

< / - >

Application of double cryofocusing method with GC-ECD to determining volatile halogenated hydrocarbons in gaseous samples

Won Tae JUNG, Masahiko FUJITA

(from the Department of Pharmaceutical Sciences, the Institute of Public Health, Tokyo.)

W. T. JUNG, Masahiko FUJITA *Application of double cryofocusing method with GC-ECD to determining volatile halogenated hydrocarbons in gaseous samples.* Bull. Inst. Public Health, 40(2), 135-140, 1991.

The double cryofocusing system for the determination of volatile halogenated hydrocarbons (VHHs) in aqueous sample was modified for automatic determination of VHHs in ambient air. Gaseous sample was absorbed by air pump at a flow rate of 20 ml/min for 3 min and VHHs in gas were trapped to a cooled (0°C) micro-trap, which was composed of Tenax® GC (beads of polymeric 2,6-diphenylphenylene oxide). Then the target compounds were analyzed by the double cryofocusing method with capillary GC-ECD reported previously. This method showed good chromatographic resolution with high sensitivity, and was successfully applied for consecutive analysis of VHHs in ambient air in every 60 min. The system is expected to give the informations which is essential for evaluating the human exposure to VHHs through respiration.

Key Words chloroform, 1,1,1-trichloroethane, carbon tetrachloride, 1,1,2-trichloroethylene, 1,1,2,2-tetrachloroethylene, purge trap/on-column cryofocusing, capillary gas chromatography, ambient air

(Accepted for publication, June 24, 1991)

INTRODUCTION

Volatile halogenated hydrocarbons (VHHs) have been widely used in various plants such as metallic machinery, integrated circuit industry, laundry shop and chlorofluorohydrocarbon maker. They are thought to be discharged mostly in gaseous phase because of their high volatilities, leading to contamination of ambient atmosphere¹⁾. VHHs in atmosphere have recently been widely determined

locally²⁻⁴⁾ and globally^{5,6)}. Understanding the distribution and fate of the trace VHHs in atmosphere has recently become a high priority in environmental sciences, because some of the VHHs have been known to have carcinogenicity⁷⁾. The data on the VHHs levels in atmosphere are essential for evaluating the human exposure to them through respiration and for assessing the risk by the long-term exposure to them. For the consecutive analysis, it is necessary to analyze the VHHs in atmosphere at regular intervals with automatic operating system⁸⁾. We have previously reported the automated purge trap/on-column cryofocusing system to determine the levels of VHHs in rainwater^{9,10)}.

In this paper, in order to apply the system to ambient air, some part of the system was improved

鄭 元台, 藤田 昌彦 (国立公衆衛生院 衛生薬学科)

[キーワード] クロロホルム, 1,1,1-トリクロロエタン, 四塩化炭素, 1,1,2-トリクロロエチレン, 1,1,2,2-テトラクロロエチレン, ページトラップ/カラム先端冷却法, キャピラリガスクロマトグラフィ, 空気

[平成3年6月24日受理]

and some basic analytical conditions were investigated. Further, the system was improved to analyze the VHHs automatically and repeatedly. Detection limits and reproducibilities of this method were also determined. This automated system ensured good resolution of trace VHHs in ambient air and made consecutive automated analysis possible in every 60 min.

MATERIAL AND METHODS

1) Apparatus

Shimadzu GC-15A gas chromatograph with ⁶³Ni-ECD and Shimadzu C-R4A integrator was used. Gas concentrator used was a D.K.K. GAS-20 with D. K.K. air sampling unit composed of air pump and flow meter. The operation system was the same as those of our previous report⁹⁾. Quadrex Halomatic[®] 624 (semi-wide bore; 0.32 mm i.d. × 30m L.) capillary column coated with a 3.0 μm film of a chemically bonded cyanomethyl phenyl silicone was used. The column oven was kept at 45°C for 5 min and then raised to 130°C with a rate of 5°C/min. Sampling pipe (stainless steel 3 mm i.d., × 3m L.) was cleaned by heating and kept at 120°C until usage.

2) Reagents

Analytical grade reagents (hexane, etc.) were purchased from Wako Pure Chemicals Industry (Tokyo, Japan) and the VHHs standards (chloroform, 1,1,1-trichloroethane, carbon tetrachloride, 1, 1,2-trichloroethylene, 1,1,2,2-tetrachloroethylene) from Tokyo Kasei CO. (Tokyo, Japan) were diluted in hexane to make standard solution. The standard solution contains chloroform 3.36 ng, 1,1,1-trichloroethane 18 ng, carbon tetrachloride 3.92 ng, 1,1,2-trichloroethylene 1.4ng and 1,1,2,2-tetrachloroethylene 0.48 ng, respectively, in 2 μl.

3) Method

The ultra pure nitrogen gas was used as a blank gas and it was absorbed through a sampling pipe into micro trap under various conditions of flow

rate, sampling time and temperature of micro trap. Standard solution 2 μl was injected in the flow of nitrogen gas and vaporized at 100°C. The VHHs were concentrated on the micro trap and then the compounds were thermally desorbed from the trap in a same manner⁹⁾ and a operating program¹⁰⁾ as that described in our previous reports. The VHHs were concentrated again on the trap capillary column 9 min after the start of program and the column oven temperature program was commenced after 4 min. The total analytical running time was 25 min. Ambient air was sampled on the roof of the Institute of Public Health (I.P.H.) during July-August in 1990 and analyzed.

RESULT AND DISCUSSION

1) Effect of sampling flow rate on recovery

To investigate the optimal sampling flow rate of gaseous sample, standard solution was spiked into the flow of ultra pure nitrogen gas and the VHHs were analyzed at flow rates of 20, 30 and 40 ml/min, respectively. As seen in Figure 1, the recoveries of chloroform, trichloroethane and carbon tetrachloride

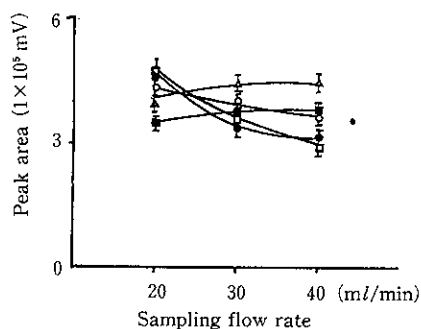


Figure 1. Effect of sampling flow rate on recovery

Injected sample; standard solution 2 μl
(containing VHHs as follows)

where; ●	chloroform	0.28ng
○	1,1,1-trichloroethane	0.60ng
□	carbon tetrachloride	0.09ng
■	1,1,2-trichloroethylene	0.23ng
△	1,1,2,2-tetrachloroethylene	0.08ng

Sampling time; 2 min

The data are given as mean ± standard deviation (n=3)

ide decreased with the rise of the flow rate. Three compounds with relative low boiling points were thought to be less trapped to the micro-trap with the increase of the flow rate. On the contrary, the recoveries of trichloroethylene and tetrachloroethylene slightly increased with the rise of flow rate. We concluded that 20 ml/min was the optimal flow rate of sampling to get good recoveries from all the compounds.

2) Effect of total sampling volume recovery

In order to investigate the optimal volume of sampling, sampling time was changed from 1 to 4 min at a constant flow rate of 20 ml/min, and the result was shown in Figure 2. Recoveries of chloroform, trichloroethane and carbon tetrachloride decreased with the increase of total volume. It is presumably due to being broken through when sampling volume is too large. Trichloroethylene and tetrachloroethylene showed gradual increase up to 60 ml (20 ml/min × 3 min.) and then decreased. So 60 ml of total sampling volume was selected as the

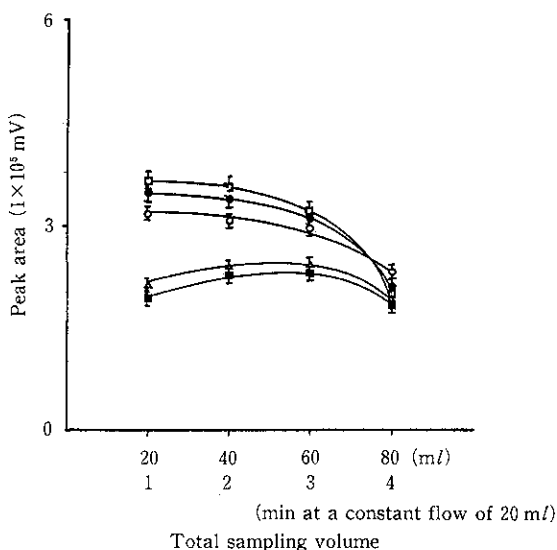


Figure 2. Effect of sampling volume on recovery

Injected sample ; standard solution 2 μl
 Sampling flow rate ; 20 ml/min
 (See legend of Figure 1.)

optimal sampling volume, therefore sampling time was thought to be optimal for 3 min.

3) Effect of micro-trap cooling on recovery

The influence of micro-trap temperature was investigated. As shown in Figure 3, the responses obtained by cooling micro-trap at 0°C were standardized as 100%. The recoveries obtained without cooling (room temperature) were compared with them as percent. All the VHHs, especially with low boiling point such as chloroform showed better recoveries by cooling the micro-trap at 0°C. From

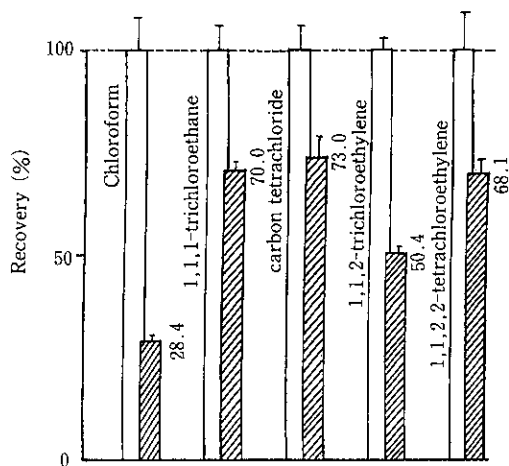


Figure 3. Effect of cooling micro-trap on recovery

Injected sample ; standard solution 2 μl
 Sampling flow rate ; 20 ml/min × 3 min
 The data are given as mean ± standard deviation (n=3)
 where ; □ Responses standardized as "100%"
 obtained from cooling micro-trap at 0°C
 ▨ Responses as compared % obtained from maintaining micro-trap at room temperature

this result, we concluded that 0°C cooling was more effective to get better recoveries.

4) Adsorption of the VHHs onto sampling pipe

To investigate the adsorption of the VHHs in gaseous sample onto the inner wall of the sampling pipe, the recoveries were compared between the data obtained from 60 ml of indoor air sampled

through sampling pipe and those without pipe. Chloroform with the lowest boiling point and tetrachloroethylene with the highest boiling point among the VHHs tested were selected for this experiment. As can be seen in the Figure 4, almost no differences were observed between the data with pipe and without it. So we concluded that the VHHs were negligibly adsorbed to the inner wall of the stainless steel pipe.

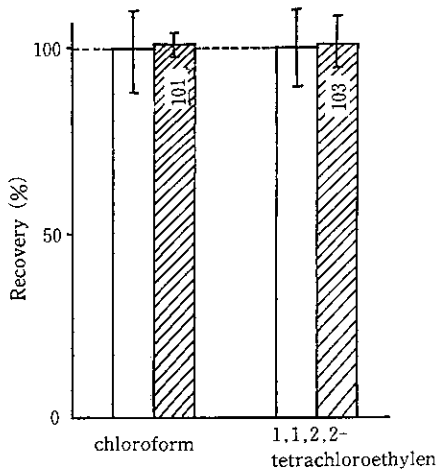


Figure 4. Adsorption of the VHHs at sampling pipe

Injected sample; indoor air
 Sampling flow rate; 20 ml/min \times 3 min
 Temperature of micro-trap; 0°C
 The data are given mean \pm standard deviation (n=5)
 Where: Responses standardized as "100%" obtained with attaching sampling pipe
 Responses as compared % obtained without sampling pipe

5) Detection limits and reproducibilities of this method

Detection limits of this method were obtained by spiking 2 μ l of standard solution into 60 ml of nitrogen gas through the sampling pipe. Detection limits were calculated by JEMCA method¹¹⁾ and shown in Table I. Those of 5 compounds were averaged 0.091 μ g/m³. The detection limits of chloroform, trichloroethane and carbon tetrachloride

with this method were much the same as those with solvent extraction method by GC/NCIMS¹²⁾, and this method was 10 times as sensitive as the solvent extraction method in cases of trichloroethylene and tetrachloroethylene¹²⁾.

Table I. Detection Limits of the VHHs with a Modified Double Cryofocusing Method for Gaseous Samples

Compounds	Detection Limit	
	ng/l	ppb
chloroform	0.071	0.014
trichloroethane	0.252	0.045
carbon tetrachloride	0.091	0.014
trichloroethylene	0.029	0.005
tetrachloroethylene	0.013	0.001

The reproducibilities of this method expressed as coefficient variation (C.V.) % were averaged 3.28% as shown in Table II.

Table II. Reproducibilities of the VHHs with a Modified Double Cryofocusing Method for Gaseous Samples

Compounds	Sampled Amounts	No. of Analysis	Responses (Mean \pm SD, mV)	C.V.(%)
chloroforms	0.28ng	5	460,452 \pm 7,197	1.5
trichloroethane	0.60ng	5	358,806 \pm 20,638	5.7
carbon tetrachloride	0.09ng	5	390,406 \pm 22,181	5.6
trichloroethylene	0.23ng	5	372,048 \pm 1,153	0.3
tetrachloroethylene	0.08ng	5	491,022 \pm 15,409	3.1
Average :				3.28%

6) Application of this method for the determination of the VHHs in ambient air

We applied the method to determining the level of 5 compounds in the ambient air at I.P.H.. The typical chromatograms of standard gas and ambient air distributed around I.P.H. were shown in Figure 5.

As can be seen in the chromatograms, the peaks of the VHHs with very closed boiling points were very clearly separated from each other. The levels of the VHHs were averaged as $10 \mu\text{g}/\text{m}^3$ for chloroform, $120 \mu\text{g}/\text{m}^3$ for trichloroethylene, $8 \mu\text{g}/\text{m}^3$ for carbon tetrachloride, $9 \mu\text{g}/\text{m}^3$ for trichloroethylene and $4 \mu\text{g}/\text{m}^3$ for trichloroethylene. The averaged levels of trichloroethylene and tetrachloroethylene were 4 times higher than those determined in Oregon, U.S. A.¹³⁾.

CONCLUSION

The optimal conditions of automated double cryofocusing system with capillary GC-ECD were established for air monitoring. This system has good sensitivities and reproducibilities with high chromatographic resolution on the VHHs with very closed boiling points. And the system established was successfully applied to determination of the VHHs at a trace level in ambient air and was able to analyze automatically and repeatedly every 60

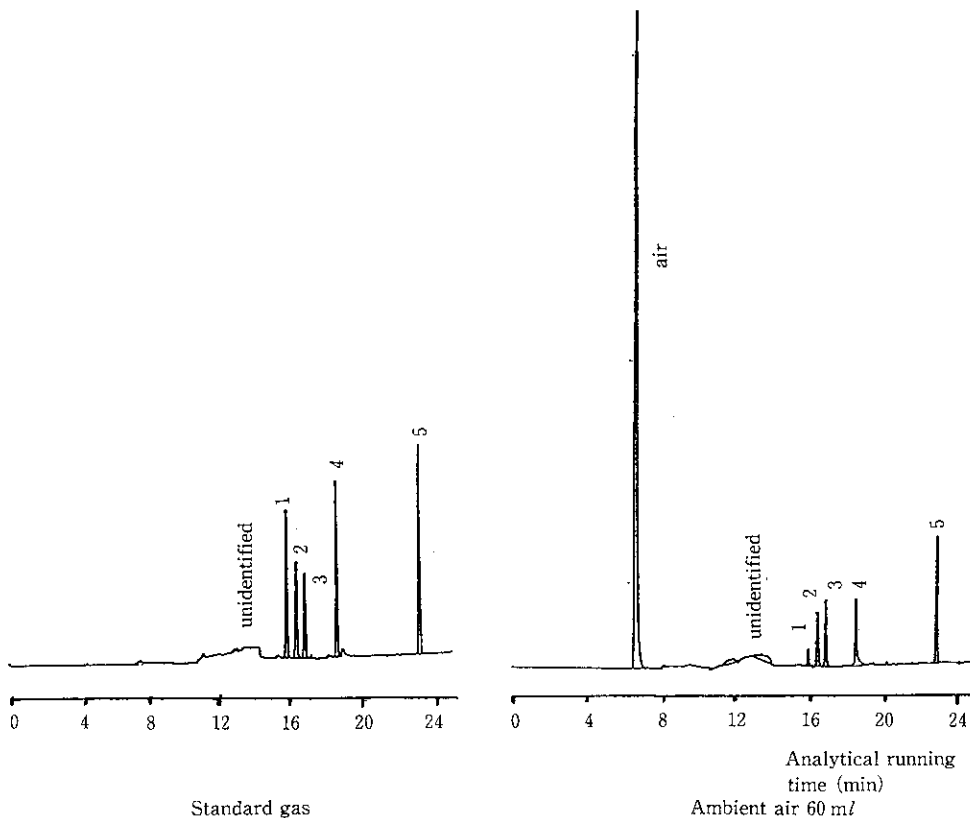


Figure 5. Chromatograms of standard gas and ambient air from Tokyo area

Standard gas; Two μl of standard solution was evaporated to ultra pure nitrogen gas with flow rate of $20 \text{ ml}/\text{min} \times 3 \text{ min}$

(See legend of Figure 1. for the concentrations of VHHs)

Ambient air; sampled with flow rate of $20 \text{ ml}/\text{min} \times 3 \text{ min}$ in Tokyo,

1: Chloroform, 2: 1,1,1-trichloroethane, 3: carbon tetrachloride, 4: 1,1,2-trichloroethylene, 5: 1,1,2,2-tetrachloro-ethylene.

min. So, the system was proved to be used also for air samples, enabling the monitoring the diurnal variation of the VHHs levels and thereby, the determination of the behavior and fate of the compounds in the atmospheric environment was made possible.

ACKNOWLEDGMENT

We express our deep thanks to Ms. Hiroko TATEMATSU and Fumiko MATSUZAWA for their devoted assistances for this work.

REFERENCES

- 1) Shah J. J., Singh H. B. : Distribution of volatile organic chemicals in outdoor and indoor air. *Environ. Sci. Technol.*, **22**, 1381, 1988.
- 2) Bozzelli J. W., Kezbekus B. B. : A study of some aromatic and halocarbon vapors in the ambient atmosphere of New Jersey. *J. Environ. Sci. Health.*, **17**, 693, 1982.
- 3) Lahl U., Cetinkaya M., Duszelin J. V., Stachel B., Thiemann W. : Health risk from volatile halogenated hydrocarbons. *Sci. Total. Environ.*, **20**, 171, 1981.
- 4) Duszelin J. V., Tiemann W. : Volatile chlorinated hydrocarbons in a coastal urban atmosphere. *Sci. Total. Environ.*, **41**, 187, 1985.
- 5) Krischmer P., Ballschmitter K. : Baseline studies of the global pollution VIII ; The complex pattern of C₁-C₄ organohalogenes in continental and marine background air. *intern. J. Environ. Anal. Chem.*, **14**, 275, 1983.
- 6) Rasmussen P., Kahlil M. A. : Latitudinal distribution of trace gases in and above the boundary layer. *Chemo. Sphere.*, **11**, 221, 1982.
- 7) Singh H. B., Salas L. J., Stiles R. E. : Distribution of selected gaseous organic mutagens and suspected carcinogens in ambient air. *Environ. Sci. Technol.*, **16**, 872, 1982.
- 8) Kawamura K., Kaplan I. R. : Compositional change of organic matter in rainwater during precipitation events. *Atmos. Environ.*, **20**, 527, 1986.
- 9) Fujita M., Jung W. T., Tatematsu H., Sohn D. H., Maeda T. : Automated analysis of volatile halogenated hydrocarbons in rainwater and ambient air by purge trap/capillary GC. *High Resol. Chromatogr.*, **14**, 83, 1990.
- 10) Fujita M., Jung W. T. : Optimal conditions of purge trap/on column cryofocusing method with GC for determination of VHHs in aqueous samples. *Eisei Kagaku*, submitted.
- 11) Japanese environmental monitoring chemical association : Analytical methods of environmental monitoring with commentary vol I. ed. by JEMCA, Maruzen Press, Japan, 1985, pp.209.
- 12) Iida Y., Daishima S., Shibata A. : Levels of volatile organochlorine compounds in environment. Proc. 30th Ann. Meet. Jpn. Soc. Air Pollut. **227**, 1989, (Abstr).
- 13) Czuczwa J., Leuenberger C., Giger W. : Seasonal and temporal changes of organic compounds in rain and snow. *Atmos. Environ.*, **22**, 907, 1988.