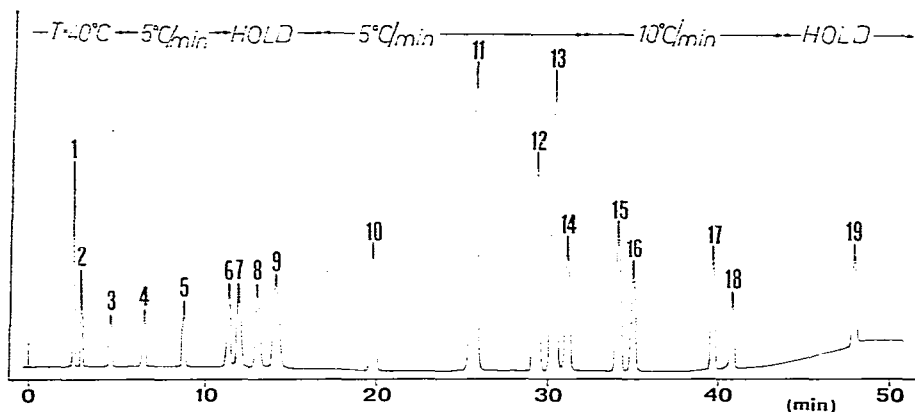
Fig. 4. Improved separation of C_1–C_2 halocarbons. Column: 3 m glass × 2 mm I.D., Carbopack B coated with 0.5% SP1000. Detector, FID; ⊿P = 4 kg/cm²; initial flow-rate, 40 ml/min (nitrogen). Peaks: 1 = CH_3Cl, 2 = F22; 3 = CH_3Br; 4 = F12; 5 = C_2H_5Cl; 6 = F21; 7 = CH_3I; 8 = CH_2Cl_2; 9 = F114; 10 = F11; 11 = 1,1-dichloroethane; 12 = $CHCl_3$; 13 = F113; 14 = 1,2-dichloroetane; 15 = CCl_3CH_3; 16 = CCl_4; 17 = 1,1,2-trichloroethylene; 18 = 1,1,2-trichloroethane; 19 = perchloroethylene. (F = Freon).

connected with the low breakthrough volumes that such compounds exhibit at room temperature on all light adsorbents. On the other hand, strong adsorbents and solvent extraction cannot be used for the reasons stated above and in this situation trapping at low temperature is necessary.

. In Table I the breakthrough volumes of some halocarbons are reported. It should be noted that most of the interesting Freons and chlorinated hydrocarbons are lost at room temperature, whereas this occurs only for CH_3Cl and Freon 22 at —93°. In fact, in order to detect the halocarbons present at lower concentrations, at least

TABLE I

APPROXIMATE BREAKTHROUGH VOLUMES OF HALOCARBONS ON CARBOPACK B

Compound	Breakthrough volume (ml) (S.T.P.)	
	20°	—93°
CH_3Cl	6.1	8000
Freon 22	6.5	10.000
Freon 12	32	65.000
C_2H_5Cl	57	310.000
Freon 21	71	100.000
CH_3I	71	100.000
CH_2Cl_2	200	>400.000
Freon 114	250	>400.000
Freon 11	400	>400.000
$CHCl_2CH_3$	450	>400.000
$CHCl_3$	500	>400.000
Freon 113	600	>400.000
CH_2ClCH_2Cl	700	>400.000
CCH_3Cl_3	2000	>400.000
CCl_4	2000	>400.000
CCl_2CHCl	>10.000	>400.000
$CHCl_2CH_2Cl$	>10.000	>400.000
C_2Cl_4	>10.000	>400.000

30 l of air should be sampled. On the other hand, the presence of water vapour in air yields a broad peak that hinders the detection of both Freon 22 and CH_3Cl in our column. To solve this problem, a different column should be used and parallel sampling should be carried out.

The operating conditions of the electron-capture detector (ECD) are extremely important. With our detector the best average conditions are the following: pulse mode, pulse amplitude 1 μsec, 18 V. In fact, these conditions are the are the best found for Freon 21, whereas for any of the other halocarbons better operating conditions might possibly be found.

For the quantitative analysis of halocarbons, calibration graphs for all of the compounds concerned should be constructed. Coupling of permeation tubes and the exponential dilution method has been found to be the best method in most instances[13]. Exponential dilution alone should be used for permanent gases. As an indicative value, the concentration of Freon 21 ranged between 10 and 20 ppt in the air sampled.

It is worth noting that the concentration of Freon 21 found by sampling under different meteorological and time conditions is constant, whereas the halocarbons with wider industrial uses vary substantially. This is particularly true with 1,1,2-trichloroethylene, chloroform, 1,1,1-trichloroethane and carbon tetrachloride.

A major difficulty in the quantitative analysis of halocarbons in the atmosphere is that some of these compounds are contained as ultra-trace impurities in high-purity commercial gases.

In Fig. 5 an example of the interferences from impurities is given, together with the solution of the problem. Two factors should be considered: under the experimental conditions the column is kept at room temperature before starting the analysis for a long period. During this period, which is necessary in order to achieve good detector stability, the column operates as a trap for the less volatile halocarbons. The same happens when purging the traps, which is carried out by passing high-purity nitrogen at 300° through the trap so that, if the trap is cooled while the carrier gas is still flowing, impurities are trapped.

Fig. 5a shows a chromatogram obtained without injection. Peaks from Freon 11, 1,1,1-trichloroethane, carbon tetrachloride, 1,1,2-trichloroethylene and tetra-chloroethylene can be identified. The same peaks are found in the chromatogram in Fig. 5b, where the contents of a trap purged with nitrogen and cooled under a gas flow were injected. In this instance the column carrier gas was further purified by placing on the gas line a molecular sieve–active charcoal trap cooled to −78° (dry-ice–acetone slush). The chromatogram in Fig. 5c, also obtained using purified nitrogen for trap purging, shows no peaks.

Measurement of hydrocarbons in the atmosphere

In connection with studies of photochemical smog, the routine qualitative and quantitative analysis of organic compounds is necessary. Although there is little doubt that for the qualitative analysis of the organics in the atmosphere glass capillary columns represent the best analytical tool[6], routine analysis, especially when a few compounds only need to be detected, can also be made with less efficient columns. In our work, micropacked columns were usefully employed to obtain comparative chromatograms of the air pollution in different urban areas in order to follow changes in concentration of less volatile compounds, say from C_5 to C_{13}.
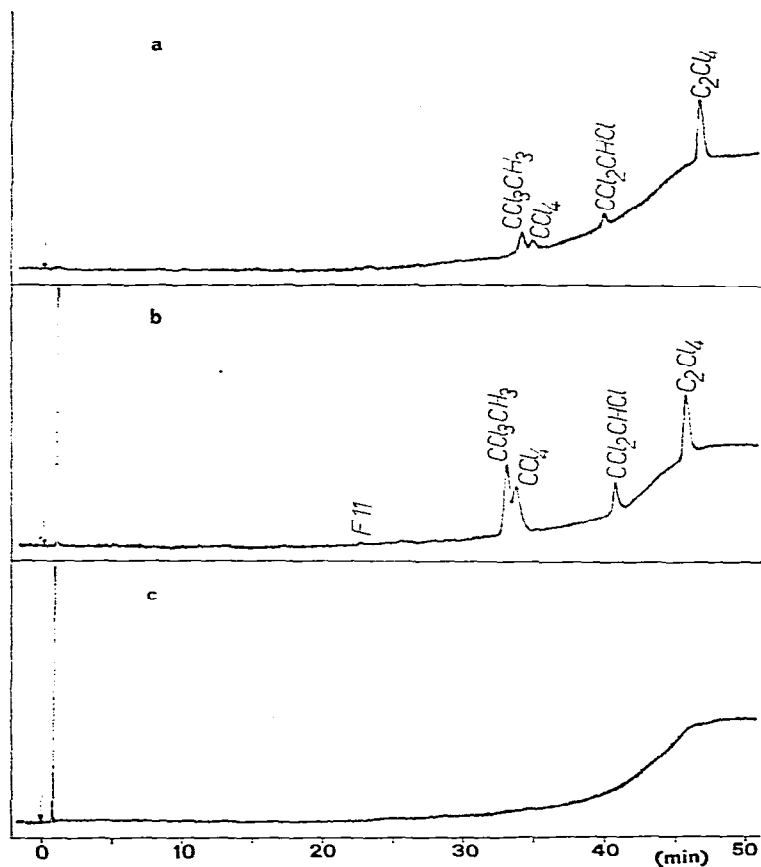
Fig. 5. Effect of halocarbon impurities contained in the carrier gas. (a) Temperature-programmed chromatogram obtained after 30-min room-temperature column operation, without carrier-gas purging: (b) same chromatogram with injection from the trap purged with unpurified nitrogen, but using purified carrier gas; (c) same chromatogram obtained using purified carrier gas and purified purging nitrogen. Conditions as in Fig. 3.

Gas–liquid–solid chromatography was again used as a separation technique. Carbopack C was coated with 0.1 % SP1000 so as to obtain a highly selective column. The surface coverage of the graphitized carbon black was, in fact, only about 30%, preserving the selectivity of the adsorbent, even though a linear isotherm is obtained for the hydrodarbons. On the other hand, the use of the same amount of a non-polar stationary phase could decrease the separation factors towards isomers[11].

The number of theoretical plates of the 1 m × 1 mm I.D. column, 170–200 mesh, is about 5000, which permits the separation of more than 50 peaks, as shown in Fig. 6. The chromatogram was obtained by trapping 1 l of air in a street of high traffic density in Rome. From the breakthrough volumes given previously[5], it should be noted that low-boiling compounds up to C_4 were partially lost during sampling. So far as as the column is concerned, this represents a good compromise between efficiency and analysis time.
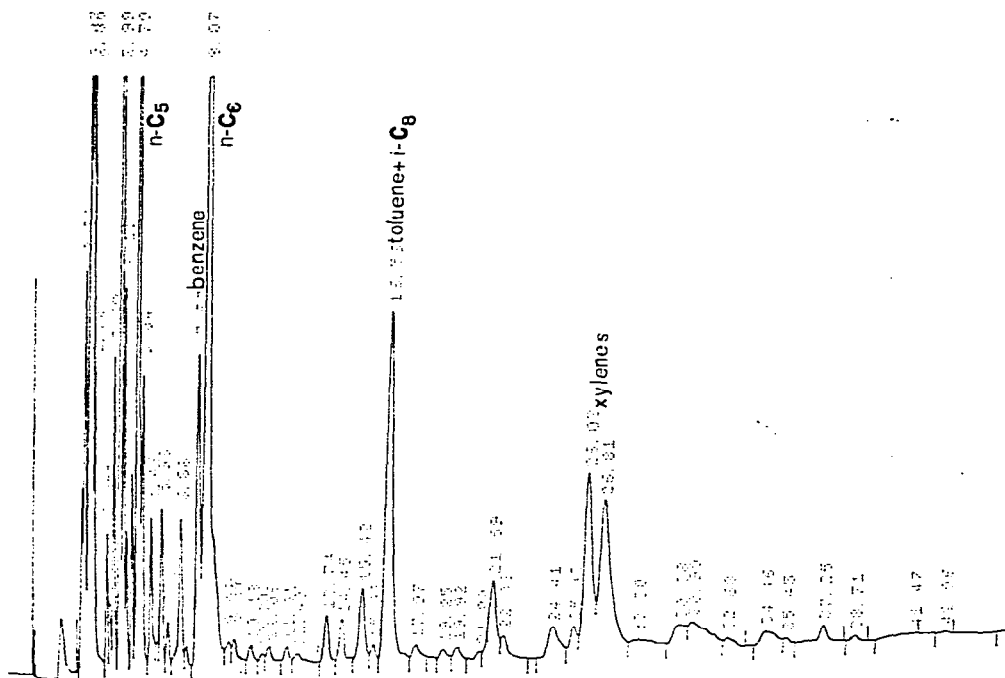
Fig. 6. Chromatogram obtained with an HP Model 3380A integrator on an air sample[12] of a street in the centre of Rome sampled with Carbopack B. Column: glass 1 m × 6 mm O.D. × 1 mm I.D., packed with Carbopack C (170–200 mesh) coated with 0.1 % SP1000. Carrier gas, helium; $\Delta P = 5$ kg/cm². Temperature programme: initial, room temperature, then programmed at 20°/min to 100° and at 5°/min to 250°.

ACKNOWLEDGEMENTS

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