

Evaluation of capillary gas chromatography for the measurement of C₂–C₁₀ hydrocarbons in urban air samples for air pollution research

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ABSTRACT

A method for the determination of speciated non-methane hydrocarbons (C₂–C₁₀ range) in ambient air samples was evaluated. The method involves a two-step cryogenic procedure: preconcentration (air sample volumes of 100–1000 cm³) and refocusing combined with capillary GC with flame ionization detection. GC columns were used under optimized temperature programming conditions (GC oven starting at above ambient temperature). Two systems were used to monitor hydrocarbon concentrations in urban air. The first system uses a megabore capillary column with a thick film of bonded non-polar silicone stationary phase (5 μm, SPB-1), which was found to be suitable for the chromatographic separation of hydrocarbons in ambient air samples without removing the moisture. To obtain a reasonable separation of volatile hydrocarbons in the C₂–C₅ range, a methylsilicone column was connected in series with a megabore methylphenylsilicone column. Better resolution of C₂–C₆ hydrocarbons was achieved on the latter system using an Al₂O₃–KCl porous-layer open tubular (PLOT) column. A dry-ice-cooled water trap was devised to remove moisture from ambient air samples. The PLOT column was not suitable for α- and β-pinene owing to decomposition. The reproducibility of GC performance (*i.e.*, retention time and peak-area integration) is discussed in detail. Both systems showed good long-term stability and gave good results for the determination of hydrocarbon concentrations ranging from several ppt to 100 ppb by volume in air samples from the Toronto urban area.

INTRODUCTION

Many non-methane hydrocarbons (NMHCs) present in the urban atmosphere are known to be toxic and certain hydrocarbons are known to participate in photochemical reactions resulting in the formation of oxidants such as ozone and peroxyacetyl nitrate (PAN) [1]. Large amounts of volatile organic substances are emitted from mobile and stationary sources [2]. With regard to anthropogenic hydrocarbons, motor vehicles make a significant

contribution to ground-level concentrations of NMHCs [3,4] at urban sites. The median profile of hydrocarbon concentrations in many USA cities is predominantly made up of alkanes, aromatics, alkenes and acetylene, whereas in many European cities the relative abundances of aromatics are dominant over alkanes [5]. There is relatively little information in the literature on the distribution of species within each type of NMHC emission or the spatial distribution of NMHC emissions in urban air. This information is necessary for assessing air quality and implementing pollution control measures. A reliable analytical system for determining the hydrocarbon concentration in air is a prerequisite for this purpose [6].

Commonly employed techniques for measuring atmospheric NMHCs include a gas chromatogra-

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phy (GC) with flame ionization detection (FID) [5,7–12] and/or photoionization detection (PID) [7,8,12] and flame photometric detection (FPD) [10]. GC combined with mass spectrometry (MS) has also been employed [8,13,14]. Columns with non-polar silicone stationary phases have been commonly employed for the analysis of multi-component hydrocarbon mixtures [15]. Their application to analyses of volatile hydrocarbons in ambient air has been reported [5,7,8,10,11,13,14,16–18]. Columns with chemically bonded phases and columns with a porous layer of adsorbents made of $\text{Al}_2\text{O}_3\text{-KCl}$ [9,12,17] and Porapak Q [10,11,17] have also been used in recent years.

Concentrations of individual NMHCs in urban air are often in the low parts per billion range and below. It is therefore necessary to employ a technique that enriches a sufficient amount of the species for analytical detection [17]. Cryogenic sample preconcentration is often employed for this purpose. The sample volume typically ranges from 100 to 1000 cm^3 . Air sample collection using stainless-steel containers with metal bellows valves combined with subsequent GC separation after preconcentration is in common use for analysing low- and medium-molecular-mass trace gases of moderate or low polarity and reasonable stability, such as hydrocarbons (see, *e.g.*, ref. 19). On-line preconcentration with GC involves cryogenic preconcentration of the hydrocarbons onto a solid substrate (solid or porous glass beads [7–11]), whereby a cooled adsorption tube retains all the atmospheric trace components except nitrogen, oxygen, carbon dioxide and methane. The trapped NMHC components are thermally desorbed quantitatively. Moisture in ambient air samples presents problems, as it can extinguish the FID hydrogen flame, plug columns at sub-zero temperatures and cause serious damage to the solid $\text{Al}_2\text{O}_3\text{-KCl}$ phase of porous-layer open-tubular (PLOT) columns [17]. Thus, the air samples are commonly dried with Nafion tubing [3], potassium carbonate [7,9,10] or magnesium perchlorate [8,18] water traps. Although these techniques remove the moisture, losses of some NMHC components {on K_2CO_3 [20], $\text{Mg}(\text{ClO}_4)_2$ [11,20]}, and contamination have been observed with the use of a Nafion dryer [20].

Adsorptive sampling of hydrocarbons in industrialized and remote areas on non-polar polymers

and carbon adsorption traps has been widely used [17,19,20]. In recent years multi-layer adsorbent cartridges have been employed [5,12,14]. This mostly solves the problem of moisture affecting the chromatography, but this enrichment process is at present not adequate for all hydrocarbons in the $\text{C}_2\text{-C}_{12}$ range. According to Rudolf *et al.* [19] and Ciccioli *et al.* [14], most affected are the $\text{C}_2\text{-C}_3$ hydrocarbons. Lancesdorfer and Puxbaum [5], however, claimed a recovery of >90% for C_2 compounds and >95% for $\geq \text{C}_3$ compounds.

This paper describes techniques employed by our group for NMHC measurements in ambient air samples from the Toronto urban area using a preconcentration system (made in-house) combined with capillary GC-FID. Problems associated with moisture in humid samples are discussed and solutions proposed. Different columns (chemically bonded non-polar dimethylsilicone phase and $\text{Al}_2\text{O}_3\text{-KCl}$ PLOT columns) were evaluated with regard to their capacity to handle moisture, the resolution of species of interest and the reproducibility of the GC performance (*i.e.*, retention time and peak integration).

EXPERIMENTAL

Preconcentration unit combined with GC

A schematic diagram of the cryogenic system combined with a gas chromatograph is shown in Fig. 1. All the gas handling lines, except the water trap, were made of chromatographic-grade stainless-steel (SS) tubing [1/16-in. SS 304 and 1/8- and 1/4-in. SS 316 (1 in. = 2.54 cm)] and connections were made by either SS 316 Swagelok or SS Valco fittings. A Valco ten-port switching valve (Model 10UWT) was used for switching both the preconcentration loop and gas flow. The preconcentration loop (16 cm in length) was constructed of 1/8-in. SS tubing packed with 60–80-mesh untreated solid glass beads. Frits (1 μm) and silanized glass-wool (Chromatographic Specialties) were placed at both ends of the tube to keep the glass beads in place. Liquid argon (-186°C) was used to cool the loop. A length of 20 cm \times 1/4-in. O.D. \times 1/8-in. I.D. FEP Teflon tubing cooled with dry-ice to -30°C was used as the water trap and was placed after the sample canister and before the preconcentration U-trap. Air samples from electropolished pressurized

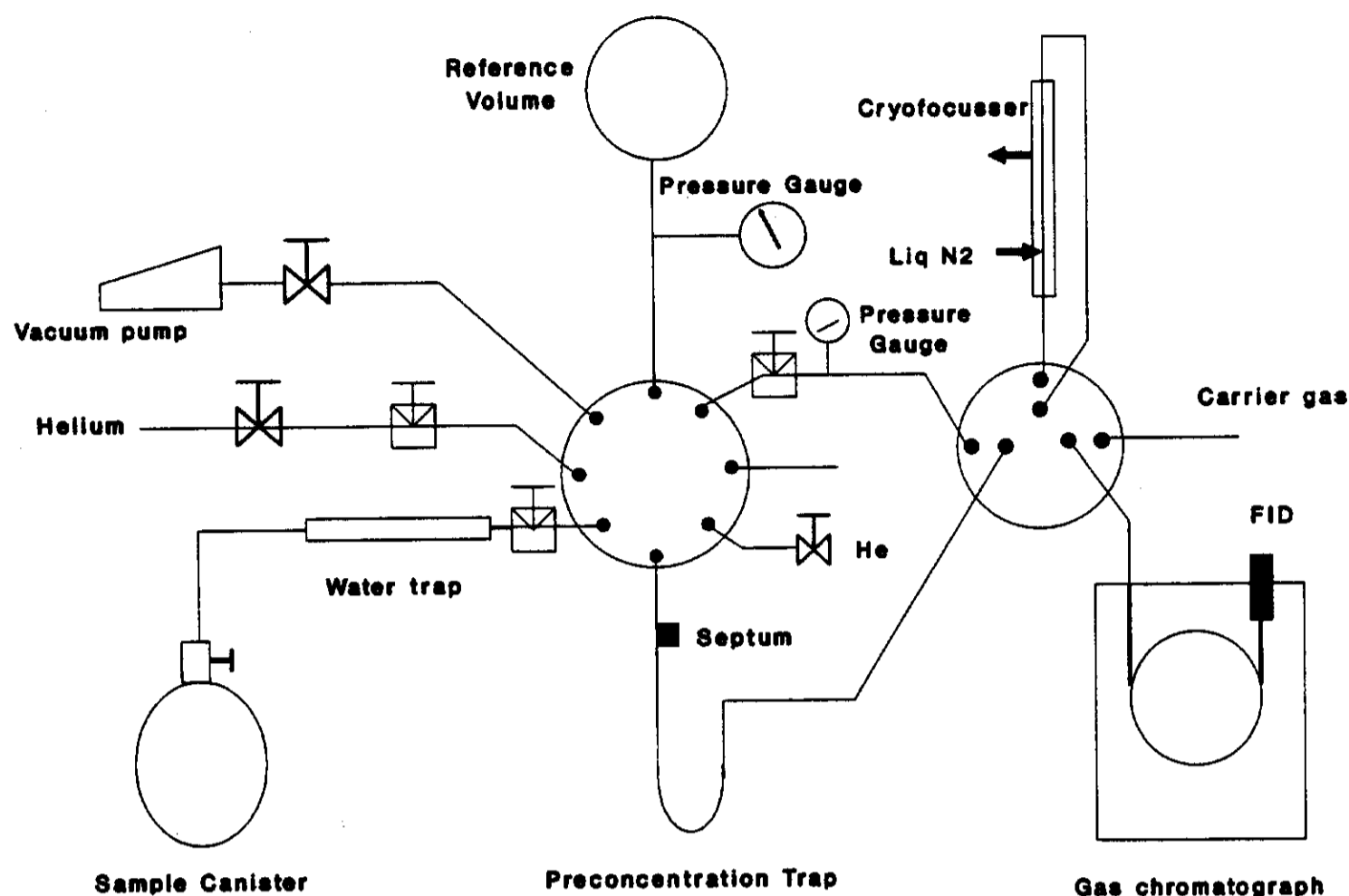


Fig. 1. Two-stage cryotrapping unit combined with capillary GC.

[ca. 40 p.s.i. (1 p.s.i. = 6894.76 Pa)] SS canisters (Biospherics) were introduced at atmospheric pressure (flow-rate 30 cm³/min) into the cryogenic U-trap. The pressure was measured by an Omega pressure gauge (Model PGS-25L-30 V/30) and adjusted by the use of a Nupro SS-4BMW needle valve placed immediately after the water trap and a second Nupro needle valve (SS-SS2) placed between the preconcentration loop and the reference volume.

In addition to the cryogenic preconcentration loop, a second cryogenic system (Cryotherm Model 100; Tekran), which can be ballistically heated, was mounted at the head of the GC column. The Cryotherm was a cryo-prefocus device (cryo-loop) employed to generate narrower hydrocarbon bands.

When the required volume of air sample (100–1000 cm³, depending on the NMHC content of the sample) was loaded, the preconcentration loop was heated to 100°C with an aluminium heating block and the sample was swept with helium (flow-rate 20 cm³/min) into the cryo-prefocusing device cooled to –180°C with liquid nitrogen. After all the NMHC had been transferred, the prefocusing device was

heated for 11 s (up to 150–200°C) and helium was used to sweep the sample on to the GC column. The reference volume (1600 cm³), made of stainless steel, along with a Barocell pressure gauge (Data-metrics, Model 600A-1000T-R12-H21X-4) was used to determine the volume of air sample that passed through the preconcentration loop.

After every cycle through the system, the reference volume was evacuated to <10⁻² Torr (1 Torr = 133.322 Pa) and ultra-high-purity (UHP) (99.995%) helium (Liquid Carbonic) was used to purge the heated lines of hydrocarbons that may have remained on the walls. Heating and back-flushing with UHP helium were also employed to purge the dry-ice water trap. During sample loading and sample purging, all the lines and valves in the system were heated at 100°C to minimize the surface adsorption of NMHC.

Two preconcentration–GC systems were used in the analysis of NMHCs. The first system employed a tandem megabore capillary arrangement [SPB-1 + DB-5; SPB-1 (Supelco), 60 m × 0.53 mm I.D. with a 5-μm bonded film thickness of dimethylsilicone phase; DB-5 (J&W Scientific) 30 m × 0.53 mm I.D. with a 1.50 μm bonded film of methyl-

phenylsilicone]. The second system used a 50 m \times 0.32 μ m I.D. Al₂O₃–KCl PLOT column (Chrom-pack) with a 5- μ m adsorbent layer. Moisture removal from this system was achieved by passing the sample through the dry-ice water trap. A conventional-bore dimethylsilicone column (DB-1, J&W Scientific; 30 m \times 0.25 mm I.D., with a film thickness of 0.25 μ m) was also tested in this system. A Hewlett-Packard Model 5890 gas chromatograph equipped with a flame ionization detector was connected to a personal computer. All GC gases (helium, hydrogen and air) were passed through a hydrocarbon trap (Supelco, Model 2-2445). The sample (after preconcentration, cryofocusing, and ballistic heating) was swept directly on to the GC column using UHP helium. All GC measurements were performed with temperature programming. Hewlett-Packard GC software (HPCHEM) was used for data collection, data display and integration purposes.

Preparation of standards for calibration

Calibration of the GC preconcentration system was accomplished by the use of multi-component gas mixtures (10–20 ppm, Scotty Can mix 2, 3, 4, 5, 6, 7, 8, 30, 54, 55 and 243) prepared by Scott Specialty Gases. Certain gas mixtures (*i.e.*, benzene, toluene, ethylbenzene, xylenes, isoprene and pinenes) were prepared in-house from pure samples. The NMHC samples were diluted with UHP helium to the level of 1 ppbv by volume (ppbv). A hydrocarbon standard of nominal 10 ppbv concentration of 103 species in the C₂–C₁₂ range was prepared gravimetrically (D. Wang). The diluted NMHC mixtures were employed as calibration gas mixtures for the preconcentration–GC system. A canister filled with UHP helium was used for blank tests on a daily basis.

RESULTS AND DISCUSSION

Two systems were evaluated and compared: (1) a megabore capillary column with a thick film of non-polar silicone; this column can be operated without removing the moisture from humid samples; and (2) a conventional methylphenylsilicone column and a Al₂O₃–KCl column PLOT; water was removed from ambient air samples before analysis with these columns.

Megabore column system

Urban air samples contain hydrocarbons at concentration levels that can be determined using sample volumes in the range 150–500 cm³ at atmospheric pressure. It has been demonstrated in this study that a thick-film megabore column with a non-polar chemically bonded silicone stationary phase is suitable for hydrocarbon analysis of ambient air without removing the moisture from the sample. In order to prevent moisture from freezing on the column and obstructing the gas flow, the GC oven was operated above 0°C. Good separation of the volatile hydrocarbons (C₂–C₅ range) was obtained using the tandem column (SPB-1 + DB-5) and the column performance was not affected by problems caused by moisture.

Particular attention was given to the resolution of isoprene from the neighbouring components. The isoprene concentration in the Toronto urban area is not usually very high as biogenic sources are not in the immediate vicinity of the sampling sites and the lifetime of isoprene can be as short as a few h. The resolution of isoprene and *n*-pentane at the optimum carrier gas flow-rate increased from 1.27 on the SPB-1 column to 1.47 on the tandem column. Satisfactory resolution of several C₃–C₅ hydrocarbons was also obtained. The increase in resolution, however, also resulted in an increase in the overall retention times. By implementing a multi-ramp temperature programme, we achieved reasonable separations of individual species of atmospheric interest in the entire C₂–C₁₀ range in addition to shortening the overall analysis time (60 min). The chromatograms of a standard calibration mixture and a real air sample are illustrated in Fig. 2.

The reproducibility tests of absolute retention times and area count measurements were performed using a commercial gas mixture (Scotty Mix 243) of C₁–C₇ *n*-alkanes with a mixing ratio of nominal 10 ppbv (*e.g.*, for *n*-butane, 100 μ l injected represent 4.74 ng) with and without (direct injections into the cryofocuser) the first preconcentration device. Good reproducibility of absolute retention times of individual species (number of measurements $n = 3$) was observed regardless of whether the sample was passed through the first preconcentration stage or was injected directly on to the cryofocuser (Table I). The relative standard deviation (R.S.D.) was between 0.01 and 0.04%. The reproducibility of rela-

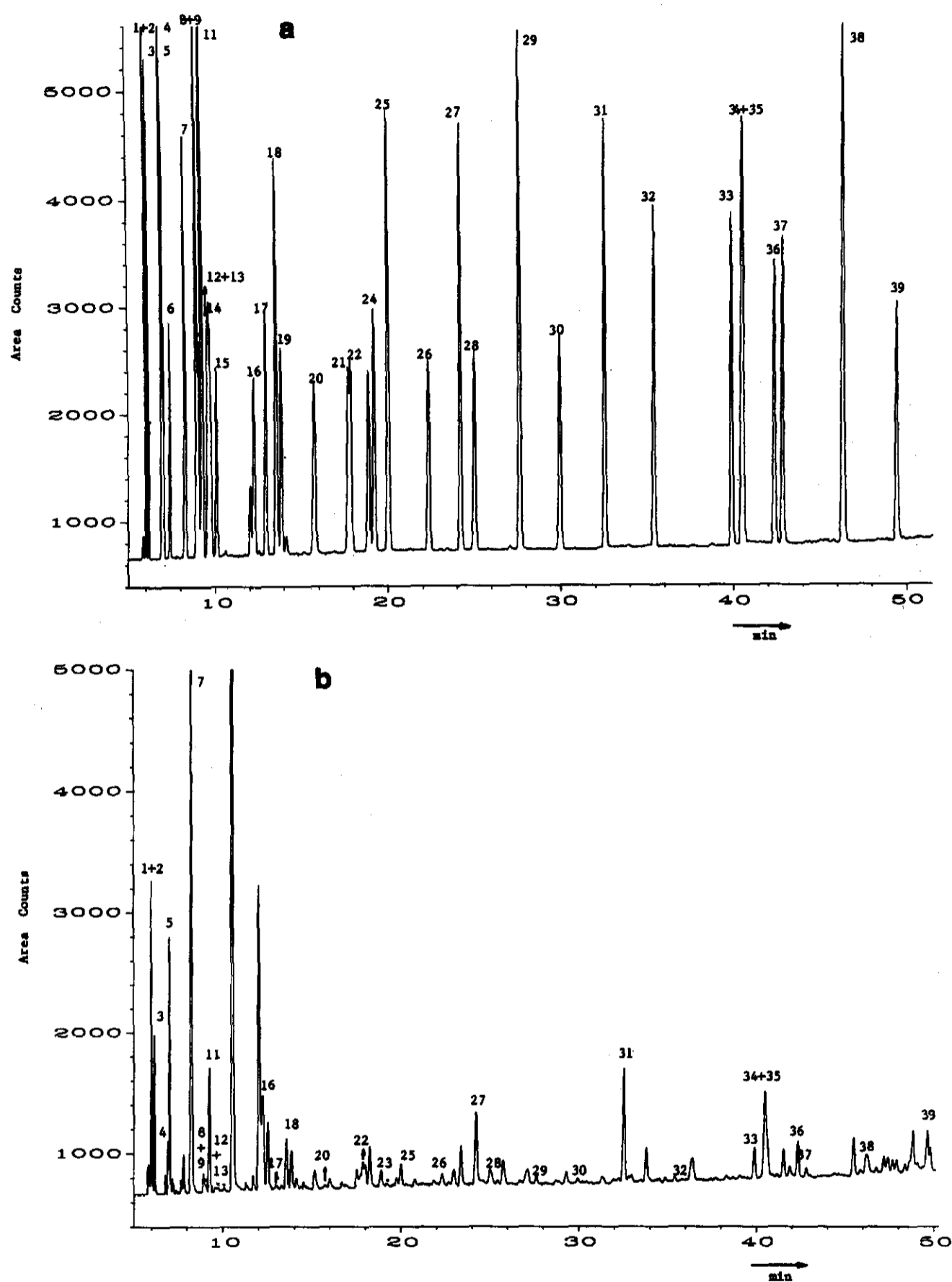


Fig. 2. (a) Separation of speciated hydrocarbons from a multi-component mixture using the tandem column (SPB-1 60 m \times 0.53 mm I.D. with 5- μ m chemically bonded non-polar dimethylsilicone plus DB-5, 30 m \times 0.53 mm I.D. with 1.5- μ m film of bonded phenylmethylsilicone) with temperature programming: initial temperature 30°C, increased at 3°C/min to 180°C, then at 25°C/min to 240°C, 15 min isothermal; carrier gas, He (linear velocity 26.65 cm/s); FID. Peak assignments: 1 = ethylene; 2 = acetylene; 3 = ethane; 4 = propene; 5 = propane; 6 = propyne; 7 = isobutane; 8 = 1-butene; 9 = isobutene; 10 = 1,3-butadiene; 11 = *n*-butane; 12 = *trans*-2-butene; 13 = butyne; 14 = 2,2-dimethylpropane; 15 = *cis*-2-butene; 16 = isopentane; 17 = 1-pentene; 18 = *n*-pentane; 19 = isoprene; 20 = 2,2-dimethylbutane; 21 = cyclopentane; 22 = 2-methylpentane; 23 = 3-methylpentane; 24 = 1-hexene; 25 = *n*-hexane; 26 = methylcyclopentane; 27 = benzene; 28 = cyclohexane; 29 = *n*-heptane; 30 = methylcyclohexane; 31 = toluene; 32 = *n*-octane; 33 = ethylbenzene; 34 = *m*-xylene; 35 = *p*-xylene; 36 = *o*-xylene; 37 = *n*-nonane; 38 = α -pinene; 39 = β -pinene. (b) Separation of speciated hydrocarbon pollutants in an urban air sample. Sampling site, Toronto, CN (Canadian National) Tower, 380 m level; collection date, September 10, 1991; sample volume, 466.7 cm³; 90% humidity. Experimental conditions and peaks assignments as in (a).

TABLE I

COMPARISON OF RETENTION TIMES AND PEAK-AREA INTEGRATIONS OF SELECTED HYDROCARBONS (ppbv) LEVEL CALIBRATION MIXTURE) USING CRYOTRAPPING FOLLOWED BY CRYOFOCUSING AND CRYOFOCUSING ALONE

Compound	Direct syringe injection with cryofocusing ^a			Cryotrapping and cryofocusing ^a		
	Peak area		Absolute retention times:	Peak area		Absolute retention times:
	Mean	R.S.D. (%)	R.S.D. (%)	Mean	R.S.D. (%)	R.S.D. (%)
Ethane	4362	2.1	0.031	4281	1.4	0.044
Propane	6254	2.7	0.038	6167	1.3	0.044
<i>n</i> -Butane	7975	4.4	0.020	7832	1.4	0.005
<i>n</i> -Pentane	9413	7.3	0.021	9261	1.4	0.023
<i>n</i> -Hexane	10 391	10.2	0.015	10 265	1.6	0.016
<i>n</i> -Heptane	10 754	12.4	0.006	10 469	1.8	0.006

^a $n = 3$.

tive retention times was checked over a period of 30 days and the results obtained are shown in Fig. 3. The reproducibility of area count measurements was considerably worse for syringe injections than with large-volume sample preconcentration. Typical R.S.D.s with sample preconcentration and direct syringe injection were 1.5% and 6.5%, respectively. The reproducibility of the system in analysing a multi-component standard mixture (ppbv concentration) is given in Table II.

The reproducibility of retention time measurements and determination of hydrocarbons concentrations in an urban sample is given in Table III. For ambient air samples, the R.S.D. for absolute retention time of individual species is better than 0.15% and for quantitative measurements the R.S.D. is less than 6% at low ppbv levels. With hundreds of sample runs as a database (the column was in continuous use for the analysis of air hydrocarbons over 1 year), this technique has proved to

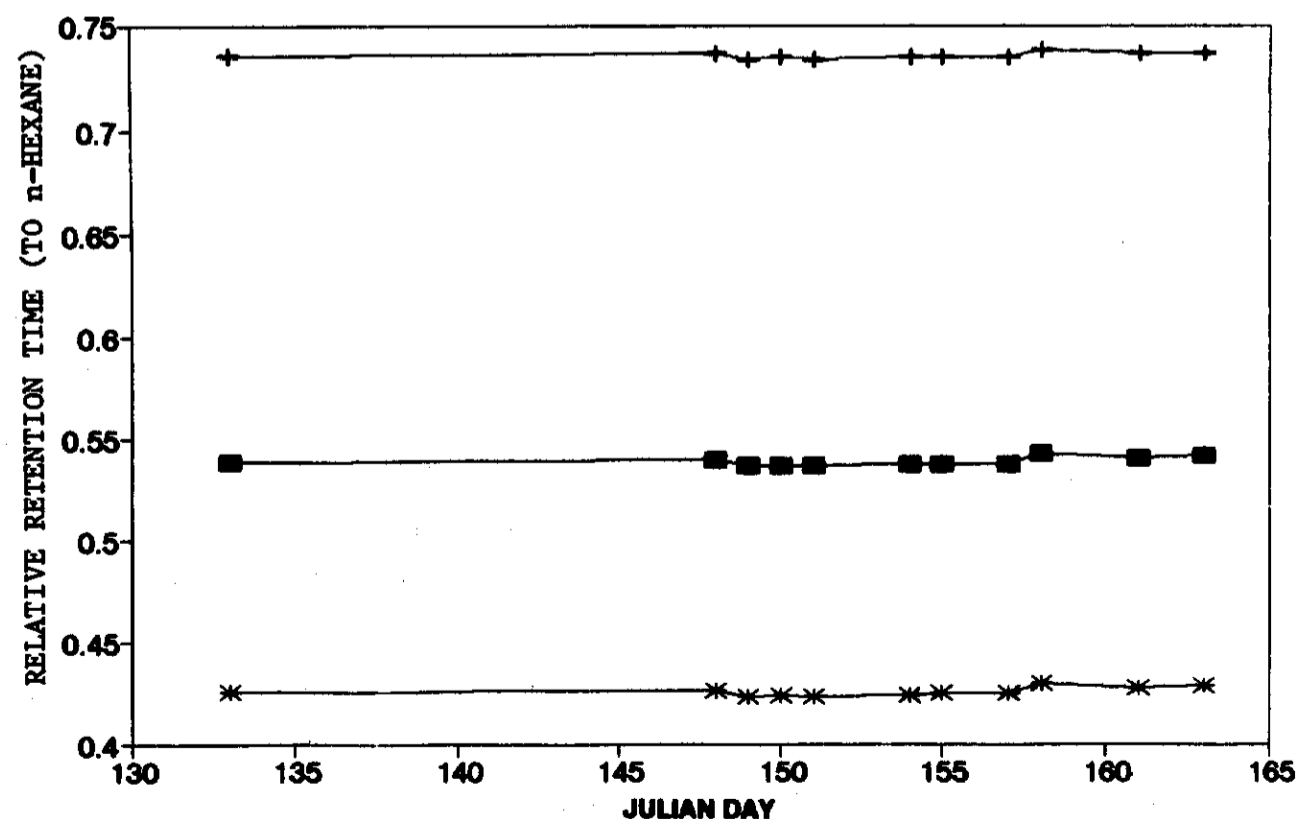


Fig. 3. Reproducibility of relative retention times of *n*-alkane standards (to *n*-hexane) measured over a period of 30 days after preconcentration and GC analysis using the tandem column (SPB-1 + DB-5). * = *n*-Propane; ■ = *n*-butane; + = *n*-pentane.

TABLE II
REPRODUCIBILITY OF CONCENTRATION DETERMINATION IN ppbv USING PRECONCENTRATION-GC AND VARYING VOLUME OF STANDARD IN THE RANGE 200–350 cm³

Compound	Mean concentration (ppbv) ^a	R.S.D. (%) ^a
<i>Alkanes</i>		
Propane	10.27	2.62
<i>n</i> -Butane	20.14	0.85
<i>n</i> -Pentane	11.89	2.23
Isopentane	10.52	2.70
Cyclopentane	2.47	2.01
<i>n</i> -Hexane	13.41	0.37
Cyclohexane	1.95	0.36
Methylcyclopentane	3.55	2.58
2,2-Dimethylbutane	10.81	1.05
2-Methylpentane	13.95	0.51
3-Methylpentane	10.36	0.44
<i>n</i> -Heptane	12.88	0.13
Methylcyclohexane	1.60	0.44
<i>n</i> -Octane	3.00	0.77
<i>n</i> -Nonane	1.47	3.76
<i>Alkyne and alkanes</i>		
Acetylene	19.84	2.24
Propene	10.79	1.79
1-Butene	30.04	3.37
<i>trans</i> -2-Butene	12.99	1.74
<i>cis</i> -2-Butene	10.72	2.67
1,3-Butadiene	10.79	0.76
1-Pentene	11.06	1.49
1-Hexene	15.97	1.46
<i>Aromatics</i>		
Benzene	6.21	0.91
Toluene	5.25	0.94
<i>o</i> -Xylene	2.53	0.84
<i>m,p</i> -Xylene	4.87	1.60
Ethylbenzene	2.35	3.61
<i>Natural</i>		
Isoprene	3.18	1.33

^a *n* = 3.

be reliable in producing qualitative and quantitative data for both calibration standards and real air samples.

Recently, a review on the performance of preconcentration units connected on-line to a GC system was published by Schaeffer [17]. He concluded that the unit constructed by Schmidbauer and Oehme [9] was the best system built up to 1989. The latter workers reported a typical R.S.D. of absolute

retention time measurement to be about 1%, with a quantitative reproducibility of about 2% for hydrocarbon concentrations in the C₂–C₆ range with a mixing ratio of 1–6 ppbv. Although the system displayed excellent precision, one drawback was the sample handling. The system was constructed with three cryo-trapping devices and required 20 min for the sample to be transferred from the second trap to the cryogenic prefocusing device in addition to the time required to transfer the sample into the first part of the preconcentration unit. The sample transfer required a long time and a correspondingly high consumption of liquid nitrogen.

Calibration of the GC-preconcentration system was accomplished using three sources of standards. The literature reveals large discrepancies using different sources of calibration standards. Hov *et al.* [21] stated a difference of up to 51% for individual species between the calibration gases from two commercial suppliers. In our laboratory the calibration gas standards from different sources (Scott Specialty Gases, C&P Gas Standards and laboratory-made standards from neat liquids) were consistent for many species, with the largest discrepancy being 12%.

Good linearity of the FID response to sample amount was found for syringe injections of standard hydrocarbon mixtures with a mixing ratio in the ppmv range. A linear dependence of FID response on sample volume (100–650 cm³) was also observed. Good reproducibility (sample volumes of 200 cm³ and higher) was found for measurements of the mixing ratios of speciated NMHCs in ambient air in the pptv to ppbv range. The detection limit was *ca.* 5 ppbv for all species. The capacity to handle moisture from humid samples and the lack of a requirement for a moisture-removal process are major advantages of using a megabore column. For highly polluted air samples, the use of a dry-ice-cooled trap is still desirable for removing high-boiling components (> C₁₀), so that peak co-elution of species from the previous run with the C₂–C₁₀ hydrocarbon analysis can be prevented. Also the removal of the heavy components extends the lifetime of the column in addition to reducing column bleeding and reducing the total analysis time. The tandem column system was checked for possible losses of species in the C₂–C₁₀ range with and without the dry-ice-cooled trap in operation. No losses were

TABLE III

REPRODUCIBILITY OF AREA COUNT AND RETENTION TIME MEASUREMENTS FOR ANALYSIS OF URBAN AIR SAMPLE USING PRECONCENTRATION-GC

Compound	Area counts ^a		Absolute retention time: R.S.D. (%) ^a	Concentration (ppbv)
	Mean	R.S.D. (%)		
<i>Alkanes</i>				
Propane	81 328	4.65	0.09	13.104
n-Butane	45 770	1.05	0.16	5.613
n-Pentane	26 693	1.61	0.07	2.871
i-Pentane	53 843	2.73	0.11	4.991
n-Hexane	34 459	1.90	0.01	3.461
Methylcyclopentane	12 737	3.42	0.01	1.052
2-Methylpentane	28 060	1.18	0.02	2.278
3-Methylpentane	15 418	3.39	0.02	1.272
n-Heptane	14 005	1.98	0.01	1.375
Methylcyclo-hexane	15 329	1.14	0.01	1.051
n-Octane	9148	4.57	0.01	0.647
<i>Alkyne and alkenes</i>				
Acetylene + ethylene	36 137	3.31	0.09	7.627
Propene	5245	4.15	0.09	0.878
1-Butene	3220	4.01	0.13	0.405
cis-2-Butene	930	3.79	0.15	0.123
1,3-Butadiene	876	4.88	0.12	0.126
1-Pentene	1731	2.66	0.07	0.133
<i>Aromatics</i>				
Benzene	12 788	3.51	0.03	0.984
Toluene	266 735	0.60	0.01	21.344
o-Xylene	16 879	3.41	0.01	1.202
m,p-Xylene	40 627	3.33	0.01	2.474
Ethylbenzene	14 410	2.14	0.01	0.909
<i>Natural</i>				
Isoprene	2385	1.53	0.06	0.278

^a n = 3.

found for trap temperatures above -30°C .

Hydrocarbon data (obtained using the tandem column system) from an urban Toronto site are shown in Fig. 4a and b. The NMHC distributions observed at the CN Tower are shown in Fig. 4a for two different height levels (ground and 380 m) on a day when the wind was blowing across Lake Ontario from the south. The hydrocarbon concentrations are seen to be generally lower by a factor of >2 at the 380 m level, but are markedly reduced for highly reactive olefinic compounds such as 1-butene (a factor of 5.5), isobutene (8.0), 1-pentene (10) and 1,3-butadiene (12). These observations are indicative of long-range transport and the corresponding ageing of the air mass aloft. Fig. 4b shows the tem-

poral distribution of hydrocarbon concentrations at an elevated level (380 m) for the CN Tower. More detailed results of hydrocarbon distributions in Toronto urban and suburban sites will be presented elsewhere [22].

Performance of narrow-bore DB-1 and Al_2O_3 -KCl PLOT columns

Capillary columns with a non-polar stationary phase (depending on the column length, inside diameter, film thickness and operating conditions) resolve many of the hydrocarbons of atmospheric importance in the C_2 - C_{10} range [14,16-18]. In our laboratory, a $30\text{ m} \times 0.25\text{ mm}$ I.D. column with a $0.25\text{-}\mu\text{m}$ film thickness was used to analyse of ambi-

ent air samples for hydrocarbons. In order to obtain good resolution of low-boiling compounds (e.g. baseline separation of *n*-pentane and isoprene in ambient air samples), it was necessary to programme the GC oven to start from -50°C . Even at this low initial temperature it was not possible to separate completely the C_2 hydrocarbons (i.e. C_2H_2 , C_2H_4 and C_2H_6). Fig. 5 shows a chromatogram of a hydrocarbon standard that was obtained using this column. With this column, moisture had to be removed from humid air samples prior to GC analysis.

PLOT columns (with an $\text{Al}_2\text{O}_3\text{-KCl}$ layer) are excellent at separating volatile hydrocarbons of atmospheric importance in the $\text{C}_1\text{-C}_6$ range [23]. Without operating the GC oven at sub-ambient temperatures, the resolution is often better than that achievable by a non-polar stationary phase column. Another advantage of PLOT columns is that they can be operated [under optimum conditions with regard to HETP (height equivalent to a theoretical plate) at high linear carrier gas velocities [24],

resulting in shorter analysis times. Hence their employment for the analysis of ambient air samples is an obvious choice. As the column can be operated at temperatures above 0°C , clogging of the column due to moisture is not a problem. However, it has been reported that water can change the adsorption properties of the solid phase and cause unpredictable changes in the retention times [9] and, in some instances, irreparable damage to the column [17].

Moisture was removed from our systems by passing the air sample through a length of FEP Teflon tubing cooled with dry-ice. After the sample had passed through, the entire tube was heated with a resistive-wire wrapping to 80°C and back-flushed with UHP helium, so that the trapped water was removed. The FEP Teflon tubing was then cooled and cycled for the next sample. Losses of aromatic components (from an ambient air sample) due to the dry-ice water trap are displayed in Fig. 6. In the temperature range $+70$ to -42°C , no significant loss of the sample species was observed. Below -42°C , however, ethylbenzene and the xylenes

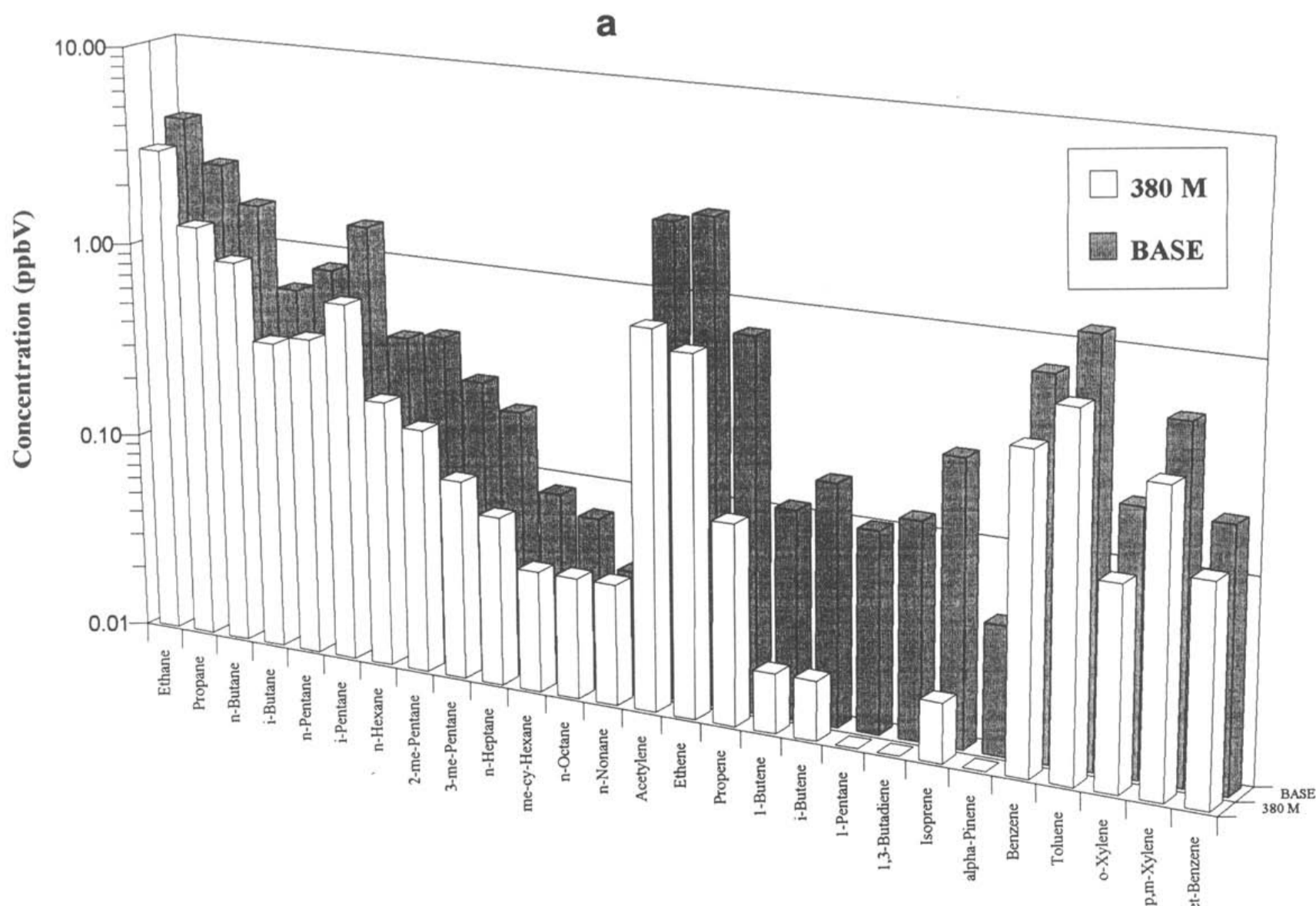


Fig. 4.

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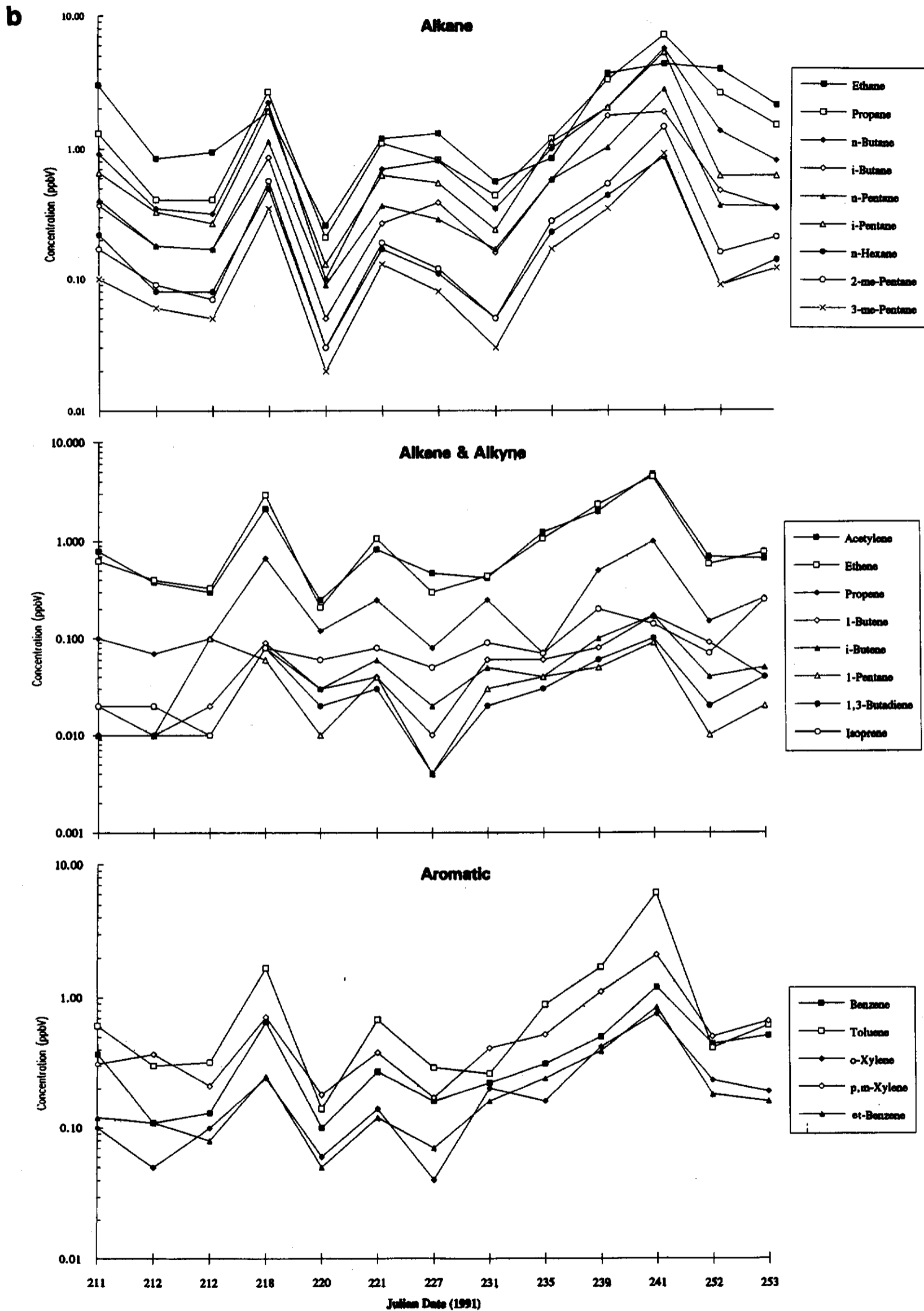


Fig. 4. (a) Hydrocarbon distribution at two height levels (ground and 380 m). Sampling site: Toronto, CN Tower, July 30, 1991. (b) Distribution of hydrocarbons (alkanes, alkenes, alkynes and aromatics) over several days (1991). Sampling site: Toronto, CN Tower, 380-m level.

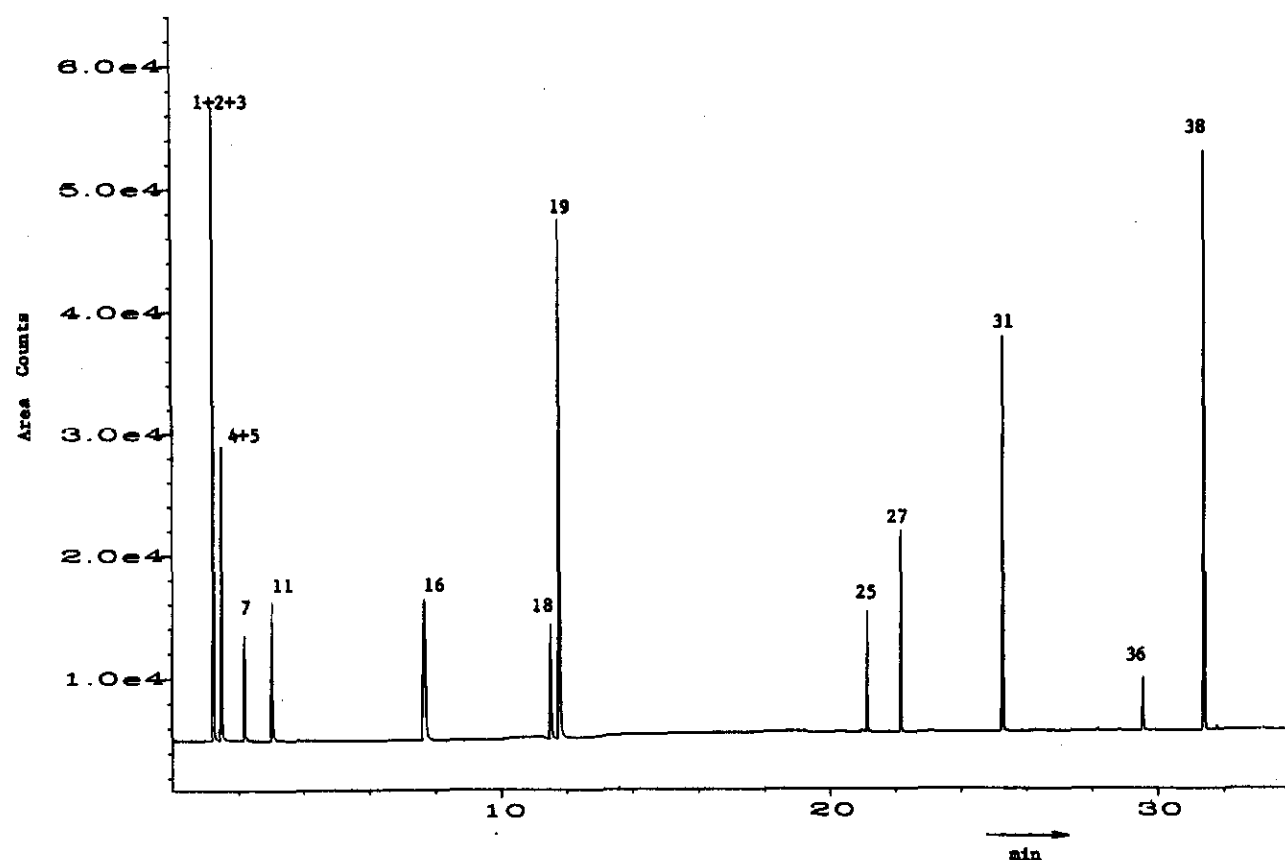


Fig. 5. Separation of hydrocarbon species of a calibration standard (using preconcentration-GC) on the DB-1 column (30 m × 0.25 mm I.D. 0.25- μ m film thickness) with chemically bonded dimethylsilicone phase with temperature programming: initial temperature, -50°C (8.00 min), increased at 5°C/min to 115°C, then at 30°C/min to 250°C, 10 min isothermal; carrier gas, He; FID.

were observed to be partially trapped in the cooled length of Teflon tubing. Benzene and toluene passed through the water trap at -60°C without being affected. It is apparent from the graph that

different components exhibit different losses with decreased temperatures. It appears that -30°C is an optimum temperature to use for removing moisture from air samples without significant losses of

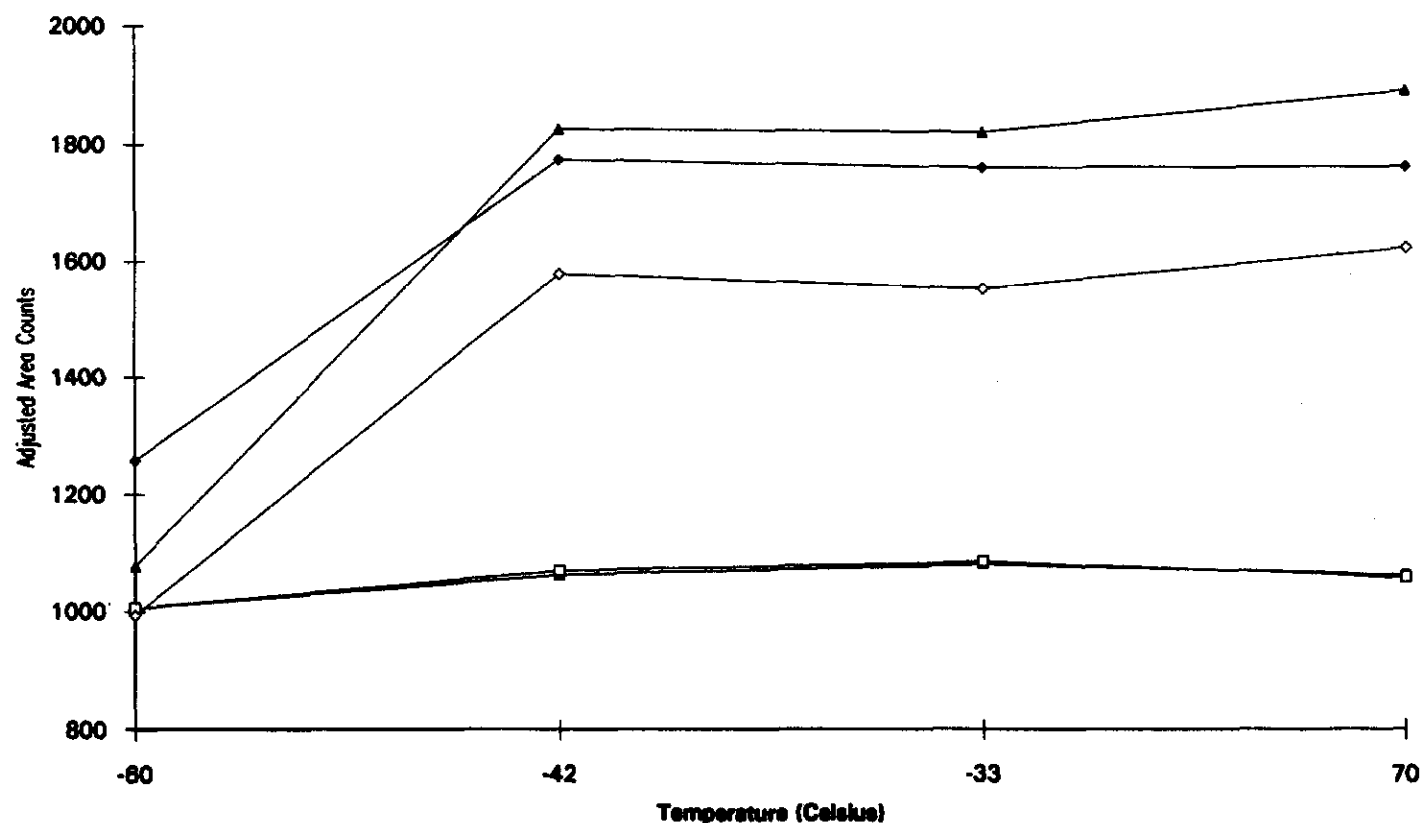


Fig. 6. Dependence of FID response (adjusted area counts) of aromatic hydrocarbons on the temperature of the dry-ice-cooled water trap. ■ = benzene; □ = toluene; ● = ethylbenzene; ◇ = p,m-xylene; ▲ = o-xylene.

analysed components. Ambient air samples with xylene concentrations ranging from 10 to 300 pptv were passed through the Teflon water trap at -30°C without significant loss. Linear behaviour was observed for the dependence of area count on sample volume in the range $100\text{--}650\text{ cm}^3$ at 1 atm (1 atm = 101 325 Pa).

Both the literature and our experience indicate

that CO_2 trapped from the preconcentration of ambient air samples is a potential interferent in the trace analysis of hydrocarbons [9,10,17,18,25,26]. In the GC analysis of urban air samples, the sample volume needed for preconcentration is small (usually $<300\text{ cm}^3$) because of the relatively high concentrations of hydrocarbon species. For this reason, the amount of CO_2 preconcentrated is sufficiently

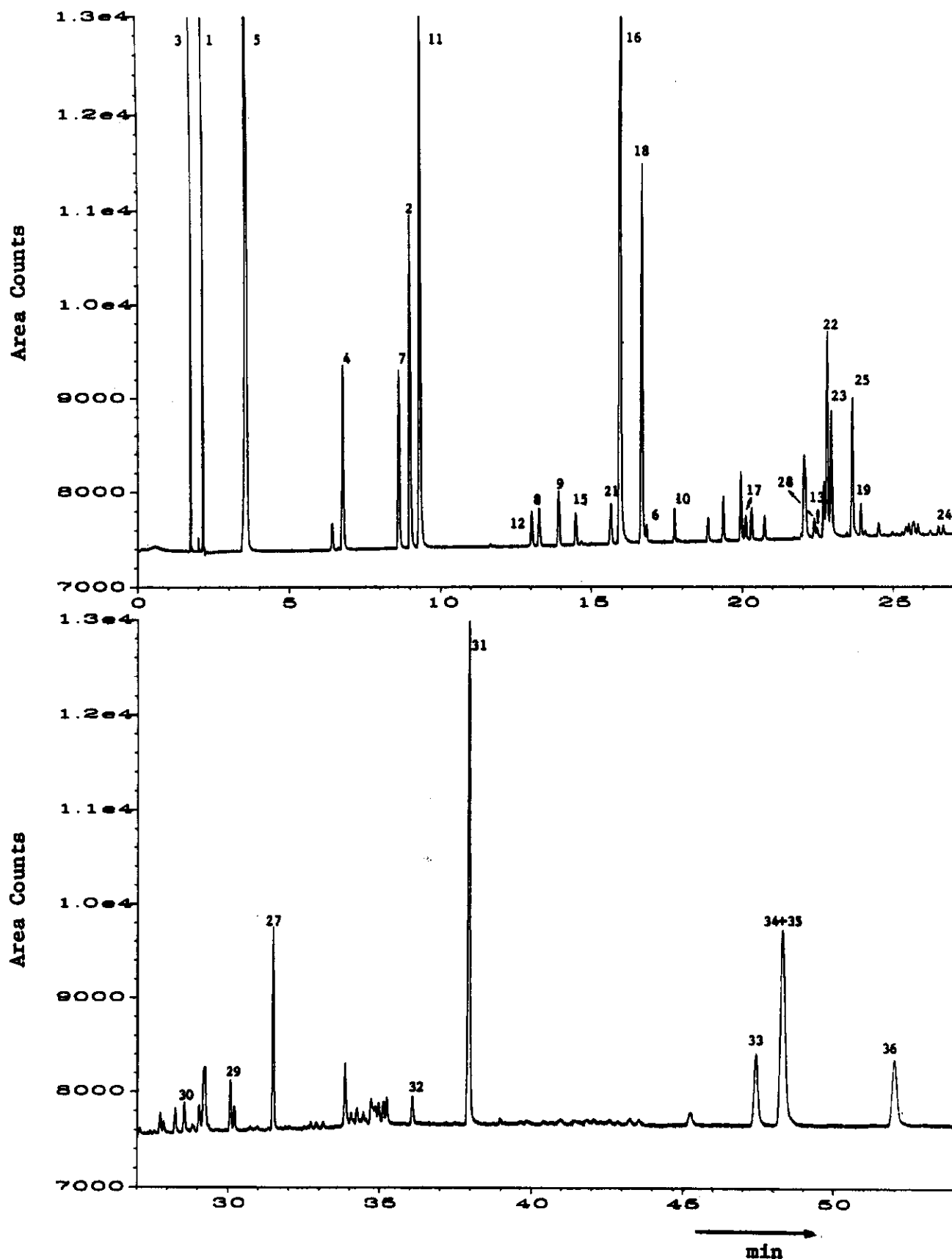


Fig. 7. Separation of urban air pollutants on $\text{Al}_2\text{O}_3\text{--KCl}$ PLOT capillary column ($50\text{ m} \times 0.32\text{ mm}$ I.D. $5\text{-}\mu\text{m}$ film thickness) with temperature programming: initial temperature 35°C (2 min), then increased at $5^{\circ}\text{C}/\text{min}$ to 200°C , 22 min isothermal; carrier gas, He (linear velocity 56.84 cm/s); sampling site, Toronto, Bay Street; sampling volume, 640 cm^3 ; Collection date: July 9, 1992. Peak assignments same as in Fig. 2a.

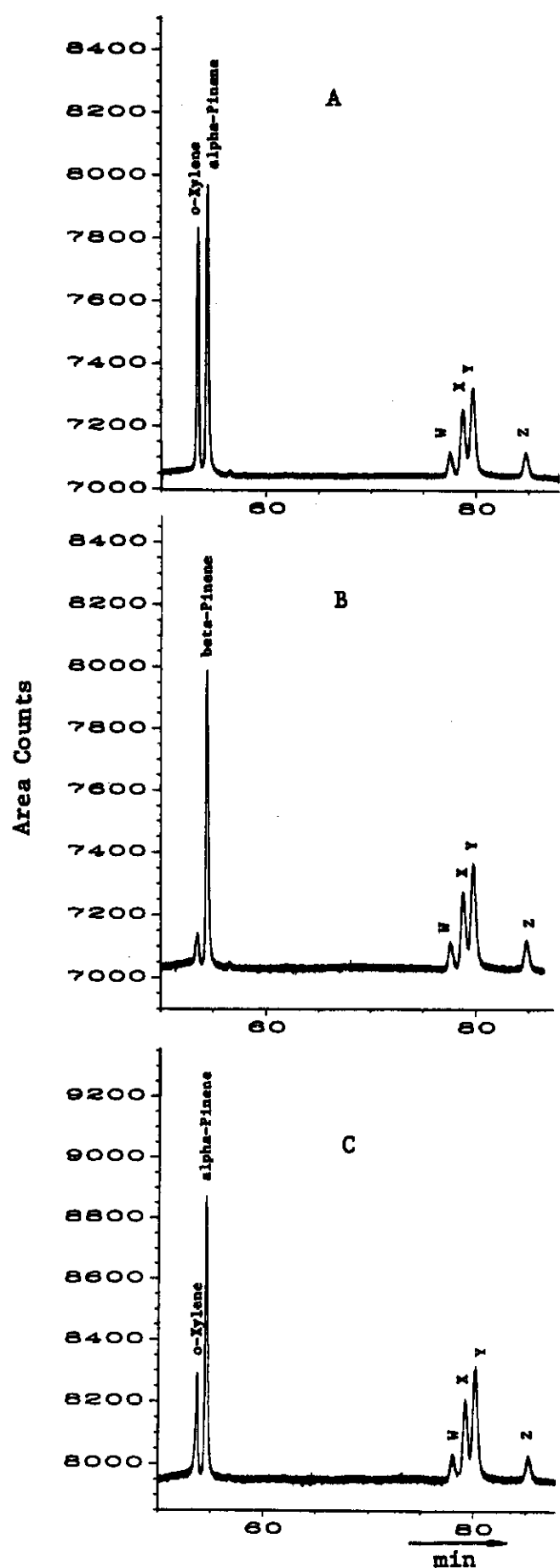


Fig. 8. Part of a chromatogram from hydrocarbons standard analysis on Al_2O_3 -KCl PLOT column. Experimental conditions as in Fig. 7 (except final isothermal period, 52 min). (A) α -pinene + *o*-xylene; (B) β -pinene; (C) NCAR (National Centre for Atmospheric Research, USA) sample containing α -pinene plus *o*-xylene; W, X, Y, Z, = assumed degradation products.

small and we did not encounter problems associated with CO_2 . A chromatogram of an air sample obtained with a PLOT column is shown in Fig. 7.

Degradation of the pinene peak was evident with this column, as peaks corresponding to decomposition products were observed with α - and β -pinene samples (Fig. 8). Degradation of the pinene peak was not observed using the non-polar silicone column and hence this became the GC column of choice for terpene analyses.

The reproducibility of the PLOT column analysis (qualitative and quantitative) of calibration standards and urban air samples has been found to be excellent. One such a column has been in continuous use for the analysis of ambient air samples for hydrocarbons for over 5 months. The relative retention times of individual components were monitored for a period of 50 days and were found to be constant. The reproducibility of peak-area integration (repeated runs) for NMHCs in ambient air samples was better for the PLOT column than for the non-polar tandem column system. The R.S.D.s were usually $<4\%$ and $<6\%$, respectively. The lower R.S.D. with the PLOT column can be attributed to better resolution of the individual components, resulting in a smaller computer integration error of area counts.

CONCLUSIONS

The analysis of urban air samples were carried out using a in-house developed preconcentration system combined with a GC capillary column and FID. For most urban measurements of C_2 - C_{10} hydrocarbons, 500-cm^3 samples provided an ample signal for analyses. Two GC columns were used for hydrocarbon separation. A megabore capillary column (DB-1) with a chemically bonded non-polar stationary phase of film thickness $5\ \mu\text{m}$ was used successfully without removal of moisture from humid samples. For increased resolution of the low-molecular-mass hydrocarbons (C_2 - C_5) the megabore column was connected with a 30-m DB-5 column to make a 90-m long tandem column system. A multi-step temperature programme was used to separate as many of the hydrocarbon components as possible in a reasonably short time (60 min) without sub-ambient oven temperatures. The PLOT column provided the better separation of low-molecular-mass hydrocarbons without the need to go to sub-ambient oven temperatures. The PLOT columns tested, however, are not suitable for α - and β -pine-

nes as these compounds were observed to degrade in the column. Because the column is sensitive to water, moisture had to be removed from the air sample using a FEP Teflon water trap cooled with dry-ice prior to GC analysis. Tests indicated that no observable amount of aromatics (up to the xylenes) was lost in the water trap when operated at -30°C .

The use of the preconcentration–GC system gave excellent reproducibility of both retention times and integration results for both calibration standards and ambient air samples. The use of the PLOT column gave better area count reproducibility than the tandem column. This can be attributed to the fact that the PLOT column was better at resolving individual components leading to a smaller computer integration error. Hundreds of urban air samples with concentrations ranging from 5 pptv to 100 ppbv have been analysed in the Toronto urban and suburban area using the two different columns over a period of 2 years.

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