



Two-dimensional gas chromatography with electron capture detection for the analysis of atmospheric ozone depleting halocarbons[☆]



Chang-Feng Ou-Yang^a, Hsi-Che Hua^b, Yu-Chieh Chou^b, Ming-Kai Teng^b, Wen-Tzu Liu^b, Jia-Lin Wang^{b,*}

^a Department of Atmospheric Sciences, National Central University, Taoyuan 32001, Taiwan

^b Department of Chemistry, National Central University, Taoyuan 32001, Taiwan

ARTICLE INFO

Article history:

Received 31 October 2016

Received in revised form 27 March 2017

Accepted 2 April 2017

Available online 4 April 2017

Keywords:

Deans switch

CFCs

Ozone depletion substance

Thermal desorption

Two-dimensional gas chromatography

Electron capture detector

ABSTRACT

This study is to develop a GC × GC method with electron capture detection (ECD) to analyze atmospheric halocarbons in the concentration range of parts per trillion by volume (pptv). To enrich atmospheric halocarbons a home-built thermal desorption (TD) device was coupled to the GC × GC-ECD. The technique of flow modulation was adopted using a Deans switch for GC × GC. Several column combinations of first and second dimensions were tested and the column set of DB-5 × TG-1301 was found to show the best orthogonality for halocarbons. A series of modulation parameters were tested for their optimal settings. The modulation period (P_M) was found to have minimal wrap-around when set at 3 s. The modulation ratio (M_R) was determined to be 7.82 to ensure reproducible results and maximum sensitivity. The modulation duty cycle (DC) was calculated to be approximately 0.17. Nine halocarbons were separated successfully and seven were calibrated with the use of a certified standard gas mixture. The correlation coefficients (R^2) were greater than 0.9972. The reproducibility was better than 1.90% as expressed in relative standard deviation (RSD; $N = 30$) and the detection limits were in the range of pptv for the target halocarbons. A field test by continuous analyzing ambient air with hourly resolution was performed to show the stability of the method as suggested by the homogeneity of certain halocarbons, while also reflecting concentration variation for others when emissions did arise.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Man-made halogenated trace gases are blamed for the stratospheric ozone depletion [1,2]. Due to the extremely long lifetimes of some selected halocarbons in the atmosphere, these compounds can drift to the stratosphere threatening the ozone layer by releasing chlorine or bromine atoms through photolysis [3]. The Montreal Protocol and its subsequent amendments were thus enacted to cease the production and consumption of anthropogenic chlorofluorocarbons (CFCs) and selected halocarbons [4,5]. Tropospheric abundances and emissions of most ozone depleting substances (ODS) hence started to decrease since mid-90s, resulting in the declines in the atmospheric burden of chlorine and bromine

[2,6–8]. Although the threat of the CFCs on ozone depletion has been greatly alleviated, the net radiative forcing of the halocarbons as greenhouse gases is still considerable since they still contribute up to 11.5% of the net radiative forcing with the inclusion of the CFC replacements of hydrochlorofluorocarbons and hydrofluorocarbons [9–13].

GC-ECD or GC-MS equipped with an enrichment device has been a common method to analyze ambient halocarbons [14–18]. The enrichment can be made either by using cryogenics (e.g., liquid nitrogen) [19] or chemical sorbents with thermal desorption (TD) [16]. As more volatile compounds are invented and emitted into the atmosphere, the complexity of air composition increases over time and; thus, the analytical techniques with higher separation resolution become ever more in demand. The conventional GC techniques are often faced with limited separation efficiency that may not be adequate in the modern era when multi-dimensional separation becomes more assessable and common. Though GC-MS is considered as a multi-dimensional technique in concept with the retention time as the first dimension (1-D) and the mass spectrum

[☆] Selected paper from the 40th International Symposium on Capillary Chromatography and 13th GC×GC Symposium (RIVA 2016), 29 May - 3 June 2016, Riva del Garda, Italy.

* Corresponding author.

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

as the second dimension (2-D), its analytical power may still be hindered by insufficient GC separation when encountering complex samples. Given the full recognition of the achievements made by the conventional GC-ECD or GC-MS in analyzing trace-level atmospheric halocarbons in the past, the comprehensive GC \times GC techniques can take the conventional halocarbon analysis to the next level by providing enhanced GC separation efficiency.

Previous work by Wang et al. has demonstrated a cryogenic GC \times GC-MS method for 30 atmospheric halocarbons [20]. Rather than using thermal modulation with a cryogen, flow modulation using a Dean switch was adopted for hardware simplicity and low cost in construction and operation. However, compared to the thermal modulation counterpart, flow modulation sacrifices some sensitivity and resolution, since minimal or no sample focusing is resulted from modulation [21]. Other than the cost and complexity issues, thermal modulation is not without drawbacks. For instance, it has potential issues with the break-through of volatile analytes [22].

This study aims at developing a comprehensive TD-GC \times GC-ECD method to analyze halogenated compounds at ambient level. ECD was employed as the detection method which is known to be extremely sensitive and rugged for highly halogenated compounds. Moreover, the high selectivity of ECD towards halocarbons can largely eliminate interferences from other air-borne volatile compounds bearing no halogen atoms to achieve rather simplified chromatography. Connecting TD-GC \times GC to a more elaborate detection method such as time-of-flight although could greatly extend the analyte coverage; the simplicity in chromatography would be lost. The sampling rate of ECD of 50 Hz makes it sufficiently fast for the flow modulated TD-GC \times GC applications. To our best knowledge, no or limited GC \times GC work has been given to the ODS analysis and only few studies have shown the potential of the applications of GC \times GC-ECD for the persistent organic pollutants such as pesticides residues, dioxins, chlorobenzenes, polychlorinated biphenyls, and fluorinated polycyclic aromatic hydrocarbons [23–27]. As a proof of concept, an analytical system of flow-modulated TD-GC \times GC-ECD was built in-house to demonstrate the feasibility of such an application. Trace-level halocarbons of significant atmospheric importance, which have been monitored by one dimensional GC with a long history [14–19,28,29], can be readily analyzed via TD-GC \times GC-ECD and viewed from a two-dimensional perspective.

2. Methodology

2.1. Halocarbon identification and quantification

An aluminum AL-150 type cylinder (Spectra Gases, Branchburg, NJ, USA) filled with compressed ambient air was employed as the working standard and air sample for testing the analytical method. In this study, 9 halocarbons, CCl_2Cl_2 (CFC-12), CCl_3F (CFC-11), methylene chloride (CH_2Cl_2), $\text{CCl}_2\text{FCFCl}_2$ (CFC-113), chloroform (CHCl_3), methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), trichloroethylene ($\text{CClH}=\text{CCl}_2$), and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$) were targeted due to their well-characterized properties, such as homogeneity, ubiquity, and the high sensitivity to ECD in detecting them [16], make them ideal targets to test the method. The concentrations of these compounds ranged from few pptv to sub-pptv, which were well above the detection limits of ECD with the use of the TD unit in the system for in-line enrichment [16]. However, ECD is less sensitive for some hydrogen-containing halocarbons at ambient level ranging from few ppt to sub-pptv even with the use of a pre-concentrator. The oxygen-doping technique by adding a small flow of zero air in the make-up gas of ultra-pure nitrogen can increase the sensitivity of ECD for the

hydrogen-containing halocarbons (e.g., CH_2Cl_2 and CHCl_3 in this study) [29,30]. The mixing was conducted by exploiting the electronic pressure controllers built in the GC to maintain very constant flows of nitrogen and air to attain the desired mixing ratio of 0.2% for oxygen in nitrogen.

Compound identification was made by spiking known compounds in both the 1-D and GC \times GC analysis, and the retention times can correlate rather well in the x – coordinate of both methods. In addition, since peaks with GC-ECD are usually very characteristic for the target halocarbons in ambient air, hence identification with spiking, assisted with characteristic fingerprinting, made identification relatively straightforward. Concentrations of the 6 target halocarbons (CFC-12, CFC-11, CH_2Cl_2 , CFC-113, CH_3CCl_3 , and CCl_4) in ambient air were calibrated with a pressurized cylinder to serve as the working standard (or secondary standard). This working standard was in term calibrated with a standard cylinder purchased from National Oceanic and Atmospheric Administration/Global Monitoring Division in the US which is traceable to National Institute of Standards and Technology to serve as our primary standard. Calibration of CHCl_3 was made by an US EPA type standard, i.e. TO-15. The concentrations of CFC-12, CFC-11, CH_2Cl_2 , CFC-113, CHCl_3 , CH_3CCl_3 , and CCl_4 in the working standard were calibrated to be 566.1, 247.9, 687.7, 75.2, 22.6, 5.7, and 94.6 pptv, respectively. Because no quality standards were available for tri- and tetrachloroethylene at the time of experiment, the concentration calibration was not possible and only compound identification was performed.

2.2. Sample pre-concentration

Fig. 1 illustrates the apparatus of the analytical system used in this study. A TD unit was built in-house with multipoint switching valves (A26UWE, Valco Instruments Co. Inc., USA) to guide sample flows during sample trapping and injection. A glass tube (10 cm \times 2 mm I.D. \times 1/8" O.D.) packed with carbon sorbent beds of Carboxen 1000, Carboxen 1003, and Carbotrap formed the sorbent trap. Each bed was about 1 cm in length isolated with glass wools. The air sample was drawn by an oil-free pump through the sorbent trap thermostated at 30 °C for 5 min or a desired time interval. The sample flow was controlled by a mass flow controller at a constant flow rate of 50 mL min⁻¹. Injection was then performed by flash heating from 30 °C to 250 °C within seconds, followed by back-flushing the sorbent trap kept at 300 °C for 30 min for conditioning. All the tubing used in the TD unit is made of Silcosteel (1/16" O.D., 0.8 mm I.D., Restek, USA). Further detailed information of the TD unit can be referred to our previous works [16,31].

2.3. Heart-cut gas chromatography

A GC (6890N, Agilent, USA) equipped with a micro-ECD thermostated at 300 °C was used. A Deans switch device comprising three micro tee unions (MT1CS6, Valco Instruments Co. Inc., USA) connected with short sections of Silcosteel tubes (3 cm \times 1/16" O.D. \times 0.1 mm I.D., Restek, USA) served as the valve-based flow modulator in this work. A three-way solenoid valve (091-0094-900, Parker, USA) was connected to the two ends of the micro tee unions to control the flow direction for modulation.

A series of column combinations for the target halocarbons were tested. A non-polar column (either DB-1 or DB-5) with a typical length of 60 m was chosen to be the 1-D column throughout the 2D optimization process. Several columns of large difference in polarity and absorptivity from the 1-D column were systematically tested for the most desired separation efficiency and orthogonality for the halocarbons. Columns of various properties such as polarity, phase types (WCOT vs. PLOT) and dimensions were tested as the 2-D column. The pressures of the auxiliary and carrier gas were setup

Download English Version:

<https://daneshyari.com/en/article/5135176>

Download Persian Version:

<https://daneshyari.com/article/5135176>

[Daneshyari.com](https://daneshyari.com)