Determination of triple oxygen isotopic compositions of atmospheric nitrous oxide by using continuous-flow isotope ratio MS

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The triple oxygen isotopic compositions ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) of nitrous oxide (N_2O) in atmosphere can be a useful tracer to clarify their sources and N cycles in atmosphere. The triple oxygen isotopic compositions of N_2O have been usually determined by using conventional IRMS system using O_2 molecule converted from N_2O through multiple reaction/purification steps. The traditional methods, however, required at least 1-100 10^3nmol quantities of N_2O so that applications of the methods to various environmental N_2O samples were difficult. Thus, we developed a rapid and sensitive analytical system to determine the triple oxygen isotopic compositions of N_2O in nmol quantities using continuous-flow IRMS (CF-IRMS) without the cumbersome and time-consuming pretreatments. We cannot determine $^{17}O/^{16}O$ ratio of N_2O directly by measuring the masses 44, 45, and 46 of N_2O introduced to IRMS, because the measured output of mass 45 from IRMS consists of $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, and $^{14}N^{14}N^{17}O$. Thus, addition to the N_2O isotopic analysis at the masses 44, 45, and 46, the $^{15}N/^{14}N$ ratio is determined separately for the same sample N_2O. To attain this purpose, two instrumental approaches were done. In the first system, the N_2^+ fragment ion beams of N_2O at masses 28 and 29 were used to determine the ^{15}N /^{14}N ratio of N_2O. While the analytical precisions better than 0.5 per mil for 20 nmol N_2O injections and better than 1.0 per mil for 7 nmol N_2O injections were obtained for 15N/14N ratio, we found that the accuracy strongly depended on the quantities introduced. In the second system, the N_2 molecules, converted from N_2O using an on line Cu reduction furnace (720 degree) was used to determine the $^{15}N/^{14}N$ ratio of N_2O. The analytical precisions better than 0.1 per mil for 5 nmol N_2O injections and better than 0.4 per mil for 1 nmol N_2O injections were obtained for $^{15}N/^{14}N$ ratio with stable accuracy irrespective of the quantities introduced. Thus, we introduced N_2 and N_2O to CF-IRMS repeatedly by using an automatic multi-injection system to improve analytical precision statistically, so that the analytical precisions in the $^{17}O/^{16}O$ ratio of N_2O and nitrate better than 1.0 per mil for 100 nmol injections and better than 4.0 per mil for 20 nmol injections were obtained. Besides to N_2O, we can also apply the method to determine the triple oxygen isotopic composition of nitrate based on the isotopic analysis of N_2O quantitatively converted from nitrate through the simple reactions using spongy cadmium and sodium azide in an acetic acid buffer. We present the triple oxygen isotopic compositions of N_2O and nitrate in atmosphere determined by using this system.