

Precise Determination of the Atmospheric CF₄ Concentration by Using Natural Kr in the Atmosphere as an Internal Reference in the Preconcentration/GC/MS Analysis

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For the precise determination of CF₄ in the atmosphere, the uniformly and constantly existing atmospheric krypton (Kr) was used as an internal reference because of its similar properties and behavior to CF₄ during the preconcentration processes and GC/MS analysis. The precision of the concentration measurement normalized with a Kr isotope was remarkably improved (to less than 1%) and the sample amount necessary was largely reduced to about one tenth.

Carbon tetrafluoride, CF₄, which is extremely stable with the strongest C–F bonds, is very inert in the atmosphere with the longest lifetime of 50000 years.¹ Its recent tropospheric concentration has been reported as 82 ± 8 pptv in the year 2000² with the increasing trend about 1 pptv/year.^{3,4} About half of the CF₄ in the troposphere has been reported as accumulated from the natural sources such as fluorite in the lithosphere.^{5–7} The rest has been believed to be released recently by the two significant anthropogenic sources: the production of primary aluminum and the use of fluorocarbons in the plasma etching process of semiconductor industry.

Since CF₄ has the extremely long atmospheric lifetime and strong infrared absorption due to C–F bond absorbance in the “atmospheric window” frequency region, CF₄ has been considered as one of the strongest greenhouse gases with the extremely large global warming potential such as 5700,⁸ resulted in the new regulation under the Kyoto Protocol adopted in December 1997 for the prevention of the global warming. On the other hand, CF₄ in the environment is expected as a useful tracer of the transport in the atmosphere and in the ocean, since their ages can be estimated from the correlation between the annual increasing trend and the distributions of CF₄ concentration.

The detection of CF₄ in the atmosphere is, however, extremely difficult due to its low atmospheric concentration and its low sensitivity to most detectors. On the other hand, its precise determination is necessary because of its small temporal trend and furthermore smaller distribution gradient due to its extremely long atmospheric lifetime. While the preconcentration of CF₄ in the atmospheric sample is inevitable due to these reasons, its boiling point is very low (–128 °C), which is close to the major components of the air, i.e., nitrogen, oxygen, and argon. Therefore, its collection has resulted in worse trapping efficiency or unreliable enrichment factor from air samples. The measurements of the atmospheric CF₄ concentration done so far are limited and contain large uncertainties such as several percents.^{2–4}

Considering these conditions, the highly efficient and reproducible preconcentration method was examined. In the course of the studies, we found that the Kr in the atmosphere (bp –153.6 °C) behaves very closely to the CF₄ during the separation and preconcentration processes with low-temperature ad-

sorption and desorption procedures. Since Kr is present permanently in the atmosphere ($1.14 \pm 0.01 \times 10^{-6}$),^{9,10} we were able to improve the precision of determination of the CF₄ concentration by using the Kr isotope peak as an internal reference in the GC/MS measurement.

A sample was introduced to GC/MS after it was enriched three times (preconcentration processes: collection process, purification process, and cryofocusing process) to remove the interfering major components before the introduction to GC. In the collection process, CF₄ and other trace gases in the atmospheric sample (at reduced pressure) are trapped in the first collection column (Tenax at liquid nitrogen temperature, 1/8-inch o.d., 30-cm long) while N₂, O₂, and Ar are not trapped and exhausted. The atmospheric sample is introduced very slowly by controlling the inlet pressure (at about 10 kPa) to avoid the condensation of liquid air or Ar.

Then the collected components in the first column is recovered by heating the column at 150 °C and transferred by helium flow to the next step. The second purification column (active alumina 80/100 mesh, 1/8-inch o.d., 20-cm long) kept at 150 °C can hold H₂O and CO₂, and other components pass through the second column to the third purification column (glass beads, 1/8-inch o.d., 30-cm long) cooled with liquid nitrogen, where the remaining N₂, O₂, and Ar are carried away by the helium flow. The target components (CF₄ and others including Kr) trapped in the third column are then heated with a hot dryer and transferred to the last cryofocusing column (Supel-Q Plot capillary, 0.53-mm i.d., 30-cm long) sunk in liquid nitrogen. The peak of the preconcentrated components broadened by the preceding purification process is sharpened by heating the last cryofocusing column with a hot dryer and was introduced into the GC/MS system.

Throughout this experiment, a new GC/MS system (Finigan Trace MS) was used by a combination with the above mentioned preconcentration system. The GC was equipped with the separation column of a CP-Silica PLOT column (0.53-mm i.d., 30-m long) and an Rts-5MS column (0.25-mm i.d., 5-m long) connected in series. The second column was introduced to meet the requirements for running MS. The separation column was held first at 32 °C for 10 min, and then raised at 10 °C/min up to the final temperature of 200 °C. The GC/MS was operated in selected ion monitoring (SIM) mode. The target ions mainly monitored were 69 for CF₄, and 80 for Kr-80. The carrier gas was helium with flow rate at 4.0 mL/min. The CF₄ and Kr detected in the blank measurements were much smaller than those in atmospheric samples and were negligible.

The CF₄ molecule consists of a carbon atom surrounded by four fluorine atoms and its chemical and physical properties are similar to rare gases. The molecular weight, boiling point and polarizability of CF₄ are very close to those of Kr, and they appear very closely in the GC/MS chromatogram. For these rea-

sons, Kr was selected to correct the collection efficiency of CF_4 and also calibrate the CF_4 peak area. Atmospheric Kr contains six stable isotopes of ^{78}Kr (natural abundance: 0.355%), ^{80}Kr (2.286%), ^{82}Kr (11.59%), ^{83}Kr (11.50%), ^{84}Kr (56.99%) and ^{86}Kr (17.28%),¹¹ and radioisotope ^{85}Kr (half life: 10.76 years). Since Kr is ten thousands times as abundant in the atmosphere as CF_4 , the peaks of other isotopes except ^{80}Kr and ^{78}Kr influenced CF_4 peak area. ^{80}Kr was used throughout this experiment due to its suitable peak size.

Although there have been no systematic studies on the distributions and the trends of stable Kr isotopes in the atmosphere, it has been considered that their global distributions are uniform and their long term trends are not observed. While the distribution and the trend of radioisotope ^{85}Kr , which is released during the reprocessing of spent nuclear fuels, have been studied extensively, its mass concentration is negligible small.

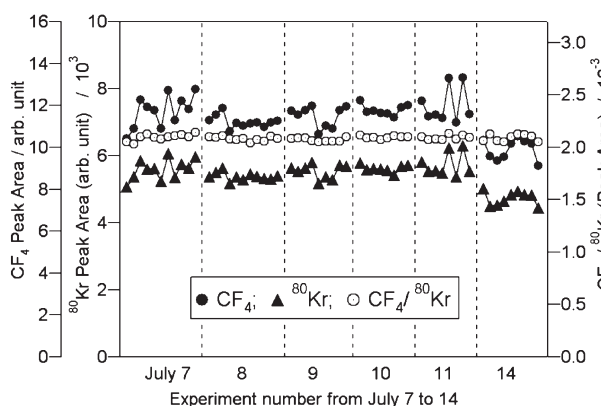


Figure 1. The changes of the GC/MS peak areas of CF_4 (●) and ^{80}Kr (▲) through a week, and those of ratios of peak areas $\text{CF}_4/^{80}\text{Kr}$ (○).

The measurement of a sample was repeated several times a day for a week to obtain the relationship between CF_4 and ^{80}Kr . Figure 1 shows the run to run change of peak areas of CF_4 and ^{80}Kr through a week, in which the averages of the relative standard deviations (RSD) for a day were 4.65 and 4.01%, respectively, and those for all the measurements through the week were 7.72 and 7.26%, respectively. Figure 1 also includes the peak area of CF_4 divided by that of ^{80}Kr as $\text{CF}_4/^{80}\text{Kr}$. The average of RSD for a day was fairly reduced to 1.09%; the RSD of all the measurements through the week was also extraordinary improved from several percents to 1.19%. The normalization of CF_4 peak area with that of ^{80}Kr attained much better RSD even if the CF_4 peak area (or sensitivity) changed in a week. This result indicates that the normalization by Kr stable isotope improves the CF_4 concentration measurements remarkably. The RSD mentioned above is not measurement precision since the experimental conditions such as sample amount, injection time, and column heating and cooling procedure were changed in this series of experiment.

Then, we investigated the measurement uncertainty of our method using natural air samples stored in cylinders. Table 1 shows an example of the result of the measurement repeated over a week on the atmospheric sample collected in Tokyo. Though RSD values of CF_4 concentration measurements with a conventional method using CF_4 calibration standards were several per-

Table 1. Atmospheric concentration (temporary values) and precision of CF_4 measurement (RSD: relative standard deviation) with a sample collected in Tokyo (on August 9th, 2003) in a metal flask

Measurement date Month/Date/Year	Conventional method		CF_4/Kr method	
	Conc. /pptv	RSD /%	Conc. /pptv	RSD /%
08/14/2003	82.14	4.24	79.75	0.97
08/18/2003	82.19	6.99	81.22	1.34
08/20/2003	80.70	4.82	80.83	0.49
08/21/2003	81.35	3.47	80.48	0.86
08/22/2003	83.55	4.73	81.16	0.96

cents, those with this CF_4/Kr method resulted in within 1%.

Not only the determination of the atmospheric CF_4 concentration was improved by introducing the $\text{CF}_4/^{80}\text{Kr}$ ratio measurement, such as from several percents to less than one percent, but also the sample volume necessary (60 mL) was largely reduced from the previous methods^{2,3} (300–600 mL) by the removal of interfering components at the improved preconcentration process and with much better precision, which makes many stored samples or volume-limited samples possible to be measured

When once the best correlation between CF_4 and Kr was established, the primary calibration standards which contain known ratios of CF_4 and Kr are able to give independent calibration standards for CF_4 concentration, if the atmospheric concentration of Kr 1.14 ± 0.01 ppmv^{9,10} is correct. However, the value of widely accepted 1.14 ppmv^{9,10} of Kr is originated from more than 50 years old unpublished data, and apparently different from our experimental value. We are now trying to determine separately more reliable accurate concentration of the atmospheric Kr.

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