Technology

Analysis of Oxygen Isotope Ratio with Multi-Turn Time-of-Flight Mass Spectrometer

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1. Introduction

Taiyo Nippon Sanso developed the world's first stable oxygen isotopes (^{17}O, ^{18}O) enrichment technology using oxygen distillation[1], and manufactures and sells isotope enriched water and oxygen gas, as well as isotope-labeled compounds from those. An accurate understanding of the ^{17}O and ^{18}O concentrations is an important element in quality assurance and evaluating the performance of production equipment. Quadrupole mass spectrometers are mainly used to acquire and calculate the concentration of the mass spectrum m/z = 32 to 36 (the dimensionless quantity that is acquired by dividing the mass of ions per unified atomic mass unit by the number of ion charges). However, the difference in mass between ^{16}O^{18}O and ^{17}O$_2$ (oxygen isotopologue) is extremely small at 0.004 Da so it cannot be directly separated and detected. When these concentrations must be known accurately, the isotope composition is probabilistically calculated from the oxygen molecules generated by water electrolysis (hereafter referred to as the "current method") [2]. This method is accurate in principle, but when the oxygen gas is analyzed, an additional process is necessary to convert it to water. This makes operation complicated and the analysis equipment also becomes larger. Therefore, we considered a method to measure isotope concentration by directly separating and detecting ^{16}O^{18}O and ^{17}O$_2$ in oxygen gas.

2. Analysis Unit

We selected a TOF-MS (time of flight mass spectrometer) unit as the best for separating and analyzing material with extremely small mass differences . The measurement principles of the TOF-MS are as follows. First, ion molecules are accelerated in a constant electric field, then sent flying a constant distance to the detector. Because the velocity of the ion molecules is different per m/z, the time it takes to reach the detector

is different. The various types of ion molecules can be separated and detected by this time difference.

There are TOF-MS units that do not have straight-line flight routes to the detector, and we selected a TOF-MS unit that uses an multi-turn system (JEOL Ltd., model JMS-MT3010HRGA (Figure 1)). Units using multi-turn system can increase their flight distances with each additional turn so that the time difference until their detection is widened and it is possible to separate milli-mass level differences. Also, the units are as small as a desktop PC, which makes it easier to install them in a factory.
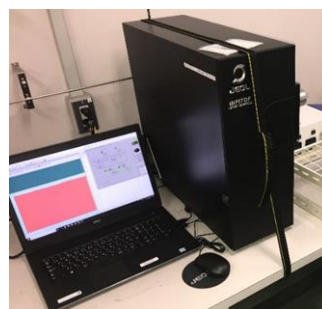

Figure 1. Multi-turn time-of-flight mass spectrometer

3. Analysis Performance Assessment

In making a quantitative assessment of oxygen isotope concentration using a TOF-MS unit, we first confirmed the peak detection for ^{16}O^{18}O and ^{17}O$_2$. The sample gas we used is generated by electrolyzing the ^{17}O-labeled water (Water-^{17}O) that we produce and sell.

3.1 ^{16}O^{18}O and ^{17}O$_2$ Mass Separation

Upon executing peak separation detection using the TOF-MS unit, in addition to the peaks of the five components m/z = 32 to 36, ^{16}O^{18}O and ^{17}O$_2$ of m/z = 34 were also separated and detected (Figure 2), so we found that the concentrations of six oxygen isotopes were quantifiable.
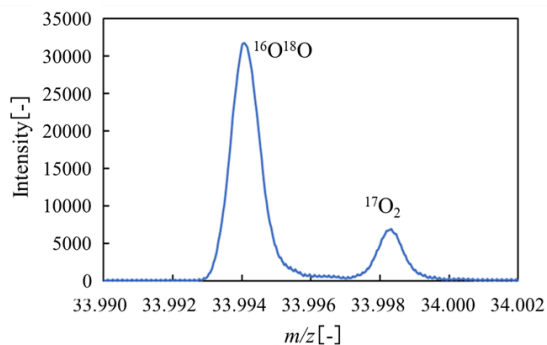
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Figure 2. Mass spectra of $^{16}O^{18}O$ and $^{17}O_2$

3.2 Analysis Trueness

Generally, analysis trueness is assessed with the calibration curve method using a standard sample with a known concentration. However, natural abundance oxygen (^{16}O: 99.757, ^{17}O: 0.038, ^{18}O: 0.205 atom%) [3] deviates considerably from the concentration of the samples enriched ^{17}O and ^{18}O. Moreover, because standard samples with high isotope concentration do not exist, assessment with the calibration curve method is not possible. Therefore, we prepared a sample quantified with the current method [2] that was put through electrolysis from our Water-^{17}O, and another company's oxygen isotope sample. By doing this, we were able to assess the trueness of two samples with different isotope concentrations by mutually comparing the TOF-MS analysis values.

3.2.1 Comparison using Water-^{17}O

First, we analyzed the oxygen gas produced by electrolysis of Water-^{17}O with the TOF-MS unit. The results matched after comparing the concentrations of the five components m/z = 32 to 36 with measured values from the current method (Table 2). Next, we also calculated the atomic concentration from a total of six oxygen isotope components that are composed of the separated and analyzed m/z =34 ($^{16}O^{18}O$ and $^{17}O_2$) and the four components m/z = 32, 33, 35, 36. When comparing with the current method, we found that each of the atomic concentration deviations was within ±0.21 atom% which was a satisfactory result (Table 3). The isotope composition of oxygen molecules acquired from electrolysis is determined probabilistically, and because the atomic concentration measurement results from the TOF-MS unit and current method matched, it can be

determined that the TOF-MS unit accurately analyzed the component concentrations of six oxygen isotopologues.

Table 2. Comparison of oxygen isotopologue concentration in Water-^{17}O

m/z	Component	TOF-MS value	Current method	Deviation
		Concentration of oxygen isotopologues (%)		
32	$^{16}O_2$	1.87	1.84	0.03
33	$^{16}O^{17}O$	3.93	3.91	0.02
34	$^{16}O^{18}O$	18.78	21.08	-0.43
	$^{17}O_2$	1.87		
35	$^{17}O^{18}O$	20.76	20.85	-0.09
36	$^{18}O_2$	52.79	52.32	0.47

Table 3. Comparison of oxygen isotope atom concentration in Water-^{17}O

Component	TOF-MS value	Current method	Deviation
	Oxygen isotope concentration(atom%)		
^{16}O	13.22	13.16	0.06
^{17}O	14.22	14.43	-0.21
^{18}O	72.56	72.41	0.15

3.2.2 Comparison of isotope concentration in Another Company's Oxygen Isotope Sample

We analyzed another company's oxygen isotope sample in the same manner with the TOF-MS unit. We calculated the atomic concentration from six components of the oxygen isotopologues. Table 4 shows the results of comparing them with the other company's analysis results (the analysis method is not known). Each of the atomic concentration deviations is within ±0.58 atom%.

Table 4. Comparison of oxygen isotope atomic concentration with another company's sample

Component	TOF-MS value	Other company's values	Deviation
	Oxygen isotope concentration(atom%)		
^{16}O	23.57	23.56	0.01
^{17}O	70.98	70.52	0.46
^{18}O	5.44	6.02	-0.58

3.3 Analysis Precision

To assess the precision of the analyses, Table 5 shows

the calculated standard deviation for short-term repeatability and long-term three-day reproducibility (acquired 5 data per day). Water-^{17}O was used for the samples. The repeatability was 0.09 to 0.56 atom% and the reproducibility was 0.28 to 0.41 atom%. Both ranges are sufficiently accurate to assess isotope concentration.

Table 5. Repeatability and reproducibility

| | | Oxygen isotope concentration(atom%） | | |
		^{16}O	^{17}O	^{18}O
Day1	Average value	13.14	14.43	72.44
	Standard deviation	0.21	0.09	0.23
Day2	Average value	13.15	14.06	72.8
	Standard deviation	0.31	0.36	0.56
Day3	Average value	13.39	14.17	72.44
	Standard deviation	0.30	0.42	0.33
Total	Average value	13.22	14.22	72.56
	Standard deviation	0.28	0.34	0.41

4. Summary

We used a TOF-MS unit to separate and detect the peaks of ^{16}O^{18}O and ^{17}O$_2$ to measure the concentration of six isotope components in oxygen gas. The trueness and precision of analysis were found to be good so we confirmed that TOF-MS units have the performance to accurately analyze oxygen isotopes.

Reference
1) Hayato SAKURAI, Hitoshi KIHARA, Takashi KAMBE; Development of Distillation and Separation Technology for Oxygen Stable Isotope ^{17}O, Taiyo Nippon Sanso Technical Report, 2019, No. 38, pp. 1-5
2) Hidetoshi YOSHIDA, Highly precision Water-^{17}O Oxygen Isotope Analysis, Taiyo Nippon Sanso Technical Report, 2019, No. 38, pp. 6-7.
3）M. Berglund, M. E. Wieser. Isotopic Compositions of the Elements 2009. Pure Appl. Chem. 2011, 83, p.397-410.