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A New Calibration Method for the Measurement of CCl_4 Concentration at 10^{-10} v/v Level and the Behavior of CCl_4 in the Atmosphere

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A new technique was developed for the accurate determination of atmospheric CCl_4 at about 100 pptv ($=10^{-10}$ v/v) concentration level, since at such extremely low concentration CCl_4 was found to be adsorbed readily and strongly on clean metal surfaces under dry conditions. The analysis of CCl_4 by gas chromatography/electron-capture detector and the preparation of CCl_4 primary calibration standard were improved by introducing water vapor into the system to prevent the adsorption of CCl_4 and to obtain stable and reproducible results. The total amount of CCl_4 in the atmosphere was studied on the basis of our newly calibrated data of CCl_4 concentration, and a reasonable lifetime of CCl_4 was obtained assuming that its sink is only the UV photodissociation in the stratosphere.

The release of chlorine atoms following UV photodissociation of man-made halocarbons (CCl_2F_2, CCl_3F, CCl_4, *etc.*) in the stratosphere is believed to change equilibria among chemical species in the stratosphere, which have been maintained for a long time.[1-9] In particular, the dissociation of ozone by Cl-induced chain reactions and the consequent change in the vertical profile of ozone in the stratosphere may end up affecting severely the earth's environment. Accumulated amounts of man-made CCl_2F_2 and CCl_3F in the atmosphere have been sharply increasing since 1950's due to their growing uses as aerosol propellants and refrigerants. Therefore, extensive efforts have been made to estimate the Cl-atom effect on the stratospheric ozone layer. While carbon tetrachloride (similar to CCl_2F_2 and CCl_3F) is almost of anthropogenic origin as well, its behavior in the atmosphere has not been understood well. During 1920 through 1940's, all the produced CCl_4 was released into the atmosphere after its uses as industrial solvent, dry cleaning agent, fire extinguisher, and grain fumigant. Since 1950's, however, CCl_4 has been mostly used as starting chemicals in the production of CCl_2F_2 and CCl_3F and its release into the atmosphere has been considered to be limited.[10-13] Accordingly its concentration in the atmosphere had been believed to remain nearly constant. The recent estimation, however, has suggested much larger release of CCl_4 in 1970's, and it has been increasing as well with the growing production of CCl_2F_2 and CCl_3F.[14] Since the reported atmospheric concentrations of CCl_4 vary among investigators, the distribution, annual change and absolute amount of CCl_4 in the atmosphere are not completely known yet. Carbon tetrachloride is an ultratrace constituent in the atmosphere at about 100 pptv (pptv$=10^{-12}$ v/v) and tends to be strongly adsorbed or decomposed on the internal surface of sample canisters, which results in poor precision and accuracy in its analysis as compared with the analyses of CCl_2F_2 and CCl_3F.[15,16] Therefore we have improved the procedure of CCl_4 analysis with a gas chromatograph/electron-capture detector (GC-ECD) and also established a new method of preparation of CCl_4 standard by adding water vapor to prevent the CCl_4 adsorption. In this paper we report a new method of preparation of CCl_4 primary standards at 100 pptv level and discuss the behavior of CCl_4 in the atmosphere based on the background atmospheric concentrations determined by our new measurements.

Experimental

Sampling Procedures. A 2-dm^3 stainless steel (SS) canister equipped with an all SS bellows valve (Nupro SS-4H) was mainly used for atmospheric sampling. The canister was made by welding a 2-dm^3 beaker and a top plate with a welded tube, all of which had been washed carefully with neutral detergent and then with acetone in an ultrasonic cleaner. Electropolishing was not used because it chemically activates the surface. After the installation of the bellows valve, the canister was evacuated overnight to below 10^{-3} Pa at elevated temperatures from 50 to 300 °C. After the evacuation, ambient air was temporarily introduced into the canister at room temperature and pumped out again in order to deactivate the internal surface with adsorbable ingredients (probably H_2O). The canisters once used for sampling in remote areas were used after only the evacuation at room temperature. Sample air was introduced into the evacuated canister up to the ambient pressure by simply opening the valve at sampling locations. Background air samples were collected on the coast of Hokkaido and west Tohoku area (in 40—45 °N) when the wind was blowing from the sea in order to avoid the pollution from industrialized areas and local sources in Japan.[17-20]

Analysis. Atmospheric samples were analyzed in the laboratory with a gas chromatograph (Varian GC3700) equipped with an ECD (8 mCi ^{63}Ni). The experimental set-up for analysis and the procedure were described in detail previously.[19,20] The vacuum line for handling of the sample and the flow path in the gas chromatograph are all made of stainless steel to avoid contaminations with halocarbons from organic polymers such as silicone and Teflon. An atmospheric sample was introduced into the 50 cm^3 sample loop to about 200 Torr (1 Torr=133.3 Pa) ($\approx$13 cm^3 STP) measuring the pressure precisely with a metal diaphragm pressure gauge and was injected to the GC. Eluted halocarbons were detected by the ECD and recorded with an analog recorder (Shimadzu R-12) and a degital integrator (Shimadzu C-R2AX). The precision in the pressure measurement was about 0.3% and the reproducibility in CCl_4 measurement was better than 1%. Pure nitrogen (Nippon Sanso, grade B) was further purified successively with molecular sieve 5A, activated charcoal, and molecular sieve 13X, and was used as the carrier gas at a flow rate of 80 cm^3 min^{-1}. Methane was added (6 cm^3 min^{-1}) to the carrier gas nitrogen at just before ECD in order to improve the stability, sensitivity and signal-to-noise ratio of the detector. Halocarbons were separated by the temperature programming of the column (4.25 mm i.d. ×3 m, packed with 10% Silicone OV-101 on Chromosorb-W HP) from −40 to 70 °C at 5 °C min^{-1}. The ECD was usually purged with the purified nitrogen at a flow rate of 80 cm^3 min^{-1} and was connected to the separation column by switching a four-way valve only when the halocarbons were eluted: air was by-passed to avoid the sensitivity change of ECD. After the elution of CCl_2CCl_2 at about 25 min, the column temperature was raised to 150 °C for 10 min to purge other high boiling components.

Preparation of the Calibration Standards of Halocarbons. An all SS vacuum line installed in a temperature controlled room was used for preparation of the calibration standards of halocarbons. Internal volume of each part of the line was determined at a precision below 1%. Calibration standards were prepared by static dilution of pure materials with purified nitrogen or zero air which had been purified in the same manner as carrier gas nitrogen. Since the atmospheric concentration of CCl_4 is about 100 pptv, the calibration standards with similar concentrations were prepared by 3-step dilutions (to about 100 ppmv, 100 ppbv, and 100 pptv). In preparation of pptv-level calibration standards of CCl_4 and CH_3CCl_3, zero air saturated with water vapor at 23 °C (H_2O saturated zero air) was introduced into the flask before the dilution so that the water vapor pressure in the standards finally becomes about 10 Torr.

Results and Discussion

Difficulty in CCl_4 Measurement. Previous data of CCl_4 measurements reported by several groups[14,21–38] are plotted in Fig. 1. Most measurements were made with GC-ECD by comparing the corresponding peaks with prepared calibration standards. As shown in Fig. 1 the reported values are widely scattered over 100—170 pptv in 1975—1980. Such a large fluctuation (≈50%) cannot be attributed to natural variation in CCl_4 concentration in view of the chemical inertness (long lifetime) of CCl_4 in the atmosphere. The measurements made by a group with the common method and secondary standard, however, showed only a small variation, indicating that the CCl_4 concentration increases by about 2% per year.[14,27,28) Therefore, the poor accuracy of CCl_4 measurements must be ascribed to the difficulty in the preparation of calibration standards. Another calibration method with GC-ECD-coulometry[12) based on several premises has produced widely scattered values due to poor reproducibility. The measurement of CCl_4 in the stratosphere has been limited only to the lower stratosphere, and it has suffered from severe problem of the decomposition of CCl_4 in metal canisters.[15,16,24,30–33,36,37) We have found that even in dry tropospheric samples (dew point below −5 °C) the CCl_4 concentrations decrease after stored in the metal canisters. On the other hand, in relatively humid surface level samples, the CCl_4 concentrations remain unchanged over a long storage time, probably due to the contained water vapor. Water can be strongly adsorbed on the metal surface of the canister and cover the active sites on it. We have confirmed this assumption experimentally; when a dry sample was introduced into a stainless steel

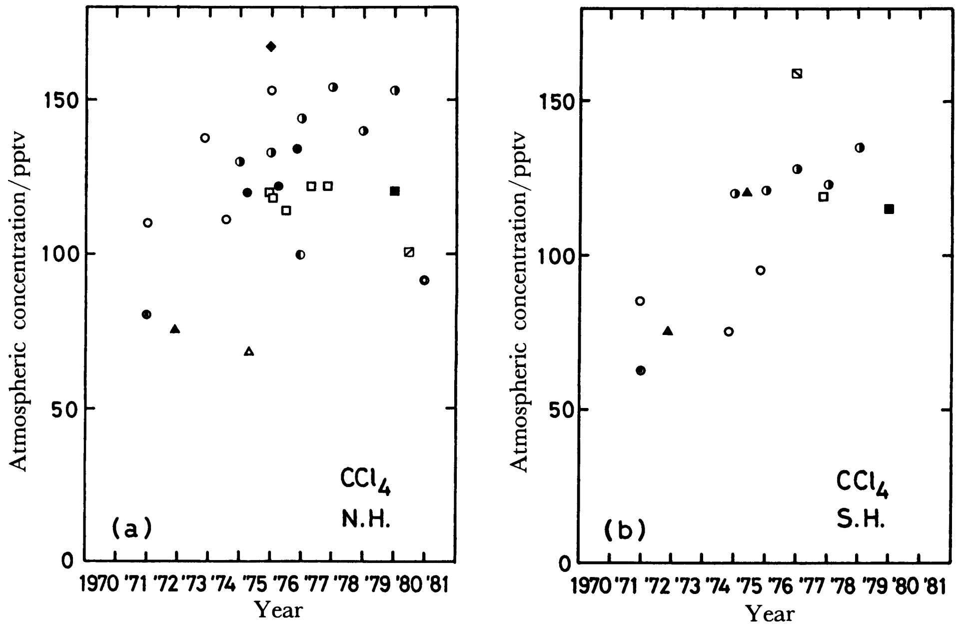

Fig. 1. Reported values of atmospheric concentrations of CCl_4 in (a) the Northern Hemisphere and (b) the Southern Hemisphere (pptv = 10^{-12} v/v). ◉: Lovelock *et al.* (Ref. 21), ○: Lovelock *et al.* (Ref. 24 and 25), ▲: Wilkniss *et al.* (Ref. 23, 34, and 35), △: Krey *et al.* (Ref. 37), ●: Robinson *et al.* (Ref. 30 and 36), Cronn *et al.* (Ref. 31), Pierotti *et al.* (Ref. 33), ◑: Rasmussen *et al.* (Ref. 28), □: Singh *et al.* (Ref. 27), ◆: Tyson *et al.* (Ref. 26), ■: Simmonds *et al.* (Ref. 14), ▨: Brice *et al.* (Ref. 29), ◐: Seiler *et al.* (Ref. 32), ⧅: Fraser *et al.* (Ref. 38), ◎: This work.

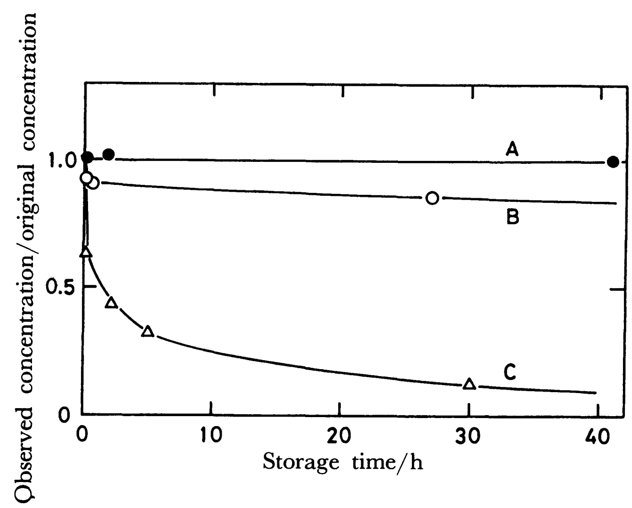

Fig. 2. Recovery of CCl_4 in dry samples stored in metal canisters: **A**, previously used for sample of background air and evacuated at room temperature; **B**, evacuated at 200 °C for 1 d; **C**, evacuated at 300 °C for 1 d.

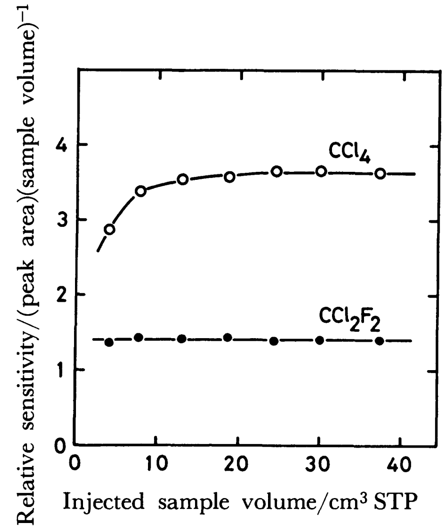

Fig. 3. Dependency of the relative sensitivity (peak area/injected sample amount) for CCl_4 and CCl_2F_2 on the injected volume of a dry sample (absolute humidity: ≈3 Torr).

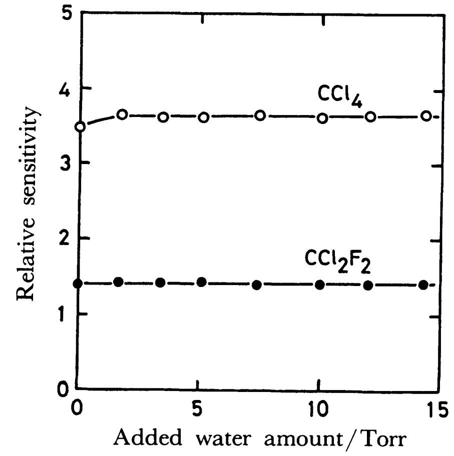

Fig. 4. The effect of preaddition of water-saturated zero air to the separation column during the analysis on the observed peak area of CCl_4 and CCl_2F_2. Water amount is shown by the corresponding vapor pressure of H_2O in the atmospheric sample.

canister baked at a higher temperature (300 °C, 1 d), much larger decrease in the CCl_4 concentration was observed as shown in Fig. 2. Furthermore, when the primary standards of CCl_4 at 100 pptv concentration level were prepared by dilution of 100 ppbv level standards in the metal canister with extremely purified dry air or nitrogen, the CCl_4 concentration found in the prepared standards was sometimes lower than expected even immediately after dilution, or often decreased drastically during the storage and completely diminished within a few days. These results must be explained in terms of the quick adsorption of CCl_4 on the inner surface (1) at the moment of introduction of the higher cocentration standard into the highly evacuated metal container to about several Torr, and (2) after the dilution with a water-free extremely pure dilution gas (air or nitrogen) which cannot cover the active sites on the metal surface.

Improvement of Analytical Procedures. Since we adopted the temperature-programming for the separation of 6 compounds (CCl_2F_2, CCl_3F, CH_3CCl_3, CCl_4, $CHClCCl_2$, and CCl_2CCl_2) with a single column, the commercially available high-pure grade nitrogen was further purified with purification columns for use as carrier gas. The concentrations of halocarbons in the purified nitrogen and in the purified zero air (processed with the same procedure) were: $CCl_2F_2 < 0.01$ pptv, $CCl_3F < 0.003$ pptv, $CCl_4 < 0.003$ pptv, and $CH_3CCl_3 < 0.01$ pptv. The separation column was therefore thoroughly cleaned by flowing the purified carrier gas nitrogen continuously for more than 5 years and by heating up to 150 °C after every run of analysis. Under these extremely clean conditions, CCl_4 in dry samples tended to be adsorbed on the column packing material during analysis and its recovery from the column was incomplete. Figure 3 shows the dependence of the relative sensitivity of CCl_4 and CCl_2F_2 (peak area/sample amount) upon the injected amount of a dry sample (dew point −5 °C, *i.e.*, absolute humidity is about 3 Torr). While the sensitivity of CCl_2F_2 was virtually independent of the injected sample amount, the CCl_4 sensitivity decreased at below 10 cm^3 STP sample injected. In order to avoid such problem, water vapor present in the purified zero air was introduced intentionally into the column at −40 °C just before the sample injection. The amount of the water-containing zero air was adjusted so as to keep the humidity in the sample constant at 15 Torr; the difference in the retention behavior of halocarbons in the GC column can also be canceled out. Each halocarbon concentration in the water saturated zero air was confirmed to be below the detection limit by GC-ECD. Figure 4 shows the change of the sensitivity of CCl_4 in the atmospheric sample (13 cm^3 STP, absolute humidity 3 Torr) with preaddition of the water-saturated zero air. Since water is introduced into the column prior to the sample injection in this case, the amount of water-containing air necessary to deactivate the reactive sites was much less than in the case of Fig. 3. The recovery of CCl_4 at plateau regions in Figs. 3 and 4 agreed well and can be considered to be complete.

Preparation of Calibration Standard. The calibration standards of CCl_2F_2 and CCl_3F prepared with dry purified zero air were stored more than 2 years without change of their concentrations (<0.5%) in the 2-dm^3 SS canister equipped with a SS bellows valve. In the dry CCl_4 calibration standards prepared in the SS canister with concentrations at and below ppbv, however, the concentration decreased rapidly (*e.g.*, 80% loss in 1 d), much more rapidly at pptv levels. In a Pyrex glass flask (2—5 dm^3) equipped with the same SS bellows valve, the dry CCl_4 calibration standards at ppbv levels were stable (<0.3%) for more than 3 months, but dry CCl_4 standards at pptv levels decreased to half in a day, probably due to the metal part connected to the glass flask (*i.e.*, SS tube and the valve). Therefore, we prepared CCl_4 calibration standards at pptv levels in the Pyrex flask using water-containing zero air. More than ten calibration standards of CCl_4 at about 100 pptv were prepared by changing the water vapor pressure. The peak area of CCl_4 observed for these standards is plotted in Fig. 5 against the water vapor pressure, where the injected pressure, the presumed CCl_4 concentration, and the detector sensitivity have been normalized. The peak area of CCl_3F diluted at the same time in the same standards showed a constant value over the whole range of water pressure. While the observed CCl_4 peak area was also constant in the presence of sufficient humidity (≥6 Torr), it became unstable (*i.e.*, poor reproducibility) and decreased with the decrease in the water vapor pressure below 5 Torr. The CCl_4 peak area without addition of water vapor in the standard was about half of that with addition of water. Therefore, the CCl_4 calibration standard was prepared hereafter in the glass flask so that the water vapor pressure became about 10 Torr. The CCl_4 calibration standard prepared by this method was very stable and reproducible (<1.5%). The reliability of the concentration value in the prepared standard (*i.e.*, accuracy) was estimated to be within 6% considering all the possible systematic and random errors involved in the system and during the procedure. By using our new calibration standards and the improved analytical method, we are now able to discuss the observed concentrations of CCl_4 and the behavior of CCl_4 in the atmosphere.

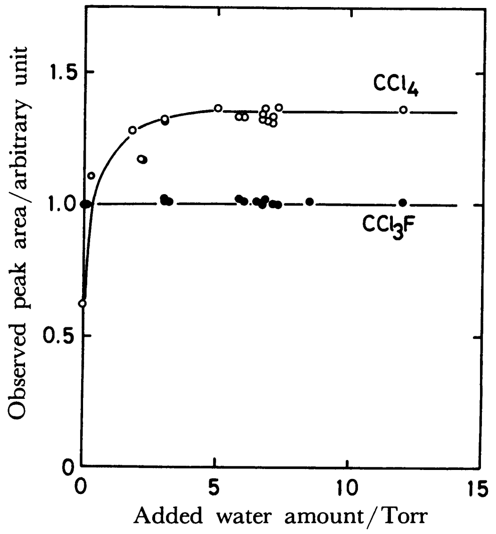

Fig. 5. The effect of water vapor pressure precedently introduced into the calibration standard at about 100 pptv concentration level prepared in a Pyrex glass flask. The peak areas of CCl_4 and CCl_3F observed in the standards are normalized for the presumed CCl_4 concentration, the injected pressure, and the ECD sensitivity.

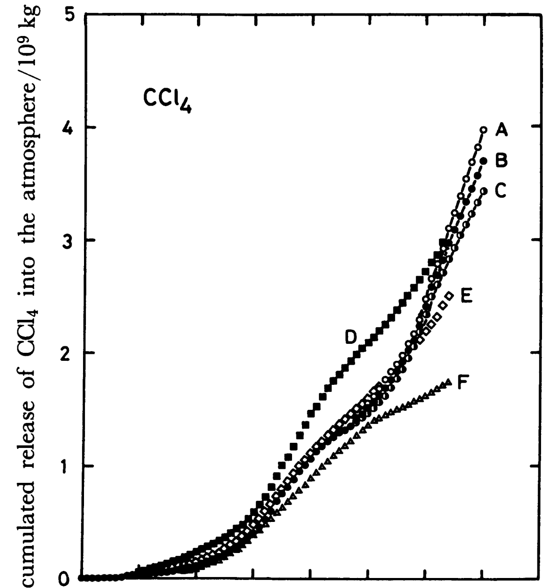

Fig. 6. Esimation of annual release of CCl_4 made by several groups: **A** (○) upper limit, **C** (◑) lower limit, **B** (●) the average of **A** and **C** by Simmonds *et al.* (Ref. 14); **D** (◆) by Galbally (Ref. 12); **E** (◇) by Singh *et al.* (Ref. 11); **F** (△) by Altshuller (Ref. 10).

The Source and Sink of CCl_4. Carbon tetrachloride has been believed to be of anthropogenic origin and no natural sources have been known.[10—14] Before 1950, most CCl_4 was used as industrial solvent, fire extinguisher and grain fumigant and eventually released to the atmosphere. However, since 1950's, CCl_4 for solvent has been replaced by other solvents such as CH_3CCl_3, CCl_2CCl_2, and $CHClCCl_2$. On the other hand, CCl_4 has mainly been consumed as starting chemicals for the production of CCl_2F_2 and CCl_3F, so that its release into the atmosphere was estimated to be only several percent of its production.[10—14] The estimates of the total release of anthropogenic CCl_4 made by several groups are shown in Fig. 6. While these estimates vary in amounts, they are similar in trend with the first release peak in 1940's as solvent and the recent increase accompanying the increase of the production of CCl_2F_2 and CCl_3F. Since the estimation by Simmonds *et al.* (curves **A**, **B**, and **C** in Fig. 6: **A**, upper limit; **C**, lower limit; and **B**, the average of **A** and **C**) is the most recent one and appears to be most reliable at present, we have compared our measurement data with their release estimation. The most effective sink of the atmospheric CCl_4 has been proved to be stratospheric UV photodissociation, and its lifetime in the atmosphere was calculated by Molina and Rowland as 30—50 years assuming vertical atmospheric transport parameters and solar flux at each altitude.[39] On the basis of recent values for such parameters (*i.e.*, about 10% lower UV-absorption cross-section of CCl_4 in 190—220 nm region,[6] and the increase of estimated solar flux due to the revised 30% lower absorption cross section of O_2[40,41]), the lifetime of CCl_4 in the atmosphere may become slightly shorter than the previous estimate. Other dissociation mechanisms of CCl_4 such as reactions with active species like OH, $O(^1D)$ in the atmosphere, or the hydrolysis in the ocean have been neglected because of their small reaction rates.[3,12,21,42,43] If the estimated lifetime based on the observed concentration is significantly shorter than the calculated ones based on the stratospheric photodissociation alone, we may have to reexamine or search for other dissociation mechanisms of CCl_4.

TABLE 1. OBSERVED CONCENTRATION OF CCl_4 IN THE ATMOSPHERIC SAMPLES COLLECTED ON THE COAST OF HOKKAIDO AND WEST TOHOKU AREA IN JANUARY 1981

Sampling location	Sampling Date	CCl_4 concentration (pptv)[a]
Setana (42.5°N, 139.9°E)	Jan. 13, 1981	91.4
Nosappu (43.4°N, 145.8°E)	Jan. 14, 1981	89.3
Nosappu (43.4°N, 145.8°E)	Jan. 15, 1981	90.7
Era (41.6°N, 140.0°E)	Jan. 17, 1981	92.0
Nyudozaki (40.0°N, 139.7°E)	Jan. 18, 1981	92.1
Nyudozaki (40.0°N, 139.7°E)	Jan. 19, 1981	92.1
	Average	91.3
	σ_{n-1}	1.1

a) pptv$=10^{-12}$ v/v in dry air.

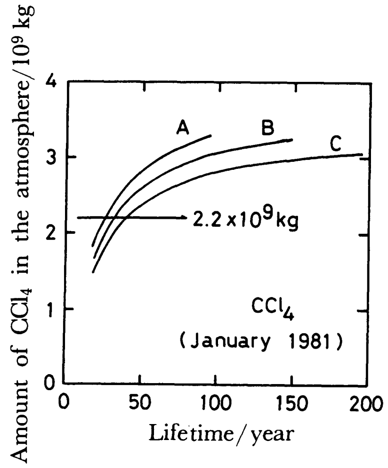

Fig. 7. Expected total amount of CCl_4 in the atmosphere in January 1981 against supposed atmospheric lifetime of CCl_4 for each emission scenario (**A**, **B**, and **C** corresponds to that in Fig. 6). The value of 2.2×10^9 kg calculated from our observation gives 33-year lifetime for the most probable emission scenario **B**.

Observed Concentration and Lifetime of CCl_4 in the Atmosphere. The background concentration is defined here as the concentration observed in remote areas far enough from local emission sources. Because each halocarbon is released continuously in specified regions on the earth, the balance of its emission, diffusion, mixing, and removal processes will give a stationary concentration in remote areas, which is considered to be the background concentration at that location. As for the halocarbons, their emission has been limited to urban areas in highly industrialized countries, predominantly in the Northern Hemisphere (N. H.) such as the United States of America, Western Europe, and Japan. Table 1 shows our data of CCl_4 concentration measured in January 1981 on the coast of Hokkaido and west Tohoku area (40—45°N). The concentration is given as in dry air. The background concentration representing the mid-latitude N. H. thus obtained was 91 pptv in January 1981. For the estimation of the total amount of CCl_4 in the global atmosphere, the concentration of CCl_4 in the Southern Hemisphere (S. H.) was obtained by referring to the S. H./N. H. ratio reported in Ref. 14; while absolute concentration values are different from ours, the latitudinal distribution profile should be free from the calibration problem as discussed before. The CCl_4 concentration in the S. H. is nearly uniform due to the absence of large source in the S. H.. The S. H./N. H. ratio of the CCl_4 concentrations at mid latitudes in January 1981 was thus calculated from Ref. 14 as $(\text{S. H./N. H.})_{\text{mid-lat.}}$=(Tasmania data+American Samoa data)/(Cape Mears data+Adrigole data)=0.92. The CCl_4 concentration at the low-lat. N. H. (represented by Barbados data[14]) was calculated as 0.96 of that at the mid-lat. N. H. Since the amount of air in high and mid latitudes (>30°) is nearly equal to that in low latitude (0—30°), the global tropospheric average concentration of CCl_4 was estimated as 0.95 (=(1.0+0.96+0.92+0.92)/4) times the mid-lat. N. H. concentration. The average mixing ratio of CCl_4 in the stratosphere (where about 20% of air exists) was calculated as 60% of the global average tropospheric mixing ratio (mixing ratio denotes pressure-normalized concentration) as in the case of CCl_3F (same with Ref. 14). Since the amount of dry air on the earth is about 5.12×10^{18} kg, the total amount of CCl_4 in the whole atmosphere was calculated to be 2.2×10^9 kg in January 1981. On the other hand, the total amount remaining in the atmosphere $S(t_1)$ at time t_1 is calculated from the worldwide CCl_4 release data $I(t)$ and

CCl_4 atmospheric lifetime τ by

$$S(t_1) = \int_{t_0}^{t_1} I(t) \exp(-(t_1 - t)/\tau) dt.$$

Figure 7 shows the expected total amount of CCl_4 in the atmosphere in January 1981 with the supposed lifetime of CCl_4 for each case of the emission scenario (*i.e.*, curves **A**, **B**, and **C** in Fig. 6). By comparing with the amount of 2.2×10^9 kg calculated from our measurement data, the lifetime of CCl_4 in the atmosphere is estimated as 33 years for the most probable emission scenario **B**, or 27 and 42 years for the emission scenarios **A** and **C**, respectively. These values are close to or slightly shorter than the lifetime of 30—50 years calculated by Molina and Rowland[39] assuming the UV photodissociation in the stratosphere as the only sink. For the global atmospheric concentration of CCl_4 118 pptv in January 1980 previously reported by Simmonds *et al.* in their Atmospheric Lifetime Experiment (ALE) program,[14] the calculated lifetime for CCl_4 should be about 70, 100, and 200 years for emission scenarios **A**, **B**, and **C**, respectively.[44] These lifetimes are even longer than those for CCl_3F and CCl_2F_2; this is unreasonable in view of their UV absorption cross-sections or their chemical reactivities. Furthermore, the larger atmospheric concentrations reported by other groups (Ref. 14, 21—38,45) and/or other scenarios with smaller emission (Ref. 10—13) will give much longer lifetime for CCl_4 and cannot be reasonably explained. We therefore suppose that such higher CCl_4 concentrations must have been based on inaccurate (unstable and overestimated) calibration standards.

Conclusion

Since CCl_4 was found to be readily and strongly adsorbed on clean metal surface under dry conditions, we developed new methods for analysis of CCl_4 and preparation of CCl_4 primary calibration standards by introducing water vapor into the system. This method is also effective for analysis and preparation of standards of high-boiling-point and readily-adsorbable compounds such as CH_3CCl_3, $CHCl{=}CCl_2$, and $CCl_2{=}CCl_2$. The absolute amount, distribution and lifetime of CCl_4 in the atmosphere were studied based on our newly calibrated measurement data.

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