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Background Atmospheric Concentrations of Halogenated Hydrocarbons in Japan

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Synopsis. The atmospheric concentrations of CCl_2F_2, CCl_3F, CCl_2FCClF_2, CH_3CCl_3, CCl_4, $CHCl{=}CCl_2$, and $CCl_2{=}CCl_2$ in remote areas in Japan and over the Japan Sea were measured in the summer of 1979. The averaged observed concentrations (in ppt: 10^{-12} v/v) for the compounds were 301 ± 12, 175 ± 7, 23 ± 2, 117 ± 11, 107 ± 6, 14 ± 10, and 19 ± 10 respectively.

Among a number of anthropogenic halogenated hydrocarbons released in large quantities into the atmosphere, greatest attention has been directed to the chlorofluoromethanes, CCl_2F_2 and CCl_3F, which have been widely used as spray propellants and refrigerants. The chlorofluoromethanes accumulated in the troposphere due to their long lifetimes rise gradually into the stratosphere, there to be decomposed by intense UV light to release atomic chlorine, which can then participate in the ClO_x-chain removal of stratospheric ozone.[1,2] While such a theoretical prediction as to stratospheric ozone depletion by chlorofluorocarbons has been essentially validated by extensive research,[3-8] precise world-wide monitoring of their background atmospheric concentrations has now become more important for the accurate estimation of possible future ozone depletion. The growing use of 1,1,1-trichloroethane (CH_3CCl_3), once classified as a 'safe' substitute for other 'labile' solvents, cannot be overlooked, since it is not decomposed completely by OH radicals in the troposphere and may similarly affect the ozone layer if the present rates of production and use continue. The development of a reliable analytical system is greatly needed in order to determine precisely its background concentration in view of the discrepancies among the reported data,[6] possibly due to contamination by the analytical systems. Measurements of unsaturated chlorocarbons, such as $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$, which are decomposed rapidly and completely in the troposphere may also be necessary for understanding their local pollution behavior, as they are extensively used as degreasing or cleaning solvents.

Since no reliable measurements of the halogenated hydrocarbons have thus far been made in Japan and 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; we have already reported the preliminary data on more or less polluted air samples.[10] In this article we wish to describe our clean analytical system for extremely accurate measurements and our results on the averaged background atmospheric concentrations of these substances in remote areas in the summer of 1979.

Experimental

Extremely Clean Analytical System and Procedures. Stainless steel canisters were specially designed for air sampling and storage. Since Teflon stopcocks or silicone rubber plugs often cause a contamination of halogenated hydrocarbons, the sampling canister was made from a stainless steel beaker (2 l) by argon-arc welding and equipped with a hermetically sealed stainless steel bellows valve (Nupro SS-4H). The inside of the canister was polished electrochemically and washed ultrasonically. After the evacuation of the canister overnight to 10^{-4} Pa at 200 °C, the dead volume between the valve and a Swagelok cap was filled with ultra-high-purity nitrogen. On sampling, ambient air was introduced into the canister by simply removing the cap and opening the valve facing the wind. The composition of the atmospheric samples remain unchanged even after storage for over a year. The calibration standard was prepared by a four- or five-step static-dilution method. An extremely clean, all-stainless-steel vacuum line was built for the final stages of dilution (*e.g.*, ppb—ppt level) with ultra-high-purity nitrogen or air. Several ambient-air samples, calibrated for all components against each standard, were used as the secondary standards in routine measurements. The halogenated hydrocarbons were determined by using a constant-current-type electron capture detector (Varian 3700 EC-GC). A Silicone OV-101 column (10 wt% coated on Chromosorb W-HP, 80—100 mesh, 5 mm i.d., 3 m long) was used as the preconcentration and analytical column. The carrier-gas (nitrogen) flow rate was 80 ml/min. Methane (4 ml/min) was mixed in between the column and the detector as a make-up gas to improve the S/N ratio and to stabilize the base line without reducing the sensitivity. An aliquot of the air sample or of the standard was introduced into an evacuated sample loop until a given pressure was reached, and then it was transferred into the column cooled at −40 °C so that halogenated hydrocarbons were kept on the head of the column. The column temperature was raised linearly at a rate of 5 °C/min up to 70 °C. After the elution of the air (oxygen), ECD was connected to the analytical column by switching the four-way valve between the column and the detector, and each component was determined.

Samples. Clean-air samples were collected in the summer of 1979 at remote areas throughout Japan and over the Japan Sea. Although sampling was not always conducted under optimum meteorological conditions, we did our best to avoid local contamination within the limited sampling periods. The locations, dates, and weather conditions are listed in Table 1.

Results and Discussion

Figure 1 shows a typical EC-GC chromatogram of the atmospheric sample No. 1, collected at Nosappumisaki, together with a chromatogram of the purified nitrogen used for the dilution of the standards to ensure the absence of any halogenated hydrocarbons during the identical analytical procedure. Since impurities in the carrier gas should also have been concentrated at the head of the analytical column during preconcentration, the possible contamination from about 500 ml of purified nitrogen can not exceed the detection limit of each compound in this system: CCl_2F_2 and

Table 1. Observed concentrations of halogenated hydrocarbons in air over Japan in the summer of 1979 (in ppt$=10^{-12}$ v/v)

Sample[a]	CCl_2F_2	CCl_3F	CCl_2FCClF_2	CH_3CCl_3	CCl_4	$CHCl=CCl_2$	$CCl_2=CCl_2$
No. 1	285	173	24	113	107	18	14
No. 2	304	179	23	121	103	5	23
No. 3	306	173	23	115	111	6	14
No. 4	288	166	27	103	112	7	8
No. 5	304	173	25	115	100	9	18
No. 6	311	181	21	136	96	19	36
No. 7	310	180	22	123	110	21	31
No. 8	278	162	23	100	108	6	3
No. 9	319	186	23	127	118	38	22
Average	301	175	23	117	107	14	19
S. D. (σ)	12	7	2	11	6	10	10
	(4%)	(4%)	(7%)	(9%)	(6%)	(71%)	(53%)

a) Sampling locations, dates, and weather conditions. Sample No. 1: Nosappu-misaki (Hokkaido) 43°23′N, 145°49′E, Aug. 3, 1979, clear, 15.7 °C, SSE 10 m/s. Sample No. 2: Nukabira (Hokkaido) 43°20′N, 143°10′E, Aug. 4, 1979, cloudy, 17.8 °C, SW, 3 m/s. Sample No. 3: Setana (Hokkaido) 42°29′N, 139°51′E, Aug. 6, 1979, cloudy, 19.5 °C, SSE, 8 m/s. Sample No. 4: Shiose-zaki (Akita) 39°51′N, 139°45′E, Aug. 7, 1979, cloudy, W, 5 m/s. Sample 5: Japan Sea (off Shimane) 38°25′N, 132°30′E, Jul. 4, 1979, clear, 22.8 °C, SW, 8 m/s. Sample No. 6: Tago (Shimane) 35°36′N, 133°06′E, Sep. 12, 1979, fair, 28.9 °C, ESE, 3 m/s. Sample No. 7: Iki-island (Nagasaki) 33°47′N, 129°48′E, Sep. 11, 1979, clear, 26.0 °C, E, 10 m/s. Sample No. 8: Muroto-misaki (Kouchi) 33°14′N, 134°11′E, Aug. 3, 1979, cloudy, 28.0 °C, W, 8 m/s. Sample No. 9: Noma-misaki (Kagoshima) 31°25′N, 130°07′E, Sep. 10, 1979, fair, 26.8 °C, NNW, 5.m/s.

$CHCl=CCl_2<0.2$ ppt, CCl_2FCClF_2, CH_3CCl_3, and $CCl_2=CCl_2<0.05$ ppt, and CCl_3F and $CCl_4<0.01$ ppt. The reproducibility of the measurement was within 2%. The absolute accuracy of the calibration under the present conditions may be less than 10 ppt. The observed concentrations (Table 1) were slightly affected by the sampling location and the meteorological conditions regarding the transport of the air mass. However, the small standard deviations in the CCl_2F_2 and CCl_3F concentrations ($\approx 4\%$) demonstrate that the relatively low local emission in the rural areas may not appreciably raise their already high concentration levels. The averaged concentrations observed in Japan are close to the background concentrations reported in the northern hemisphere after the correction for the monthly increase in concentrations. The fluctuations in the $CHCl=CCl_2$ and $CCl_2=CCl_2$ concentrations may be ascribed to their short lifetimes and relatively high emissions even in remote areas in Japan. The averaged concentrations of these halogenated ethylenes have been observed to be hundreds-fold higher in Tokyo.[11)]

In conclusion, it is made clear that we can measure the background concentrations of the halogenated hydrocarbons even in Japan only if we carefully choose favorable locations and meteorological conditions. Further studies regarding the profile of local pollution in urban areas are also in progress in our laboratory.

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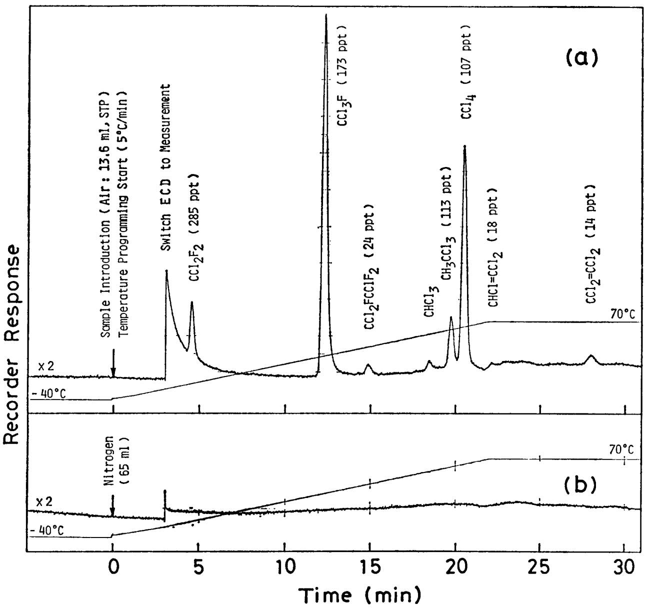

Fig. 1. Typical temperature program EC-GC chromatograms of (a) the atmospheric sample collected at Nosappu-misaki, Hokkaido (Sample No. 1 in Table 1), and (b) the instrumental background noise level in the identical analytical procedure. (Conditions are given in the text).

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