Determination of Halogenated Hydrocarbons in the Air by Cryogenic Preconcentration and Gas Chromatography- Quadrupole Mass Spectrometry

by

Katsuhiko Fushimi and Yukio Sugimura

Meteorological Research Institute, Tsukuba, Japan

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Abstract

A simple method is described for the preconcentration and determination of some of the atmospheric chlorofluorocarbons by using the GC-QMS method. The halogenated hydrocarbons in 100 ml of air sample were preconcentrated into 1.7 ml of cold trap by using helium stream and were injected into a GC column. The determination of F-11 and F-12 was done by electron impact mode of the GC-QMS method. Recovery of this method is 100% and the results of replicate determinations are in good agreement with each other within the analytical error.

1. Introduction

In the last three decades, chlorofluorocarbons have been continuously and increasingly introduced into the global atmosphere mainly through their use as refrigerant, aerosol propellant and foaming agent of plastic rubber. Owing to their chemical inertness, accumulation in the troposphere has been pointed out by many researchers (Lovelock et al., 1973; Su and Goldberg, 1973). Subsequent diffusion to the stratosphere followed by the generation of chlorine through photolysis has attracted worldwide attention to possible future reduction of the stratospheric ozone content (Cicerone et al., 1974; Crutzen, 1974; Molina and Rowland, 1974).

Most determinations of halogenated hydrocarbons in the air have been carried out by the electron capture detector with a highly selective GC column, and also by the GC-MS methods (Grimsrud and Rasmussen, 1975; Bortoli and Pecchio, 1976; Pack et al., 1977;

Makide et al., 1980; Bruner et al., 1981).

To separate chlorofluorocarbons from the air effectively, most of these methods proceed as follows: the GC column is maintained at dry ice temperature first and then the separation of chlorofluorocarbons takes place on the GC column at elevated temperatures, taking great care against contamination of the sampling tube and the analytical system.

For increasing the detection limit of the trace constituents, a method of sample concentration by freezeout was reported by Rasmussen et al. (1977). In their method, an air sample was preconcentrated in a sample loop as the first step, and then the contents of the sample loop were transferred onto the head of the GC column kept at -10°C .

As a more simple preconcentration and injection method, the present authors intended to report here a modified method of analysis after the cryogenic preconcentration of halogenated hydrocarbons in a small cold trap followed by determination of the GC-QMS

method.

2. Experimental

2.1 Instrument: A gas chromatograph coupled with a quadrupole mass spectrometer (Varian TE-600) was used to determine chloro-fluorocarbons in the air. Throughout this work, the following analytical condition of gas chromatography was used:

GC column: Stainless steel column of 2 mm dia and 2 m long packed with 10% Silicone OV-1 on 80 to 100 mesh Neopak 1A.

Temperature: 70°C

Carrier gas: He (99.995%) at the flow rate of 10 ml min⁻¹.

After gas chromatographic separation, chloro-fluorocarbons are injected into QMS of electron impact mode and the intensities of induced ions of CF₂Cl⁺ and CFCl₂⁺ were determined by multi-ion detectors at m/e 85 and 101 respectively.

2.2 Sampling and storage of air samples: Samples were collected in 100 ml of gas collecting tube of glass made with two stop cocks by using an air pump. Before sampling, the inside of the sampler was flushed with ambient air for 5 min at a flow rate of 1 to 2 liters per minute and each stop cock was closed after the pressure was equilibrated. The sample tube was stored at ambient temperature and pressure.

During the storage for several months,

Fig. 1. A schematic diagram of the preconcentration system and GC-QMS for the determination of halogenated hydrocarbons in the air.

neither loss nor gain was observed on the concentration of halogenated hydrocarbons in the sample tube as shown in Fig. 2. The average concentrations of F-11 and F-12 in stored samples were 215±18 ppt and 326±11 ppt respectively. The result shows that the standard deviations of the analytical values are within the reproducibility of the analyses.

3. Analytical procedure

The following procedure was used for the determination of halogenated hydrocarbons in surface air in this study. A schematic diagram of preconcentration line and GC-QMS is shown in Fig. 1.

(1) Clean up the line: The sample tube was set into the analytical line and before opening the stop cocks of the sampler, the line was evacuated and washed with He stream repeatedly.

(2) Blank run: To examine a blank value of the analytical line, helium gas was passed through bypass line to sample loop at 10 ml min⁻¹ for 2 hours. Trace contaminants in the carrier gas and the line were trapped into the sample loop at liquid nitrogen temperature and the concentration of F-11 and F-12 was determined as blank value.

(3) Preconcentration step: After the blank run, the stop cocks of the sample tube were opened and halogenated hydrocarbons in the sample air were transferred into a small trap of 1.7 ml at liquid nitrogen temperature

Fig. 2. Change of the concentration of halogenated hydrocarbons during the storage of the air sample in the glass sample tube.
○: CF₂Cl₂, △: CFCl₃

by means of helium stream at the flow rate of 10 ml min^{-1} for 2 hours.

(4) Determination of halogenated hydrocarbons: After the preconcentration step, a six-way valve was turned to the analyzer line and the sample loop was warmed with hot water. The concentrated halogenated hydrocarbons in the cold trap were liberated and introduced into GC-QMS system with helium stream at the flow rate of 10 ml min^{-1} . The separation of halogenated hydrocarbons by gas chromatograph was done at the isothermal condition of 70°C and identification and determination of each chlorofluorocarbon were done by the quadrupole mass spectrometer in an electron impact mode at m/e 85 and 101 using multi-ion detectors respectively.

After the first run, the second determination was repeated under the same conditions to confirm the completeness of elution from the sample tube and sample loop, and also to confirm the blank value.

(5) Regeneration of the GC column: At the end of each determination, the GC column was allowed to remain at 150°C for 1 hour to remove the less volatile materials from the column before the next analysis.

4. Examination of the analytical procedure

4.1 *Recovery*: In order to determine the recovery of this method, diluted standard gases each containing 100 ppb of CF_2Cl_2 and CFCl_3 in helium were used. The results of determination indicate that $98 \pm 4\%$ for CF_2Cl_2 and $102 \pm 2\%$ for CFCl_3 were recovered from the first run. The result of the second determination is that only a trace amount of halogenated hydrocarbons is observed which has nearly the same value as those of blank ones.

4.2 *Reproducibility and precision of the method*: The result of four replicate analyses of known amounts of F-11 (378 ppt) and F-12 (388 ppt) in helium showed a good agreement within the analytical error with the standard deviation of 3.9% and 1.7% respectively.

The results of determination of four aliquots of the same air sample at Tsukuba showed good agreement as shown in Table 1,

Table 1. Determination of four aliquots of the same air at Tsukuba.

Sample No.	CF_2Cl_2 (ppt)	CFCl_3 (ppt)
1	339	187
2	343	231
3	313	199
4	321	202
Average	329 ± 14	205 ± 19
c. v. (%)	4	9

Fig. 3. Calibration curves for F-11 and F-12.

○: CF_2Cl_2 , △: CFCl_3

with the standard deviation of 9% and 4% respectively for F-11 and F-12.

4.3 *Detection limit*: Detection limit of this method is obtained as 20 ppt and 78 ppt for CF_2Cl_2 and CFCl_3 respectively, taking into account two sigma of the variation of the blank value.

4.4 *Calibration curve*: A series of F-11 and F-12 standard concentrations from 18 to 99 ppb were made by dynamic dilution system by using the standard gas generator (Standard Tech., SGGU-72), starting from commercially prepared 10 ppm standard of F-11 and F-12. Helium was used for the dilution of the standard gases.

Using one ml sample loop, the diluted standard gases were introduced into GC-QMS. Plots of peak areas generated from these standards against their known concentrations illustrate the linearity of the method as well as similar sensitivity for F-11 and F-12 as shown in Fig. 3.

5. Results and discussion

Some of the examples of determination

Table 2. Results of analysis of halogenated hydrocarbons in the surface air.

Date	Location	CF ₂ Cl ₂ (ppt)	CFCI ₃ (ppt)
June 19, 1981	Tsukuba	329	205
July 1, 1981	Tsukuba	332	211
July 3, 1981	Tsukuba	374	197
July 21, 1981	Tsukuba	476	302
Oct. 6, 1980	Kagoshima	424	176

of F-11 and F-12 in surface air at Tsukuba are shown in Table 2. In the same table, an example of the air collected at Kagoshima is given.

A detailed report on the distribution of F-11 and F-12 on land and over the Pacific, the Indian and the Southern Ocean will be given later elsewhere, but as shown briefly in the table, the concentration in the air on land is in the same order of magnitude as given by other researchers (Grimsrud and Rasmussen, 1975; Bortoli and Pecchio, 1976; Makide et al., 1980; Bruner et al., 1981).

It is concluded that the present method for preconcentration and determination of halogenated hydrocarbons in the air compares favorably with those previously used, because it can easily handle a large volume of sampled air, the instrument needs no modification, and the determination can attain high precision.

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低温濃縮，ガスクロマトグラフ・四重極質量分析計を用いる 大気中のハロゲン化炭化水素の分析

伏見克彦・杉村行勇

空気試料中のハロゲン化炭化水素を、あらかじめ低温で濃縮したのち、ガスクロマトグラフ・四重極質量分析計 (GC-QMS) を用いて分析する方法を述べる。100 ml の空気試料をガラス球にとり、ヘリウム気流を用い、液体窒素温度に冷却した 1.7 ml のトラップに、ハロゲン化炭化水素を凍結捕集する。この濃縮試料を GC カラムに、ヘリウム気流を用いて移し、F-11 と F-12 を、電子衝撃モードによってイオン化したのち GC-QMS により定量した。この方法の回収率は 100% で再現性もよく、濃縮系をとりつけるだけで簡便に分析を行えることがわかった。