Gas-Chromatographic Measurements of Atmospheric Sulfur Hexafluoride

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Synopsis. From air samplings on aircraft in February and December 1982 and in February 1983, and from gas-chromatographic measurements, the background volume mixing ratio of sulfur hexafluoride(SF_6) over Japan was found to be about (0.72±0.13) ppt, where ppt=10^{-12}. Since the first observation by Lovelock in 1970 (0.03 ppt), SF_6 seems to have been increasing steadily.

Sulfur hexafluoride(SF_6) is a very stable compound which has been used for gas insulation since the 1960's[1]; it has also been used as an atmospheric tracer because a electron-capture detector(ECD) has very high sensitivity for it.

With the increasing use of SF_6, it is being accumulated in the atmosphere; its background volume mixing ratio was about 0.5 ppt in 1978.[2] Because its use as a tracer for long-range-transport experiments is not considered to be suitable, it is being replaced by C_6F_{12} and C_8F_{16}.[2] However, it can still be used as a tracer of global atmospheric circulation like CF_2Cl_2, $CFCl_3$,[3] and ^{85}Kr.[4] Furthermore, it has the anvantage that, like them, its emission is due only to man's activities.

In this paper, our preliminary findings regarding its vertical distribution in the troposphere and the time trend of its background volume mixing ratio will be reported.

Experimental

The details of our air sampling and gas-chromatographic measurements have been described in Refs. 5 and 6. Therefore, except for some changes, only a brief description will be presented here.

Sampling of Air. Air samples were collected on an aircraft (Aerocommander 685 or Cessna 404) by means of an air pump (NRK, UP-2) into stainless steel cylinders (0.3 l, Nupro SS-4JB or B-4H valves were used). The SF_6 concentration was almost constant for several months in the cylinder.

Gas-Chromatographic Measurements. SF_6 was analyzed using a Shimadzu Gas Chromatograph GC-6AM equipped with an ECD. The sample air in the cylinder was transferred into a gas sampling tube (Shimadzu MGS-4, 2 ml) and then into a glass column (3 m×5 mm o.d., 90 °C) filled with molecular sieve 5A (30—60 mesh). An ECD (^{63}Ni 10 mci) was used at 300 °C. Ultra-pure N_2(>99.9995%), which had been passed through a drier tube filled with molecular sieve 5A(1/16″ pellets), was used as the carrier gas at a flow rate of 30 ml $min.^{-1}$

SF_6 was eluted before CF_2Cl_2 and O_2. Though CF_3Cl has nearly the same retention time as SF_6, its sensitivity was about 10^2 times lower.

A reference gas was made by diluting pure SF_6 (Takachiho, >99.8%) with ultra-pure N_2 into a *tedlar* bag (20 l). The SF_6 in the *tedlar* bag was constant in a few days. By a two-step static dilution, a reference gas of SF_6 in N_2 was made. The peak height of SF_6 was proportional to the amount of SF_6 in the range from 0 to 0.33×10^{-12} g, which was equal to the amount of 25 ppt SF_6 in a 2-ml sample air. The error in repeated measurements at 1.0 ppt was ±10%. In practice, the volume mixing ratios of SF_6 were calculated from those of CF_2Cl_2[7] by making use of the fact that the peak height of SF_6 was about 20 times (20.8±0.6) higher than that of CF_2Cl_2, which was eluted about 20 s after SF_6. In the measurement of the sensitivity ratio, a mixed gas of 10 ppt SF_6 and 400 ppt CF_2Cl_2 in N_2 was used. The detection limit was 0.3 ppt (S/N~1).

Results and Discussion

The vertical distribution of SF_6 in February 1982 is shown in Fig. 1. In every flight, the Cessna 404 took off and landed at Haneda Airport. The flight courses ranged from Sendai to Hachijo-jima. As with CF_2Cl_2 and $CFCl_3$,[7] higher mixing ratios were often observed over urban areas up to an altitude of 2 km. Above 2 km, nearly constant mixing ratios were observed; the mean value (0.64 ppt) for 17 samples was considered as the background mixing ratio in the troposphere. Subsequent air samplings were performed on 20 and 21 December 1982 over the Kanto Mountains and on 7 February 1983 between Hamamatsu and Nii-Jima. Above 2 km, the mean values and standard deviations were 0.85 and 0.06 ppt for 7 samples in December 1982 and 0.83 and 0.07 ppt for 5 samples in February 1983. The mean value for the total of 29 samples and its standard deviation were 0.72 and 0.13 ppt. The increase in the mean value from February 1982 to December 1982 and February 1983 seems attributable mostly to the experimental uncertainties.

The background mixing ratios of SF_6 which were obtained in both this study and earlier works are shown in Fig. 2. The (a) value, which was obtained for the first time by Lovelock in 1970, was 0.03 ppt.[8] Observations after Lovelock have shown that the atmospheric SF_6 is increasing steadily.

The (b), (d), (g), (i), (j), and (l) values were obtained by aircraft observations. Except for the lower values of (e), (h), and (k), which were obtained in Antarctica or in the southern hemisphere, samples were obtained in the mid-latitude of the northern hemisphere. The values of this study((i), (j), and (l)) were in agreement with a higher value of Rasmussen and Khalil (0.75 ppt, (k)) which was obtained in the Pacific Northwest(≈45° N).[15]

The main sink for atmospheric SF_6 would be photodecomposition by solar ultraviolet radiation in the upper atmosphere. The rate of this process, however, must be very slow in the stratosphere, as SF_6 is photoionized only in the wavelength region below 81 nm.[16-18]

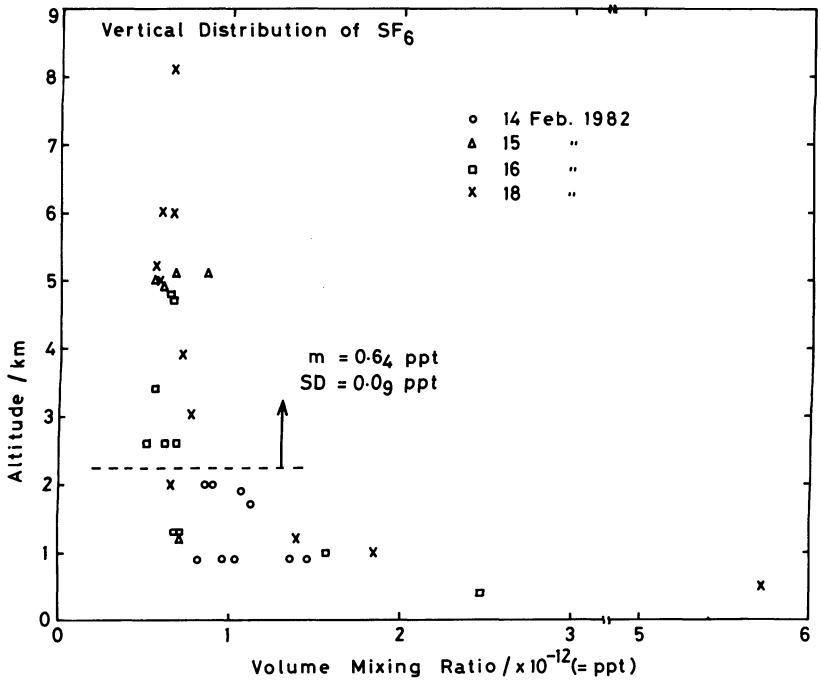

Fig. 1. Vertical distribution of SF_6.
Cessna 404 was used. Flight courses ranged from Sendai to Hachijo-jima.

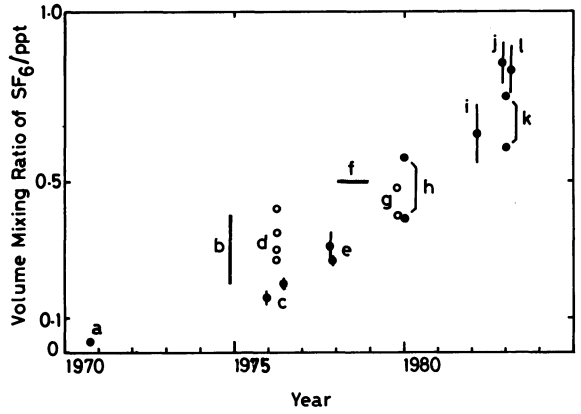

Fig. 2. Volume mixing ratios of SF_6.
○: individual value, ⊕: mean value and standard deviation.
In (b) and (f), only approximate values were reported. Individual values in (i) are shown in Fig. 1. In (j) and (l), samples were collected around Kanto Mts., and between Hamamatsu and Nii-jima.
(a): Lovelock,[8] (b): Elias et al.,[9] (c): Singh et al.,[10] (d): De Bortori and Pecchio.,[11] (e): Singh et al.,[12] (f): Pack et al.,[2] (g): Leifer et al.,[13] (h): Rasmussen et al.,[14] (i),(j), and (l): this study, (k): Rasmussen and Khalil[15].

The emission rate of SF_6 from gas-insulation instruments is not known. If the global mean mixing ratio is assumed to be about 0.5 ppt(≈1980), the total amount of SF_6 in the atmosphere is about 1.3×10^7 kg, assuming that the total air is 5.137×10^{18} kg.[19] The total world use was estimated to be 2.5—4.5×10^6 kg/year about 1980.[20] From these facts and also the development of SF_6 production since 1960's, a rather large part of the SF_6 may be supposed to have been released into the atmosphere in the several years since its production.

In this study, CF_2Cl_2 was used as the standard because a very dilute reference gas, such as SF_6, was not needed. However, the ratio in the senstivities of SF_6 and CF_2Cl_2 is not necessarily independent of the experimental conditions, and so further improvements are now in progress.

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