Estimation of Mass Discrimination Factor for a Wide Range of *m/z* by Argon Artificial Isotope Mixtures and NF₃ Gas

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Absolute isotope ratio is a critical constituent in determination of atomic weight. To measure the absolute isotope ratio using a mass spectrometer, mass discrimination factor, f_{MD}, is needed to convert measured isotope ratio to real isotope ratio of gas molecules. If the f_{MD} could be predicted, absolute isotope ratio of a chemical species would be measureable in absence of its enriched isotope pure materials or isotope references. This work employed gravimetrically prepared isotope mixtures of argon (Ar) to obtain f_{MD} at *m/z* of 40 in the magnetic sector type gas mass spectrometer (gas/MS). Besides, we compare the nitrogen isotope ratio of nitrogen trifluoride (NF₃) with that of nitrogen molecule (N₂) decomposed from the same NF₃ thermally in order to identify the difference of f_{MD} values in extensive *m/z* region from 28 to 71. Our result shows that f_{MD} at *m/z* 40 was −0.044 % ± 0.017 % ($k = 1$) from measurement of Ar artificial isotope mixtures. The f_{MD} difference in the range of *m/z* from 28 to 71 is observed −0.12 % ± 0.14 % from NF₃ and N₂. From combination of this work and reported f_{MD} values by another team, IRMM, if f_{MD} of −0.16 % ± 0.14 % is applied to isotope ratio measurement from N₂ to SF₆, we can determine absolute isotope ratio within relative uncertainty of 0.2 %.

Key Words : Atomic weight, Absolute isotope ratio, Mass spectrometer, Mass discrimination factor, Artificial isotope mixture

Introduction

Atomic weight, the basic physical property of elements, has been reported by numerous research groups. International Union of Pure and Applied Chemistry (IUPAC) has reviewed reported values from past and present, and published biennial reports on standard atomic weights of various elements.[1] Atomic weight of an element is determined by two components: isotope abundance and their atomic masses. With the current advances in instrumentation, the atomic mass could be measured within a relative uncertainty of 1×10^{-7}, whereas the isotope abundance has large relative uncertainty of 1×10^{-3}.[2] Isotope abundance is computed by absolute isotope ratios.

Nowadays, needs for more precise atomic weight are growing in variety of scientific research fields, such as for preparation of reference gas mixtures by gravimetric method,[3,4] for correction of the buoyancy effect on the comparison of mass standards in air,[5,6] for precise determination of the triple point temperature of neon (Ne) and the Avogadro constant using silicon single crystals,[7,8] and for re-defining the International System (SI) unit of temperature, the Kelvin, by acoustic technique.[9]

In gas metrology, the molecular weight of a source gas is crucial constituent in gravimetric technique. Gravimetry is the primary method for preparation of reference gases.[3,4] In the international comparison on gravimetry organized by Gas Analysis Working Group of Consultative Committee for Amount of Substance (CCQM GAWG), it is found that isotope variation of reference gases can remarkably affect to the measurement value.[10,11] For this reason, it is recommended to check or verify the isotopic composition of source gases.

To measure the isotope ratio, a mass spectrometer is generally used. In the mass spectrometric measurement, the mass discrimination effect presents in the instrument must be identified and applied to the results.[12] The most common way for determination of mass discrimination factor (f_{MD}) is to employ isotopic reference materials. In 1950, Nier measured isotope ratios of five elements including atmospheric nitrogen, oxygen and argon (N₂, O₂, and Ar).[13] In order to determine the f_{MD} of the mass spectrometer, he employed single isotope reference, which was prepared by volumetrically mixing of ³⁶Ar and ⁴⁰Ar isotope enriched gases. Recently, a research team of Institute for Reference Materials and Measurements (IRMM, Belgium) of European Commission investigated f_{MD} values of the mass spectrometer (which is called Avogadro II Amount Comparator) using several kinds of isotope mixtures.[14-18] In 1996, De Bièvre *et al.* suggested a theoretical and experimental correction value for N₂ isotope ratio measurement based on gas kinetics in the Avogadro II mass spectrometer without any isotope reference material.[19]

Recently, the precision of gravimetric preparation for reference gas mixtures reached the level of 0.02 %.[4] If isotope enriched gases are available, isotope mixtures can be prepared and employed to determine the f_{MD}. In the real experimental fields, isotopic enriched gases with required component are not readily available, and not many laboratories have a gravimetric preparation system for isotope references.

If the f_{MD} is predictable over a wide range of mass-to-charge ratio (m/z) with mass dependent property, a mass spectrometer can be used conveniently to determine the absolute isotope ratio of various elements.

This work studied whether the f_{MD} is constant over a wide range of m/z in a magnetic sector type mass spectrometer with a molecular flow gas inlet system. If in that case, the f_{MD} obtained from single specific isotope reference within a certain m/z range can be used to convert from the measured isotope ratio (such as ion current ratio) to the real absolute isotope ratio. The gravimetrically prepared Ar isotope gas mixture was used to determine the f_{MD} at m/z of 40. In addition, the nitrogen ion current ratio of nitrogen trifluoride (NF$_3$) gas which has mono-isotopic fluorine atom was compared to that of N$_2$ gas obtained from thermal decomposition of the NF$_3$ in order to check the difference of f_{MD} values at m/z of 28 and 71.

Experimental

Preparation of Isotope Mixtures. To determine the f_{MD} in the mass spectrometer, Ar isotope mixtures, one of the most stable gas species, was prepared using the gravimetric technique. In addition, Ar is a mono-atomic molecule, any ion exchange during the ionization process by the electron impact do not occur. Therefore, Ar isotope gas mixture is suitable to directly observe the f_{MD} inside the mass spectrometer. In gas metrology, gravimetry is used as the primary method to produce a reference gas mixture.[3,4] Hence if isotope enriched gases are mixed using this method, very precise isotope gas mixtures can be prepared. The molar mass and weight of two isotope enriched gases (A and B) are used to calculate the mole fraction of i isotope (x_i) of the gravimetrically prepared gas mixture in Eq. (1).

$$x_i = \frac{n_{i,A} + n_{i,B}}{n_A + n_B} = \frac{x_{i,A} \times \frac{m_A}{M_A} + x_{i,B} \times \frac{m_B}{M_B}}{\frac{m_A}{M_A} + \frac{m_B}{M_B}} \quad (1)$$

where, $n_{i,A}$ and $n_{i,B}$ are moles of i isotope, and n_A and n_B are total moles, introduced from two parent gases of A and B, respectively. Additionally, $x_{i,A}$ and $x_{i,B}$ represent mole fractions of i isotope, m_A and m_B are masses determined by weighing, and M_A and M_B are molar masses of source gases. As seen in Eq. (1), vital components in gravimetric technique are abilities to measure the mole fraction and to weigh the

mass of source materials. The gravimetric system used here is described in detail in previous works.[5,20]

Argon is the most abundant noble gas in the atmosphere, and exists as three stable isotopes in nature, ^{36}Ar, ^{38}Ar, and ^{40}Ar. In this work, only ^{36}Ar and ^{40}Ar were measured due to their relatively large peaks of artificially prepared Ar isotope mixtures. Any impurities which are overlapped with Ar ion peaks at m/z of 36 and 40 were not detected in the Ar isotope mixtures. The source materials of Ar isotope mixtures were 99.999 % of pure Ar gas (Deokyang Co. Ltd., Rep. of Korea) and two kinds of Ar isotope enriched gases (^{36}Ar > 99.5 %, ^{40}Ar > 99.95 % from Oak Ridge National Laboratory, USA). The purity of the source materials was assessed using the gas/MS, as presented in Table 1. The initial abundance of each isotope of Ar source gases was corrected by the f_{MD} determined using isotope gas mixtures after being prepared and validated. The cylinders used for the gas mixtures were made of aluminum. The volumes of cylinders were 75 mL (Swagelok, USA) for R1 and R2, 6 L (Luxfer, Australia) for R3. Pressures of Ar isotope mixtures, R1, R2 and R3 were approximately 0.8 MPa, 8 MPa, and 0.3 MPa, respectively. After preparation, the isotope mixtures were allowed to undergo rotation for an hour to improve the homogeneity. As expected, no chemical reaction or adsorption effect inside the cylinders or the instrument was found due to the stable nature of Ar.

The gravimetrically prepared isotope ratio, R(^{40}Ar/^{36}Ar), of each Ar isotope mixture is 2.8251 ± 0.0026, 39.596 ± 0.037, and 330.30 ± 0.34 for R1, R2 and R3, respectively, and shown in Table 2. The uncertainty in this paper is expressed as a standard uncertainty ($k = 1$) and numbers in the parenthesis in the tabled values indicate standard uncertainties in the last digit. Major uncertainty factors in gravimetric isotope ratios were isotopic impurity of source materials and reproducibility in weighting. The uncertainty in the isotope ratio was evaluated by the GUM Workbench Pro software (Version 2.3.6.141). Especially, Ar isotope mixtures (R1, R2 and R3) have been used for the research on redetermination of the isotopic abundance of atmospheric Ar.[20]

Mass Spectrometer. The gas mass spectrometer (gas/MS, Finnigan MAT271, Thermo Scientific, Germany) employed in this work is a single focusing magnetic sector type mass spectrometer with a molecular flow gas inlet system. Recently, the gas/MS was used to determine neon isotope abundances of artificial isotope mixtures as a part of neon International Project named 'Euromet Project 770' mainly organized by

Table 1. Composition of Ar source gases (This table is cited from Lee *et al.*[20])

Source gases	Mole fraction of Ar isotopes and impurities (mmol/mol)									
	^{36}Ar	^{38}Ar	^{40}Ar	H$_2$	He	CH$_4$	CO$_2$	O$_2$	N$_2$	H$_2$O
Normal Ar	3.291 (4)	0.634 (4)	995.947 (7)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002 (1)	0.013 (4)
^{36}Ar enriched	998.15 (5)	0.775 (3)	0.112 (3)	0.32 (2)	0.40 (3)	< 0.001	0.006 (2)	0.008 (2)	0.17 (1)	0.05 (2)
^{40}Ar enriched	0.273 (3)	0.163 (3)	999.486 (9)	0.009 (4)	< 0.001	0.004 (2)	0.049 (5)	< 0.001	0.013 (3)	0.003 (2)

*Numbers in parenthesis indicate the standard uncertainties in the last digit ($k = 1$). *A mole fraction entry such as < 0.001 mmol/mol indicates the detection limit of the instrument used, gas/MS.

Table 2. Gravimetric mixing of Ar isotope mixtures and their real isotope ratio (This table is cited from Lee *et al.*[20])

Isotoe mixtures	Weight of source gases (g)			Mole of Ar isotopes (mmol)		Real isotope ratio, R ($^{40}Ar/^{36}Ar$)
	Normal Ar	^{40}Ar enriched	^{36}Ar enriched	^{40}Ar	^{36}Ar	
R1	0.718 45 (20)	/	0.2262 (2)	17.913 (5)	6.341 (6)	2.8251 (26)
R2	9.619 98 (20)	/	0.1896 (2)	239.847 (6)	6.057 (6)	39.596 (37)
R3	/	33.0394 (20)	0.081 98 (3)	826.378 (51)	2.502 (3)	330.30 (34)
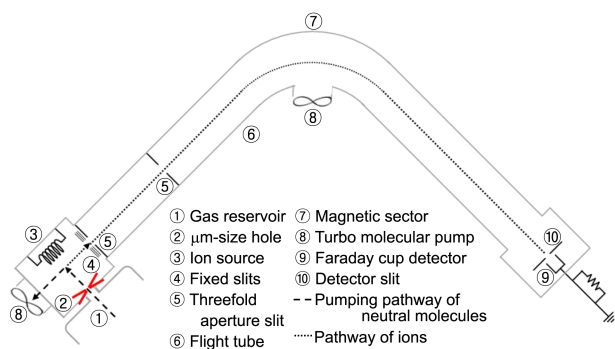
Figure 1. Schematics of MAT271 gas mass spectrometer with the neutral and ion travel path.
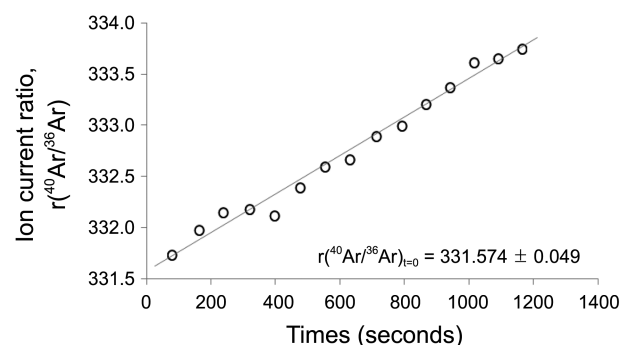
Figure 2. Regression curve of ion current ratio on ^{40}Ar over ^{36}Ar.

INRIM (Istituto Nazionale di Ricerca Metrologica, Italy).[21] Also it is the same model with mass spectrometer (Avogadro II Amount Comparator) employed to measure isotope ratios in 'Avogadro Project' conducted by IRMM.[22]

Figure 1 shows the schematics of gas/MS used in this work. A gas sample with pressure greater than 0.1 MPa was directly connected to the inlet system using a VCR fitting (1/4" stainless steel, HYLOCK). Then the sample was injected into the gas reservoir with a Baratron pressure gauge of 10 Pa (①). To reduce molecular adsorption and to stabilize the speed of molecules, the temperature of gas reservoir was set to be (60.0 ± 0.1) °C by implementing a heater. A gold plate (②) with a μm-size orifice was placed between the gas reservoir and ionization chamber to allow the effusion of gas with molecular flow. The gas pressure in the ionization chamber was controlled not to exceed 1×10^{-4} Pa during measurements. A tungsten filament was used as an ionization source (③). The emission current of filament and electron energy were 50 μA and 100 eV, respectively. Ionized molecules were accelerated by high voltage of 8 kV towards the flight tube. To improve stability of our measurement, we properly adjusted a set of ion beam slits (④ and ⑤) in order to ion beams were maintained homogeneous with low resolution. From this condition, we could obtain sufficient data point at the top plateau of each ion peak. To prevent neutral molecules to collide with the ion, a separated turbo molecular pumps (⑧) were attached to the ionization chamber and flight tube (⑥) and keep the internal pressure below 1×10^{-5} Pa. Single Faraday cup detector (⑩) was used with 1×10^{10} Ω of resistance to ion current measurements.

Isotope Ratio Measurement. The ion current measured by the MAT271 gas/MS is proportional to the number of molecules effused from the inlet gas reservoir. When isotopes transfer from the gas reservoir to the ionization chamber, they have molecular flow governed by kinetic gas theory. During effusion, the speed of isotope depends on the square root of its atomic mass. In other words, lighter isotope effuses to ionization chamber faster than heavier isotope. So the ion current ratio of two isotopes, r(i/j), where $m_i > m_j$, increases with time as shown in Figure 2. It was proven with numerous reports from IRMM researchers that mass discrimination effect during the effusion process in the gas/MS agrees well with the theoretical projection by gas kinetics.[22-24] The gas/MS used in this work (located at Korea Research Institute of Standards and Science, KRISS) shows the same characteristic with IRMM's instrument.

The r(i/j) was measured through symmetric method,[25] and analyzed by simple linear regression method with elapsed time. The r(i/j) at time zero, r(i/j)$_{t=0}$, was used as a measured isotope ratio. Figure 2 shows an example of Ar isotope measurement of R3 mixture. The uncertainty of r(i/j) was calculated from noise of ion currents and deviations from duplicated measurements. The ion current for each isotope was measured over 15 times during approximately 20 minutes for single run.

Nitrogen Isotope Ratios in NF_3 and its Decomposed N_2. To measure the nitrogen isotope ratio at different *m/z* positions, we used NF_3 and N_2 gas decomposed from the same NF_3 gas. Since the fluorine atom in NF_3 is a mono-isotopic element, the r(i/j) of NF_3 depends on the isotope ratio of nitrogen in NF_3. So from the comparison of r(i/j) between NF_3 and N_2 decomposed from the same NF_3 gas, we can investigate whether f_{MD} values are constant at different *m/z* positions of 28 and 71. Each isotope ratio was measured more than two times independently.

In the gas/MS, molecules are effused to the ionization

chamber, and fragmented by electron impact. From NF_3 molecules, a set of fragmentation ions including NF_3^+, NF_2^+ and NF^+ are produced. In this work, the r(i/j) of NF_3 was obtained from three fragmented ions with significant peak heights; NF^+ (*m/z* of 33 and 34), NF_2^+ (*m/z* of 52 and 53), and NF_3^+ (*m/z* of 71 and 72).

To obtain N_2 from NF_3 gas, we applied thermal decomposition method.[26,27] Copper chips and 0.05 MPa of NF_3 gas (> 99.99 %, Hankook Special Gases Co. Ltd., Rep. of Korea) were placed inside a Pyrex tube, and heated to approximately 500 °C. During the reaction, the tube was carefully shaken and blended to prevent any mass discrimination effect to the sample. After 20 minutes of reaction, it was confirmed that more than 80 % of NF_3 had been converted into N_2 gas. To remove by-products of the reaction, mostly SiF_4, the Pyrex tube was treated with liquid oxygen to separate N_2 from gas sample. For N_2 isotope ratio measurement, N_2^+ ion was only used because the abundance of N_2^+ peak accounted for above 90 % among all nitrogen ions including doubly charged and fragmented ions.

Mass Discrimination Factor. The factor to correct the mass discrimination effect, f_{MD}, can be calculated from Eq. (2).

$$f_{MD}(\%) = \left(\frac{R(i/j)_{ref}}{r(i/j)_{ref}} - 1\right) \times \frac{100}{\Delta m} \qquad (2)$$

where, $\Delta m = m_i - m_j$, $(m_i > m_j)$

$$R(i/j)_{sp} = \left(\frac{f_{MD}}{100} \times \Delta m + 1\right) \times r(i/j)_{sp} \qquad (3)$$

In Eq. (2), i and j represent the isotopes those masses of m_i and m_j, and $R(i/j)_{ref}$ and $r(i/j)_{ref}$ are the real isotope ratio and measured isotope ratio of the isotope reference material composed of isotopes, i and j. Δm represents the mass difference in the two isotopes and has been included in the calculation of f_{MD} to address the previous reports that mass discrimination is generated with mass dependency from a variety of origins.[28,29] The obtained f_{MD} using the reference material is then used to convert the unknown sample's measured isotope ratio, $r(i/j)_{sp}$, to real isotope ratio, $R(i/j)_{sp}$, shown in Eq. (3). Often, the mass discrimination correction factor is noted by K, as shown in Eq. (4).[12,14-18]

$$K = \frac{R(i/j)_{ref}}{r(i/j)_{ref}} \qquad (4)$$

Results and Discussion

f_{MD} from Ar Isotope Mixtures. The mass discrimination factor, f_{MD}, obtained by gas/MS measurement of each Ar
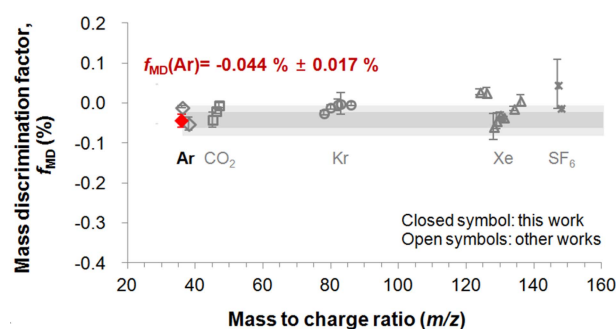

Figure 3. Mass discrimination factors, f_{MDS}, reported in this work and other studies (Closed symbols: Ar in this work, Open diamond: Ar from Valkiers *et al.*,[14] open square: CO_2 from Valkiers *et al.*,[15] open circle: krypton (Kr) from Aregbe *et al.*,[16] open triangle: xenon (Xe) from Aregbe *et al.*,[17] and asterisk: sulfur hexafluoride (SF_6) from Ding *et al.*[18]). The dark and bright gray colored areas signify standard and expanded uncertainty of the $f_{MD}(Ar)$ in this work.

isotope mixture is shown in Table 3. The weighted average of $f_{MD}(Ar)$ from three isotope mixtures is $-0.044\% \pm 0.017$ %, being close to zero. Although isotope ratios from three different isotope mixtures were varied by a factor of 100 times or greater, f_{MD} values of mixtures were well agreed within their uncertainties. This confirmed that not only all artificial isotope mixtures were reproducibly well prepared by the gravimetric technique, but the linearity in Faraday cup detector of gas/MS would not be an issue in this work. The relative uncertainty in gravimetric preparation and isotope ratio measurement of Ar was precisely determined to be less than 0.16 %, allowing $f_{MD}(Ar)$ of low uncertainty.

Mass Discrimination Factors from other Literatures. In Figure 3 we plotted f_{MD} values of five chemical elements including Ar, carbon dioxide (CO_2), krypton (Kr), xenon (Xe) and sulfur hexafluoride (SF_6) from the same type of gas/MS by other research groups including IRMM team.[14-18] Actually, they reported mass discrimination correction factor (K) instead of mass discrimination factor (f_{MD}) which is used in this paper. Therefore, we converted their reported K value to f_{MD} by using Eq. (5).

$$f_{MD} = (K - 1) \times \frac{100}{\Delta m} \qquad (5)$$

All f_{MD} values from previous literatures were located in certain narrow boundaries of ± 0.06 % in the *m/z* range from 40 (for Ar)[14] to 146 (for SF_6).[18] Figure 3 also shows that the $f_{MD}(Ar)$ of $-0.044\% \pm 0.017$ % from gravimetric prepared isotope mixtures in this work agrees well with f_{MD} values from other literatures.

Mass Discrimination Factor in Expanded *m/z* Range.

Table 3. Mass discrimination factor (f_{MD}) of isotope gas mixtures

Isotope mixtures		Real isotope ratio, R	Ion current ratio, r	f_{MD} (%)	
$^{40}Ar/^{36}Ar$	R1	2.8251 (26)	2.8292 (19)	−0.036 (28)	
	R2	39.596 (37)	39.652 (14)	−0.035 (25)	−0.044 (17)
	R3	330.30 (34)	331.57 (52)	−0.095 (47)	

In order to check the f_{MD} difference over a wide range of m/z, NF_3 gas was used. The isotope ratio of NF_3 in mass spectrometer depends only upon the isotope ratio of nitrogen which consists of NF_3 molecule because of the mono-isotope fluorine. If f_{MD} is almost constant in the m/z range from 28 to 71, the nitrogen isotope ratio of NF_3, $r(^{15}N/^{14}N)_{NF3}$, must be the same with nitrogen isotope ratio of thermally decomposed N_2 from same NF_3, $r(^{15}N/^{14}N)_{N2}$.

To compare $r(^{15}N/^{14}N)$ values of NF_3 and N_2, we computed $r(^{15}N/^{14}N)_{NF3}$ from isotope ratio and its abundance of three fragmented ions of NF_3, such as NF_3^+, NF_2^+, and NF^+, as shown in Eq. (6). This computation allows us to eliminate any discrimination effect occurring by ion fragmentation from $r(^{15}N/^{14}N)_{NF3}$. In the Eq. (6), $f(NF_i)$ represents the abundance of fragmented ion of NF_3.

$$r\left(\frac{^{15}N}{^{14}N}\right)_{NF_3} = \Sigma r\left(\frac{^{15}NF_i}{^{14}NF_i}\right) \times f(NF_i) \ (i = 1, 2, 3) \quad (6)$$

The $r(^{15}N/^{14}N)_{N2}$ is a half of $r(^{29}N_2/^{28}N_2)_{N2}$ according to the statistics of isotope abundance, as shown in Eqs. (7) to (9). In the equations, P_i represents the probability fraction of atomic or molecular nitrogen isotope, i.

$$P_{29_{N_2}} = 2 \times P_{14_N} \times P_{15_N} \quad (7)$$

$$P_{28_{N_2}} = P_{14_N} \times P_{14_N} \quad (8)$$

$$r\left(\frac{^{29}N_2}{^{28}N_2}\right) = \frac{P_{29_{N_2}}}{P_{28_{N_2}}} = \frac{2 \times P_{14_N} \times P_{15_N}}{P_{14_N} \times P_{14_N}} = 2 \times \frac{P_{15_N}}{P_{14_N}} = 2 \times r\left(\frac{^{15}N}{^{14}N}\right) \quad (9)$$

Table 4 shows the results of $r(^{15}N/^{14}N)_{NF3}$ and $r(^{15}N/^{14}N)_{N2}$ measured by the gas/MS with the same condition above. $r(^{15}N/^{14}N)$ values of NF_3 fragmented ions were in agreement within their measurement uncertainties with approximately 95 % confidence level. The uncertainty of each isotope ratio was calculated from the standard deviation of ion current of each ion and the instrumental noise. The maximum relative difference of $r(^{15}N/^{14}N)$ of three NF_3 ions was 0.04 %.

The values of $r(^{15}N/^{14}N)_{NF3}$, and $r(^{15}N/^{14}N)_{N2}$ were 357.1 $\times 10^{-5} \pm 0.5 \times 10^{-5}$ and $356.65 \times 10^{-5} \pm 0.22 \times 10^{-5}$, respectively. The relative difference between $r(^{15}N/^{14}N)_{NF3}$ and $r(^{15}N/^{14}N)_{N2}$ was −0.12 % with standard uncertainty of 0.14 %.

Figure 4. Over to Figure 3, we added the f_{MD} values obtained from NF_3 and N_2 produced from decomposition of the same NF_3 gas (closed squares).

This means that the relative difference of f_{MD} between m/z positions of 28 and 71, $\Delta f_{MD}(N_2, NF_3)$, is confined with −0.12 % ± 0.14 %.

With combining the results from this work and previous researches as shown in previous sections, we can expect the f_{MD} from m/z 28 (N_2) to m/z 146 (SF_6) as follows;
(a) f_{MD} in the m/z range of 40 (Ar) and 146 (SF_6) is found to be −0.044 % ± 0.017 %, as shown in Figure 3, hence, we can expect the same $f_{MD}(NF_3)$ value with $f_{MD}(Ar)$;
(b) f_{MD} between m/z of 28 (N_2) and 71 (NF_3) can be calculated from expected $f_{MD}(NF_3)$ and $\Delta f_{MD}(NF_3, N_2)$, and is in the range of −0.16 % ± 0.14 %. This f_{MD} value can be applied to expanded m/z range to 146 (SF_6) linked to the statement (a), as shown in figure 4.

Source of Mass Discrimination. Molecules injected into the instrument travels along the path in the gas/MS as shown on Figure 1. During this processes mass discrimination effect could influenced to the isotope ratio measurement. Neutral molecules effuse from the gas reservoir into the ionization chamber are evacuated from the chamber by a turbo molecular pump. During these two processes, the movement of each molecule strongly depends upon their molecular mass so that molecules with different mass has been discriminated on their velocity in the gas/MS. Mass discrimination effect can be presented in some other processes not only while the positive ions being formed from the neutral molecules by electron impact, but throughout the acceleration, focusing processes and producing a signal at the detector.

Table 4. Nitrogen ion current ratio of NF_3 and N_2 decomposed from NF_3

Measured ions	Relative abundance, $f(NF_i)$	Ion current ratio, $r(^{15}N/^{14}N)$ ($\times 10^{-5}$)						Difference (%)
		Independent measurements				Weighted average		
NF_3^+	0.211 (6)	358.1 (1.6)	358.3 (1.9)	357.7 (1.9)	358.1 (3.8)	358.1 (1.2)	357.1 (0.5)[c]	−0.12 (0.14)
NF_2^+	0.600 (12)	356.9 (0.6)	356.7 (0.8)	356.5 (0.7)	357.1 (1.2)	356.8 (0.4)		
NF^+	0.189 (10)	356.5 (2.9)	357.1 (3.4)	356.8 (3.2)	357.0 (2.0)	356.9 (1.5)		
$N_2^{+ \ d}$	/	356.69 (0.29)		356.61 (0.32)		356.65 (0.22)		

[c]Nitrogen isotope ratio of NF_3 from three fragmented ions, $r(^{15}N/^{14}N)_{NF3} = \Sigma[r(^{15}NF_i/^{14}NF_i) \times f(NF_i)]$, $i = 1, 2, 3$. [d]Nitrogen isotope ratio of N_2, $r(^{15}N/^{14}N)_{N2} = \dfrac{r(^{29}N_2/^{28}N_2)_{N2}}{2}$
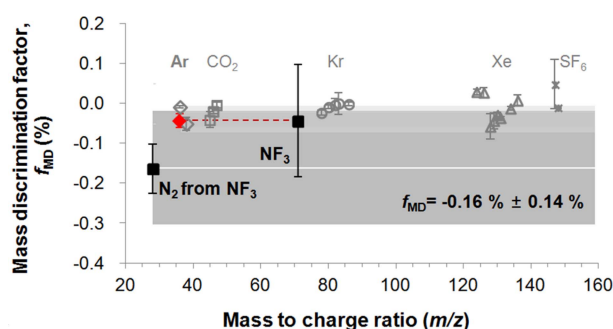
When isotopes with different masses effuse from the gas reservoir through μm-size orifice with molecular flow, lighter isotopes travel with a higher speed governed by the kinetic gas theory.[18,19,22] In the ionization chamber maintained a high vacuum (less than 1×10^{-4} Pa), neutral molecules which avoid to be any ions by electron impact immediately evacuated by the turbo molecular pump. Under our experimental condition, the estimated ionization efficiency (the number of Ar ions arrived at the detector relative to the number of injected molecules) reached only less than 0.01 %. And during these processes, the pressure in the ion source chamber remains almost constant even through molecules continuously flow into the source. It demonstrates that the amount of gas entering the ionization chamber equals to the amount of gas leaving.

The f_{MD} in the effusion process can be theoretically estimated due to the molecule's movement speed with molecular flow governed by the kinetic gas theory. The f_{MD} on effusion $f_{MD(Effusion)}$, for two isotopes of ^{36}Ar and ^{40}Ar can be estimated using the Eq. (10),[18] and computed as 1.4 % per unit mass. While the $f_{MD}(Ar)$ obtain using gravimetrically prepared Ar artificial isotope mixtures is very close to zero. Therefore, we can experimentally expect that most of the mass discrimination effect due to effusion of molecules at the entrance of ion source chamber can be canceled out due to the pumping. In the same manner of Ar, the $f_{MD(Effusion)}$ of N_2 and NF_3 can be calculated to be 1.8 % and 0.7 %, respectively. According to the equation 10, $f_{MD(Effusion)}$ values of heavier molecules are getting closed to zero, that means lighter molecules could be affected more with the mass discrimination, as previously reported by Wood *et al.*[29]

$$f_{MD(Effusion)} = \left(\frac{m_{40Ar}}{m_{36Ar}}\right)^{0.5} - 1 \qquad (10)$$

The mass discrimination factor on ionization has not been independently reported, but we can estimate it with the ion current ratios of three fragmented ions of NF_3 (NF_3^+, NF_2^+, and NF^+). Because NF_3 mother molecules of three fragmented ions were neutral molecules before being ionized, they have the same $f_{MD(Effusion)}$. However these neutral molecules produce different ion beams in accordance with their m/z after being ionized and fragmented. Therefore the difference of ion current ratios in nitrogen isotope of NF_3 ions can be expressed as the f_{MD} on ionization, $f_{MD(Ionization)}$. Although ion current ratios of NF_3^+ and NF_2^+ show the difference of 0.4% as shown in Table 4, they agreed well to each other within measurement uncertainties. It can be expected that $f_{MD(Ionization)}$ does not have a significant effect on f_{MD}.

Conclusion

This work explored the mass discrimination factor (f_{MD}) that is used to convert the ion current ratio into the real ratio when measuring the absolute isotope ratio using a single magnetic sector type mass spectrometer with a dynamic gas inlet system.

Artificial argon (Ar) isotope gas mixtures were gravimetrically prepared to obtain f_{MD} values in the gas/MS at m/z positions of 40. f_{MD} of Ar isotope mixture was −0.044 % with the standard uncertainty of 0.017 %. From the comparison of this work and previous works done by another research group, we confirm that f_{MD} values of molecules heavier than Ar, molecular weight of 40 g/mol, are almost constant and very close to zero. To investigate the f_{MD} over a wide range of m/z, we measured and compared nitrogen isotope ratios of NF_3 (m/z of 71 and 72) and N_2 (m/z of 28 and 29) which was thermally decomposed from the same NF_3. As shown in Figure 4, the relative difference between the isotope ratio of nitrogen in NF_3 and the isotope ratio of N_2 decomposed from NF_3, is −0.12 % ± 0.14 %. With combining all results in Figure 4, we can apply f_{MD} as −0.16 % ± 0.14 % in a wide m/z range from N_2 to SF_6 in our gas/MS.

When an artificial isotope mixture that has been prepared using a gravimetric technique, f_{MD} can be very accurately obtained within the uncertainty of 0.05 %. However, if preparation of any isotope references is not possible due to the absence of a gravimetric mixing system or the enriched isotope materials, the estimate f_{MD} described in this study can be applied to measure isotope ratios for most of gases within the relative uncertainty of 0.2 %. Also, we anticipate that this method can be used to check the validity of the previously reported, and currently used absolute isotope ratios of the gas molecules.

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