



A method for determining the isotopic composition of dissolved zinc in seawater by MC-ICP-MS with a ^{67}Zn – ^{68}Zn double spike



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ARTICLE INFO

Article history:

Received 9 December 2015

Received in revised form 22 January 2016

Accepted 22 January 2016

Available online 29 January 2016

Keywords:

Zinc isotopes

Double spike

Chemical oceanography

GEOTRACES

ABSTRACT

The biogeochemical cycling of dissolved zinc in seawater is dominated by biological uptake in the surface ocean and its regeneration at depth leading to a large concentration gradient between the surface and deep ocean. The advent of multi-collector inductively coupled mass spectrometry (MC-ICP-MS) provides the marine community with a new way of probing the biogeochemical zinc cycle through changes in its isotope composition. In this paper we document the mathematical and analytical procedures involved in determining the dissolved zinc isotopic composition of seawater using the double spike technique. Seawater samples were spiked with a ^{67}Zn – ^{68}Zn double spike, before processing. Measurement of zinc by the MC-ICP-MS requires the sample to be free of the seawater matrix and other interfering elements; for this purpose Toyopearl AF-Chelate 650 M and AG1X8 resins were used to pre-concentrate zinc from seawater and separate it from major cations and anions. The optimum pH range for loading zinc for affinity chromatography was between 5 and 8. After pre-concentration, zinc was purified from other trace element by anion exchange chromatography. The reproducibility of the procedure was excellent for a deep water sample [$6.55 \pm 0.34 \text{ nmol L}^{-1}$ and $0.59 \pm 0.02\%$ ($n = 9$) w.r.t. JMC-Lyon] and a shallow water sample [$0.05 \pm 0.01 \text{ nmol L}^{-1}$ and $0.08 \pm 0.02\%$ ($n = 3$) w.r.t. JMC-Lyon] analyzed over a period of 1 year. Analysis of GEOTRACES IC1 BATS and SAFE inter-calibration samples produced data in good agreement with data published by other groups. As a further test of the methodology, we determined the isotopic composition of dissolved zinc for samples collected at various depths from station 40°S, 162°E located in the Tasman Sea, SW Pacific Ocean. The $\delta^{66}\text{Zn}$ vs. depth profile showed isotope variability in the upper water column (0–200 m) with values ranging between -0.03% and 0.53% . These variations were attributed to biological activity. In deep waters the isotope composition of dissolved zinc ($0.50 \pm 0.10\%$) is comparable to other data published.

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1. Introduction

Zinc acts as cofactors in many important enzymes within marine phytoplankton and hence plays a significant role in controlling the biology of oceans [1]. Thus changes in its bioavailability may influence biological production and hence the marine carbon cycle. Isotopic fractionation of zinc isotopes in the natural waters can occur as a result of variety of process, including complexation with organic ligands [2], biological uptake [3,4], and particle scavenging [5]. Therefore knowing the potential processes that can lead to zinc isotope fractionation may facilitate its use as a biogeochemical tracer for oceanographic research.

The mass dependent fractionation of zinc isotopes in nature is relatively small [6] and hence requires accurate and precise zinc isotope determination, which can be achieved by using the multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [7,8]. One disadvantage of MC-ICP-MS is that instrumental mass bias can

occur whereby a measured isotope ratio is different to the “true” isotope ratio.

Mass fractionation (mass bias) of zinc isotopes induced within the mass spectrometer can be corrected by the following methods [8,9]: a) conventional standard-sample-standard bracketing; b) doping samples with copper of a known isotope composition; and c) zinc double spike correction.

a) The conventional method of standard-sample-standard bracketing involves running a zinc standard with a known isotopic composition before and after every sample measurement.

b) To further account for mass bias samples during zinc isotope analysis samples are usually doped with copper of a known isotopic composition [10]. While this procedure generally works well mass bias can still occur and not be adequately accounted for during analysis [8].

c) The double spike (DS) technique can be used to circumvent these issues [2]. The DS technique involves spiking the sample with a mixture of two artificially enriched isotopes of the target element of a known isotope composition [8,10,11]. The DS method is only suitable for elements which have four or more naturally occurring stable isotopes. Zinc has five stable isotopes ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn and ^{70}Zn with natural abundances of 48.6%, 27.9%, 4.1%, 18.8% and 0.62%, respectively; thus it

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is well suited for the DS methodology. In addition, the DS methodology can also be used to correct for mass dependent isotope fractionation that might occur during sample preparation. Appreciable mass dependent isotope fractionation can occur during ion exchange chromatography as result of zinc interacting with the ion exchange resin and during the elution process [12]. These fractionation processes can be corrected for by adding the DS to the sample before processing. Thus, full recovery of element during sample preparation is not essential, although it is desirable.

1.1. Calibration of the double spike

In this study, the zinc DS was calibrated against the certified zinc standard IRMM-3702 utilizing an in-house copper standard (Fluka, USA) to correct for mass dependent fractionation of zinc during the initial DS calibration. At the start of each analytical session mass dependent fractionation of the zinc standard in the MC-ICP-MS was corrected using copper by applying the exponential mass bias expression [10]:

$$R_{a/b} = r_{a/b} \left(\frac{m_a}{m_b} \right)^P \quad (1)$$

where ($R_{a/b}$) is the true ratio of isotopes a and b, ($r_{a/b}$) is the measured ratio, and m_a/m_b is ratio of the atomic masses for a and b and P is the exponential mass fractionation factor.

The following steps were undertaken to calibrate the DS solution at the start of each session:

1. An IRMM-3702 zinc standard solution ($100 \mu\text{g L}^{-1}$) containing copper ($50 \mu\text{g L}^{-1}$) was measured by MC-ICP-MS.
2. Based on the measured copper isotope values, the exponential fractionation factor (P') was determined and used to calculate instrumental mass bias

$$P' = \frac{\ln \left(\frac{^{63}\text{Cu}}{^{65}\text{Cu}} \text{ true} / \frac{^{63}\text{Cu}}{^{65}\text{Cu}} \text{ measured} \right)}{\ln (62.9296/64.9280)} \quad (2)$$

3. The newly calculated P' was then used to correct the measured ^{66}Zn – ^{64}Zn isotope. If the mass bias corrected ^{66}Zn – ^{64}Zn isotope was not equal to the certified value IRMM-3702 ratio, P' was adjusted until they agreed. This new fully corrected exponential fractionation factor was termed P .
4. Using the new P factor the copper isotope composition in the IRMM-3702 standard solution was recalculated.
5. Next a DS solution ($100 \mu\text{g L}^{-1}$) containing the same copper standard ($50 \mu\text{g L}^{-1}$) was measured by MC-ICP-MS.
6. Based on the newly calibrated copper isotope composition and the measured copper isotope value for the DS solution, a fractionation factor was calculated and used to correct measured zinc isotope ratios (^{64}Zn – ^{68}Zn , ^{66}Zn – ^{68}Zn , ^{67}Zn – ^{68}Zn and ^{66}Zn – ^{64}Zn) for the DS.

This procedure of calibrating the DS was undertaken at the beginning of each analytical session [10]. The zinc isotope composition of natural samples was determined using the DS method and solved iteratively. The mass balance equations and how they were used and solved are detailed below.

1.2. Isotope dilution equation

If we consider a standard (Std) or a sample (Sa) – spike (Sp) mixture (Mix), the zinc isotope composition of the mixture will be equal to the total amount of zinc in the sample plus the spike:

whereby,

$$^{67}\text{Zn}_{\text{Mix}} = ^{67}\text{Zn}_{\text{Sa}} + ^{67}\text{Zn}_{\text{Sp}} \quad (3)$$

and

$$^{68}\text{Zn}_{\text{Mix}} = ^{68}\text{Zn}_{\text{Sa}} + ^{68}\text{Zn}_{\text{Sp}} \quad (4)$$

Thus

$$^{67}\text{Zn}_{\text{Sp}} = ^{68}\text{Zn}_{\text{Sp}} \times ^{67}\text{Zn}_{\text{Sp}} / ^{68}\text{Zn}_{\text{Sp}} \quad (5)$$

$$^{67}\text{Zn}_{\text{Sa}} = ^{68}\text{Zn}_{\text{Sa}} \times ^{67}\text{Zn}_{\text{Sa}} / ^{68}\text{Zn}_{\text{Sa}} \quad (6)$$

Combining Eqs. (3) and (4) we can write following equation:

$$\frac{^{67}\text{Zn}_{\text{Mix}}}{^{68}\text{Zn}_{\text{Mix}}} = \frac{^{67}\text{Zn}_{\text{Sa}} + ^{67}\text{Zn}_{\text{Sp}}}{^{68}\text{Zn}_{\text{Sa}} + ^{68}\text{Zn}_{\text{Sp}}} \quad (7)$$

Rearranging Eq. (7) we get:

$$\frac{^{67}\text{Zn}_{\text{Mix}}}{^{68}\text{Zn}_{\text{Mix}}} \times (^{68}\text{Zn}_{\text{Sa}} + ^{68}\text{Zn}_{\text{Sp}}) = ^{67}\text{Zn}_{\text{Sa}} + ^{67}\text{Zn}_{\text{Sp}} \quad (8)$$

Combining Eq. (8) with Eqs. (5) and (6) gives:

$$\frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} \times ^{68}\text{Zn}_{\text{Sa}} + \frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} \times ^{68}\text{Zn}_{\text{Sp}} = ^{68}\text{Zn}_{\text{Sa}} \times \frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Sa} + ^{68}\text{Zn}_{\text{Sp}} \times \frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Sp} \quad (9)$$

This can be rearranged and simplified to give:

$$^{68}\text{Zn}_{\text{Sa}} \left(\frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} - \frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Sa} \right) = ^{68}\text{Zn}_{\text{Sp}} \left(\frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Sp} - \frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} \right) \quad (10)$$

Eq. (10) can also be written as:

$$\frac{^{68}\text{Zn}_{\text{Sp}}}{^{68}\text{Zn}_{\text{Sa}}} = \frac{\left(\frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} - \frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Sa} \right)}{\left(\frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Sp} - \frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} \right)} = Q \quad (11)$$

We can write a similar equation whereby,

$$\frac{^{68}\text{Zn}_{\text{Sp}}}{^{68}\text{Zn}_{\text{Sa}}} = \frac{\left(\frac{^{66}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} - \frac{^{66}\text{Zn}}{^{68}\text{Zn}} \text{ Sa} \right)}{\left(\frac{^{66}\text{Zn}}{^{68}\text{Zn}} \text{ Sp} - \frac{^{66}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} \right)} = Q \quad (12)$$

Combining Eqs. (11) and (12) gives:

$$\frac{\left(\frac{^{66}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} - \frac{^{66}\text{Zn}}{^{68}\text{Zn}} \text{ Sa} \right)}{\left(\frac{^{66}\text{Zn}}{^{68}\text{Zn}} \text{ Sp} - \frac{^{66}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} \right)} = \frac{\left(\frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} - \frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Sa} \right)}{\left(\frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Sp} - \frac{^{67}\text{Zn}}{^{68}\text{Zn}} \text{ Mix} \right)} \quad (13)$$

If we generalize Eq. (13), the following isotope dilution equation can be written:

$$\frac{(\text{Mix1} - \text{Sa1})}{(\text{Sp1} - \text{Mix1})} = \frac{(\text{Mix2} - \text{Sa2})}{(\text{Sp2} - \text{Mix2})} \quad (14)$$

where 1 and 2 denote isotopic ratios with the same denominator.

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