

Monitoring of Atmospheric Concentration of Chlorodifluoromethane (HCFC-22) by Automated GC / O₂-doped-ECD

Sakae Toyoda, Takeshi Tominaga, and Yoshihiro Makide
Radioisotope Center, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113

(Received September 30, 1996)

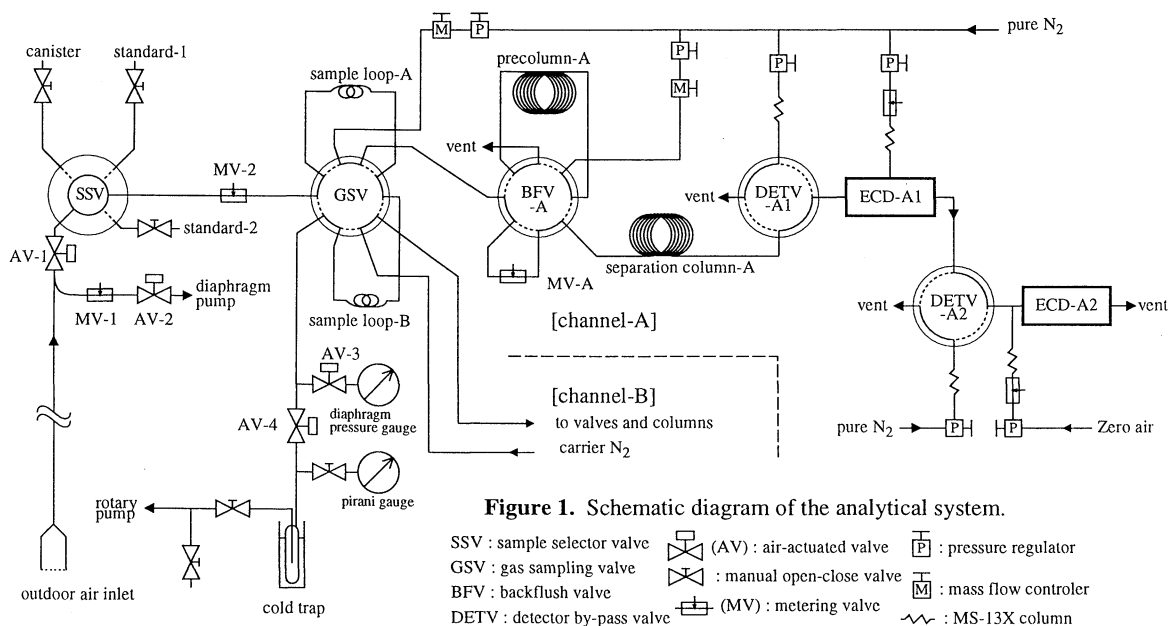
An automated gas chromatograph/electron capture detector (GC/ECD) system was developed to monitor the concentration of HCFC-22 in the urban atmosphere at intervals of 90 min. By using two columns in series we avoided the use of cryogen and dryer for preconcentration or sample drying. Oxygen was doped into the N₂ carrier gas to sensitize the ECD. Serial measurements of atmospheric HCFC-22 concentration were attempted in the central area of Tokyo.

The production and consumption of ozone-depleting chlorofluorocarbons (CFCs) were phased out by the end of 1995 in developed countries in accordance with the international regulation of their emissions based on the 1987 Montreal Protocol and the subsequent revisions. On the other hand, their substitutes have been developed and are now being widely used. Chlorodifluoromethane (CHClF₂: HCFC-22) is one of typical substitutes, hydrochlorofluorocarbons (HCFCs), which can be decomposed by OH radicals in the troposphere. It has been used for a long time as a refrigerant and its production has grown in recent years; the production and consumption of HCFC-22 and other HCFCs have also been regulated since 1996 because they still have potential of depleting ozone when they enter the stratosphere and release chlorine atoms by photolysis. Nevertheless, their distribution and behavior in the troposphere are not well understood and frequent monitoring of their concentration is needed. Until recently, there have been only several researchers including us who reported the measurement

of atmospheric concentration of HCFC-22 by GC/ECD¹⁻³ or GC/MS.^{1,4,5} However, they need cryogen or cooling devices for preconcentration of the compound from large volume of air samples because of its extremely low concentration in the pptv (pptv=10⁻¹² v/v) range and low sensitivity to detectors. In addition, they use chemical or physical dryers for water removal in large volume of samples introduced, which may cause contamination and/or adsorption of the target compound.

In this paper, we report an automatic analytical system for HCFC-22 measurement which can be operated at unattended monitoring station. It requires sample amount of only below 20 ml STP and hence there is no need to use cryogen for sample preconcentration or any dryer while the detection limit is a little higher than other methods.

The analytical system consists of an outdoor air inlet line, a vacuum line, valves, and two gas chromatographs (Shimadzu GC-14A and GC-17A) equipped with three constant current type ECDs (Figure 1). All the analytical lines are made of stainless steel except switching valves and air-actuated open-close valves. Since this system was developed as annex to the system designed for measurement of several CFCs and major chlorinated hydrocarbons, the details of the system will be described elsewhere and the procedures are mentioned briefly here. The system consists of dual analytical lines each of which contains a sample loop, a precolumn, and a main separation column. One line is mainly used for the separation of CFCs (channel-A), and the other for heavy halocarbons (channel-B).



HCFC-22 was separated in channel-A and detected by ECD-A2 which was placed downstream the ECD-A1.

Prior to the measurements, the diaphragm pump of the outdoor air inlet line is turned on and driven continuously. Sample to be analyzed is selected by switching SSV to outdoor air, sample in a canister, or one of standards, and the vacuum line including the sample loop is evacuated. Then the sample air is introduced into the vacuum line by opening AV-1 and closing AV-2 (for outdoor air sampling), or by opening a Nupro valve manually (for a canister sample or standard). After inner pressure is equilibrated and measured, GSV is switched for injection of the sample in the loop-A into the precolumn-A (Silicone OV-101, 10% on Chromosorb W HP). The temperature of precolumn-A is programed from 50 °C to 90 °C and the lighter halocarbons including HCFC-22 are sent to the main separation column-A (Porapak Q). BFV-A is then reversed in order to vent heavier compounds retained in the precolumn. Among the compounds separated in the main column by temperature programing from 70 °C to 160 °C, CFCs are measured by ECD-A1, while HCFC-22 is hardly sensitive to the normally operated ECD with typical carrier gas such as N₂ or Ar/CH₄. Hence we improved its sensitivity with ECD by addition of oxygen as a dopant of the carrier gas.^{2,3,6} After passing through ECD-A1, HCFC-22 was detected by ECD-A2, immediately before which O₂ was doped in the form of zero air (research grade, Takachiho Chemical Industrial Co., Ltd.) to the N₂ carrier gas (99.9995% minimum, Nihon Sanso Co., Ltd.).

A typical O₂-doped ECD gas chromatogram of the HCFC-22 as well as CH₃Cl and CFC-12 (CCl₂F₂) is shown in Figure 2.

Sensitivity of the detector and signal-to-noise (S/N) ratio were investigated by changing the amount of O₂ added and the detector temperature. It was found that the detector response to HCFC-22 increased with O₂ concentration up to 1% and detector temperature from 240 to 320 °C, while S/N ratio decreased. We determined the best conditions among them.

It was found that the connection of a normal ECD and an O₂-doped ECD in series makes it possible to measure major CFCs and HCFC-22, respectively, and simultaneously without

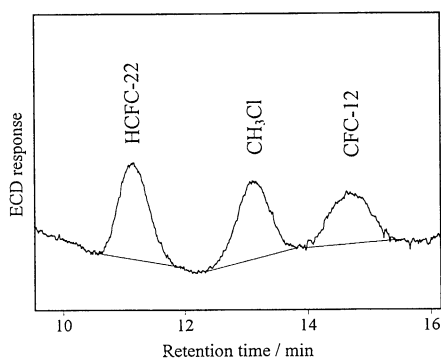


Figure 2. Typical O₂-doped ECD gas chromatogram of tropospheric urban air. About 18 ml STP sample was introduced from outside the laboratory, the University of Tokyo, on April 1, 1996. HCFC-22 concentration is 1260 pptv. About 0.7% O₂ relative to N₂ was added to the carrier gas. GC columns: Silicone OV-101, 3 m long, 1/8 inch o.d. and Porapak Q, 3 m long, 1/8 inch o.d. in series; column temp.: 1 °C/min from 50 °C to 90 °C for Silicone col., 3 °C/min from 70 °C to 160 °C for Porapak col.; det. temp.: 300 °C; N₂ carrier gas flow rate: 40 ml/min.

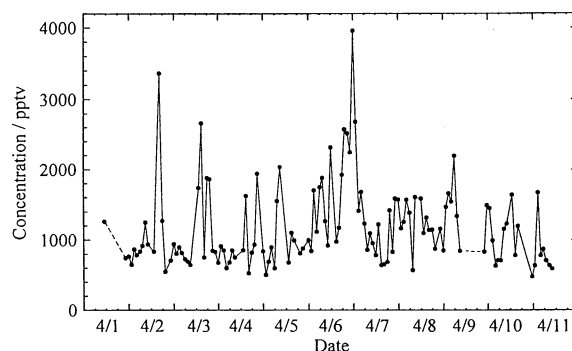


Figure 3. Monitoring of HCFC-22 in the air outside the laboratory for a period from April 1 to 11, 1996.

interfering each other as mentioned by Sturrock et al.³

Replicate analyses of air in canisters showed the average precision to be better than 10%. The linearity of detector response was confirmed by changing sample size. Peak area of HCFC-22 was calibrated by an urban atmospheric sample whose HCFC-22 concentration had been determined by our original standard prepared by three-step dilution.^{2,7} The detection limit (S/N=2) was 0.1 pmol, which corresponds to 120 pptv of HCFC-22 at 18 ml STP sample air and is close to the background atmospheric concentrations in the troposphere.

An example of monitoring of HCFC-22 in the air outside the laboratory is shown in Figure 3. Measurements were carried out once every 90 minutes including analyses of other halocarbons on the both channels and conditioning of columns, though HCFC-22 itself can be measured in much shorter time.

The variation of HCFC-22 concentration shown in Figure 3 was generally related with those of CFCs (CFC-11: CCl₃F, CFC-12, and CFC-113: CCl₂FCClF₂) and CH₃CCl₃ being affected by meteorological conditions, but it had a wider range of variation in concentration. This may suggest that large amount of HCFC-22 has recently come to be used in industry in place of CFCs and regulated chlorinated hydrocarbons, and its release takes place often incidentally.

It was found that our analytical system is useful to monitor the emissions of HCFC-22 in the urban area. Since CH₃Cl can also be detected with this procedure, it will provide us with information regarding the behavior of CH₃Cl in the urban area.

Although the detection limit of HCFC-22 is not low enough for background air monitoring under the current conditions, it can be improved by optimizing the analytical conditions for HCFC-22 measurement alone. Then the improved system will be possibly used even at unattended remote monitoring stations.

References and Notes

- 1 R. A. Rasmussen, M. A. K. Khalil, S. A. Penkett, and N. J. D. Prosser, *Geophys. Res. Lett.*, **7**, 809 (1980).
- 2 L. Chen, Y. Makide, and T. Tominaga, *Chem. Lett.*, **1994**, 2423.
- 3 G. A. Sturrock, P. G. Simmonds, and G. Nickless, *J. Chromatogr.*, **707**, 255 (1995).
- 4 S. A. Montzka, R. C. Myers, J. H. Butler, and J. W. Elkins, *Geophys. Res. Lett.*, **20**, 703 (1993).
- 5 P. G. Simmonds, S. O'Doherty, G. Nickless, G. A. Sturrock, R. Swaby, P. Knight, J. Ricketts, G. Woffendin, and R. Smith, *Anal. Chem.*, **67**, 717 (1995).
- 6 E. P. Grimsrud and D. A. Miller, *Anal. Chem.*, **50**, 1141 (1978).
- 7 L. Chen, Y. Makide, and T. Tominaga, *Chem. Lett.*, **1994**, 571.