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Journal of Chromatography A, 676 (1994) 389–398

JOURNAL OF CHROMATOGRAPHY A

Fully automated gas chromatograph–flame ionization detector system for the *in situ* determination of atmospheric non-methane hydrocarbons at low parts per trillion concentration

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First received 2 February 1994; revised manuscript received 31 March 1994

Abstract

A completely automated gas chromatography–flame ionization detector system with cryogenic sample freeze-out for measuring atmospheric non-methane hydrocarbons was deployed at the Mauna Loa Observatory, Hawaii during the MLOPEX II experiment, September 1991 through August 1992. The system was designed to (1) rapidly trap air samples of up to 4 litres volume to allow for sub-parts per trillion detection limits, (2) eliminate interferences from ambient ozone, water vapor and carbon dioxide, (3) reduce to negligible levels any contamination in the analytical systems, and (4) allow for continuous, unattended operation. The instrumentation consisted of two parallel analytical systems, employing packed and capillary chromatographic columns, which allowed quantification of C_2–C_{10} non-methane hydrocarbons from sub-parts per trillion to parts per million concentrations. A dynamic dilution system was used to calibrate the analytical system over the range of concentrations measured (low parts per trillion to parts per billion) at this site.

1. Introduction

Atmospheric non-methane hydrocarbons (NMHCs) play an important role in the atmospheric chemistry of the troposphere. They are central to the production and destruction of atmospheric oxidants and oxidant precursors, such as OH, O_3, organic peroxides and peroxy radicals [1]. The annual global emissions of NMHCs into the atmosphere exceed that of methane [2], and, therefore, represent a major component of the atmospheric carbon budget. Because of their higher chemical reactivity, however, NMHCs are often found at a few parts per billion (ppb) to low parts per trillion (ppt) levels in the remote troposphere, compared to approximately 1.7 parts per million (ppm) for methane [3].

Atmospheric NMHCs have been measured both by *in situ* analysis and by sample collection in canisters, bags, or adsorbent cartridges, with subsequent laboratory analysis. The latter strategy has disadvantages, which may include artifact formation in the storage medium, storage losses or transformations, sample recovery, and sample size constraints [2]. More recently, measurements have been reported which utilized *in situ* methods [4–6]. The in situ techniques also have revealed analytical problems, which include chemical or chromatographic interferences as a

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SSDI 0021-9673(94)0321-Y

result of simultaneously collected water vapor, ozone, and CO_2. Problems with high blank or background levels have also been noted. For any sampling and analysis strategy, calibration over the entire range of concentrations in the remote troposphere can present problems. These include difficulties in producing and maintaining accurate and stable standards at low concentrations, the unavailability of standards for all NMHCs and other trace gases detected, linearity of detector response, etc. [7]. Finally, experimental requirements in some cases include the continuous operation of sampling and analytical instrumentation on a 24-hour basis for up to several months.

We have designed and successfully deployed a fully automated gas chromatography–flame ionization detection (GC–FID) system for the determination of atmospheric NMHCs at the Mauna Loa Observatory, Hawaii, as part of the Mauna Loa Photochemical Experiment II (MLOPEX II), from September 1991 to August 1992 [8,9]. The analytical system was designed to satisfy the following fundamental criteria: (1) the system should operate unattended on a 24-hour basis, (2) atmospheric samples of volumes of up to 4 litres should be collected in less than 30 minutes and analyzed for C_2–C_{10} NMHCs down to low ppt concentrations, (3) the analytical system should have blanks sufficiently low for the quantitation of the corresponding NMHCs, (4) interferences of water, CO_2, and O_3 should be eliminated, and (5) calibrations should be made over the entire dynamic range of measurements.

2. Experimental

The measurement of atmospheric NMHCs was based upon a two-stage cryogenic sample trapping strategy. The first stage sample trap was designed to rapidly and efficiently trap C_2 and heavier NMHCs; it had sufficient capacity and cross section so that water vapor trapped simultaneously with the sampled air would not impede the sample air flow at cryogenic trapping temperatures. Traps for removal of O_3 and, in some analyses, CO_2 were placed upstream of this trap. The first stage was then heated slowly and NMHCs trapped were quantitatively transferred to a micro-volume, cryogenically cooled second stage trap. The programmed heating of the first stage prevented the bulk of the trapped water vapor from being transferred to the second-stage, analytical trap. The small effective volume (less than 100 μl after packing, see below) and rapid heating of the second stage trap insured that NMHCs would be transferred to the GC analytical column in the smallest possible volume in order to avoid broad peaks early in the chromatogram.

2.1. Components

The NMHC analytical system is depicted in Fig. 1. The sample inlet was located at an elevation of approximately 9 m; the sample line was 12.7 mm O.D., 10.5 mm I.D. (0.5" O.D., 0.412" I.D.) electropolished stainless steel tubing. The inlet was fitted with a Teflon filter holder which contained a Teflon coated glass fibre filter, in order to remove particulates. Sample air was continuously pulled through the sample line at a flow rate of approximately 10 l min^{-1} with a diaphragm pump. The sample line was routed very close to the sample collection system inside the laboratory to minimize the distance between the sample line and the sample collection/introduction system to approximately 20 cm.

All tubing from the sample inlet to the sample transfer tubing of the sample collection/introduction system was wrapped with nickel-coated copper braided wire 0.7 mm diameter (Teflon insulated); AC current (approximately 10 A at 7 V) was passed through the wire in order to heat these components to approximately 50°C. Valves V1, V2, E1, E2, and SS were heated to 60°C by individual valve heaters (VALCO Model HA2). The heating of these components reduced blank levels from sample carryover, especially of higher boiling components, to well below equivalent ppt concentrations measured.

Samples were collected in sample traps SL1 and SL2 (Fig. 1). These traps were cooled by

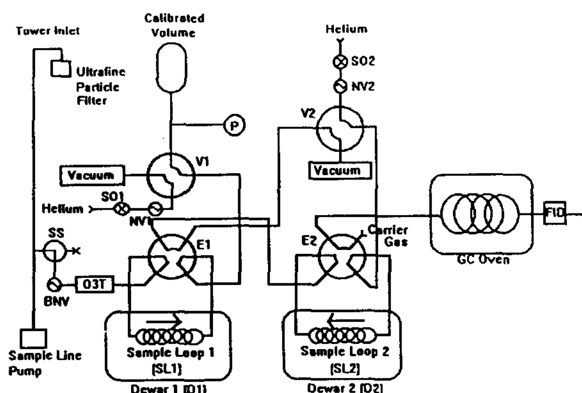

Fig. 1. Schematic of the sample collection/introduction system in the sample collection mode. The system consisted of the following components: 2-position, air actuated switching valves (Valco, Houston, TX, USA): V1 and V2: flow direction valves, 4-port, Models #4UWP (1/4″ tubing ports, 1″ = 2.54 cm) and C4WP (1/16″ tubing ports), respectively; E1 and E2 : 6-port sample trap valves, Models #6WP (1/8″ tubing ports) and #C6WP (1/16″ tubing ports) respectively; SS: stream selector valve, 3-port, Model #C3WP (1/16″ tubing ports). Pumps: sample line pump: diaphragm pump, Model #N035ATP (KNF Neuberger, Princeton, NJ, USA); VP: vacuum pump: Welsh Model #R1405 (Welsh, Skokie, IL, USA) (liquid nitrogen cooled vapor trap placed on low pressure side). Needle valves, shutoff valves (NUPRO, Willoughby, OH, USA); BNV: stainless steel bellows needle valve, Model #SS-4BMW; NV1 and NV2: stainless steel needle valves, Model #SS-SS1; SO: stainless steel bellows pneumatic shut-off valves, Model #SS-4BK-1O. Pressure measurement (MKS Instrument Co., Andover, MA, USA): P: pressure transducer Model #127AA-01000B, power supply and display, Model PDR-C-2C. Miscellaneous: SL1: 1st stage cryogenic sample trap, 16″ × 0.190″ ID stainless steel packed with 0.18–0.23 mm diameter glass beads (Alltech, Deerfield, IL, USA); SL2: 2nd stage cryogenic sample trap, 8″ × 0.085″ I.D. stainless steel packed with 60/80 mesh glass beads; D1 and D2: liquid nitrogen dewars, Model #10LD (Taylor-Wharton, Theodore, AL, USA); O_3T: ozone trap, KI impregnated glass wool Ultrafine particle filter, Teflon coated glass fiber filter, Pallflex T60A20 (Putnam, CT, USA); CV: calibrated volume, 35 litre, electropolished stainless steel, rigid tank.

immersion in liquid nitrogen (Fig. 2). SL1 and SL2 were located inside a plastic pipe (43 mm I.D.), which was placed in a liquid nitrogen dewar. The pipe was sealed on its outside to the top of the dewar, but the inside of the pipe was open to the atmosphere. The bottom end of the pipe extended below the liquid nitrogen level in the dewar. When SL1 or SL2 cooling was re-

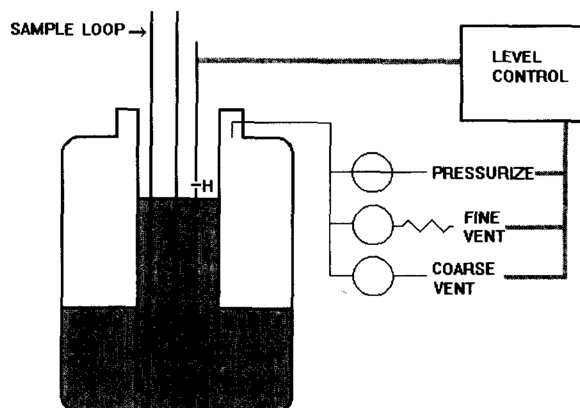

Fig. 2. Schematic of the automated cryo-trapping system. The system is in the activated, level control mode. Liquid nitrogen level is maintained between the high (H) and low (L) resistor level sensors, located 1 cm apart, by pressurizing or venting the dewar headspace.

quired, a level sensing circuit was activated. This circuit closed the dewar vent and pressurized the dewar (10 p.s.i. nitrogen or helium, 1 p.s.i. = 6894.76 Pa) which would force liquid nitrogen up the central tube containing the sample loops. A two-resistor sensing circuit maintained the liquid nitrogen level between the resistors (1 cm apart) by alternately pressurizing and venting the inside of the dewar. The sensors were fixed to appropriate positions on the sample loops. When the loops required heating (for transfer, sample injection, or backflush), the liquid nitrogen level was dropped by venting the dewar to atmospheric pressure. The sample loops were heated electrically by passing 110 V AC current directly through the stainless steel tubing of the trap. Heating rates and temperature setpoints were controlled by temperature controllers (Model #2050, West Instruments, Schiller Park, IL, USA), using a thermocouple sensor attached directly to SL1 or SL2. Separate dewars were used for SL1 and SL2. Cryogen consumption was approximately 2 litres per day for each dewar, when approximately 8 samples were collected daily.

An ozone trap (O_3T) was installed upstream of SL1 to remove ambient O_3 from the air sampled, since O_3 would also be condensed in SL1 at the cryogenic trapping temperatures and would react with unsaturated NMHCs during

sample heating and transfer from SL1 to SL2 [3]. These traps were prepared by soaking glass wool in a solution of potassium iodide (3 g), methanol (5 ml), water (10 ml) and glycerol (2 ml). The impregnated glass wool was then dried by inserting it in a glass tube and purging it with UHP zero air. The O_3 trap consisted of a short length of stainless steel tubing (51 mm × 5.3 mm I.D.) packed with this impregnated glass wool.

An additional trap (76 mm × 10.5 mm I.D. length stainless steel), packed with Ascarite (NaOH coated silica, A.H. Thomas Co., Philadelphia, PA, USA), was used downstream of the O_3T in the packed column system (see below), in order to remove carbon dioxide (CO_2), which would otherwise interfere with the chromatographic determination of ethane and ethylene. The Ascarite trap was not used with the capillary column system (see below), since a corresponding interference was not found and the Ascarite increasingly removed the higher boiling NMHCs eluting after benzene (retention index 642, DB-1).

NMHC measurements were made by gas chromatography using a Model HP 5890A dual flame ionization detector gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA). Two analytical columns were used: (1) DB-1 fused silica capillary column, 30 m × 0.32 mm I.D., 1 μm film thickness (J and W Scientific, Folsom, CA, USA), −50°C to 200°C at 4°C/min, used for C_3–C_{10} NMHCs; (2) Gas Chrom PICN, 0.14–0.18 mm diameter range (Alltech, Deerfield, IL, USA), 6 m × 0.2 mm I.D. stainless steel packed column, isothermal at 40°C, used for C_2–C_4 NMHCs. Two completely separate automated, analytical systems, one with the capillary and the other with the packed chromatographic column, were operated in parallel, and were used to sample ambient air alternately, every two hours.

Chromatographic signals were sent to HP 3396 integrators; raw signal files were further transferred to and stored by a personal computer, where they were reintegrated using ChromPerfect Ver 3.0 software (Justice Innovations, Palo Alto, CA, USA).

Automation of the sampling process was controlled by a STD-Bus single-board computer (OSC 9600 systems card, Octagon System Corp., Westminster, CO, USA), running STD BASIC III. The automation computer was responsible for initiating and executing the sample collection sequence every two hours on the hour. As illustrated in Fig. 1, sample valves E1 and E2 (to which were attached SL1 and SL2, respectively), flow directing valves (V1 and V2), dewar level control circuitry, and heater power were all switched by a 24-channel digital I/O card (OSC 805 I/O card) controlling standard size OPT022 optically isolated I/O modules mounted on a 24-channel opto relay rack (PB-24 opto rack). GC start, integrator start, and start signals for the West temperature controllers were provided by relay contact closures from an eight-channel relay card (OSC 502 relay card). Sample volumes were determined by analog-to-digital conversion (OSC 860 analog input card) of the pressure of calibrated volumes (CV) from the pressure transducer, P (samples volumes of 2 and 4 litres were approximately 50 and 100 torr above the calibrated volume (CV) pressure at the beginning of the sample collection procedure, respectively). The BASIC automation program was written and compiled on an IBM compatible PC, then downloaded to the Octagon system computer. Diagnostics and housekeeping data were stored on a 256K RAM memory board (OSC 829A 64/256K memory card), before being stored to disk.

Subsequently, the OCTAGON STD-Bus single board computer was replaced by an IBM compatible PC with menu driven software (CONTROL-EG, Quinn Curtis, Needham, MA, USA). This change eliminated the need to write control code in BASIC and considerably reduced the lines of instruction code. It also reduced hardware requirements. All control and sensing in the revised PC system were accomplished using two I/O cards in the PC (Computer Boards Inc., CIO-DIO24 and CIO-DAS08) and one external 16-channel analog input multiplexer board (Computer Boards Inc. CIO-EXP16). Each of the two internal cards had 24 I/O channels which controlled a 24-channel opto relay card (Computer Boards, Inc., SSR-Rack24) with standard size OPTO22 digital I/O

modules. The DAS08 card also had eight A/D channels, several of which were used by the analog input multiplex card for temperature sensing and control, and another two were used for pressure readings on the two parallel analytical channels. In this configuration, the temperatures of SL1 and SL2 were controlled by proportional-integral-differential control (PID) loops run in the background of the Control-EG software.

2.2. Automation sequence

The sample collection/introduction system was completely automated to execute the following sampling sequence:

(1) Initial (default) configuration. The CV was connected to the vacuum pump through switching valve V1 and CV was evacuated to less than 5 torr. Concurrently, the first stage sample trap (SL1) was heated (110°C) and backflushed through the stream selector valve (SS) with UHP helium (50 ml min^{-1}) directed through V1; the second stage sample trap (SL2) was also heated and backflushed with UHP helium (10 ml min^{-1}) directed to vacuum through switching valve V2. Carrier and backflush UHP helium was further purified by passing it through a molecular sieve 5A trap (450 mm × 10.5 mm I.D.) immersed in liquid nitrogen.

(2) Sample collection. SS was switched to the closed (no flow) position, isolating the sample collection system. V1 was switched to connect CV to SL1 on sample valve E1. Simultaneously, the liquid nitrogen level control was activated to immerse SL1 in the cryogen. (The temperature of liquid nitrogen (−196°C) was sufficiently low to trap the lowest boiling NMHCs and immersion in the cryogen eliminated the need to control the trapping temperature.) After a 3-min SL1 temperature equilibration pause, SS was returned to the open (flow) position. The vacuum of the CV pulled sample air from the sample line through a stainless steel bellows needle valve (BNV) used to control sampling rate (125 ml min^{-1}), the ozone trap (O_3T), and SL1. The volume of air pulled through SL1 was related to the pressure change in CV (N_2 and O_2, which constitute approximately 98% of air sampled, pass quantitatively through the trap), which was measured by a pressure transducer (P). A pressure change in CV of 50 torr (used for capillary column system) and 100 torr (used for packed column system) corresponded to approximately 2 and 4 litres air sampled, respectively. At system pressures under approximately 200 torr, liquid nitrogen could be used as a cryogen to trap atmospheric NMHCs without the coincident trapping of atmospheric O_2 and N_2. SL1 had a sufficiently large volume and cross section that lighter NMHCs (ethane, acetylene, ethylene) were trapped at 100% efficiency up to sample flow rates of approximately 200 ml min^{-1} and that simultaneously trapped water vapor would not inhibit sample flows with the large sample volumes passing through SL1.

(3) Sample transfer. After the required volume was passed through SL1, SS was changed to the closed position (no flow). The helium backflush flow through switching valve V2 was stopped by closing shut-off valve SO2 and the position of V2 was changed from the backflush to the SL1–SL2 transfer position. The second stage sample loop (SL2) was then immersed in liquid nitrogen by activating its level control circuit. After SL2 temperature equilibration, the transfer flow of helium through V2 (10 ml min^{-1}) was turned on by opening SO2. E1 position was then changed to put SL1 in series with SL2, the liquid nitrogen level of SL1 was lowered and SL1 was heated to 80°C in 3 min in order to transfer the trapped volatile trace gases to SL2. This slow, controlled heating minimized the transfer of water vapor to SL2, since the water vapor pressure was low over most of the temperature programmed transfer. Coincident with this transfer, the control computer started the HP 5890 gas chromatograph temperature program (contained in its own memory) and the GC oven temperature was lowered to its initial program value (−50°C).

(4) Sample injection. After the sample transfer time expired and the initial oven temperature of the gas chromatograph was reached, sample valve E2 was switched to the inject position, the liquid nitrogen level was lowered and SL2 was

heated to 80°C in approximately 15 s to transfer the sample to the analytical column. The effective dead volume of SL2 after packing with glass beads was less than 100 μl, therefore, minimizing the transfer volume. C_3 and heavier NMHCs were again cryofocused on the GC column. In most samples, the low dead volume of SL2 allowed separation of C_2H_4 from C_2H_6 and C_2H_2 (these NMHCs are not cryofocused on the capillary column). Sample valve E2 was returned to the initial (load) position 45 s after injection. The sample collection/introduction system was returned to its initial default configuration 30 s later. The gas chromatograph continued to execute its temperature program to completion, at which time it held a post-run temperature of 150°C. Detector signals were communicated to the HP 3396 integrator, which was also programmed to store raw data files to a host PC.

2.3. Other analytical details

System blanks were run periodically with zero gas introduced at the beginning of the sample collection system and at the sample inlet atop the tower. Zero gases from high pressure cylinders included UHP nitrogen, UHP helium, and ultrapure zero air. These cylinder zero gases contained numerous trace contaminants, including NMHCs, which were, in some cases, at mixing ratios over 100 ppt. There was considerable variability in the levels of contamination for each of these zero gases and among cylinders of individual zero gases. All required additional purification. Repurification was achieved by passing the zero gas through a molecular sieve 5A trap (450 mm × 10.5 mm I.D.) that was maintained at −80°C in an ethanol–liquid nitrogen bath. The boil-off from the liquid nitrogen tanks was more consistently near appropriate background levels for NMHCs and most other trace gases and was used without additional purification in some tests. Blank levels of NMHCs (and all other trace gases normally detected in routine ambient sampling were negligible (less than 1 ppt) when these repurified zero gases were analyzed.

Experiments were also made to determine the necessity and efficiency of the O_3 traps. O_3 traps were checked at first daily and later weekly. The efficiency of these traps was near 100%, when ambient air (which typically contained 35–45 ppb O_3) was passed through the trap at flow rates up to 1 litre per min (the NMHC sample collection rate was approximately 125 ml min^{-1}). O_3 was measured using a commercial ozone detector (Model #1003-AAS, Dasibi Environmental Corp., Glendale, CA, USA). The traps were efficient for several months under the sampling conditions (up to 25 litres per day or 1.5 m^3 of sample air in a 2 month period). Blank levels for individual NMHCs were not increased by the addition of the O_3 trap and there were no differences in calibration response factors measured with and without the O_3 trap included.

FID signals were processed both with a HP Model 3396-Series II integrator and with ChromPerfect PC software (which allowed for storage of raw signal data and their subsequent reanalysis). The reintegration of the stored raw data file proved essential, since at the low mixing ratios encountered, individual NMHCs often were near their detection limits. The HP 3396 integrator did not conveniently provide adequate integration control. Reintegration of the signal file with ChromPerfect software allowed on-screen baseline placement and integration control, which resulted in satisfactory precision of integration.

3. Calibration and standards

3.1. Standards

Several primary gravimetric standards were used in the course of the experiment: (1) 1 ppm (±1%) propane in nitrogen, National Institute of Standards and Technology (NIST) SRM #1660a; (2) 10.53 ppb (±3%) *n*-butane and 10.30 (±2%) ppb benzene in nitrogen, NIST special mixture; (3) 7-component mixture: ethane, ethylene, acetylene, propane, propylene, *i*-butane, *n*-butane in nitrogen, 15 (±2%) ppm each, Scott Specialty Gases, Plumsteadville, PA, USA; (4) 201 (±2%) ppb 2,2-dimethyl butane

in nitrogen, Scott Specialty Gases. These primary standards were intercompared on a response per carbon basis [7,10,11] and were in agreement within the confidence limits reported by the preparer. In addition to the primary standards, a secondary standard was prepared from the dilution of an aliquot of the 7-component primary standard to the 10 ppb level with zero air.

A dynamic dilution system [12] was used to dilute a flow of the primary 7-component standard to concentrations from 15 ppm down to 650 ppt. These dilutions were used to calibrate the secondary standard made from the 7-component primary standard. The dynamic dilution system was again used to dilute the secondary 7-component standard (approximately 10 ppb for each component) down to 15 ppt/component. High-pressure cylinder ultra-pure zero air (Scott-Marrin, San Bernadino, CA, USA) was used as the diluent gas; however, the NMHC levels in these cylinders were of the order of several tens of ppt for some individual NMHCs and cylinders also contained numerous other trace gas components. Consequently, it was necessary to purify the dilution gas by passing it through a molecular sieve 5A trap (450 mm $\times$ 10.5 mm I.D.) immersed in a liquid nitrogen–ethanol bath maintained at $-80°C$. This additional purification reduced NMHC mixing ratios to levels below 2 ppt and removed most other constituents. Dilutions to lower concentrations were not made because, at dynamic dilution flow rates (>1 l min^{-1}), the diluent zero air levels of several NMHCs could not be reduced further. (At purification flow rates of the order of 100 ml min^{-1}, used to determine system blanks, sub-ppt levels were obtained for all NMHCs).

3.2. Calibration

Calibration of the NMHC system was performed over the mixing ratio range 15 ppt to 15 ppm and the response of both FID systems proved linear over the entire range (Fig. 3). In addition, we compared the response factors for individual NMHCs (Table 1). The relative response factors measured, when the mixing ratios were expressed as parts per trillion of carbon, are within a few percent of each other. For the calibration of NMHCs sampled, the actual response factor for each individual NMHC in the calibration mixture was used. Where there was no response factor measured for a specific

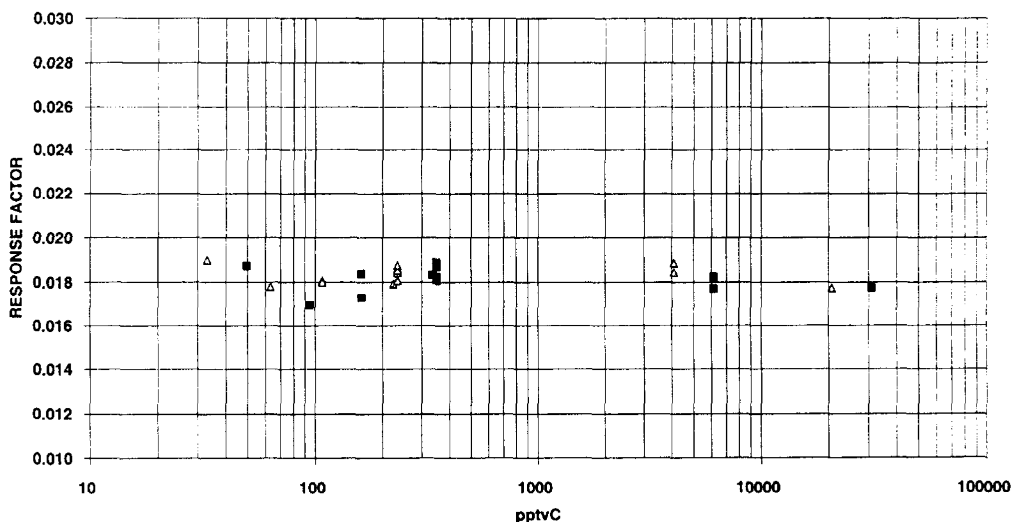

Fig. 3. Response factors calculated for the calibration of ethane (△) and propylene (■), shown in mixing ratios of parts per trillion by volume carbon. The FID system gave a linear response on the pptvC basis over the dynamic range of approximately 30 pptvC (the lowest measured) to 30 ppmvC.

Table 1
Relative FID response factors ($RF_x/RF_{n\text{-butane}}$)

NMHC	Response factor
C_2H_6	1.03 (±0.06)
C_2H_4	1.01 (±0.06)
C_3H_8	1.03 (±0.06)
C_3H_6	0.98 (±0.07)
i-C_4H_{10}	1.02 (±0.06)
C_6H_6	0.98 (±0.03)

RF = [NMHC]/area; concentrations are computed as pptvC. C_2H_6, C_2H_4, C_3H_8, C_3H_6, and i-C_4H_{10} relative response factors were based upon the 7-component NMHC standard; the relative response factor for C_6H_6 was based on the NIST n-butane–benzene standard. Uncertainties were computed from propagation of errors, considering uncertainties in standard calibrations, dilution factors, and standard deviation of area response from multiple analyses of individual components.

NMHC (*i.e.*, the component was not a included in a primary standard), the average of the response factors from Table 1 was used.

3.3. Detection limits and uncertainties

Detection limits for individual NMHCs were determined empirically from the precision of the measurements and are reported as 3 times the uncertainty of the determination for the smallest detected peaks (Table 2). Differences in sample volume, chromatography, and background signal resulted in some differences in the detection limits between the packed and capillary column systems.

Table 2
Detection limits (ppt) for individual NMHCs determined for the system described

NMHC	Packed column	Capillary column
C_2H_6	1	
C_2H_4	1	2
C_2H_2	1	
C_3H_8	0.5	0.5
C_3H_6	0.7	0.5
i-C_4H_{10}		0.4
n-C_4H_{10}	0.4	0.4
n-C_5H_{12}		0.3
C_5H_8		0.3
C_6H_6		0.3
C_7H_8		0.3

Sample sizes were 4 and 2 litres for the packed column and the capillary column systems, respectively.

Uncertainties in the determination of individual NMHCs were determined by a propagation of errors technique, and included errors in the determination of sample volume, temperature, chromatographic integration, and calibration. Uncertainties for NMHCs computed were approximately 5% at mixing ratios above 50 ppt, 7% at 10 ppt, and 10% at 3 ppt (20% for ethylene); errors for acetylene were higher because of incomplete separation from another constituent and sometime were as high as 20%.

4. Conclusion

Concentrations of atmospheric NMHCs measured during the year-long MLOPEXII experiment varied seasonally and diurnally, as well as with synoptic meteorological conditions [8]. These concentrations varied from several thousand ppt for the longest lived NMHC, ethane, to sub-parts per trillion levels for others. Representative chromatograms for the packed column and capillary column techniques are shown in Fig. 4. Numerous peaks corresponding to trace gases other than NMHCs were also detected and appear in these chromatograms. These were often chlorofluorocarbons, aldehydes, and ketones. In cases where identifications were confirmed by *in situ* GC–MS measurements [13], identifications are presented on the chromatograms of Fig. 4. Quantitation of trace species other than NMHCs was not made. Of particular interest in the capillary chromatogram are the occurrence of a series of n-alkyl aldehydes, which appeared as the major features of most chromatograms in samples analyzed on the capillary column. Similar observations have been made by others [14,15]. Actual mixing ratios of these aldehydes may differ from the relative abundances indicated in Fig. 4, since the analytical system was not characterized for the quantitation of aldehydes. Analytical discussions regarding these are presented elsewhere [8].

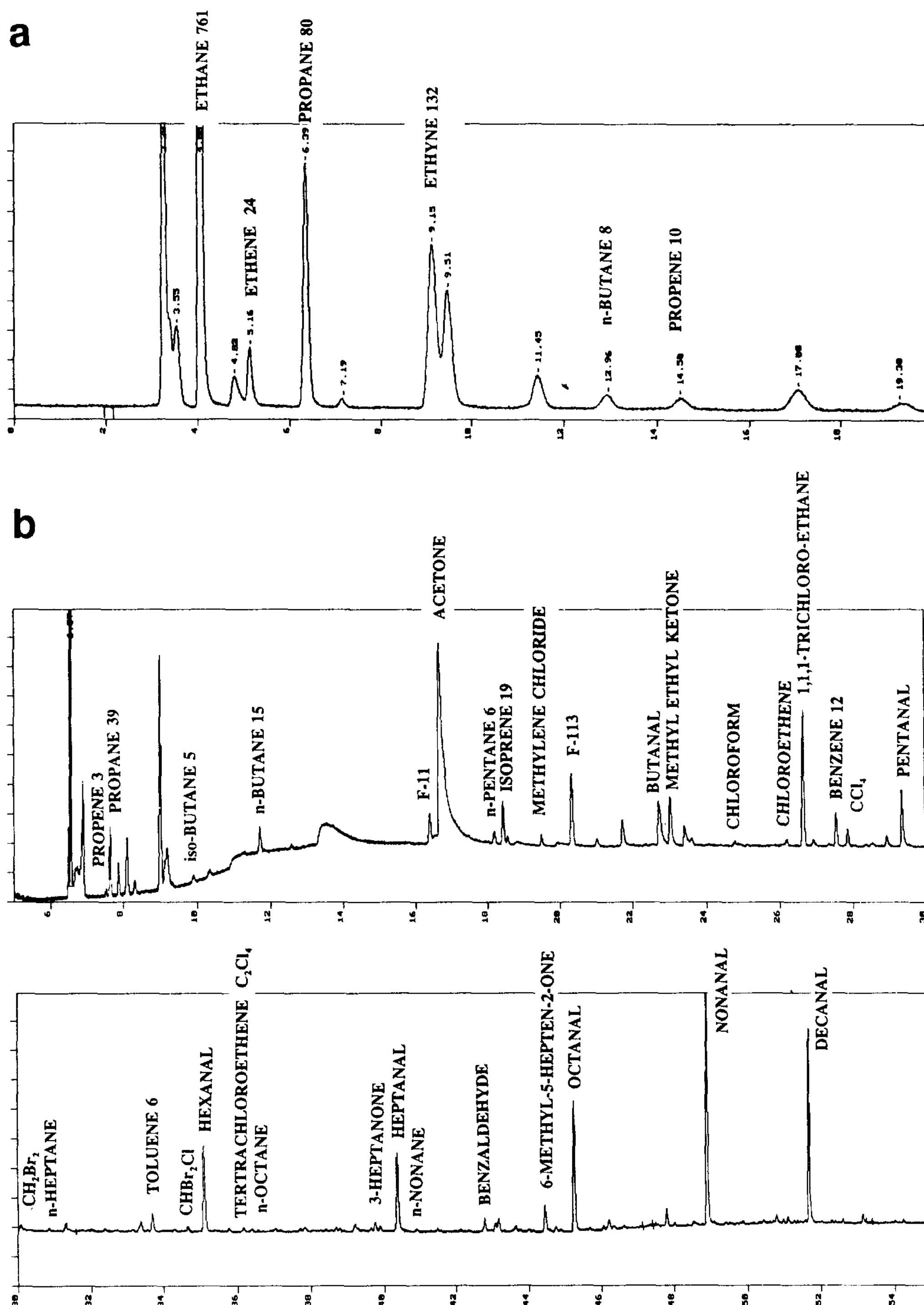

Fig. 4. Sample chromatograms from the MLOPEX II experiment. Mixing ratios in ppt are shown next to NMHC label; other trace gases identified are labeled only. (a) Packed column chromatogram for C_2–C_4 NMHCs, January 29, 1992, 21.00–21.30 local time; (b) capillary column chromatogram for C_3–C_{12} NMHCs, July 22, 1992, 16.00-16.15 local time.

The system described here successfully met the design criteria of continuous, automated, unattended operation; wide dynamic range and sub-ppt detection limits; freedom from water vapor, O_3, and CO_2 interferences; negligible analytical blanks levels; and linear calibration response over the entire range of measurements.

Acknowledgements

We thank E. Ellert, who contributed significantly to the fabrication of the instrument and who wrote the BASIC program instructions to control the instrument. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

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