

Determination of atmospheric concentrations of halocarbons in Beijing area

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Abstract— Gas chromatography with ambient temperature injection and frozen-trapped techniques was used to determine the atmospheric concentrations of halocarbons over Beijing. Halogenated compounds such as CFC-11, CFC-12, CHCl_3 , CCl_4 , CH_2Cl_2 , $\text{CHCl}=\text{CCl}_2$, and $\text{CCl}_2=\text{CCl}_2$ were measured and their concentrations are 109 ± 8 , 234 ± 13 , 47 ± 22 , 97 ± 24 , 88 ± 29 , 11 ± 1 and 17 ± 3 (pptv), respectively.

Keywords: GC-ECD; atmospheric halocarbons; Beijing.

INTRODUCTION

It is well known that trace gases such as chlorofluorocarbons (CFCs), carbon dioxide have greatly increased in the past decades and that anthropogenic sources are responsible for the increase. Chlorofluorocarbons are important compounds not only causing the stratospheric ozone depletion but also as greenhouse gases increasing the earth surface temperature. Organochlorine compounds play the same role as CFCs in the atmosphere. In addition, they have poisonous effects on human being and plants (Pellizzari, 1976; Bruner, 1978; Grimmer, 1986; Frank, 1988). Ozone depletion may lead to the increase of UV-B radiation reaching the ground. It has been predicted that for 1% ozone reduction UV-B radiation will increase 2% (Gerstle, 1981). Although the Montreal Protocol has made limitations on CFCs production and consumption, its potential effects on environment still exist. Model calculations indicate that ozone depletion will be 7–10% at 50° N and about 3–8% at 50° S by 2060s if assumed that currently observed trends in CO_2 , CH_4 , N_2O , CCl_4 and CH_2Cl_2 ,

will continue and that future emissions of the Montreal products (CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, and the halons 1211 and 1301) will remain fix at the production levels estimated for 1985 (WMO, 1990). Another calculation shows that greenhouse forcing of CFCs will increase from 0.04 to 0.07 °C by 2020s if the emission fluxes keep as present rates (Ramanathan, 1987). Therefore, CFCs damage effects on human and ecosystems is an important concern of the public and need further study. Analysis of CFCs atmospheric concentrations is the main topic in this paper.

Analytical techniques have been widely developed since Lovelock *et al.* first presented GC-ECD method to determine the concentrations of CFC-11 and CFC-12 (Lovelock, 1973; 1974). At present, three techniques are used: GC-ECD, GC-MS, and IR (Wang, 1990). In China, Wang and Tang (1991) used GC-ECD with a gas-liquid and a gas-solid column to determine the concentrations of halocarbons over Beijing. In this paper, we made an improvement on the previous analytical technique and measured some halocarbons across Beijing.

EXPERIMENTAL

Instruments and reagents

GC-7A with a constant-current-type electron capture detector was used. A gas-solid column (2m×3 mm i. d. stainless-steel packed with Carbo-pack C-HT, 80–100 mesh) was chosen (Vidal-Madjar, 1978; 1981). CFC-12 standard gas (53ppm) was used to prepare CFC-12 calibration gas in concentrations of parts per trillion by a three-step static-dilution method. Other halocarbon standard gases such as CFC-11, CHCl₃, CCl₄, CH₂Cl₂, CHCl=CCl₂ and CCl₂=CCl₂ were not available, so we used liquid calibration solutions (Ballschmitter, 1986; Frank, 1988). By using liquid volumetric dilution with isooctane as diluent the calibration curves were obtained (Ballschmitter, 1986).

Analytical conditions

High-purity nitrogen is used as carrier gas with a flow-rate of 30 ml/min. The column temperature was kept constant at 50 °C and the detector temperature was at 270 °C. 1.0 nA was chosen as reference current. More detailed descriptions of each analytical condition can be found elsewhere (Wang, 1993).

Samples

A stainless steel canister with "summa" polished surface was used to collect air samples. This surface was inert and it has been proved that the concentrations of compounds stored in the canister did not change after a few years (Rasmussen, 1980). Before sampling, the canister was evacuated and washed with high-purity nitrogen three times and kept vacuum. On sampling, ambient air was pumped into the canister until the interior pressure up to 13 psi and then the sample was taken back to laboratory for analysis.

Cold trap for CFC-12 analysis

The GC-ECD method for analyzing atmospheric halocarbons by directly injecting air into column was performed by several researchers (Makide, 1981; 1983; Wang, 1991) and was proved to be prompt and effective. But O_2 can often disturb CFC-12 detection. Two approaches are keys for solving the problem. One is to use temperature-programming from below $0^\circ C$ to higher level and the other is cryogenical technique. Because the GC-7A is not equipped with temperature programming, here we employed a cold trap for sample preconcentration (Heidt, 1975; Rasmussen, 1977). Fig. 1 shows the structure of analytical system. First, 100 ml gas sample was slowly injected into a stainless steel tube (immersed in a solution of liquid nitrogen and alcohol at a temperature of $-90^\circ C$). And then after two minutes cold trap, the tube was taken out and immersed into boiling water. Finally, the injection valve was opened and the analysis started. In order to make sure that CFC-12 and other halogenated compounds are fully trapped, the experiments on trap efficiency were made (Table 1). It can be seen that halocarbons concerned were all trapped at over ninety percent. But CFC-12 trap efficiency is lower, its efficiency coefficient was used for correction in concentration calculation.

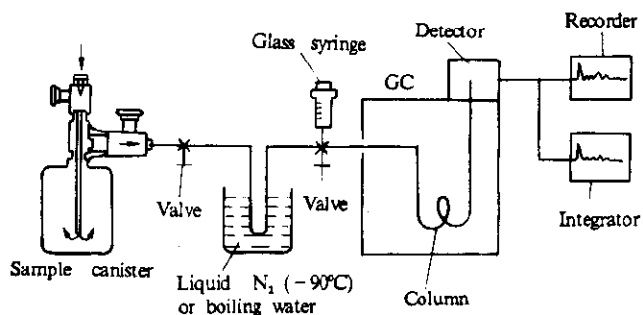


Fig. 1 Diagram of analytical system

Table 1 Trap efficiency of halocarbons at $-90^\circ C$

CFC-12	CFC-11	$CHCl_3$	CH_2Cl_2	CCl_4	$CHCl=CCl_2$	$CCl_2=CCl_2$
0.90	0.98	0.97	0.96	1.00	0.94	0.98

RESULTS AND DISCUSSION

Atmospheric samples were collected in the suburbs of Beijing including Xiangshan Mountain, Plant Garden, Lishui Bridge, the Research Academy of Chinese Environmental Sciences (RACES), Huagong Road, and Nanyuan Airport. Fig. 2 shows a typical GC-ECD chromatogram of an atmospheric sample. It can be seen that in direct injection peak of all compounds are fully separated except for oxygen and CFC-12. CFC-12 is undetectable (Fig. 2a). However, cryogenical technique showed its advantages (Fig. 2b). In Fig. 2b, there appears unknown peak *A* and peak *B*. Peak *A* may be assigned to CH_2Cl_2 or CFC-113 while peak *B* is possibly $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ or CFC-114, which need further judgment.

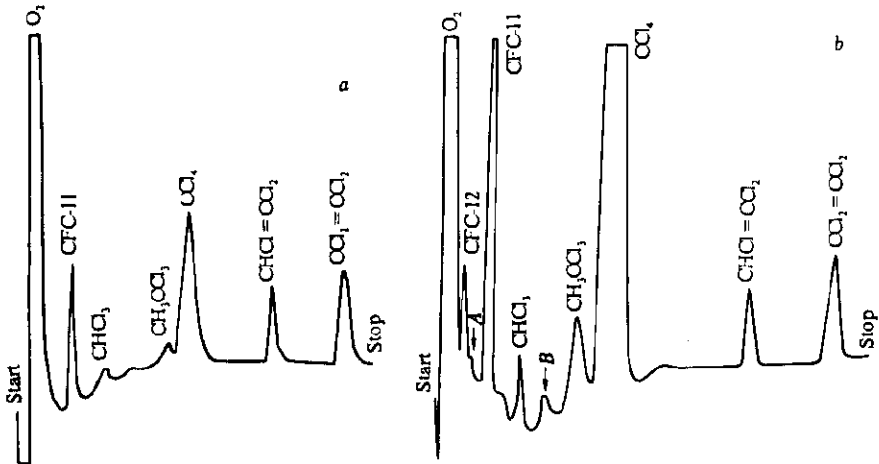


Fig. 2 GC-ECD chromatogram of an atmospheric sample in Beijing area
Column temperature $50\text{ }^{\circ}\text{C}$; carrier gas N_2 30 ml/min; detector temperature $270\text{ }^{\circ}\text{C}$;
reference current 1.0 nA; attenuation $2^x=16$ (a. 10 ml sample; b. 100 ml sample)

Linear ranges of each compound in this compounds are shown in Fig. 3. The upper limits for higher sensitive compounds such as CCl_4 , CFC-11 and C_2Cl_4 are about 1.0 ng; for C_2HCl_3 and CH_3CCl_3 , the limits are 2.5ng; and for the lower sensitive compounds CFC-12 and CHCl_3 , the limits are 4.0 ng. Detection limits of each compound for 10 ml sample are 0.9 ppt for CFC-11, 10 ppt for CFC-12, 8 ppt for CHCl_3 , 4 ppt for CH_3CCl_3 , 0.8 ppt for CCl_4 , 4 ppt for C_2HCl_3 , and 3 ppt for C_2Cl_4 .

All sample results are listed in Table 2. The observed concentrations were slightly affected by the sites and meteorological conditions. In Huangong Road, concentrations of organochlorine compounds are higher than that of any other places. This may be

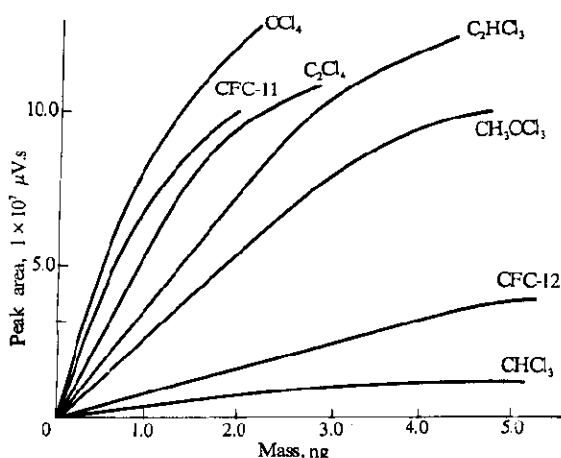


Fig. 3 Linear ranges of halocarbons on GC-ECD

attributed to the chemical plant activities nearby. The average concentrations are close to the previous data but still lower than that of reported data elsewhere. The discrepancy may be due to several factors. Concentration of CFC-12 standard gas (53 ppm) was not precisely measured. It can be changed owing to the wall absorption and heterogeneously chemical dissociation (Harrison, 1986). Errors in static-dilution processes may also be a contributor. And sample preconcentration, if not complete, is another cause.

Class and Ballschmiter (1986) proposed that due to atmospheric diffusion, lower emission, and long lifetime, concentration of CCl_4 in the northern and southern hemisphere are nearly in equivalence. Its annual increase rate can be precisely determined. Therefore, CCl_4 is usually taken as a stable reference in the troposphere. Define $R_r(A)$ as following:

$$R_r(A) = [A]/[\text{CCl}_4], \quad (\text{pptv}/\text{pptv})$$

$[A]$ and $[\text{CCl}_4]$ denotes concentration of organochlorine compound and CCl_4 , respectively. $R_r(A)$ represents relative concentration of compound A which eliminates system errors induced by sampling, injection volume, and sample transport. Table 3 shows $R_r(A)$ of organochlorine compounds in Beijing and other places. The results show that $R_r(A)$ of each organochlorine compound in Beijing is close to that in Northern Hemisphere except for CHCl_3 . This indicates that although observed concentrations of each halocarbon in Beijing are lower than that in other places,

Table 2 Concentrations of halocarbons in Beijing (pptv)

Sites	CFC-12	CFC-11	CHCl ₃	CH ₂ Cl ₂	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄
Xiangshan Mountain	225 ± 18	107 ± 6	75 ± 4	120 ± 7	107 ± 4	12 ± 1	20 ± 1
Plant Garden	244 ± 17	109 ± 11	38 ± 2	104 ± 10	100 ± 9	12 ± 1	20 ± 1
Lishui Bridge	224 ± 23	112 ± 8	29 ± 1	109 ± 4	107 ± 9	10 ± 1	13 ± 1
RACES	212 ± 4	98 ± 4	26 ± 1	96 ± 2	89 ± 6	10 ± 1	14 ± 1
Huagong Road	214 ± 14	106 ± 1	142 ± 6	218 ± 10	403 ± 2	23 ± 1	25 ± 1
Nanyuan Airport	163 ± 3	122 ± 12	66 ± 5	56 ± 1	37 ± 4	12 ± 1	19 ± 1
$\bar{X} + S^*$	224 ± 13	109 ± 8	47 ± 22	97 ± 24	88 ± 29	11 ± 1	17 ± 3
Wang and Tang, 1993	275 ± 12	127 ± 24	49 ± 32	80 ± 27	60 ± 18	8 ± 2	30 ± 17
WMO/UNEP	484	280		158	146		
Frank, 1986	374	—	59	217	81	56	93

Notes: pptv: parts per trillion (10^{-12}) by volume (ml)

RACES: the Research Academy of Chinese Environmental Sciences

\bar{X} : Average concentration

S: Standard deviation

*: The point of Huagong Road is not included in calculation for CHCl₃, CH₂Cl₂, CCl₄, CHCl=CCl₂, CCl₂=CCl₂.

their relative concentrations are in approximate. As for CHCl₃, its higher $R_p(A)$ reflects the local emission and its short lifetime.

In conclusion, GC-ECD is an effective means in analyzing atmospheric halocarbons. The determined concentrations of halocarbons in Beijing are lower than that of global concentrations, however, their concentrations relative to CCl₄ are close.

Table 3 Comparison of halocarbons' $R_p(A)$

Sites	CHCl ₃	CH ₂ Cl ₂	C ₂ HCl ₃	C ₂ Cl ₄
Beijing	0.53	1.10	0.13	0.19
NH (Class, 1986)	0.2	1.1	0.15	0.2
SH (Class, 1986)	0.1	1.01	0.06	0.15
τ_p (Class, 1986)	100d	7y	3-7d	70d

∴ NH—Northern hemisphere; SH—Southern hemisphere

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REFERENCES

- Ballschmiter, K., *Fresenius Z. Anal. Chem.*, 1986, 323: 334
- Bruner, F., *J. Chromatogr.*, 1978, 167: 399
- Class, Th. and K. Ballschmiter, *Fresenius, Z. Anal. Chem.*, 1986, 325: 1
- Class, Th., *Chemosphere*, 1986, 15: 413
- Frank, H. and W. Frank, *J. High Resolution Chromatogr. & Chromatogr. Comm.*, 1988, 11: 51
- Gerstle, S. A. W., *Nature*, 1981, 294:352
- Grimmer, G. and W. Schmidt, *Angew. Chem.*, 1986, 98: 807
- Harrison, R. M. and R. Perry, *Handbook of air pollution analysis* (2nd. edition), London: Chapman and Hall Press, 1986: 453
- Heidt, L. E., *Geophys. Res. Lett.*, 1975, 2: 445
- Lovelock, J. E., *Nature*, 1973, 241: 194
- Lovelock, J. E., *Nature*, 1974, 252: 292
- Makide, Y., *Nippon Kagaku Kaishi*, 1981, 133
- Makide, Y., *J. Trace Microprobe Tech.*, 1983, 1: 265
- Pellizzari, E. D., *Anal. Chem.*, 1976, 48: 803
- Ramanathan, V., *Rev. Geophys.*, 1987, 25: 1441
- Rasmussen, R. A., *J. Air Pollut. Contr. Assoc.*, 1977, 27: 579
- Rasmussen, R. A., *J. Geophys. Res.*, 1980, 85: 7350
- Vidal-Madjar, C., *J. Chromatogr. Sci.*, 1978, 16: 190
- Vidal-Madjar, C., *J. Chromatogr.*, 1981, 203: 247
- Wang Shaobin, Graduate thesis. Peking University, 1990
- Wang Shaobin and Tang Xiaoyan, *Acta Sci. Circum.*, 1993 (in press)
- WMO, *Scientific Assessment of Stratospheric Ozone: Vol. 1*, World Meteorological Organization, Geneva, 1990
- WMO/UNEP, *Climate change, The IPCC scientific assessment*, Cambridge: Cambridge University Press, 1990

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