The Concentration of Krypton in the Atmosphere —Its Revision after Half a Century—

Nobuyuki Aoki and Yoshihiro Makide*
Radioisotope Center, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-0032

(Received June 22, 2005; CL-050801)

During our attempt of the precise determination of trace gases in the atmosphere by using atmospheric krypton (Kr) as an internal standard, we noticed that the atmospheric Kr concentration of 1.14 ± 0.01 ppmv which had been quoted through half a century was different from the observation. The Kr concentration we obtained with three step concentration followed by GC/MS measurement was 1.099 ± 0.009 ppmv, about 4% lower than the currently used value.

Carbon tetrafluoride, CF_4, which consists of extremely stable C–F bonds corresponding to the longest atmospheric lifetime of 50,000 years, is almost the strongest greenhouse gas with an extremely large global warming potential such as 5700; resulted in the new regulation under the Kyoto Protocol adopted in December 1997 for prevention of the global warming. In our attempt of the precise determination of the atmospheric concentration of CF_4, we developed a new method using the atmospheric Kr as an internal reference.[1] Atmospheric Kr is believed to be uniformly distributed horizontally and vertically on the global scale with no temporal trend because it has neither source nor sink in the atmosphere.

Since the precise determination of CF_4 in the atmosphere is extremely difficult because its boiling point is very low (−128 °C) which is close to those of the major components of air, its preconcentration had resulted in worse trapping efficiency or unreliable collection factors from air samples. In the course of the studies, we found that the Kr in the atmosphere (bp −153.6 °C) behaved very closely to CF_4 during the separation and preconcentration processes with low-temperature adsorption and desorption procedures; the chemical and physical properties of CF_4 are very similar to those of Kr due to its molecular shape completely surrounded with fluorine atoms. Actually, CF_4 in the atmosphere had been detected for the first time in the Kr fraction separated from air.[2]

However, the concentration values of CF_4 directly obtained by comparing with prepared CF_4 standards showed clearly smaller ones than those based on the Kr concentration beyond the experimental errors when we used the widely accepted Kr concentration in the atmosphere of 1.14 ± 0.01 ppmv.[3,4] Therefore, we tried to determine the atmospheric concentration of Kr by modifying our measurement system to the Kr concentration determination also with several gravimetrically-prepared Kr primary standards.

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%);[5] the variation of their isotopic abundance in the atmosphere has never been reported. The Kr is mainly transported to the Earth's surface via volcanic activity from the mantle, while its emission is a negligible amount.

Table 1. Reported Kr concentration in the atmosphere

Investigators	Year	Kr Concentration
Moureu and Lapape[7]	1926	$1.0 \pm 0.1 \times 10^{-6}$
Damkolher[8]	1935	$1.08 \pm 0.10 \times 10^{-6}$
Glueckauf and Kitt[9]	1951	$1.14 \pm 0.01 \times 10^{-6}$
Glueckauf and Kitt[12]	1956	$1.139 \pm 0.01 \times 10^{-6}$
This Work	2004	$1.099 \pm 0.009 \times 10^{-6}$

Though the atmosphere also contains man-made radioactive ^{85}Kr (half life: 10.76 years), which is released mainly from the nuclear energy use, its absolute amount is negligible small ($^{85}\mathrm{Kr}/\mathrm{Kr} \approx 10^{-11}$) which does not affect the total Kr concentration, and the stable isotope abundance of Kr can be considered to be constant all over the world in the atmosphere.

The atmospheric Kr concentration was for the first time observed as about 1 ppmv more than 100 years ago by Ramsay and Travers.[6] Other groups reported the values about 30 years later[7,8] as shown in Table 1. The latest Kr concentration of value of 1.14 ± 0.01 ppmv was obtained by Glueckauf and Kitt and reported in 1951.[9] This unpublished value was quoted in the "U.S. Standard Atmosphere 1962"[4] and again in the "U.S. Standard Atmosphere 1976,"[3] then in most handbooks and textbooks.[10,11] Glueckauf and Kitt published later the Kr concentration as 1.139 ± 0.01 ppmv in 1956,[12] though the quotation has been limited.

For the method by Glueckauf and Kitt,[12] about 200 to 400 litter of air was used, since about 0.1 mL of Kr was necessary finally for the determination by the mercury gas bullet. They removed the air constituents except Kr by distillation and chemical reactions. The loss of the Kr during their enrichment processes was corrected by the radioactivity measurement of artificially added radioactive ^{85}Kr as a tracer. While their method was the latest in those days, it needed sophisticated and complicated separation processes. On the other hand, much smaller amount of air is enough in our measurement, which enabled us to attain more reproducible and reliable preconcentration and GC/MS determination.

In our measurement method, sample was concentrated three times (collection, purification, and cryofocusing) and then introduced to the GC/MS system. The Kr in samples was trapped initially in the first collection tube packed with Tenax at liquid nitrogen temperature at reduced pressure below 10 kPa, where major component of air such as N_2, O_2, and Ar were mostly exhausted. In the next step, the trapped components in the first column were flowed out at 150 °C with purified helium flow, and H_2O and CO_2 were captured with a purification column (Active Alumina) kept at 150 °C, then the remaining N_2, O_2, and Ar were removed with a column packed with glass beads at liquid nitrogen temperature using the difference of retention behavior in the column. Finally, the broaden peak by these

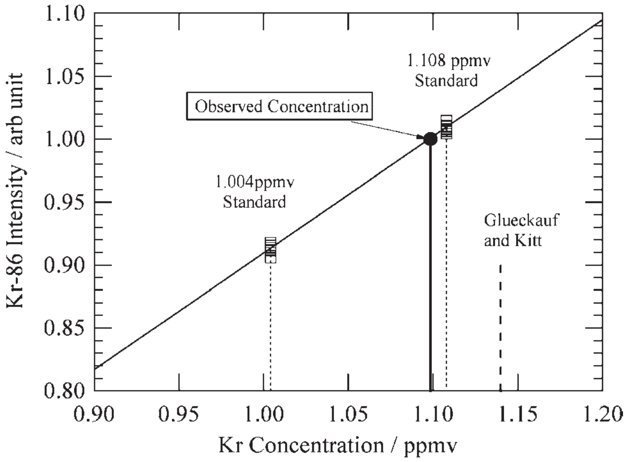

Figure 1. Determination of atmospheric Kr concentration by using two calibration standards. The concentration given by Glueckauf and Kitt (Refs. 9 and 12) is also indicated.

preconcentration processes was sharpen by the last cryofocusing capillary column (Supel-Q PLOT). The concentrated sample was analyzed with a newly installed GC/MS (Finnigan Trace MS). The GC/MS was operated at selected ion monitoring (SIM) mode and the target ions monitored were 84 and 86 for ^{84}Kr and^{86}Kr which are most abundant isotopes. The ion of 86 was mainly used for the determination of Kr concentration. Air sample volume introduced was 20 mL STP, which is about one ten-thousandth of that used by Glueckauf and Kitt.

The Kr concentration was determined by comparing the peak area of the sample air and that of the primary standards.

The accuracy of the whole measurements was obtained as follows. Precision of Kr peak measurement in the sample: 0.36%; Precision of Kr peak measurement in the standard: 0.59%; Accuracy of the pressure gage: 0.25%; Precision due to the variation of temperature: 0.17%. Since the several standards prepared separately gravimetrically and volumetrically showed similar results, the final determinative standards were prepared gravimetrically (with possible error of 0.09%; by Japan Fine Products Corporation) as 1.004 ppmv and 1.108 ppmv which are very close to the atmospheric Kr concentration. The final standards had been diluted with synthetic air in order to avoid the matrix effect by the difference between constituents of air samples and standards. We analyzed and confirmed that the oxygen used for dilution did not contain Kr. Figure 1 shows one of the calibration curves with peaks of Kr isotopes using the standards, which passes through the origin of the correlation. The responses of other isotopes and the linearity of the peak area to the introduced sample amount were examined and confirmed as well. The total accuracy thus obtained was estimated to be 0.76%.

In the present paper, the air samples analyzed were collected in Hokkaido (Japan), Syowa Station (Antarctica), and Tokyo (Japan). Each sample was analyzed three or five times and three samples at each location were measured.

Table 2 shows the atmospheric Kr concentration thus determined. The concentration of Kr in the atmosphere obtained by our measurement was 1.099 ppmv with the standard deviation of 0.004 ppmv from the nine samples. The difference among the locations was not observed.

Table 2. Obtained atmospheric Kr concentration

Location		Kr Concentration /ppmv	S.D.
Japan	Hokkaido	1.1008 1.0933 1.0995	0.0040
	Tokyo	1.0930 1.0996 1.0988	0.0036
Antarctica	Syowa Station	1.1009 1.0975 1.1047	0.0036
	Average	1.099	
	S.D.	0.004	

Considering the accuracy of our measurements, the global atmospheric Kr concentration was concluded to be 1.099 ± 0.009 ppmv, which is about 4% lower than that of 1.14 ppmv reported by Glueckauf and Kitt about 50 years ago and then quoted for half a century without any revision.

While isotope dilution method could be applied to the determination of atmospheric Kr concentration, it will not be easy because of the need of separation of more abundant noble gases in the atmosphere. Other GC methods need the quantitative pre-separation of Kr from the major components of the air with close properties, which is difficult as mentioned in this paper.

Therefore, we hope the value of 1.099 ± 0.009 ppmv will be widely accepted as the standard concentration of Kr in the atmosphere hereafter in reference books and textbooks.

References

1 N. Aoki and Y. Makide, *Chem. Lett.*, **33**, 1634 (2004).
2 M. Gassmann, *Naturwissenschaften*, **61**, 127 (1974).
3 "U.S. Standard Atmosphere 1976," Washington, D.C. (1976).
4 "U.S. Standard Atmosphere 1962," Washington, D.C. (1962).
5 Atomic Weights of The Elements: Review 2000 (IUPAC Technical Report), *Pure Appl. Chem.*, **75**, 683 (2003).
6 W. Ramsay and M. Travers, *Proc. R. Soc.*, **A63**, 405 (1898).
7 L. Moureu and A. Lepape, *Compt. Rend.*, **183**, 171 (1926).
8 V. G. Damköhler, *Z. Elektrochem.*, **41**, 2, 171 (1935).
9 T. F. Malone, "Compendium of Meteorology," American Meteorological Society, Boston (1951), p 5.
10 M. Ozima and F. A. Podosek, "Noble Gas Geochemistry," 2nd ed., Cambridge University Press, Cambridge (2002), p 11.
11 "CRC Handbook of Chemistry and Physics," 83rd ed., CRC Press, Florida (2002), p 14.
12 E. Glueckauf and G. P. Kitt, *Proc. R. Soc.*, **A234**, 557 (1956).