Examination of analytical accuracy of GC/IRMS: Nitrogen isotopic composition of ^{15}N-enriched amino acids

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Nitrogen consists of two stable isotopes (^{14}N: 99.63% and ^{15}N: 0.37%). The ratio of $^{15}N/^{14}N$ is expressed as $\delta^{15}N$ notation in per mill (‰) relative to the standard ratio in terrestrial atmospheric air (Air). The variation of $\delta^{15}N$ in the terrestrial materials generally falls within ±20‰, but even such little variations tell us a lot of information for studying environmental and physicochemical processes that the molecules has experienced. Unlike the terrestrial materials, extraterrestrial materials, especially pristine solar system materials such as comets and chondrites, exhibit extremely high $\delta^{15}N$ values more than +1000‰ [e.g., 1], and even +5000‰ as a nanometer scale materials (which is called a hot spot [e.g., 2]).

However, there are problematic issues on the analytical accuracy in calculating the $\delta^{15}N$ values of such ^{15}N-enriched materials, because the conventional $\delta^{15}N$ analysis has been developed for measuring the ratio in terrestrial materials and focusing very little amount of ^{15}N (˜0.4%) in them. For the $\delta^{15}N$ analysis by gas chromatography / isotope-ratio mass spectrometry (GC/IRMS), the nitrogen in the organic materials are converted to N_2. There are three combinations of the nitrogen isotopes: $^{14}N≡^{14}N$ (*m/z* 28), $^{15}N≡^{14}N$ (*m/z* 29), $^{15}N≡^{15}N$ (*m/z* 30). Among these three combinations, it is assumed that the existence of $^{15}N≡^{15}N$ (*m/z* 30) are negligible, because the amount of ^{15}N on the Earth is very small against that of ^{14}N. On the other hand, the applicability of this assumption has not been examined to the isotope analysis of ^{15}N-enriched materials. If $^{15}N≡^{15}N$ are produced significantly in the analytical procedure, the $\delta^{15}N$ calculation will include a large uncertainty.

To examine the accuracy in the $\delta^{15}N$ analysis for ^{15}N-enriched materials, we evaluate the GC/IRMS results for several ^{15}N-labelled amino acid samples. The samples were prepared by mixing ^{15}N-labelled and non-labeled amino acids, resulting in a variation in the $\delta^{15}N$ value from 0‰ to +1000‰ based on the mathematical calculation from the mixing ratios. The amino acid samples were then derivatized and analyzed by GC/IRMS, according to the standard procedure [3]. The results reveals that the measured $\delta^{15}N$ values certainly deviate from the calculated $\delta^{15}N$ values, with a linear relationship between the $\delta^{15}N$ values and the deviation: the deviation is close to zero for the 0‰ samples but reaches ˜ +90‰ for the +1000‰ sample accompanied by *m/z* 30 signals on the GC extracted ion chromatograms. This deviation would be critical to understand the physicochemical processes occurring in the extraterrestrial environments. These results demonstrate the importance of the inclusion of the *m/z* 30 signal area for the calculation of the $\delta^{15}N$ values of ^{15}N-enriched materials. Further detailed studies including memory effects [4] are necessary to investigate the factors on potential inaccuracy to form $^{15}N≡^{15}N$ during GC/IRMS analysis.

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