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Construction and evaluation of automated gas chromatography for the measurement of anthropogenic halocarbons in the atmosphere

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Abstract

An automated gas chromatography system for analyzing atmospheric halocarbons was constructed and evaluated. A cryogenic trap was developed to facilitate automation and, at the same time, conserve liquid nitrogen. Concentration calibration was accomplished by the use of multi-component gas mixtures with ambient concentration levels. Reproducibility was evaluated with replicate precision of about 1–2% for most of the measured halocarbons, substantially better than that of our previous manual system of 4–6%. The linearity of this automated system was confirmed by two independent methods, with one varying injection volume and the other varying injection concentration, and both were in excellent agreement. The system was successfully employed in canister and in-situ measurements. Concentrations of CCl_4 was found to be extremely uniform with average concentration of 102 pp (v/v), very close to its global background value. The standard deviation of 106 samples was 1.5% for CCl_4 which is almost equivalent to its analytical precision. This uniform property associated with CCl_4 atmospheric distribution can be a useful tool for testing system's reproducibility and stability. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Air analysis; Environmental analysis; Automation; Instrumentation; Halocarbons; Organochlorine compounds

1. Introduction

The release of chlorofluorocarbons (CFCs) has resulted in ozone depletion in the Antarctic stratosphere [1–5]. Measurement of long-lived halocarbons, mainly the chlorofluorocarbons, has been carried out continuously on remote sites either by canister method or in-situ on-site method for the past two decades [6,7]. The objective was mainly to deduce the lifetimes of the monitored species, and the trend of their atmospheric growth [6–9]. The trend is of particularly importance in recent years

after the implementation of the Montreal Protocol in 1987 and its subsequent amendments [10–12].

Most of the industrialized nations have dramatically reduced their usage and therefore the emissions, and the result has been well reflected on the background measurement data in which a slow-down trend or even a decline trend has been observed [6–9]. However, many developing nations may have not completely abandoned the CFC applications, which may result in a much slower recovery for the stratospheric ozone [13]. As a result, to locate and cease the fugitive sources may become an important task in the future worldwide. Nevertheless, passive monitoring of atmospheric CFC background levels can not provide the capability to locate fugitive

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emissions. Instead, direct sampling in the possible areas is the only effective method in locating sources [14,15].

A large quantity of air sample canisters are often needed in order to sample a large area and to provide statistically significant data, and an automated analytical system can facilitate the analysis with superb precision and efficiency. We therefore designed and successfully employed a fully automated gas chromatograph with electron-capture detection (ECD) for measuring halocarbons in air canisters or directly from open atmosphere. The system was design to meet the criteria of continuous, automated, and precise measurements, so that minimum man-

power was required to perform quality halocarbon measurements.

2. Instrumentation

A Varian 3400 GC equipped with an electron-capture detector provided the base for the automated system to build upon. Fig. 1 displays the systematic diagram of this system with emphasis placed on valve configuration. Three Valco air actuated multiport switching valves, i.e., a 3-port, a 4-port, a 6-port (Model 3UWT, 4UWT, and 6UWT), and a pneumatic bellows valve (Parker; 4A-P4K-11AC-

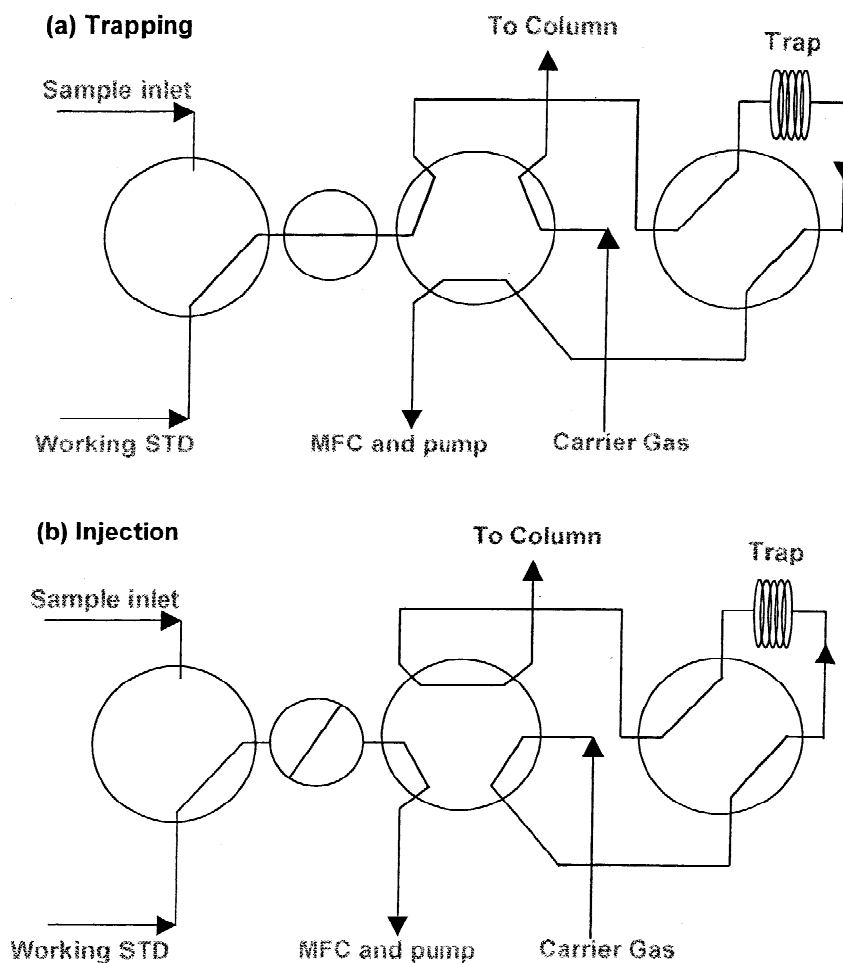


Fig. 1. Valve configuration in (a) sample trapping and (b) sample injection modes. Details of the cryo-trap are shown in Fig. 2.

SS) were placed up-stream of the trap. The valve bodies were heated at about 60°C at all times to minimize surface absorption. Actuating these 4 valves was made possible by four 110 VAC 4-way solenoid air valves (Valco, model 41E1) controlled by a relay board with each responsible for routing compressed air to actuate its corresponding switching valve. All the connecting plumbing for transferring sample air used 0.32 cm O.D. treated tubing (Silco-steel, Restek, Bellefonte, PA, USA) to minimize possible transfer loss due to surface adsorption [16]. The plumbing for actuating valves used 0.32 cm O.D. PTFE tubing with air pressure set at about 56 kPa. The outlet of the valve system was connected to a vacuum line evacuated by a mechanical pump. A cold trap submerged in liquid nitrogen dewar was placed between the valve system and the pump to prevent oil vapor from back-diffusing into the gas line. To accurately measure the amount of air drawn through the cryo-trap and to monitor the vacuum condition of the system, a mass flow controller

(Sierra Instrument, 840L-1-OV1-SV1-E-V1-S1), a capacitance manometer (MKS, model 622A), and a thermocouple gauge (Edwards, Thermocouple 507) were installed on the vacuum line.

The complete cryo-trap unit was placed right on top of a flange-sealed 10-l liquid nitrogen dewar with a head pressure of 20 p.s.i., see Fig. 2 (1 p.s.i. = 6894.76 Pa). A cryo-trap was made of a piece of 10 cm long, 0.32 cm O.D. stainless steel tubing filled with 4 cm long, 120–180 μm glass beads. Cooling of the trap for trapping halocarbons was performed by purging liquid nitrogen into the housing to maintain temperature at -180°C . During injection, the trap was rapidly heated up by supplying a low voltage high electrical current (4 V; 30 A) to both ends. A solenoid valve was connected to the vent port of the purge housing. Whenever the trap was called for cooling, the solenoid valve was opened to inject liquid nitrogen into the housing by relieving the head pressure in the dewar. As soon as the temperature reached -180°C , the solenoid valve was

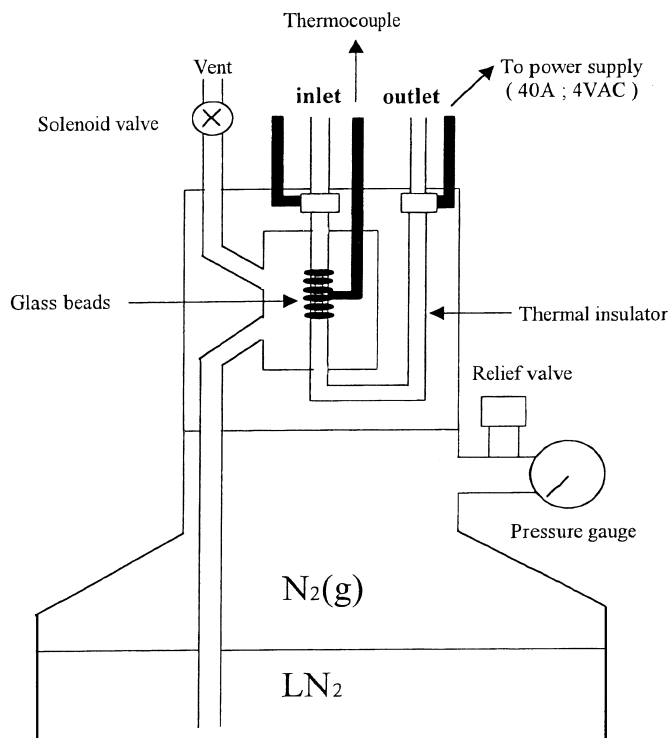


Fig. 2. The cryo-trap, constructed from a piece of 0.32 cm stainless steel tubing packed with glass beads, is placed on top of a sealed 10 l LN₂ tank to reduce the transfer loss.

shut off. The temperature setpoints, the feedback, and the control of the solenoid valve for cooling were performed by a temperature profile controller (Powers 535, Powers Process Controls, Skokie, IL, USA). The use of PID (proportional-integral-derivative) control algorithm enabled a small temperature fluctuation around the temperature setpoints.

The purpose of this cryo-trap design was to conserve liquid nitrogen by reducing vaporization due to long-distance transfer. As a result, more than 30 sample analyses could be made by one LN₂ filling (about 8 l). The trap was designed to be removable from the housing, so that traps with different packing material could be employed. Although packing with chemical absorbent elevated the cooling temperature significantly, which in turn conserved more LN₂, the glass beads were preferred in this work for its rapid and complete desorption, which resulted in a very clean baseline.

In this study, a DB-1 column (J&W Scientific; 60 m×0.32 mm, $d_f=1.0\mu\text{m}$) was used for canister analysis, and a DB-624 column (J&W Scientific, 70 m×0.53 mm; $d_f=3.0\mu\text{m}$) was used in the field deployment without GC oven cooling. The temperature program for the DB-1 column was: -50°C isothermal for 2 min followed by a ramp of $8^\circ\text{C}/\text{min}$ to 180°C and maintained at 180°C for 8 min. For the DB-624 column, the temperature program started at 35°C , isothermal for 5 min followed by a ramp of $5^\circ\text{C}/\text{min}$ to 180°C .

Data acquisition and integration were made by a commercial chromatographic software package (Star, provided by Varian, Walnut Creek, CA, USA). The control of valve switching, GC on/off, cryo-trap, and graphic display of system actions were performed by a self-developed software.

The 2-l stainless steel canisters used in this study were purchased from Rowland–Blake Laboratory, University of California, Irvine, CA, USA. Prior to analysis, a batch of canisters was cooled with ice for at least 20 min to condense excess water to prevent the cryo-trap from being plugged up during trapping. To determine if cooling resulted in surface effect, humid ambient samples were tested with and without cooling and no signs of removal occurred for compounds like CH₃CCl₃ and CCl₄, which are more subject to adsorption [17]. The remaining water vapor in the canisters was necessary to prevent

surface adsorption on canister or tubing wall [17]. Alternatively, a Nafion tubing, 65 cm long, membrane O.D.=0.32 cm, and shell O.D.=0.635 cm, was used before the sample inlet to yield a dew point of approximately -10°C . Again, humid air samples were tested with the Nafion tubing and no noticeable reduction in peak height for CH₃CCl₃ and CCl₄ was found. We also use this device in our in-situ mode, which has been a convenient solution to remove water in some long-term monitoring stations measuring halocarbons [18,19].

A 30-l reference cylinder (Acufife treated, provided by Scott, San Bardino, CA, USA) was filled with ambient air to about 700 kPa to maximize the number of aliquots and hence prolong the usage time. The stability of the analytical system was monitored by analyzing this air in between sample runs. This reference air was calibrated with synthetic standard mixtures prepared by a 4-step static dilution of the pure halocarbons with UHP zero air [20–22]. Hence, it also served as a working standard for deducing concentrations of selected halocarbons in the samples.

3. Automation sequence

Detailed time events and their corresponding analytical significance of a complete cycle are described in Fig. 3. The 4-valve system with the cryo-trap mainly executes the following analytical steps.

(1) Sample trapping, see Fig. 1a. The 3-port switching valve routed the air either from the sample canister or the reference cylinder. Aliquots of air sample going to the cryo-trap was controller by a mass flow controller with a fixed duration prescribed in the time event table. The reproducibility of aliquots controlled by the mass flow controller was checked by repeatedly monitoring the pressure drop of sample canisters of ambient pressure with the capacitance manometer (MKS, model 622A), and the 1σ was better than 0.04%

Whenever a new canister was attached to the sample inlet and ready to be analyzed, the valve on the canister was opened after the line was evacuated to $<10^{-2}$ Torr (1 Torr=133.322 Pa). The first half a minute of sample air flow was used to flush tubing

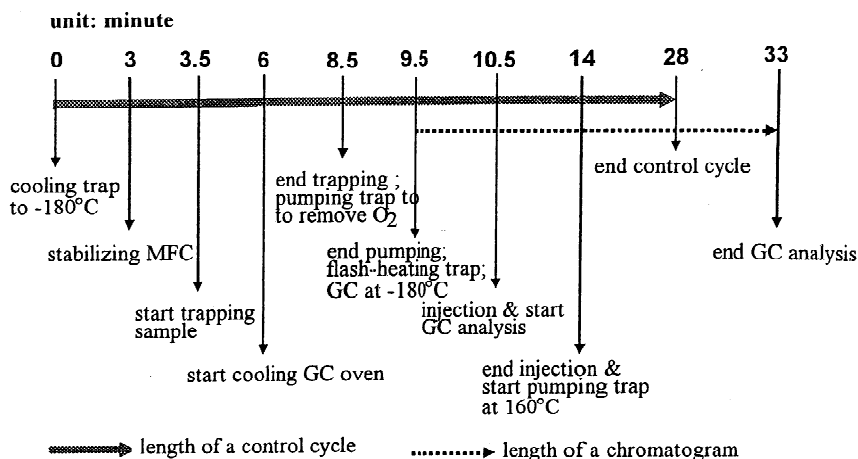


Fig. 3. Time events of a complete analytical cycle.

and to stabilize the mass flow controller. As soon as the cold-trap has been cooled to -180°C , the sample flow was routed to the trap for enrichment.

(2) Oxygen removal. After the trapping was completed, the pneumatic valves was shut off while the cold-trap was still under vacuum for another minute to evacuate residual air in the cryo-trap maintained at -180°C to remove oxygen, which otherwise would overload the ECD system and seriously interfere or reduce the sensitivity of the early eluting halocarbon peaks, such as CFC-12 (CCl_2F_2), H-1211 (CBrClF_2), CFC-11 (CCl_3F), and CFC-113 ($\text{CCl}_2\text{FCClF}_2$).

(3) Sample injection, see Fig. 1b. The trap was then heated up rapidly from -180°C to 60°C in a few seconds, and flushed the enriched sample onto the column. After flushing for 3.5 min, the 6-port valve was switched and the trap was immediately ramped to 160°C to allow the less volatile compounds and water to be pumped away, which otherwise tended to accumulate in the trap and affected later injections. This pumping continued into next running cycle until sample air started to be drawn through the system by opening the pneumatic shut-off valve (see Fig. 1a). Immediately after the trapping has finished and the pneumatic valve was shut off, the sample can be taken off from the inlet and replaced by a new one. Depending upon the length of a chromatogram, a time window of more than 20 min was available for changing canisters.

Fig. 4 exhibits the resulting chromatograms for separation and detection of halocarbons in a typical air sample collected in Taipei area with injection volume of 250 ml.

To facilitate analyses of large amount of samples, a canister rack system to accommodate multi-canisters for batch analysis, was constructed from 110 VAC 4-way solenoid air valves (Valco, model 41E1) and pneumatic bellows valves (Parker; 4A-P4K-11AC-SS), similar to the design described earlier. When batch analysis was needed, the outlet of this rack was connected to the sample inlet shown in Fig. 1. A subroutine was written for this canister rack to perform analysis in a subsequent order or a prescribed order. Before starting analysis on a batch, all the connecting tubing was evacuated to $<10^{-2}$ Torr. Leak was checked prior to opening the canister valves. As soon as the computer routine was started, the system can run continuously unattended until a batch was finished. A new batch of canisters, which has been cooled with ice for sufficient time, was then attached to the rack to start a new round of analysis.

4. Control hardware and software

The software and hardware components provided a generic means to bridge our valve system to GC systems of different manufacturers. The control hardware used in this study consisted of a digital/

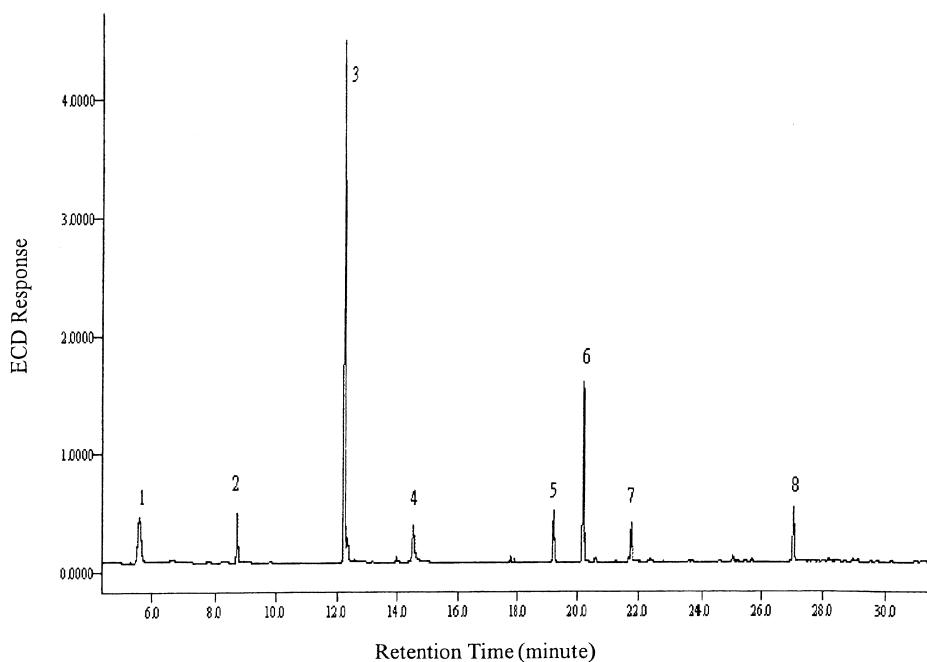


Fig. 4. Separation of halocarbons on the DB-1 column for a typical sample collected in Taipei City. Peak assignments: (1) CFC-12, (2) H-1211, (3) CFC-11, (4) CFC-113, (5) CH_3CCl_3 , (6) CCl_4 , (7) $\text{CClH}=\text{CCl}_2$, (8) $\text{CCl}_2=\text{CCl}_2$.

analog conversion card (PCL-818L), a signal conditioning board (PCLD-8115), a 16-channel power relay output board (PCLD-885; Advantech, Taiwan). A Windows-based software platform (Genie; Advantech, Taiwan) was used to provide a Visual Basic programming environment for writing control code. Six relays were used to drive valves, initialize the temperature profile controller, and start/stop the GC system. Another set of relays was used to control a canister rack system. We also designed the software to include a graphic display of the valve actions using icons with color change to indicate on/off modes while an analysis was proceeding. This feature provided an instant understanding of the system status for operators. Manual control of the system was also possible through highlighting icons for valves, cryo-trap, GC systems, or individual sample inlet on the rack system.

This automated system was not designed and constructed for measuring halocarbons alone, measurements of non-methane hydrocarbons were also made using this system with different columns and

chromatographic conditions. This will be discussed in later publications.

5. Analytical precision

The analytical precision was tested by analyzing the pressurized reference air sample, which permitted hours of unattended injections. Table 1 lists the 1σ replicate precision of halocarbons resulting from repeated injections of this sample, as shown in the third column. Also listed in Table 1 is the reproducibility compiled from archived data over a period of a month to demonstrate the system stability, as shown in the fourth column. The power and gas supply of the system was turned off at the end of a day, which may have caused a small drift in gas flow settings and hence the slightly worse precision compared to the replicate precision. Improvement in precision was dramatic when compared to our previous manual system with replicate precision between 2 and 6% at similar concentration levels. Inaccuracy

Table 1
Analytical precision for selected halocarbons in the reference air

Compound	Concentration (pptv)	Replicate (1 σ %) (n=17)	Long-term stability (1 σ %) (n=7)
CFC-12 (CCl ₂ F ₂)	540	0.62	1.40
CFC-11 (CCl ₃ F)	320	0.68	1.20
CFC-113 (CCl ₂ FCClF ₂)	105	1.21	2.83
CHCl ₃	60	0.82	0.95
CH ₃ CCl ₃	130	0.87	0.90
CCl ₄	105	1.11	1.13
C ₂ HCl ₃	65	0.81	1.75
C ₂ Cl ₄	210	0.65	3.69

in timing when manually turning valve-knobs as well as inconsistency between different operators was the main reasons for the inferior precision.

6. Linearity study

Linearity of this automated system was investigated by analyzing a synthetic gas mixture at nominal concentrations. Gas mixtures containing measured halocarbons were made by static volumetric dilution method with concentrations, e.g., for CFC-12 and CCl₄ being 500 and 100 pp (v/v) (pptv) respectively, close to their background levels. Detailed description of such a method is published elsewhere [20–22]. Fig. 5a and b show the linearity of the two halocarbons, i.e., CFC-12 and CCl₄, of significant volatility difference. Two methods were employed in this study. In the first method, the linearity was examined by injecting five different amounts of this standard covering the working range with the median injection volume of 250 ml. The amount of each injection was determined by measuring the pressure drops in a fixed volume holding the gas standard. The volume coordinate can be directly converted into concentration coordinate, provided that the halocarbons are consistently trapped. In order to verify this argument a conventional method was used by running another 4 standards of different concentrations, with the original standard being the median concentration. The injection volume was kept the same as 250 ml for all the standards, and the data point for original 500 pptv standard for CFC-12 and 100 pptv standard for CCl₄ run at 250 ml was

directly combined in this method. Hence, both methods shared this common data point in Fig. 5a and b. The fact that both methods agreed well and had near-zero intercepts suggests the cryo-trapping and ECD response over this concentration range are proportional and linear, which otherwise would result in two curves crossing at the common data point.

7. Field measurement

The spatial and temporal variability of anthropogenic halocarbons varies from compound to compound. For halocarbons, such as CFC-11, CFC-113, and CCl₄, their usage has rapidly declined in recent years, hence their long atmospheric lifetimes render them mix homogeneously in the air. As a result, their concentration variability is smaller than those of other halocarbons, such as CFC-12 and CH₃CCl₃, whose usage is still significant, and occasionally elevated concentrations can be encountered in urban samples [14,15]. The degree of concentration variation of halocarbon concentrations was used as a basis for determining the existence or the extent of anthropogenic halocarbon emissions. The automated system was employed in a field mission to measure ambient air samples collected in Taipei metropolitan area. A total of 106 air samples were collected on 7 August, 1998 in Taipei metropolitan area with one half of the samples collected between 5:00 and 5:30 a.m. and the other half collected between 6:00 and 6:30 p.m. This sampling strategy was designed to obtain a near snapshot effect of the spatial dis-

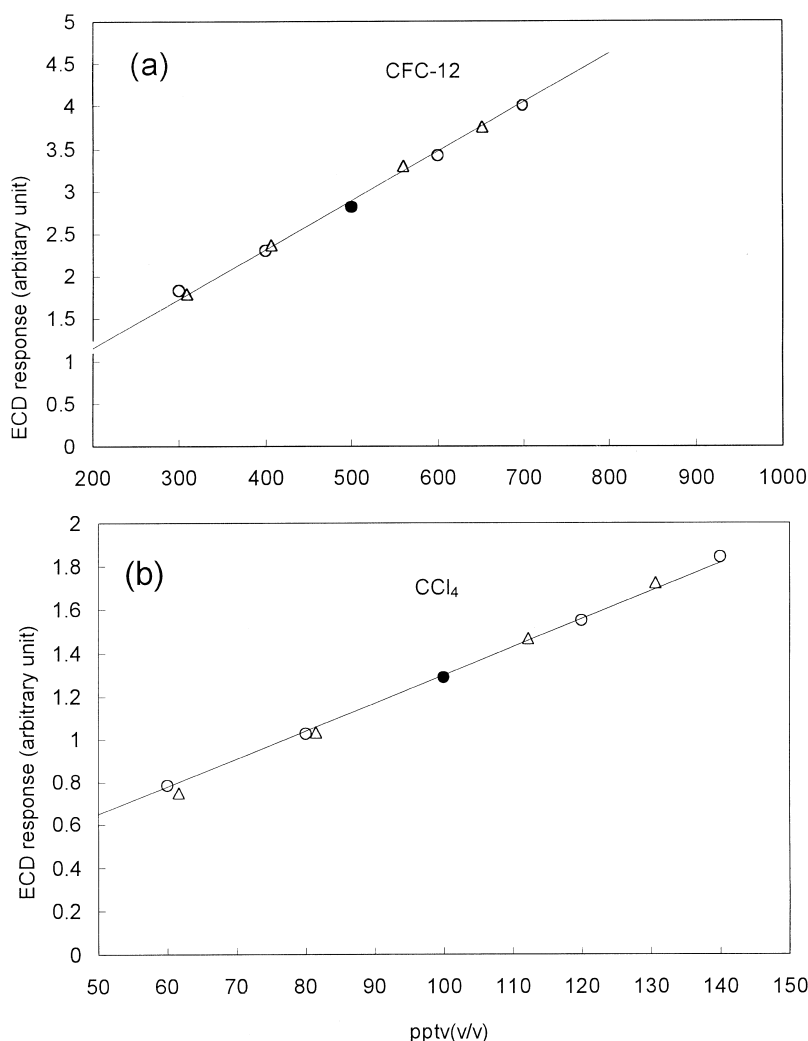


Fig. 5. Linearity of cryo-trapping and ECD response using (a) CFC-12 and (b) CCl₄ for illustration. Circles are standards of 5 different concentrations with 500 pptv and 100 pptv being the median concentrations for CFC-12 and CCl₄, respectively, and injected at a fixed volume of 250 ml. Triangles denote the 500 pptv and 100 pptv standards for CFC-12 and CCl₄, respectively, injected at five different volumes with the median volume being 250 ml. The solid circle denotes the common data point of median standards injected at 250 ml. The best fit to circles and triangles combined in (a) $y=0.0058x$, $R^2=0.996$; (b) $y=0.013x$, $R^2=0.995$, with intercept deliberately set at zero.

tributions of anthropogenic halocarbon sources. All samples were collected in open field such as parks or schoolyards to avoid direct influence by point sources. Of all the measured species, CCl₄ had the smallest concentration variation with 1σ relative standard deviation of only 1.5% around its average concentration of 102 pptv, almost equivalent to the global background level [23], suggesting CCl₄ had

no usage and therefore emissions in Taipei area. Fig. 6a and b display the concentrations of CFC-12 and CH₃CCl₃ with respect to CCl₄ for the 106 samples. Clearly, the concentrations of CFC-12 and CH₃CCl₃ were significantly more variable, suggesting the emissions of CFC-12 and CH₃CCl₃ were still significant. The fact that all 106 samples were continuously analyzed within 4 days and showed CCl₄ standard

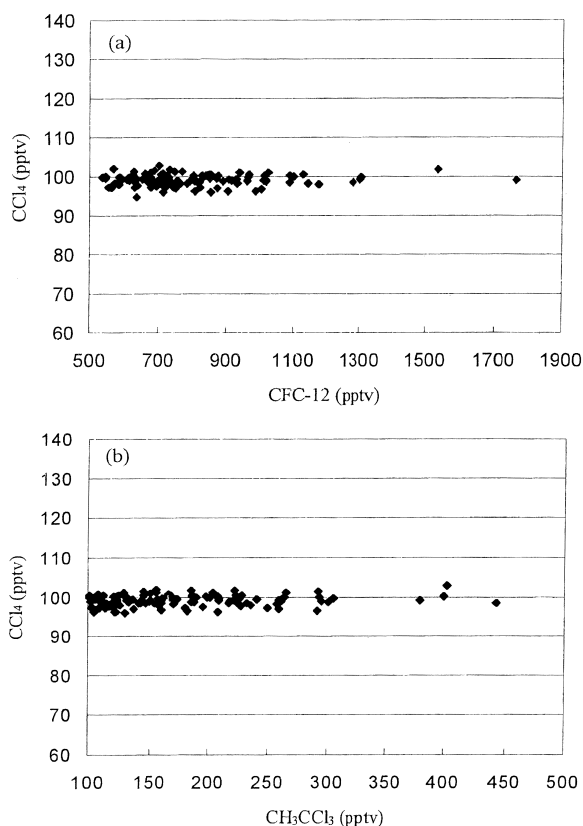


Fig. 6. Concentrations of (a) CFC-12 and (b) CH_3CCl_3 with respect to those of CCl_4 for the 106 samples.

deviation almost equivalent to its replicate precision demonstrated the system was highly reproducible and stable. Four refills were made during analyzing the 106 canisters, plus runs for the reference air. The limiting factor in sustaining the continuity of the analysis was the size of the LN_2 tank. In most cases, we ran smaller numbers of canisters, and using a larger tank ended up wasting the remaining LN_2 .

As part of the field measurement to supplement the near real-time variability with temporal variability, the system was placed at a field site to perform unattended in-situ measurement of atmospheric halocarbons, see Fig. 7. Since the concentration differences between measured halocarbons were rather large; examining their relative change in concentration facilitated comparison of temporal variation between compounds in a similar scale. The

relative percent concentration change of each halocarbon was calculated as

$$\text{Relative concentration change (\%)} = (A - B)/B \times 100$$

where A is the concentration of a halocarbon of any injection; B is the lowest concentration found among all injections.

Large temporal variation in concentration was found for CFC-12, C_2HCl_3 , and CH_3CCl_3 . The concentrations for $\text{C}_2\text{Cl}_3\text{H}$, CH_3CCl_3 , and CFC-12 declined as time elapsed into the evening, whereas for CFC-11, CFC-113, and CCl_4 their concentrations were rather uniform throughout the measurement period. The minimum concentration for CFC-12 was about 5ppbv, about an order of magnitude higher than the background level of about 520 pptv [6,7], indicating a source existed near our station. This dramatic change in concentrations for $\text{C}_2\text{Cl}_3\text{H}$, CH_3CCl_3 , and CFC-12 was likely to be associated with the change of wind directions. Again, the uniform concentrations for CFC-11, CFC-113, and CCl_4 provided a good indication that the analytical conditions were robust. Hence, an automated system with the ability to detect very small variability or fugitive emissions of anthropogenic halocarbons was proven to be useful for monitoring the degree of compliance to the Montreal Protocol in certain parts of the world.

8. Conclusion

The precision of halocarbon measurements of about 1–2% at pptv levels was achieved by automating the analytical procedure on a GC-ECD system. A cryo-trap system was built in an attempt to conserve liquid nitrogen and therefore facilitate field deployment. The computer based control hardware and software were developed to synchronize the valve actions, the cryo-trap system, and the canister rack with the GC system, so that the system successfully met the design criteria of continuous, automated, and unattended operation. Linearity of this system was demonstrated by employing two independent methods to vary the injection content of halocarbons of interest over the range of measurement, and both methods were in good agreement. The robustness of

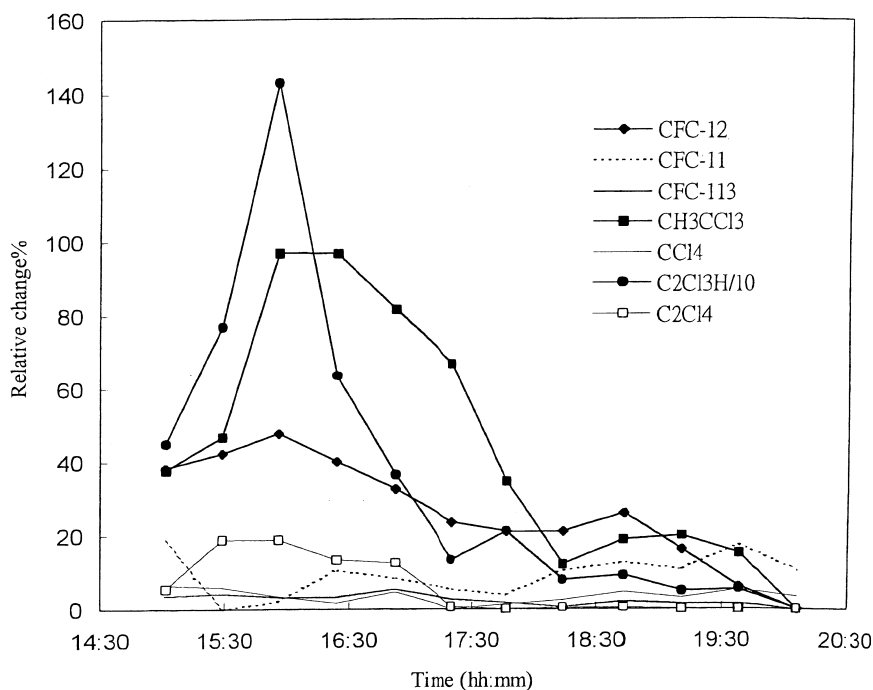


Fig. 7. Continuous measurements of halocarbons in open air for determining temporal variation in concentrations.

this system was tested with a field mission with grasp and in-situ sampling. The small variability of atmospheric CCl_4 provided a useful reference to examine the system's stability and reproducibility. In addition, the ability to determine the variability associated with the anthropogenic halocarbons with high precision and efficiency is useful for certain areas to assess the degree of compliance to the Montreal Protocol.

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