



Simultaneous analysis of atmospheric halocarbons and non-methane hydrocarbons using two-dimensional gas chromatography

Chieh-Heng Wang^b, Sen-Wei Chiang^a, Jia-Lin Wang^{a,*}

^a Department of Chemistry, National Central University, Chungli 320, Taiwan

^b Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu 300, Taiwan

ARTICLE INFO

Article history:

Received 11 September 2009

Received in revised form

17 November 2009

Accepted 17 November 2009

Available online 26 November 2009

Keywords:

Heart-cut

Deans switch

Ozone depletion substances (ODSs)

Ozone formation precursors

Internal standard

ABSTRACT

A gas chromatographic system was constructed to simultaneously measure ambient non-methane hydrocarbons (NMHCs) and halocarbons, which play significant roles in tropospheric ozone formation and stratospheric ozone loss, respectively. A heart-cut device based on a Deans switch was connected to two capillary columns to cover the full range of NMHCs and halocarbons. Analytes more volatile than C₆ NMHCs and the halocarbon CFC-113 were separated with a PLOT column, while the remaining less volatile compounds were separated with a DB-1 column. Merge-and-split of the flows at the end of the two columns allowed the NMHCs and halocarbons to be observed simultaneously by electron capture detection (ECD) and flame ionization detection (FID). To avoid peak-overlap from the two columns while merging, programmed pressures were incorporated to control the Deans switch. In addition to the advantage of measuring two important classes of compounds in the atmosphere at the same time, this method has the additional benefit of using the homogeneity of atmospheric CFC-113 as an "intrinsic" internal reference. Thus, better data continuity, less consumption of gas standards, and real-time quality control can all be achieved.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Ozone plays many pivotal roles in the atmosphere, despite its relatively low abundance in comparison to other atmospheric constituents. In recent decades, the natural atmospheric abundance and distribution of ozone have been seriously perturbed by human activities. In the lower atmosphere, emitted pollutants such as volatile organic compounds (VOCs) and NO_x (NO + NO₂) react to form ozone and fine particles in the presence of sunlight, leading to adverse health effects and indirectly influencing climate. Non-methane hydrocarbons (NMHCs) constitute a major portion of volatile organic compounds in terms of composition and abundance, and thus present major ozone formation reactivity in most environments. Accurate monitoring composition of NMHCs in air with adequate time resolution is crucial in determining the source types, strength, and apportionment; with this knowledge, effective ozone abatement strategies can be planned. Given the high complexity and low abundance of ambient NMHCs, chromatographic methods are preferred for their efficient separation and sensitivity relative to other analytical means [1–4].

In contrast to the ozone forming mechanisms present in the lower atmosphere, anthropogenic chlorofluorocarbons (CFCs) are

known as ozone depleting substances (ODSs) [5]. These persistent gases are also potent greenhouse gases [6,7]. Although their total abundance is only a minute fraction of that of carbon dioxide, they contribute nearly 42% of the total radiative forcing exerted by increased CO₂ in the period from 1970 to 2000 [8]. The advent of the Montreal Protocol two decades ago, which called for a total phase-out of ODSs, has achieved unprecedented success, leading to a decline or leveling-off of these compounds to various degrees in the atmosphere [9,10].

In order to gain a better understanding of ozone formation in the troposphere and ozone depletion in the stratosphere over time, systematic monitoring of ambient NMHCs and halocarbons is required. A gas chromatographic (GC) system with integrated capabilities allowing for the simultaneous measurement of these gases offers attractive benefits. The GC system discussed in this study employed a Deans switch-based heart-cut technique to perform two-dimensional gas chromatography (2D-GC) [11,12]. In this design, two columns with different properties, a PLOT (porous layer open tubular) column and a WCOT (wall-coated open tubular) column, were connected to the Deans switch. The PLOT column provided sufficient retention for highly volatile compounds that cannot be adequately retained and separated by WCOT columns. Conversely, less volatile compounds are too retentive on PLOT columns, and were thus separated by the WCOT column and detected by flame ionization detection (FID). Consequently, the 2D-GC configuration provided an easy method for analyzing the full range of

* Corresponding author. Fax: +886 34277972.

E-mail address: cwang@cc.ncu.edu.tw (J.-L. Wang).

ambient NMHCs. This 2D configuration also took into account the volatility of the ambient halocarbons.

In addition to the major objective of targeting two classes of gases simultaneously, the CFC-113 in every sample aliquot was used as an internal reference for real-time quality control of the continuous measurements [13,14].

The most obvious benefit of this 2D configuration is that it can maximize the number of monitored gases with important environmental implications using a single gas chromatograph. Compared to cases where multiple GCs are used for various classes of gases in laboratory or field monitoring tasks, this new configuration dramatically reduces instrument redundancy, size, cost, and complexity, while at the same time enhancing the data quality of unattended field monitoring tasks.

2. Experimental

2.1. Sample pre-concentration

A pre-concentration unit was constructed in our laboratory that was coupled to a GC (Agilent 6890) to perform automated analysis. This unit used a multi-sorbent trap made by packing several carbon sorbents, i.e., Carboxen 1000, Carboxen 1003, and Carbo-trap (Supelco, Bellefonte, PA, USA) (in that order), into a stainless tube (3 mm I.D. \times 10 cm). Each sorbent filled roughly 1 cm in length inside the trap tube, and glass wool plugs were used to separate the sorbents. The packing sequence and flow direction for sorption and desorption are critical to ensure complete desorption, optimal peak shape, and thus resolution [15]. The sorption of an air sample was performed at 30 °C to enrich the VOCs without C₂ compounds. The quantitative trapping of three C₂ species, ethane, ethene, and ethyne, requires cooling of the trap to subambient temperatures. This can be achieved using common cooling methods, such as a vortex tube, a refrigeration compressor, or a thermoelectric cooler based on the Peltier effect, provided that the use of cryogenics is avoided. We designed a cooling device using a thermoelectric device to trap the three C₂ compounds with satisfactory performance [16], but in this study, the device was omitted to simplify construction.

Thermodesorption for injecting VOCs was performed by resistive heating of the stainless trap tube. A process controller (Powers 535, Moore Industry, North Hills, CA, USA) regulated a 4 V AC current to the stainless-steel trap tube for flask heating; heating occurred from a setpoint of 30 °C to 250 °C within 7 s, with small fluctuations within ± 1 °C at the high and low setpoints.

2.2. Standard gas mixture and chromatographic conditions

To test the separation of NMHCs, a standard mixture gas cylinder containing 56 NMHCs from C₂ to C₁₂ at sub-ppb (v/v) levels (Spectra, USA) was used. The 2D-GC separated NMHCs smaller than C₆ using a PLOT column (10 m \times 0.32 mm I.D. \times 8 μ m *d_f*; Agilent) and C₆–C₁₂ NMHCs using a DB-1 column (60 m \times 0.32 mm I.D. \times 1 μ m *d_f*; Agilent). All NMHCs were detected by FID.

To test the separation of halocarbons, room air was analyzed by the 2D-GC. The common halocarbons in ambient air that can easily be seen by electron capture detection (ECD) are trichlorofluoromethane (CFC-11), dichlorofluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), trichloroethane, tetrachloromethane, trichloroethene, and tetrachloroethene [17,18]. Calibration of halocarbons was performed by a pressured ambient air cylinder to serve as a working standard whose concentrations were calibrated by a NOAA standard.

Both columns and the Deans switch (except the solenoid valve) were placed in the same GC oven. The temperature in the GC oven

was initially set at 40 °C for 5 min, increased at 6 °C/min to 100 °C, increased at 5 °C/min to 120 °C for 6 min, increased at 5 °C/min to 170 °C, and finally increased at 10 °C/min to 200 °C for 12 min. The pressure of the carrier gas (high-purity He) was controlled via an electronic pneumatic controller (EPC) at a constant pressure of 2.8 kg/cm² (40 psi). The pressure of the switching flow (high-purity He) for the Deans switch was programmed to create the desired heart-cut effect, which will be discussed below.

3. Results and discussion

3.1. Basic heart-cutting

A basic Deans switch consists of a solenoid valve placed outside the GC oven, three low dead volume tee connectors installed inside the GC oven, and stainless-steel tubes connecting these components (see Fig. 1a for the basic configuration of the Deans switch). The DB-1 column is used not only as the pre-column for the PLOT for delivering chunks of highly volatile compounds, but also the analytical column for the less volatile species. The solenoid valve controls an auxiliary flow (helium) for directing the carrier gas to either the PLOT or the uncoated column. At the onset of an injection, the carrier gas is directed to the PLOT for separating compounds more volatile than C₆ (see Fig. 1a for the flow path), followed by a swing in the auxiliary flow to direct the carrier gas to the other side (uncoated column) to elute the less volatile compounds from the DB-1 [12] (see Fig. 1b for the heart-cutting results). Two FID detectors were required for this basic configuration.

3.2. Merging of two columns into one detector

The most straightforward way to achieve the goal of using one detector for two columns is to merge the two flows at the column ends, which would enter into a single detector to produce a combined chromatogram (this configuration is similar to that shown in Fig. 2a). Peak-overlap is to be predicted while merging because peaks from the PLOT and DB-1 columns may have similar retention times, and simple merging will inevitably result in a co-elution problem for the combined chromatogram. To circumvent this problem, one alternative is to delay the elution of the C₆–C₁₂ species from the DB-1 column, causing them to lag behind the C₃–C₅ species from the PLOT; thus, the C₃–C₅ peaks would precede the C₆–C₁₂ peaks in the combined chromatogram. Although this concept is straightforward, the technique used to delay the C₆–C₁₂ species in the DB-1 column is not trivial. It requires an abrupt stop of elution in the DB-1 column until the C₃–C₅ species cut to the PLOT column have advanced in the PLOT column for some time. The C₆–C₁₂ species are only released from the DB-1 column after a delayed time period. This can be accomplished by delicately controlling the timing and pressure of the switching flow in the Deans device. The pressure of the switching flow determines whether the switching to either column is complete. If the switching flow pressure is lower than required, a complete switch is not possible, and leakage to the undesired column will occur [12]. In contrast, partial or complete blockage of effluents from the pre-column will take place if the pressure is too high; this phenomenon was exploited to delay the elution. After the lighter component of the VOCs was cut to the PLOT column, the switching pressure was abruptly increased from its normal cutting pressure, causing the elution of C₆–C₁₂ species in the DB-1 column to stop temporarily. After a 4 min hold-up time, the switching pressure was then rapidly released to elute the C₆–C₁₂ species to the short uncoated column. The resulting combined chromatogram is shown in Fig. 2b, where the heavier compounds from the DB-1 column trail behind the lighter compounds from the PLOT column. In this procedure,

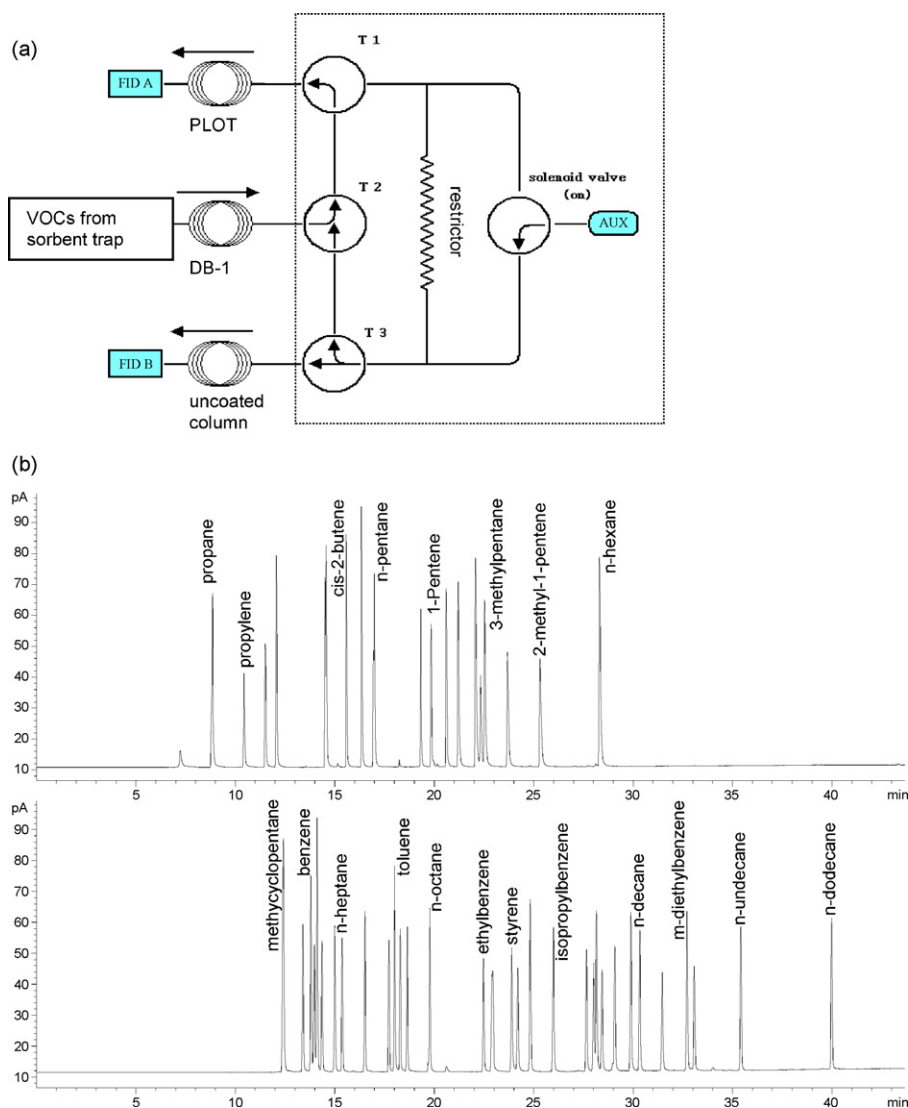


Fig. 1. A standard heart-cut configuration based on a Deans switch (a), and its resulting chromatograms, in which the PLOT column separates C_3 – C_5 (upper trace) and the DB-1 column separates C_6 – C_{12} (lower trace) (b). Selected compounds are labeled.

two pressure settings for the switching flow were required (see Fig. 3 for the switching pressure program, as well as the programs for other GC conditions).

The second objective was to include ambient halocarbons in the list of desired analytes within the same air sample aliquot. To achieve this goal, the merged flow was further split into the FID and ECD separately (Fig. 4a). The same hold-up technique was also applicable to the separation of halocarbons. Using the same conditions presented in Fig. 3, more volatile halocarbons, such as CFC-11, CFC-12, and CFC-113, which were not well separated by the DB-1 pre-column, were cut to the PLOT column for better separation. The remaining species, e.g., CH_3CCl_3 , CCl_4 ,

$CHCl=CCl_2$ and $CCl_2=CCl_2$, whose separation was already satisfactory, were eluted to the uncoated column (data not shown). The split ratio of FID versus ECD was approximately 10:1, resulting from unevenly adjusting the length of the two uncoated columns (0.1 mm I.D.) after the splitter (a micro-Tee connector), as the sensitivity of ECD is far better than that of FID. Fig. 4b shows the results for halocarbons and NMHCs from a typical analysis of laboratory air. Note that although both NMHCs and halocarbons were seen by either detector, the low sensitivity of FID towards ambient halocarbon levels and no sensitivity of ECD towards NMHCs resulted in each detector only sensitive to one type of compounds.

Table 1

Linearity and precision for selected target compounds. For the halocarbons, the atmosphere was analyzed; for the NMHCs, a gas standard mixture was analyzed.

	Halocarbons ($n=152$)		Hydrocarbons ($n=7$)							
	CFC-113	CCl_4	Propane	Isobutane	n-Butane	n-Pentane	Benzene	Toluene	Ethylbenzene	m,p-Xylene
Mean conc. (ppbv)	0.084 ^a	0.090 ^a	15.3	8.4	15.2	7.8	5.5	35.6	7.7	10.2
R^2	0.997 ^b	0.995 ^b	0.735	0.994	0.998	0.998	0.974	0.998	0.991	0.990
RSD (%)	2.39	12.28	1.73	2.37	0.60	1.26	1.36	1.90	1.29	1.15

^a Values are given to three decimal places for CFC-113 and CCl_4 due to low levels.

^b Ambient air in a canister analyzed for five trapping time intervals.

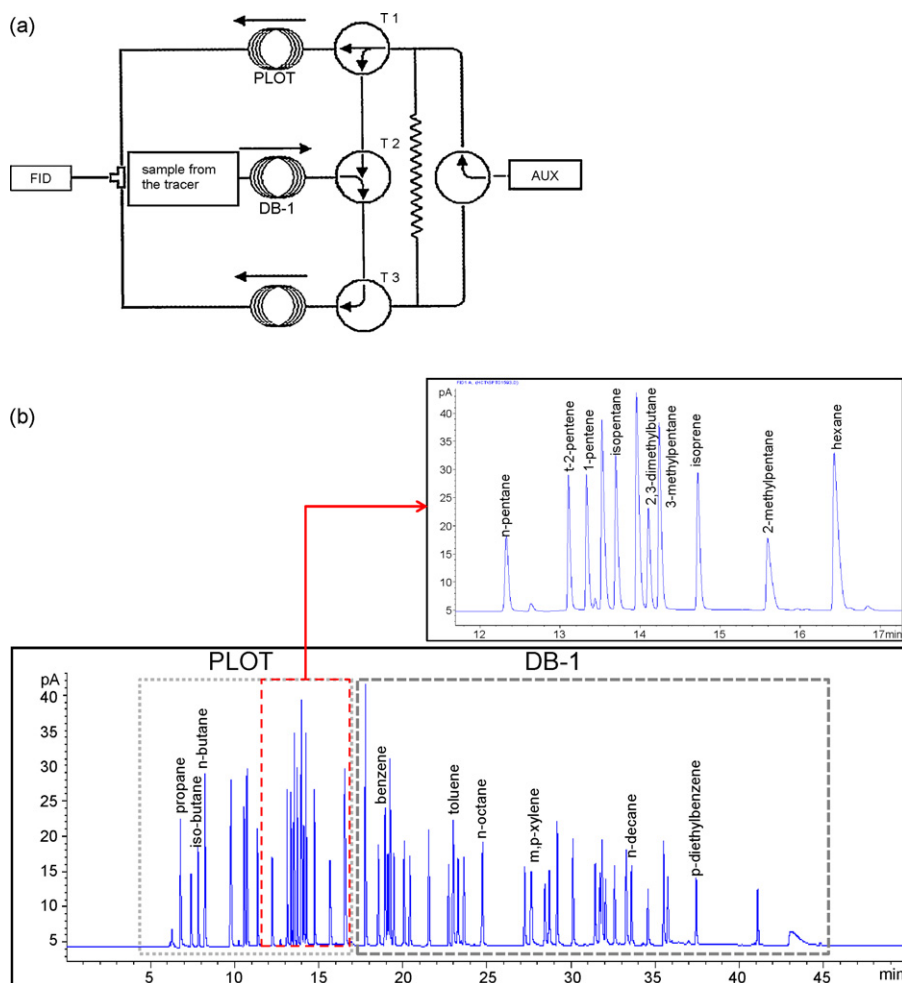


Fig. 2. Combined 2D chromatogram for the target compounds. The light gray dashed portion was generated using the PLOT column, and the dark gray dashed portion was generated using the DB-1 column. The red dashed portion is enlarged to present greater details. Selected compounds are labeled. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

3.3. Quality control with external and internal checks

The robustness of the system was first tested for linearity and reproducibility. A standard mixture containing 56 NMHCs at ppb (v/v) levels was analyzed. By varying the trapping time of this standard gas, the correlation coefficients (R^2) for most NMHCs were greater than 0.99 (Table 1). Subsequently, outdoor air was continuously analyzed using this system for 1 week with hourly data resolution. The NMHC standard gas mixture was inserted between ambient air runs, and seven standard runs in total were made, which are referred to as the external standard runs. Fig. 5 demonstrates the results for ambient NMHCs and halocarbons from this continuous measurement test. The ambient concentrations of NMHCs varied drastically during the measurement period, while compounds from the external standard runs (represented by toluene in Fig. 5) were extremely constant by comparison. The inter-day analytical precision, as assessed by the seven external standard runs, was better than 3% in terms of the relative standard deviation (RSD) (see Table 1 for the selected NMHCs). The good linearity and reproducibility suggest that measurements of NMHCs were robust and that the variability in the detected NMHC levels was a true reflection of their ambient abundance. Intriguingly, the RSD for CFC-113 in ambient air was as small as 2.15% (Table 1), which was very close to or even better than that for the NMHCs of the external standard runs. As shown in Fig. 5, the stable response of CFC-113 during the measurement period

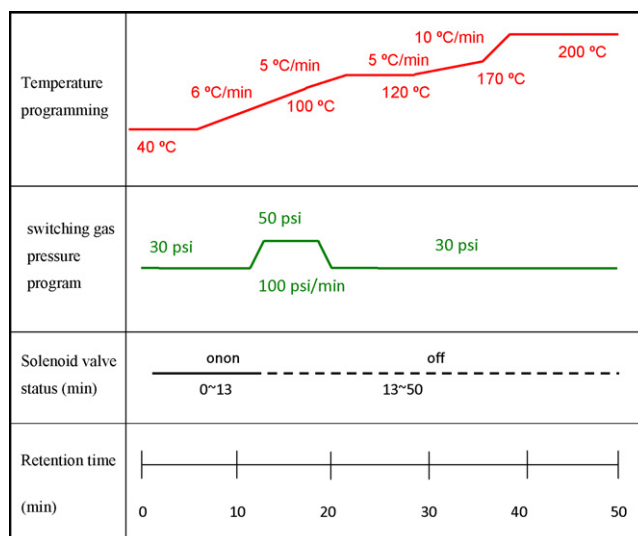


Fig. 3. GC programs for oven temperature, carrier gas, auxiliary gas, and valve action.

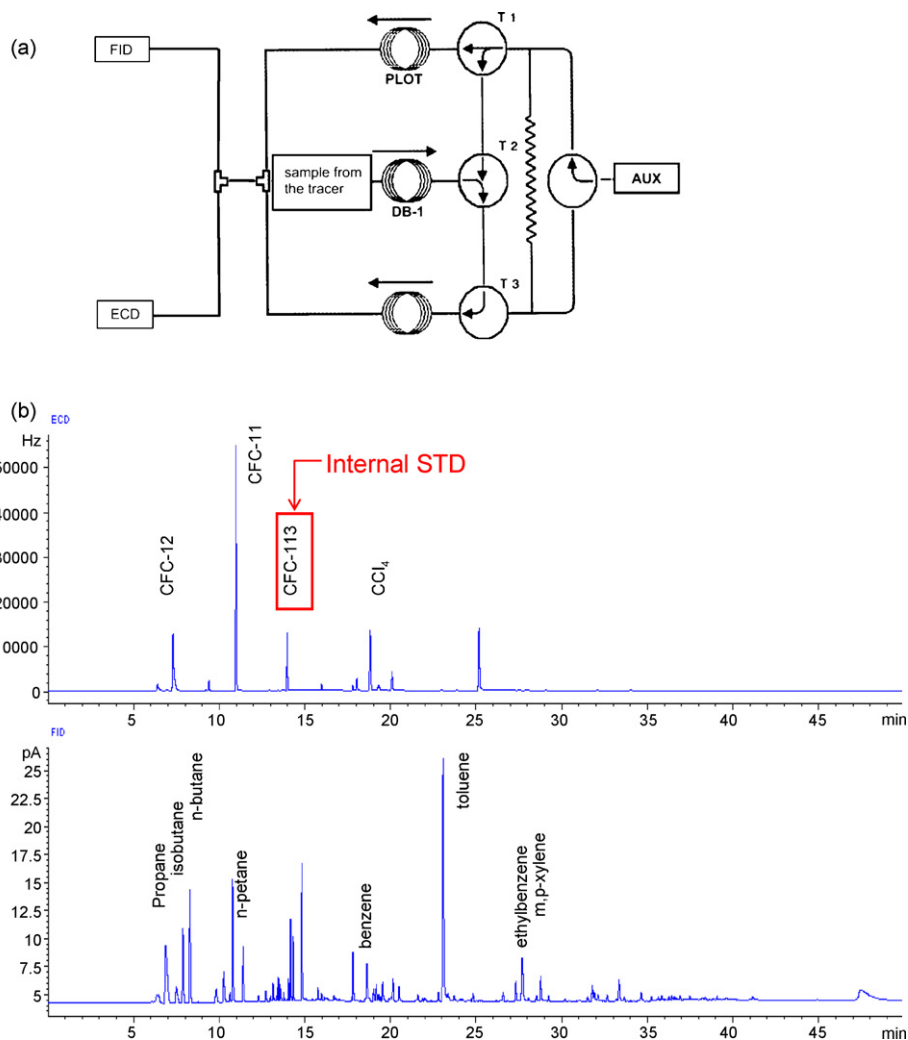


Fig. 4. Simultaneous analysis of ambient NMHCs and halocarbons resulting from the merge-and-split configuration of the Deans switch. (a) Merge-and-split configuration. (b) The ambient halocarbons detected by ECD (upper trace) and C_3 – C_{12} NMHCs (bottom trace). Selected compounds are labeled.

(red line in Fig. 5) closely matched the external standard values (represented by toluene only), demonstrating their high level of agreement. The small variability in the ambient CFC-113 compared to that in the ambient NMHCs was mainly due to the successful

phase-out of ODSs, as required by the Montreal Protocol [9,10]. In addition, the extremely long lifetimes of CFCs contributed to their homogeneity in the atmosphere [19]. The near-zero emissions of CFC-113 and its lifetime of about 90 years [20] led not only to a

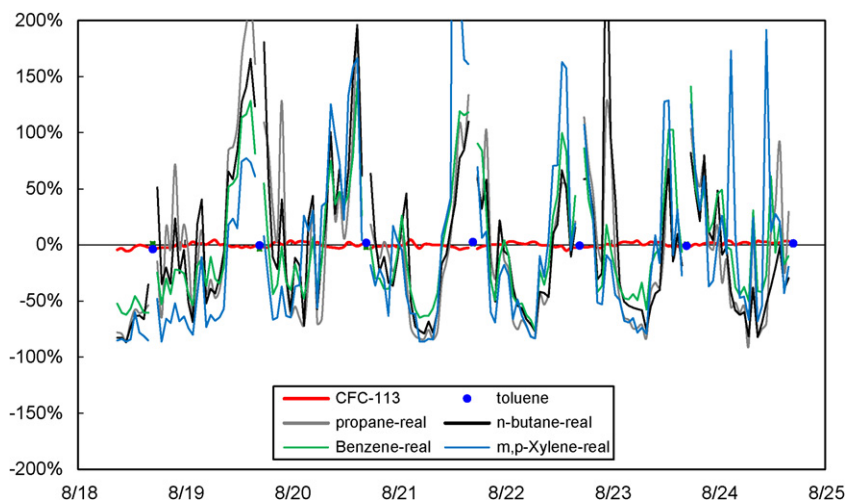


Fig. 5. Concentration variations of ambient NMHCs and halocarbons from continuous measurements (shown by solid lines). External standard runs are also shown (toluene in blue dots). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

small concentration variability, but also to a stable ambient level over a considerably long period of time. For instance, remote measurements have shown that the global background concentration of CFC-113 is slightly below 80 ppt (v/v), decreasing at the rate of 0.6–0.7 ppt/year over the last decade. No discernable change is expected for a laboratory or field measurement study carried out over a period of weeks or months. As a result, in this study, ambient CFC-113 was exploited as a real-time “intrinsic” internal reference in our 2D-CG analysis of both NMHCs and halocarbons. Thus, the need for frequent external standard runs between sample runs can be greatly alleviated, as CFC-113 can now take the place of an external standard to validate the system’s stability and hence the quality of the data. As a result, fewer external standard injections are needed, and only for the purpose of concentration calibration. The major benefits of using CFC-113 as an intrinsic internal reference include less consumption of the standard gas, better data continuity without interruption due to the insertion of external standard runs, and an easier quality-control algorithm for automated data reduction.

4. Conclusions

An automated thermal-desorption 2D-GC system was configured to simultaneously analyze ambient NMHCs and halocarbons due to their great atmospheric significance. The system employed a device with a heart-cut configuration based on a Deans switch and two columns to obtain complete separation of ambient halocarbons and NMHCs (C₃–C₁₂). The merge-and-split configuration at the end of the two columns allowed these two classes of compounds to be detected simultaneously by FID and ECD.

CFC-113 was employed as an internal reference to provide real-time quality control of ambient NMHC and halocarbon measurements, due to its homogeneity and slow decay rate in the atmosphere. Thus, reliance on an external standard to assess the stability of the system during a continuous measurement study can be greatly alleviated.

Acknowledgements

This work was supported by the National Science Council (NSC), EPA, Taiwan, and the Ministry of Economic Affairs, Taiwan under the contracts NSC96-2745-M-008-004, EPA-97-U1L1-02-101, and ITRI: 8355FA2120.

References

- [1] T. Maeda, S. Onodera, H. Ogino, J. Chromatogr. A 710 (1995) 51.
- [2] K.D. Oliver, J.R. Adams, E.H. Daughtrey Jr., W.A. McLenny, M.J. Yoong, M.A. Pardee, Atmos. Environ. 30 (1996) 2751.
- [3] J. Dewulf, V. Langenhove, J. Chromatogr. A 843 (1999) 163.
- [4] D. Helmig, J. Chromatogr. A 843 (1999) 129.
- [5] M.J. Molina, F.S. Rolwand, Nature 249 (1974) 810.
- [6] V. Ramanathan, Science 190 (1975) 50.
- [7] V. Ramanathan, R.J. Cicerone, H.B. Singh, J.T. Kiehl, J. Geophys. Res. 90 (1985) 5547.
- [8] IPCC/TEAP Special Report. Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons. Technical Summary, 2005.
- [9] United Nations Environmental Program (UNEP). Montreal Protocol on substances that deplete that ozone layer. September 16, Montreal, 1987.
- [10] United Nations Environmental Program (UNEP). Report on the forth meeting of the parties on substances that deplete the ozone layer. Copenhagen, 1992.
- [11] J.H. Wang, C.C. Chang, J.L. Wang, J. Chromatogr. A 1087 (2005) 150.
- [12] C.H. Wang, C.C. Chang, J.L. Wang, J. Chromatogr. A 1163 (2007) 298.
- [13] J.L. Wang, C. Chew, S.W. Chen, S.R. Kuo, Environ. Sci. Technol. 34 (2000) 2243.
- [14] C.M. Karbiwnyk, C.S. Mills, D. Helmig, J.W. Birks, Environ. Sci. Technol. 37 (2003) 1002.
- [15] J.M. Sanchez, R.D. Sacks, Anal. Chem. 75 (2003) 978.
- [16] J.L. Wang, G.Z. Din, C.C. Chan, J. Chromatogr. A 1027 (2004) 11.
- [17] R.G. Prinn, P.G. Simmonds, R.A. Rasmussen, R.D. Rosen, F.N. Alyea, C.A. Cardelino, A.J. Crawford, D.M. Cunnold, P.J. Fraser, J.E. Lovelock, J. Geophys. Res. 88 (1983) 8353.
- [18] C.C. Chang, C.H. Lai, C.H. Wang, Y. Zhang, N.N. Lin, J.L. Wang, Atmos. Environ. 42 (2008) 6973.
- [19] B.T. Jobson, S.A. McKeen, D.D. Parrish, F.C. Fehsenfeld, D.R. Blake, A.H. Goldstein, S.M. Schauffler, J.W. Elkins, J. Geophys. Res. 104 (1999) 16091.
- [20] P.J. Fraser, D.M. Cunnold, F.N. Alyea, R.F. Weiss, R.G. Prinn, P.G. Simmonds, B.R. Miller, R.L. Langenfelds, J. Geophys. Res. 101 (1996) 12585.