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Absolute Isotopic Composition and Atomic Weight of Commercial Zinc Using Inductively Coupled Plasma Mass Spectrometry

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Inductively coupled plasma mass spectrometry is introduced as a method for determining the absolute isotopic composition of zinc. The high ionization efficiency and time-independent characteristics of the mass spectrometry permit the absolute isotopic composition of high ionization potential elements. The mass discrimination of the instrument is calibrated by synthetic isotope mixtures prepared from highly enriched isotopes of zinc. The resulting isotope ratios yield atomic percents of ^{64}Zn, 49.188 ± 0.030; ^{66}Zn, 27.792 ± 0.041; ^{67}Zn, 4.041 ± 0.009; ^{68}Zn, 18.378 ± 0.050; and ^{70}Zn, 0.600 ± 0.003. This isotopic composition is different from those of conventional mass spectrometric measurements. Their differences depend on the mass differences about 0.8−1.2%/amu with enhancement of heavier isotopes. The atomic weight calculated from our isotopic composition is 65.3756 ± 0.0040. The obtained atomic weight is fully consistent with that of a precise coulometric measurement in contrast to the previous mass spectrometric measurements. An isotopic variation of commercial zinc reagents has been investigated. A mass-dependent fractionation of 0.12%/amu is observed in a high-purity metal zinc, NIST-SRM 682, among five reagents. This mass dependence is probably inherited through their purification process.

Atomic weights of elements are fundamental constants in analytical chemistry because they relate mass to the amount of substance in chemical reaction, and these values must be determined accurately. Atomic weights of polyisotopic elements are precisely calculated from isotope ratios determined by mass spectrometry. However, the observed isotope ratios are not always accurate. To obtain accurate isotope ratios, it is necessary to calibrate the mass discrimination of a mass spectrometer using samples of accurately known isotope ratios of the element under study. The double-spike method is the most common approach to correct the mass discrimination. This method involves the synthesis of a mixture from two solutions of the element, each enriched in a different isotope. As the isotopic abundances of the mixture are accurately known gravimetrically, a correction factor for the mass discrimination of the instrument can be determined from the observed isotope ratios of the mixture. Then observed isotope ratios of the element with normal isotopic abundances are calibrated by the correction factor to absolute ratios.

Thermal ionization mass spectrometry (TIMS) has been employed for the double-spike analysis, especially for elements with relatively low first ionization potentials. For the high first ionization potential elements, several techniques have been introduced into TIMS to enhance ionization efficiency.[1] The superior points of TIMS are stability of ionization source and low background. However, a major problem of TIMS is the time-dependent isotopic fractionation during analysis. This time dependence is attributed to mass-dependent fractionation during evaporation of isotopes from the filament in the ionization source. Thus, accurate isotope ratios are only obtained by measuring the synthetic mixture and natural samples under identical conditions of the fractionation.

Inductively coupled plasma source mass spectrometry (ICPMS) is a recently developed technique initiated for the determination of trace element abundances[2] using the strength of its argon plasma source, which achieves high ionization efficiency of >90% for most elements as calculated from the Saha equation. The magnetic sector multiple-collector ICP mass spectrometer is designed to provide high-precision isotopic data by eliminating the instability of ICP by simultaneous ion detection,[3] and precise analyses have been carried out.[4−7] In contrast to TIMS, the mass discrimination of the instrument remains relatively constant over time and is dependent on the relative mass difference of isotopes.[8] These unique characteristics of ICPMS permit the identical analytical conditions between the synthetic mixture and natural samples in the double-spiking method.

In this study, we introduce the double-spike method into ICPMS and examine the applicability of the magnetic sector multiple-collector ICP mass spectrometer as an instrument to

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obtain absolute isotopic composition of elements. An absolute isotopic composition of zinc is determined by calibrating the mass discrimination of the instrument. As is expected for such a high ionization potential element as zinc, the development of a suitable ion source is difficult, and the absolute isotopic composition and atomic weight of zinc are not defined well by conventional mass spectrometry. An absolute isotopic measurement by Rosman,[9] which has been adopted by IUPAC Commission on Isotopic Abundance,[10] yielded the atomic weight of 65.396 ± 0.005, whereas a chemical determination by Marinenko and Foley[11] obtained 65.377 ± 0.003. This discrepancy was not resolved by a recent isotopic determination.[12] The currently recommended value for the atomic weight of zinc is 65.39 ± 0.02,[13] and zinc is listed as one of the elements whose standard atomic weights are estimated to be uncertain by 0.015% or more.[14] The large discrepancy provided impetus for utilization of the new ionization source.

We will also examine zinc isotopic compositions of commercially available zinc reagents including zinc metal standards provided from NIST. From isotopic variations of the terrestrial zinc samples, the practical uncertainties of the zinc isotopic composition and atomic weight are estimated.

EXPERIMENTAL SECTION

Instrument Information. The magnetic sector multiple-collector ICP mass spectrometer employed in this study is a Nu instruments (Wrexham, Wales, U.K.) Nu Plasma 500. This Nier-Johnson-type double-focusing mass spectrometer achieves an effective mass dispersion of 500 mm and produces flat-topped, symmetrical peak shapes. Twelve fixed Faraday collectors are supplied for ion detection. The magnification of the spectrometer can be adjusted with a pair of quadrupole lenses that act as zoom lenses, focusing the ion beams electrically into the Faraday collectors. The lenses were set to detect the following isotopes by the Faraday collectors (in parentheses) simultaneously: ^{64}Zn (low 4), ^{66}Zn (low 2), ^{67}Zn (axial), ^{68}Zn (high 2), and ^{70}Zn (high 5), respectively. Input signals are converted to voltages through 10^{11}-Ω feedback resistors. The relative differences in the amplifier resistors were calibrated against the axial Faraday collector by passing a constant current electronically. The relative differences in ion input efficiency among the Faraday collectors were checked using a ^{64}Zn ion beam in the range $0.4 \times 10^{-11}-4 \times 10^{-11}$ A and were found to be negligible within ±0.01%. Operating conditions of the instrument are detailed in Table 1.

Background Spectrum. It is widely recognized that ICPMS potentially suffers from interferences from various polyatomic species, which originate from argon, water, and air. Moreover, the washing-out time of sample solutions to background level must be investigated, because we analyze the synthetic isotopic mixtures and natural samples in turn in the double-spiking method. As their isotopic abundances are quite different, the memory effect of a previous solution may cause a fatal interference in the following measurement. To evaluate the washing-out time, the ion beam intensity of ^{64}Zn was monitored as a 0.5 μg g^{-1} zinc solution was introduced into the instrument and washed out over 30 min with pure water. Approximately 1 min after pure water was introduced, the ^{64}Zn beam intensity exhibited a sharp drop to less than 0.1% of its peak value of 5×10^{-12} A (Figure 1). Afterward, the beam intensity remained constant at $\sim 5 \times 10^{-16}$ A, which was accepted as background. Similar results were obtained for a 5 μg g^{-1} zinc solution. The background intensity is probably the result of polyatomic interferences, such as ArN_2 or some other species.

Table 1. Typical ICPMS Operating Conditions

ICP Ion Source[a]	
rf frequencies	27.12 MHz
rf power	1.35 kW forward, <3 W ref
Fassel-type torch Ar gas flow rates	
outer	14.0 L min^{-1}
intermediate	0.70 L min^{-1}
central	0.95 L min^{-1}
nebulizer	Glass Expansion Micromist
spray chamber	Scott type glass chamber (3 °C)
sample uptake rate	0.4 mL min^{-1} (free aspiration)
torch−interface distance	5.5 mm
Mass Spectrometer	
ion energy	4000 V
extraction	2400 V
transmission	2×10^{-11} A per μg g^{-1} zinc
Data Acquisition	
integration time	10 s
no. of ratios per run	60 (20 cycles × 3 blocks)

[a] The central argon gas flow rate was adjusted to maximize the transmission of zinc signal.

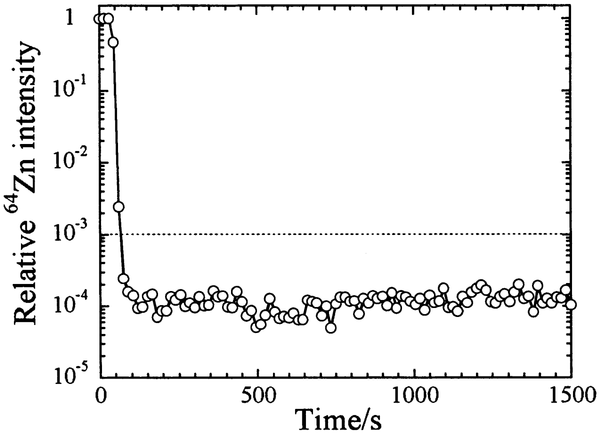

Figure 1. Washing-out profile of a zinc solution with time. Data were obtained every 15 s.

During analyses, background intensities were measured after washing out for 30 min and subtracted from zinc ion beam intensities of the following sample. This correction for background was less than 0.01%. The isobaric interferences of ^{64}Ni and ^{70}Ge were monitored from ^{60}Ni and ^{74}Ge before each analysis, and no interferences were observed.

Preparation of Highly Enriched Isotope Solutions. Two samples of metal, highly enriched in ^{64}Zn (sample A) and ^{68}Zn (sample B), were obtained from Oak Ridge National Laboratory. The two metal plates of about 5 mm × 5 mm were washed with diluted HNO_3 for a few minutes in room temperature to remove oxidized layers on their surfaces. After the plates were rinsed with

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Table 2. Observed and Absolute Zinc Isotope Ratios of Two Highly Enriched Isotopes, Samples A and B[a]

		observed		step 1		step 2		step 3	
A	B	A	B	A	B	A	B	A	B
^{64}Zn/^{64}Zn	^{64}Zn/^{68}Zn	1	0.005473 ± 8	1	0.006254	1	0.006269	1	0.006269 ± 9
^{66}Zn/^{64}Zn	^{66}Zn/^{68}Zn	0.002831 ± 5	0.004112 ± 7	0.002648	0.004396	0.002645	0.004401	0.002645 ± 5	0.004401 ± 6
^{67}Zn/^{64}Zn	^{67}Zn/^{68}Zn	0.000349 ± 5	0.001226 ± 5	0.000316	0.001309	0.000315	0.001309	0.000315 ± 5	0.001309 ± 5
^{68}Zn/^{64}Zn	^{68}Zn/^{68}Zn	0.001494 ± 5	1	0.001307	1	0.001304	1	0.001304 ± 5	1
^{70}Zn/^{64}Zn	^{70}Zn/^{68}Zn	0.000046 ± 5	0.000170 ± 5	0.000038	0.000159	0.000038	0.000159	0.000038 ± 5	0.000159 ± 5
atomic weight		63.9420 ± 7	67.8942 ± 8	63.9408	67.8905	63.9408	67.8904	63.9408 ± 7	67.8904 ± 8
synthetic mixture									
$R^{\text{obs}}_{68/64}$		0.37027 ± 19		0.37027		0.37027		0.37027 ± 19	
$R^{\text{abs}}_{68/64}$		0.32399 ± 32		0.32325		0.32324		0.32324 ± 32	
$K_{68/64}$		0.87500 ± 98		0.87301		0.87298		0.87298 ± 98	

[a] The absolute isotope ratios were obtained by an iterative calculation of $K_{68/64}$ (see text). The analytical uncertainties apply to last digits throughout the tables. The uncertainties during the iterative calculation are not shown in this table. The synthetic mixture is identical to mix 1 on day 1 in Table 3. The choice of the other mixtures, mix 2 and mix 3, does not affect the results in Table 3 within significant figures.

pure water and ethanol, they were dried in an oven for one week at 110 °C in a dry argon atmosphere. The plates were weighed daily during drying, and no increase in weight was observed. About 0.1 g of the metal plates was accurately weighed and dissolved in ultrapure 1 M HNO_3 (Tamapure-AA10) to prepare stock solutions. All possible impurities in the solutions were measured by argon plasma spectrometry. The analyses indicated the presence of the following impurities of more than 0.01%: 0.04% In and 0.01% Fe in solution A, and 0.25% Cu and 0.07% Fe in solution B. Thus, the chemical purity of sample A is 99.95% and that of sample B is 99.68%. Zinc concentrations of the stock solutions were 1018.5 μg g^{-1} for solution A and 998.5 μg g^{-1} for solution B. All synthetic mixed solutions were prepared from the stock solutions and diluted to ~3 μg g^{-1} zinc with pure water immediately before isotopic analyses.

Correction for Mass Discrimination. Various physical and chemical mechanisms conspire to alter ion beams within mass spectrometers so that the observed ratios R^{obs} are not identical to the absolute ratios R^{abs}. These mechanisms typically produce mass-dependent isotope discrimination. The relationship between the observed and absolute isotope ratios is described by the expression

$$R^{\text{abs}} = KR^{\text{obs}} \tag{1}$$

where K is a mass discrimination correction factor. In this study, the absolute isotope ratio of the synthetic mixture is calculated gravimetrically from the following formula:

$$R^{\text{abs}}_{68/64} = \frac{W^{\text{A}}C^{\text{A}}\gamma^{\text{A}}_{68} + W^{\text{B}}C^{\text{B}}\gamma^{\text{B}}_{68}}{W^{\text{A}}C^{\text{A}}\gamma^{\text{A}}_{64} + W^{\text{B}}C^{\text{B}}\gamma^{\text{B}}_{64}}, \tag{2}$$

where W^{A} and W^{B} are the weights of solutions A and B, C^{A} and C^{B} are the molar concentrations of solutions A and B, and γ^{A}_{68}, γ^{B}_{68}, γ^{A}_{64}, and γ^{B}_{64} are the atomic percents of ^{68}Zn and ^{64}Zn in solutions A and B, respectively. From the obtained $K_{68/64}$ value, the correction factors for the other isotope ratios are calculated using the power law as follows: $K_{66/64} = K_{68/64}{}^{1/2}$, $K_{67/64} = K_{68/64}{}^{3/4}$, and $K_{70/64} = K_{68/64}{}^{3/2}$.

RESULTS AND DISCUSSION

Isotopic Composition of Highly Enriched Isotopes. Absolute isotopic abundances of the highly enriched isotope solutions of samples A and B were determined by iterative calculation. Isotope ratios of solutions A and B alone and a synthetic mixture were individually measured on the mass spectrometer. Initial atomic weights of A and B and the gravimetric ^{68}Zn/^{64}Zn ratio of the mixture ($R^{\text{abs}}_{68/64}$; see eq 2) were calculated from the observed isotope ratios as listed in Table 2. From $R^{\text{abs}}_{68/64}$ and $R^{\text{obs}}_{68/64}$ of the mixture, an initial discrimination correction factor $K_{68/64}$ was estimated (eq 1). Then, the first-order corrected isotope ratios and atomic weights of samples A and B were recalculated using this initial correction factor. New values for the correction factor were calculated iteratively (see steps 1−3 in Table 2) until $K_{68/64}$ became constant. The obtained isotopic composition (in atomic percent) is as follows: For of sample A, ^{64}Zn, 99.5716 ± 0.0010; ^{66}Zn, 0.2634 ± 0.0005; ^{67}Zn, 0.0314 ± 0.0005; ^{68}Zn, 0.1298 ± 0.0005; and ^{70}Zn, 0.0038 ± 0.0005. For sample B, ^{64}Zn, 0.6194 ± 0.0009; ^{66}Zn, 0.4348 ± 0.0006; ^{67}Zn, 0.1294 ± 0.0005, ^{68}Zn, 98.8008 ± 0.0013; and ^{70}Zn, 0.0157 ± 0.0005. The calculated atomic weights are 63.9408 ± 0.0007 and 67.8904 ± 0.0008, respectively.

Absolute Isotopic Composition of Zinc. Four synthetic mixed solutions were prepared from different proportions of solutions A and B. After thorough mixing, each of the mixtures and a natural zinc solution were analyzed one after the other in two days. The natural zinc solution, JMC Zn, is a laboratory standard solution prepared from a zinc metal wire with 99.9985% purity, purchased from Johnson Mattey. The correction factor $K_{68/64}$ was calculated from $R^{\text{abs}}_{68/64}$ and $R^{\text{obs}}_{68/64}$ of each mixture with eq 1 as shown in Table 3. Then, the observed isotope ratios of JMC Zn were corrected to absolute ratios using the $K_{68/64}$ values (Table 3). There is a difference in the observed isotope ratios between day 1 and day 2 of ~0.1%/amu, due to a slight change in the instrumental condition. However, their absolute isotope ratios are quite consistent between the two days. These data demonstrate isotopic analyses under identical conditions by ICPMS between the synthetic mixtures and the natural sample. From this result, we obtain the absolute isotopic composition of JMC Zn in atomic percent as shown below: ^{64}Zn, 49.188 ± 0.030; ^{66}Zn, 27.792 ± 0.041; ^{67}Zn, 4.041 ± 0.009; ^{68}Zn, 18.378 ± 0.050; and ^{70}Zn, 0.600

Table 3. Instrumental Calibration and Absolute Zinc Isotope Ratios of JMC Zn

	calibration			observed ratios				absolute ratios			
mixture	$R^{\mathrm{abs}}_{68/64}$	$R^{\mathrm{obs}}_{68/64}$	$K_{68/64}$	^{66}Zn/^{64}Zn	^{67}Zn/^{64}Zn	^{68}Zn/^{64}Zn	^{70}Zn/^{64}Zn	^{66}Zn/^{64}Zn	^{67}Zn/^{64}Zn	^{68}Zn/^{64}Zn	^{70}Zn/^{64}Zn
day 1											
mix 1	0.3240	0.37027	0.8730	0.604183	0.090848	0.427229	0.014915	0.56451	0.08205	0.37296	0.01217
	±3	±1	±9	±7	±2	±8	±1	±56	±8	±37	±1
mix 2	1.8229	2.07635	0.8753	0.604226	0.090861	0.427290	0.014922	0.56529	0.08222	0.37400	0.01222
	±18	±3	±9	±7	±2	±9	±2	±57	±8	±37	±1
mix 3	0.7900	0.90163	0.8741	0.604291	0.090871	0.427387	0.014924	0.56498	0.08215	0.37360	0.01220
	±8	±2	±9	±6	±2	±7	±2	±56	±8	±37	±1
day 2											
mix 4	0.9310	1.05759	0.8782	0.603186	0.090630	0.425873	0.014845	0.56527	0.08222	0.37401	0.01222
	±9	±2	±9	±8	±2	±9	±2	±57	±8	±37	±1
mix 4	0.9310	1.05915	0.8769	0.603483	0.090697	0.426276	0.014867	0.56513	0.08219	0.37381	0.01221
	±9	±2	±9	±7	±2	±8	±2	±57	±8	±37	±1
mix 1	0.3240	0.36964	0.8745	0.603608	0.090720	0.426414	0.014871	0.56446	0.08204	0.37289	0.01216
	±3	±1	±9	±5	±2	±5	±1	±56	±8	±37	±1
mix 2	1.8229	2.07299	0.8767	0.603713	0.090744	0.426542	0.014882	0.56527	0.08222	0.37394	0.01222
	±18	±7	±9	±6	±2	±7	±2	±57	±8	±37	±1
mix 2	1.8229	2.07338	0.8765	0.603754	0.090758	0.426591	0.014890	0.56525	0.08222	0.37392	0.01222
	±18	±4	±9	±6	±3	±6	±3	±57	±8	±37	±1
mix 3	0.7900	0.90056	0.8752	0.603897	0.090785	0.426823	0.014883	0.56495	0.08215	0.37355	0.01218
	±8	±2	±9	±10	±3	±12	±2	±56	±8	±37	±1
average								0.56501	0.08216	0.37363	0.01220
2SD								±75	±17	±100	±5

[a] After stock solutions A and B were diluted to 49.61 and 55.52 μg g^{-1}, the synthetic mixtures were produced from mass ratios of 0.3459/1.1214 for mix 1, 1.3381/0.7618 for mix 2, 0.7803/1.0320 for mix 3, and 0.8478/0.9504 for mix 4 (in g/g), respectively. The total uncertainty during the weighing procedure was assumed to be ±0.1%.

Table 4. Observed Isotope Ratios of Commercial Zinc Reagents and Their Relative Deviations from JMC Zn (Four Replicates)[a]

sample name/ source	form/ nominal purity	observed isotope ratio				deviation from JMC Zn			
		^{66}Zn/^{64}Zn	^{67}Zn/^{64}Zn	^{68}Zn/^{64}Zn	^{70}Zn/^{64}Zn	^{66}Zn/^{64}Zn	^{67}Zn/^{64}Zn	^{68}Zn/^{64}Zn	^{70}Zn/^{64}Zn
JMC/	zinc metal wire/	0.60418	0.09086	0.42725	0.01492	1	1	1	1
Johnson Mattey, UK	99.9985%	±25	±6	±36	±3				
NIST-SRM 682/	zinc metal bar/	0.60272	0.09053	0.42522	0.01482	0.99760	0.99636	0.99525	0.99321
Cominco American, Canada	99.9999%	±15	±3	±19	±1	±18	±33	±41	±203
NIST-SRM 683/	zinc metal bar/	0.60424	0.09087	0.42732	0.01493	1.00007	1.00003	1.00010	1.00027
Cominco American, Canada	99.998%	±20	±4	±28	±2	±7	±30	±14	±158
Nilaco/	zinc metal sheet/	0.60425	0.09088	0.42735	0.01493	1.00013	1.00016	1.00024	1.00041
Nilaco, Japan	99.5%	±12	±3	±15	±2	±22	±45	±48	±149
Cica-Merck/	std soln for AA	0.60422	0.09087	0.42731	0.01492	1.00007	1.00012	1.00015	1.00015
Kanto Chemical, Japan		±31	±6	±42	±2	±26	±41	±50	±130

[a] The uncertainties for the observed ratios were two standard errors, while those for the relative deviations were calculated after the observed ratios were normalized to JMC Zn in each data set.

± 0.003, respectively. The atomic weight is calculated to be 65.3756 ± 0.0040 from the absolute isotope ratios.

Isotopic Variation of Commercial Zinc Reagents. A limitation to the uncertainty associated with an atomic weight is that caused by natural variations in the isotopic compositions of the element itself. To determine the isotopic variations in commercially available zinc, zinc isotope ratios of five zinc reagents were investigated. Their sources and nominal purities are listed in Table 4. The metal reagents were dissolved in the same manner as the enriched isotopes of samples A and B and diluted with pure water to volumes sufficient to give concentrations of 1 μg g^{-1} zinc. To avoid any cross contamination from the synthetic mixed solutions, a different set of glassware was used. Measured zinc isotope ratios and relative deviations from JMC Zn are given in Table 4. The isotope ratios listed are observed ratios, not corrected for the mass discrimination of the instrument. The isotope ratios of the NIST-SRM 682 high-purity zinc are clearly different from those of the other reagents. The differences from JMC Zn were plotted in Figure 2 against zinc isotopes. The relative isotopic deviation of NIST-SRM 682 depends on the mass differences of ~0.12%/amu with depletion of heavier isotopes. The mass-dependent fractionation of NIST-SRM 682 reduces the atomic weight relatively from 65.3756 to 65.3732.

Such a large mass-dependent fractionation might be present in the source material through some geological process,[15] but it is more likely the result of an industrial process in this case. Most

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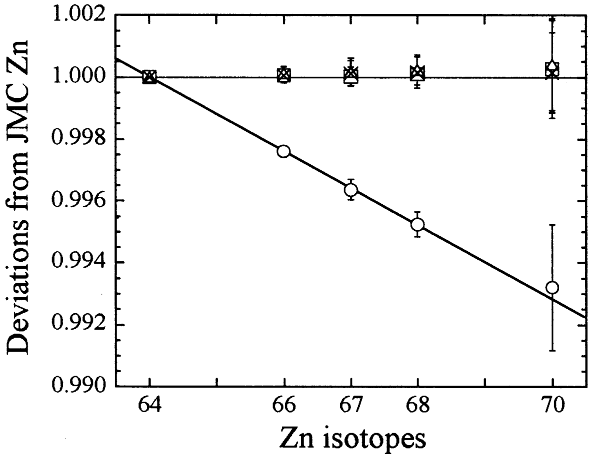

Figure 2. Relative zinc isotopic deviations of commercial zinc reagents from JMC Zn. The isotope ratios of NIST-SRM 682 (open circles) are clearly different from those of NIST-SRM 683 (open squares), Nilaco Zn (triangles), Cica-Merck Zn (crosses), and JMC Zn.

commercial zinc metal is now made by electrolysis, which yields purity from 99.99 to 99.999%. NIST-SRM 682 and 683 were prepared by Cominco American, Inc., from a special lot of high-grade electrolytic zinc, and NIST-SRM 682 was further purified by vacuum distillation, zone refining, and degasification. Distillation can produce depletions in heavier isotopes in products. Thus, the mass-dependent fractionation of NIST-SRM 682 relative to JMC Zn can be explained by the distillation process. The good agreement of the other reagents on the isotope ratios indicates homogeneity in their sources and no isotopic fractionation by electrolysis. Prior to this study, such a small variation could not be detected, because the reproducibility of previous analyses was restricted to ∼±0.1%/amu.[9] The time-independent feature of ICPMS improved the reproducibility and allowed detection of the zinc isotopic variation.

Evaluation of Accuracy. Different measurements of the isotopic composition of zinc have been reported by several authors. Electron impact ionization was shown to be a successful ion source for the zinc isotope analysis,[16−18] but this method suffered from a hydrocarbon background interference. By reducing the hydrocarbon background from an improvement of the ion source,[19] an absolute zinc isotopic composition was estimated by Rosman.[9] Recently, a new absolute determination by TIMS was reported[12] using activators to enhance ionization efficiency. Their values are significantly fractionated from our result in linear arrays as a function of mass (Figure 3). These linear correlations obtained from different mass spectrometry prove that background interferences of ICPMS are negligible or at least subtracted well for zinc. These two sets of previous results deviate by about 0.8 and 1.2%/amu from our results, far beyond the isotopic variation we detected in the commercial zinc.

The literature atomic weights of zinc calculated from the previous mass spectrometric measurements above are 65.396 ± 0.005[9] and 65.409 ± 0.006, [12] while a precise coulometric measurement by Marinenko and Foley[11] from five metal samples yielded 65.377 ± 0.003. Our mass spectrometric result of 65.3756 ± 0.0040 is quite consistent with the coulometric measurement. Also, the atomic weight of NIST-SRM 682 calculated above (65.3732 ± 0.0040) is within analytical uncertainty of the coulometric value of NIST-SRM 682 alone (65.377 ± 0.004[11]).

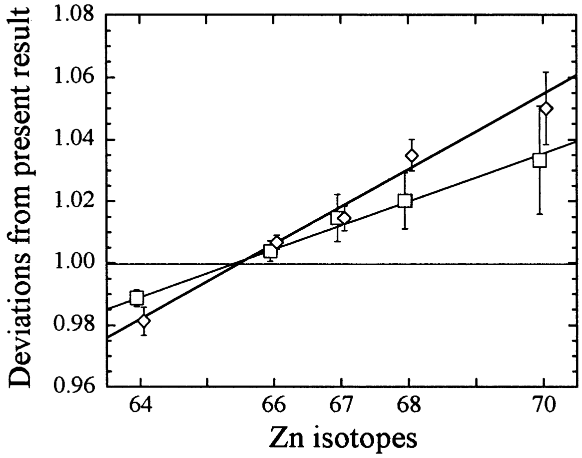

Figure 3. Comparison of reported absolute zinc isotope compositions using our data as reference. Data from Rosman[9] (open squares) and Chang et al.[12] (diamonds) are fractionated from our result.

The validity of our results can be assessed from an independent line of reasoning. As described above, the mass discrimination of ICPMS is independent of time. Though no theoretical model has been published to explain the mass discrimination effect, the space-charge effect is assumed to have the strongest influence,[20] which results in the preferential transmission of heavier ions. As the magnitude of the discrimination is similar among different elements over a limited mass range, an element with known isotopic composition in the same mass range is used as an internal standard to correct the discrimination.[8,21−23] Such mass dependence of the discrimination near zinc is presented from nickel, copper, and galium in Figure 4. To calculate their mass discrimination correction factors, ^{60}Ni/^{58}Ni, ^{65}Cu/^{63}Cu, and ^{71}Ga/^{69}Ga isotope ratios of isotopic standard reference materials provided by NIST were measured under identical instrumental conditions. The correction factor for the synthetic mixtures of zinc ($K_{68/64}{}^{1/4}$; from Table 3) falls clearly close to the line obtained from the correction factors for Ni, Cu, and Ga, while large deviations are recognized if the previous zinc isotope ratios are referred[9,12] (Figure 4). The cause of such fractionations of the previous results is uncertain, but it is possible that variations in sample preparation affected their reproducibilities of the absolute isotopic analysis.[27]

The mass discrimination correction factor of zinc agrees well with the mass discrimination trend in the same mass range,

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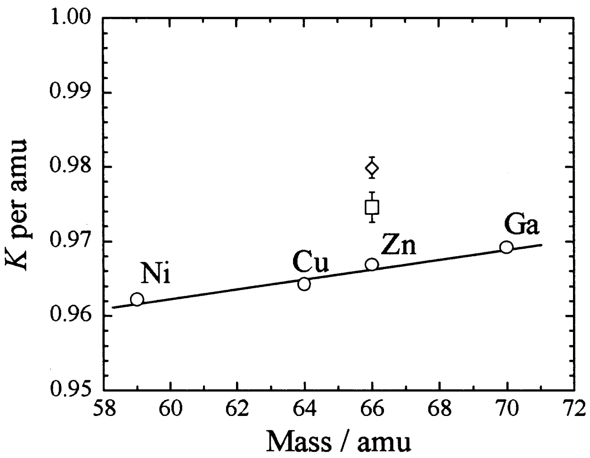

Figure 4. Mass discrimination correction factors per mass unit near the zinc mass range. This analysis was carried out after the absolute zinc isotope analysis on day 1 (Table 3). The factors of $K_{60/58}{}^{1/2}$, $K_{65/63}{}^{1/2}$, and $K_{71/69}{}^{1/2}$ are calculated from eq 1 using the observed ratios of ^{60}Ni/^{58}Ni = 0.4161 ± 0.0001, ^{65}Cu/^{63}Cu = 0.4792 ± 0.0001, and ^{71}Ga/^{69}Ga = 0.7066 ± 0.0001 and their recommended values.[24−26] The $K_{68/64}{}^{1/4}$ value obtained in this study falls on the straight line, which was obtained from the $K^{1/2}$ values (open circles), whereas deviations are observed from the line if previous ^{68}Zn/^{64}Zn of Rosman[9] (open square) and Chang et al.[12] (diamond) are used as references against the observed ^{68}Zn/^{64}Zn of JMC Zn (Table 3). Although the K values change day by day, their trend against mass number does not change.

though the ionization efficiency of zinc by the argon ICP is ∼70% as estimated from the Saha equation. This result suggests that the mass discrimination is not produced during ionization. Hirata[8] reported that neither accelerating voltage nor plasma settings affected the degree of the mass discrimination in magnetic sector ICP mass spectrometers. These results demonstrate that the mass discrimination possibly takes place in the region from the sampler cone to the skimmer cone of the instrument.

CONCLUSIONS

The absolute isotopic composition and atomic weight of zinc were obtained using ICPMS. The presently accepted atomic weight of zinc is 65.39 ± 0.02,[13] but our results indicate that this value should be revised to 65.3756 ± 0.0040. This estimate is 1 order of magnitude more precise and, more importantly, is fully consistent with a precise chemical determination[11] and a mass discrimination trend of the instrument. A precise isotopic analysis of commercial zinc reagents resolved an isotopic variation probably resulting from industrial purification. This result indicates that a knowledge of purification processes is necessary to select a reference material. NIST-SRM 683 is a currently favorable reference material in its availability, purity, and isotopic composition.

The magnetic sector multiple-collector ICP mass spectrometer can be utilized as a tool to determine absolute isotopic composition of elements, especially for the high first ionization elements, if the background spectrum and memory effects are carefully addressed. The mass discrimination of the instrument is larger than that of TIMS, but its time independence during analyses and identical condition among samples permit accurate calibration of the instrument. As the degree of the mass discrimination in the instrument is a function of mass, the absolute isotopic composition of elements can be verified, except for some volatile elements.[8]

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