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Determination of 1,2-dichlorotetrafluoroethane (CFC-114) Concentration in the Atmosphere

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Atmospheric concentration of 1,2-dichlorotetrafluoroethane (CFC-114) was determined accurately by the complete separation of its isomer 1,1-dichlorotetrafluoroethane (CFC-114a). The trends of atmospheric CFC-114 concentrations since 1986 were observed in Hokkaido, Japan (40-45 °N), and Syowa Station, Antarctica (69 °S). The atmospheric CFC-114 concentration in the mid-latitude Northern Hemisphere increased by 0.75 pptv / year over the period 1986-1990, and 0.6 pptv / year over 1990-1993. Vertical distribution of CFC-114 was also obtained up to mid-stratosphere.

Increasing abundances of man-made halocarbons in the atmosphere have been the cause of the extensive ozone depletion. Five kinds of chlorofluorocarbons (CFCs) and three kinds of halons have been subjected to the international regulation of emissions according to the Montreal Protocol. Among them, CFC-114 ($CClF_2CClF_2$) which has been used for blowing agent of polyolefin foams, aerosols sprays and long-lived refrigerants but emitted in smaller amount than other CFCs, has a high ozone depletion potential (ODP), high global warming potential (GWP) and extremely long lifetime (~220 years) in the atmosphere.1) Although the CFC-114 concentration in the Northern Hemisphere in 1975 was reported as about 12 pptv (pptv=10^{-12} v/v),2) it was far beyond the possible concentration estimated from the world CFC-114 production up to that time. Thus, reliable concentration of CFC-114 in the atmosphere has not been reported because of its very low concentration and interference by its isomer CFC-114a (CCl_2FCF_3). We have established an accurate measurement system for CFC-114 and observed the trend of its atmospheric concentration and vertical distribution.

Atmospheric sample canisters were made by argon arc welding of a 12-L or 2-L stainless steel beaker and equipped with a stainless steel bellows sealed valve (Nupro SS-4H). Tropospheric air samples were collected in Hokkaido, Japan (40-45 °N) and Syowa Station, Antarctica (69 °S): tropospheric air was simply introduced into the evacuated canister up to the ambient pressure.3,4) Stratospheric samples were collected by liquid helium cryogenic sampling over Sanriku, Japan (37-39 °N, 140-142 °E): this balloon-borne sampling system was developed and launched by the Institute of Space and Astronautical Science, Japan.5)

The analytical system consists of a stainless steel vacuum line and a gas chromatograph equipped with a constant current type electron capture detector (Shimadzu GC-14A). A sample aliquot about 100 ml STP (standard temperature and pressure) from the canisters was introduced into a U-shaped preconcentration trap (SS tube packed with Flusin GH, glass beads) at liquid nitrogen temperature; CFC-114 was separated by Carbopack B / 5% Fluorcol column (60 / 80 mesh, 10 inch long, 1/8 inch o.d. SP Alloy) at 40 °C and determined with the electron capture detector (ECD, temp: 250 °C). Research grade nitrogen (99.9995% minimum, Nihon Sanso Co., Ltd.) was used as carrier gas (flow rate: 30 ml / min) after further purification with columns of molecular sieve 5A, active charcoal, and molecular sieve 13X connected in series.

The calibration standard for each compound was prepared by three-step static dilution using different vacuum lines according to the concentration level. Zero air or research grade nitrogen was further purified similarly as the carrier gas nitrogen before the usage for dilution. At each step of dilution, the gaseous mixture in a glass flask was mixed actively by warming and cooling the flask several times to cause convection within. The final primary standards for calibration were prepared in concentrations close to the background atmospheric samples. Several ambient air samples in large containers were calibrated and used as the secondary standards in routine measurements.

The samples stored in our laboratory were analyzed after the method was established. The composition of the atmospheric samples remained unchanged even after storage for over several years in the all-stainless steel sample canisters. About 100 ml of tropospheric sample was used in an analytical run, and the coefficient of variation for repeated measurements of these samples was about 5% for CFC-114. Figure 1 shows a typical ECD gas chromatogram of tropospheric air sample.

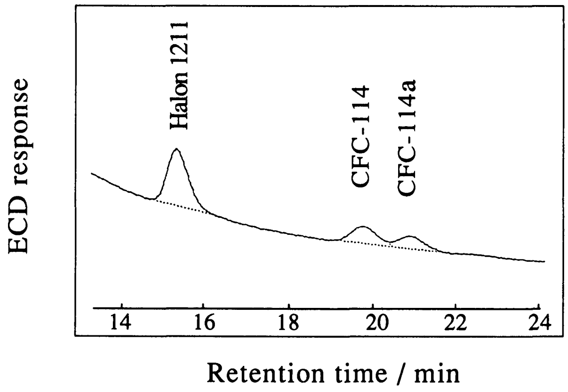

Fig. 1. Typical ECD gas chromatogram of a tropospheric air sample. Sample: 105.4 ml STP, collected in Hokkaido on 3 Aug., 1992; GC column: 60 / 80 mesh Carbopack B/ 5% Fluorcol, 10' long x 1/8' o. d. SP Alloy; col. temp: 40 °C; det. temp: 250 °C; flow rate: 30 ml / min N_2.

Most serious problem in the determination of CFC-114 is the interference by its isomer, CFC-114a. Commercially available CFC-114 contains CFC-114a as a by-product: their physical and chemical properties are extremely similar (e.g., the boiling point for CFC-114, 3.8 °C; CFC-114a, 3.6 °C). It is not easy to separate them by gas chromatography. Furthermore, ECD response of CFC-114a was 15.5 times as high as that of CFC-114 (Fig.2). Only 5% of CFC-114a in the atmospheric CFC-114 sample showed nearly equal peak area to that of CFC-114. On the other hand, the CFC-114 gas in a lecture bottle (95% minimum, Tokyo Kasei Kogyo Co., Ltd.) used for preparing the standard was found to contain 2.4% CFC-114a by our calibration: the content of ECD sensitive CFC-114a in the CFC-114 standard was obtained by using pptv concentration level standards of CFC-114a (97% minimum, PCR Inc., U.S.A.). Unless resolved, CFC-114a and CFC-114 produce a composite peak which appear like a single peak in the gas chromatogram. An atmospheric sample

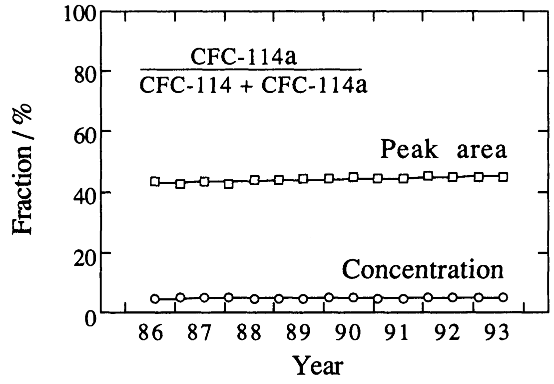

Fig. 2. Fraction of CFC-114a in CFC-114 in the atmosphere

containing 15 pptv CFC-114 (including 5% CFC-114a), for example, may appear as containing 19.2 pptv CFC-114 by using the standard which contains 2.4% CFC-114a, or 25.9 pptv by using pure CFC-114 standard. These overestimates due to interference of CFC-114a depend on the fraction of CFC-114a in the standard used.

For determining CFC-114 in extremely low concentrations, stratospheric samples were introduced in amounts from 100 to 500 ml STP according to their altitude. The response of the ECD shows very good linearity over the range from 3.0 x 10^{-14} to 4.2 x 10^{-13} mole (or 50 to 700 ml STP sample size). Furthermore, this result also proves that the sample size does not affect the efficiency in cold trapping.

The vertical distribution of CFC-114 shown in Fig.3 indicates that CFC-114 is one of the most stable compounds in the atmosphere: not only in the troposphere like CFC-11, CFC-12 and CFC-113, but also in the stratosphere where the photodecomposition rate of CFC-114 is found to be much smaller than other CFCs.

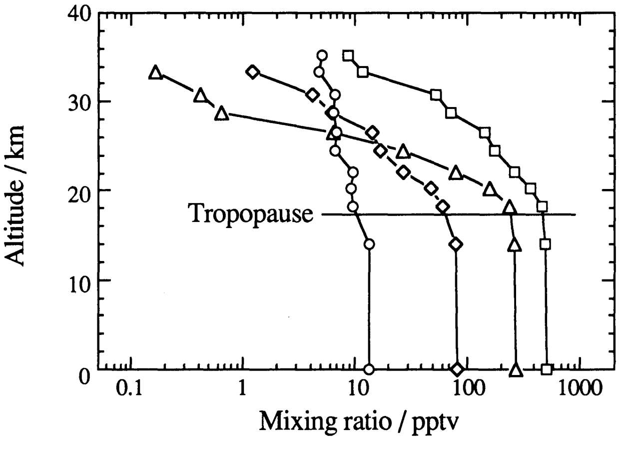

Fig. 3. Vertical distributions of CFC-12, CFC-11, CFC-113 and CFC-114 over Sanriku on 29 Aug., 1991.
-□-: CFC-12, -△-: CFC-11, -◇-: CFC-113, -○-: CFC-114.

The current tropospheric concentrations of CFC-114 were found to be about 15 pptv in the mid-latitude Northern Hemisphere and about 14 pptv in the Southern Hemisphere (Fig.4). The CFC-114 concentration in the Southern Hemisphere has been 10 to 15 percent lower than that in the Northern Hemisphere. Global CFC-114 concentration has increased by 0.75 ± 0.05 pptv per year (6% per year) over the period 1986-1990, and 0.60 ± 0.05 pptv per year (4% per year) over the period 1990-1993. Based on these data, we can estimate that the annual emission of CFC-114 (including CFC-114a) into the atmosphere was about 22 metric kilotons over the period 1985-1989. Recently, it has been reported that CFC-114 emission was about 16 metric kilotons per year according to the statistics which covered 85% of world production during the same period based on the survey of CMA FPP (the Fluorocarbon Program Panel of the Chemical Manufacturers Association).$^{6)}$ The global emission based on this estimates is about 15% smaller than our estimates from the atmospheric concentration. Although the growth rate of CFC-114 in the atmosphere was reported at a workshop as 6% per year by the OGIST (Oregon Graduate Institute for Science and Technology) flask sampling from 1979 to 1990, its absolute concentration was not mentioned.$^{7)}$

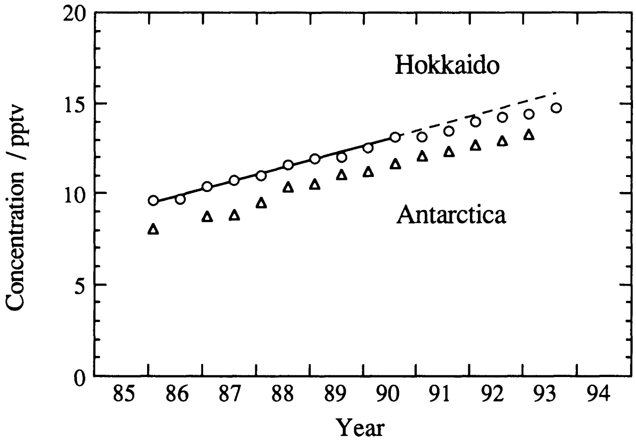

Fig. 4. Observed tropospheric concentrations of CFC-114 in the Northern and Southern Hemispheres. Solid line shows the least squares fitting of 1986-1990 data and dashed line shows its extrapolation.

Our result indicates that the trend in 1993 (4% per year) is lower than that in 1990 (6% per year). The growth rate of CFC-114 in the atmosphere starts slowing down possibly due to the international regulation of CFC productions and emissions. However, it will need a long time before the concentration begins to decrease: even after the phase out of all CFCs, CFC-114 will survive extremely long time in the atmosphere and remain affecting both the stratospheric ozone depletion and the global warming. Hence, accurate measurements of its concentration in the atmosphere will become more and more necessary and important.

References

1) Scientific Assessment of Ozone Depletion: 1991, *WMO Report No.25,* (1992) Chap. 8.
2) H. B. Singh, L. J. Salas, H. Shigeishi, and E. Scribner, *Science*, **203**, 899 (1979).
3) Y. Makide, Y. Kanai, and T. Tominaga, *Nippon Kagaku Kaishi,* **1981**, 133.
4) Y. Makide, A. Yokohada, and T. Tominaga, *J. Trace Microprobe Tech.,* **1**, 256 (1982/1983).
5) H. Honda, *Inst. Space Astron. Sci. Res. Note,* **433**, 1 (1990).
6) D. A. Fisher and P. M. Midgley, *Atmos. Environ.,* **27A**, 271 (1993).
7) Scientific Assessment of Ozone Depletion: 1991, *WMO Report No.25,* (1992) Chap. 1.

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