CHEMISTRY LETTERS, pp. 355-358, 1979. Published by the Chemical Society of Japan

GAS CHROMATOGRAPHIC ANALYSIS OF HALOGENATED HYDROCARBONS IN AIR OVER JAPAN

Yoshihiro MAKIDE, Takeshi TOMINAGA, and F. Sherwood ROWLAND*
Department of Chemistry, Faculty of Science, The University
of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
*Department of Chemistry, University of California, Irvine,
California 92717, U. S. A.

Preliminary measurements were conducted of atmospheric concentrations of CCl_2F_2, CCl_3F, CCl_2FCClF_2, CH_3CCl_3, CCl_4, $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ in remote and urban areas in Japan to determine accurate background levels as well as the profile of local pollution. Samples collected in all-metal canisters were analyzed with an extremely clean stainless steel high vacuum sampling and calibration system and an EC-GC.

Great concern has been expressed recently for the environmental impact of chlorofluorocarbons (CCl_2F_2, CCl_3F and CCl_2FCClF_2) released into the atmosphere following their extensive use as aerosol propellants, refrigerants and solvents. These compounds with extremely long tropospheric lifetimes diffuse into the mid-stratosphere, and are decomposed by solar u.v. radiation to release chlorine atoms which in turn participate in catalytic removal of stratospheric ozone.[1,2] In contrast, unsaturated chlorocarbons such as $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ (degreasing or cleaning solvents) are subject to photochemical or chemical decomposition in the troposphere, and suspected as a source of photochemical smog. Although methylchloroform CH_3CCl_3 has been classified as 'safe' solvent and its usage has been growing rapidly as a substitute for the labile molecules, the role of CH_3CCl_3 in the stratospheric ozone depletion is not clear yet. This is also considered as a key compound to understand the atmospheric behavior of other hydrogen-containing halocarbons ($CHClF_2$ etc.) which will decompose through similar reactions with OH radicals in the troposphere.[3-5] In view of the environmental aspects of such halogenated hydrocarbons, world-wide monitoring of their atmospheric concentrations is urgently needed to make accurate estimates of the possible ozone depletion. Since no accurate measurements of these compounds at ppt (10^{-12}) level have been undertaken in Asia, we have initiated a systematic survey of the atmospheric concentrations of CCl_2F_2, CCl_3F, CCl_2FCClF_2, CH_3CCl_3, CCl_4, $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ over Japan and the western Pacific.

In the present article are reported data of our preliminary measurements made to determine background atmospheric concentrations as well as to examine the profile of local pollution in Japan. Extreme care has been taken in the experiments so as to minimize any possible contamination during sampling and analysis, and thus to ensure very accurate measurements.

Analytical system and procedures. Atmospheric air samples were collected in stainless steel canisters equipped with stainless steel bellows valves, which had been evacuated to 10^{-6}mm Hg at 200°C. It has been confirmed that contamination or change of composition during storage of sample is unlikely. Calibration standard for each compound was carefully prepared from the pure compound by four-step static dilution method. Heating-cooling cycles and spinning of a flask were adopted to ensure complete mixing of gases in the flask. For the 3rd and 4th steps of dilution of the standard as well as introduction of the air samples into the analytical system, was usually employed an extremely clean high-vacuum sampling system all made of stainless steel and equipped with stainless steel bellows valves (free from any Teflon-containing valves or rubber gaskets). We have found that halogenated hydrocarbons tend to be adsorbed into the synthetic polymers during the handling of high concentration gases, and then they are desorbed very slowly causing contaminations. Brand new valves, regulators or flow controller were often contaminated by chlorinated solvents used for degreasing them. With our clean analytical system, the contamination level for each compound was bellow the detection limit of 0.5 ppt for CCl_2F_2, CCl_3F, CH_3CCl_3 and CCl_4, and of 1 ppt for CCl_2FCClF_2, $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$. An aliquot of the air sample was introduced into a sampling loop, while the pressure was measured with a precision metal diaphragm gauge, and then transferred into a short preconcentration column (Chromosorb 102 or Silicone OV-101, cooled to $-40\sim-30$°C) with an ultra-high purity helium flow. After the air passed through the preconcentration column, the helium flow was switched to ultra-high purity argon (carrier gas) so that the trapped components were eluted according to temperature programming. Further separation was attained with a main column (Silicone OV-101, kept isothermal) and, after addition of 5 % methane to the carrier gas argon, each component was determined with a constant current type EC detector (Hewlett Packard #5710A EC-GC).

Atmospheric samples. Sample No.1 was obtained in summer 1978 at Katsuura (on a cliff overlooking the Pacific Ocean), when a tropical depression to the south and a high pressure to the east of Japan brought an oceanic air to the land. Sample No.5 was collected on Tokyo Tower in downtown Tokyo, when photochemical smog was slightly observed under hazy sunshine. Samples No.2-4 were obtained in summer or winter on the mountains to the northwest or southwest of Tokyo.

Typical ECD chromatograms of an atmospheric sample are illustrated in Fig.1 (a) and (b). Table 1 summarizes the observed atmospheric concentrations of halogenated hydrocarbons in the samples No.1-5. The concentrations of such compounds in sample No.1 (Katsuura) were reasonably close to the northern hemisphere background concentrations measured in the continental North America,[6-8] after corrected for monthly increases, indicating the absence of local contamination. However, all the other samples collected inland showed higher concentrations as the result of local pollution due to human activities. The concentrations of CCl_2F_2, CCl_3F and CCl_2FCClF_2 in samples No.2-4 were 20-50% higher than the background concentrations ($3\sim9$-fold increased in Tokyo), in accordance with their long tropospheric residence times and recent increase in applications. In contrast, the atmospheric concentrations of CCl_4 were close to the background concentration at all locations except in Tokyo (with high local contamination level), reflecting

Table 1. Atmospheric concentrations of halogenated hydrocarbons in Japan (in ppt = 10^{-12} v/v)

Sample	Sampling Location*	Date	CCl_2F_2	CCl_3F	CCl_2F-$CClF_2$	CH_3-CCl_3	CCl_4	$CHCl$=CCl_2	CCl_2=CCl_2
No.1	Katsuura (Chiba-pref.)	July 22 1978	268	159	25	96	104	2	7
No.2	Mt. Fuji (Yamanashi-pref.)	July 8 1978	335	193	37	269	108	106	66
No.3	Kirizumi (Gunma-pref.)	Dec. 1 1977	316	207	41	599	93	573	163
No.4	Hakone (Shizuoka-pref.)	Dec. 9 1977	360	215	43	841	102	768	195
No.5	Tokyo Tower (Tokyo)	July 7 1978	962	372	234	10100	342	3950	719

* All located between latitudes 35°N and 37°N.

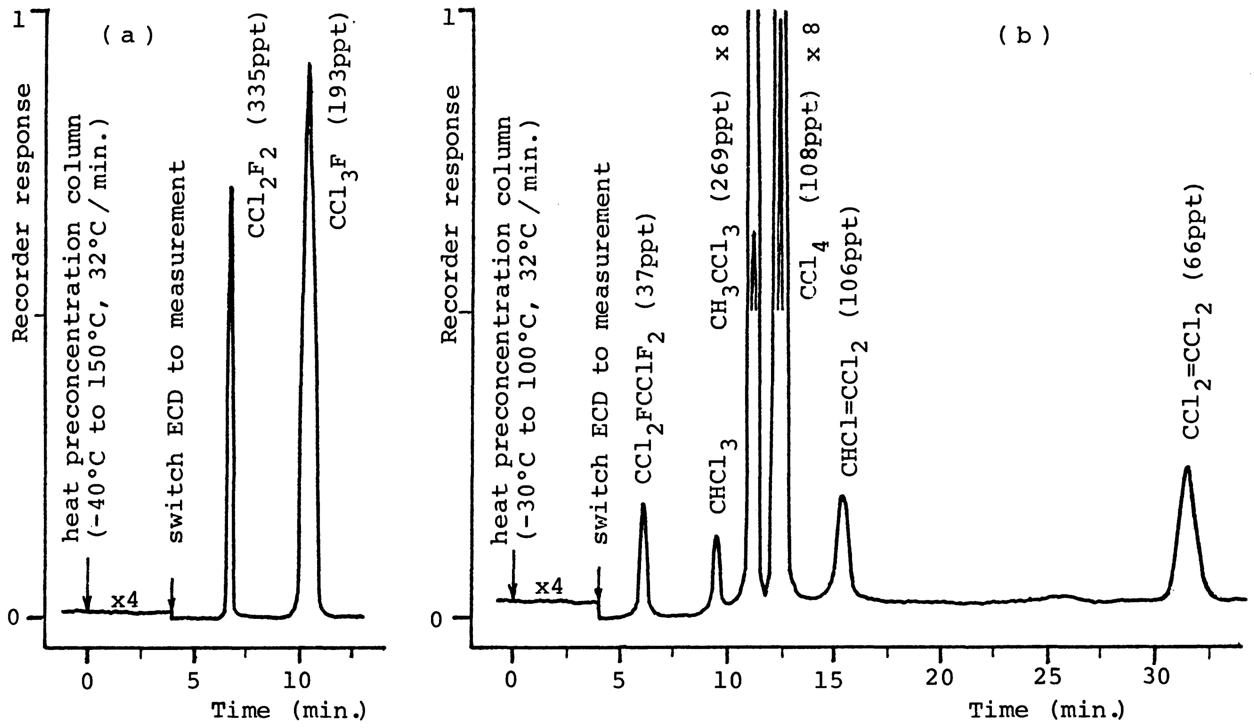

Fig. 1. Typical ECD chromatograms of an atmospheric air sample: Sample No.2 collected on the northern side (elevation 2270 m) of Mt. Fuji on July 8, 1978.

(a) Analysis of CCl_2F_2 and CCl_3F. Preconcentration column: Chromosorb 102 (80-100 mesh, 5.3 mm i.d., 30 cm long, -40°C to 150°C), analyzing column: Silicone OV-101 (10 wt % on Chromosorb W-HP, 80-100 mesh, 5.3 mm i.d., 450 cm long, 70°C), carrier gas: argon (60 ml/min.), sample size: 20 ml (STP).

(b) Analysis of CCl_2FCClF_2, CH_3CCl_3, CCl_4, $CHCl$=CCl_2 and CCl_2=CCl_2. Preconcentration column: Silicone OV-101 (10 wt % on Chromosorb W-HP, 80-100 mesh, 5.3 mm i.d., 45 cm long, -30°C to 100°C), the other conditions are the same as in (a).

that current emission of CCl_4 is small as compared with the total atmospheric burden of this compound. The atmospheric concentrations of $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ (with short tropospheric lifetimes) were greatly influenced by local pollution: for instance, the concentrations in Tokyo were 100~1000-fold higher than the background concentration, indicative of marked local emission in urban-industrial area. The concentrations of CH_3CCl_3 in most inland area were several times as high as in the background air; the sample from Tokyo indicated almost 100-fold increase in its concentration, in accordance with the heavy use and relatively long tropospheric lifetime.

In conclusion, accurate measurements of the background atmospheric concentrations of CCl_2F_2, CCl_3F, CCl_2FCClF_2 and CH_3CCl_3 at selected locations in Japan will be of primary importance for estimation of the possible depletion of stratospheric ozone. Furthermore, measurements of $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ in air may afford clues to understand the local pollution behavior of such compounds in the troposphere.

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(Received February 15, 1979)