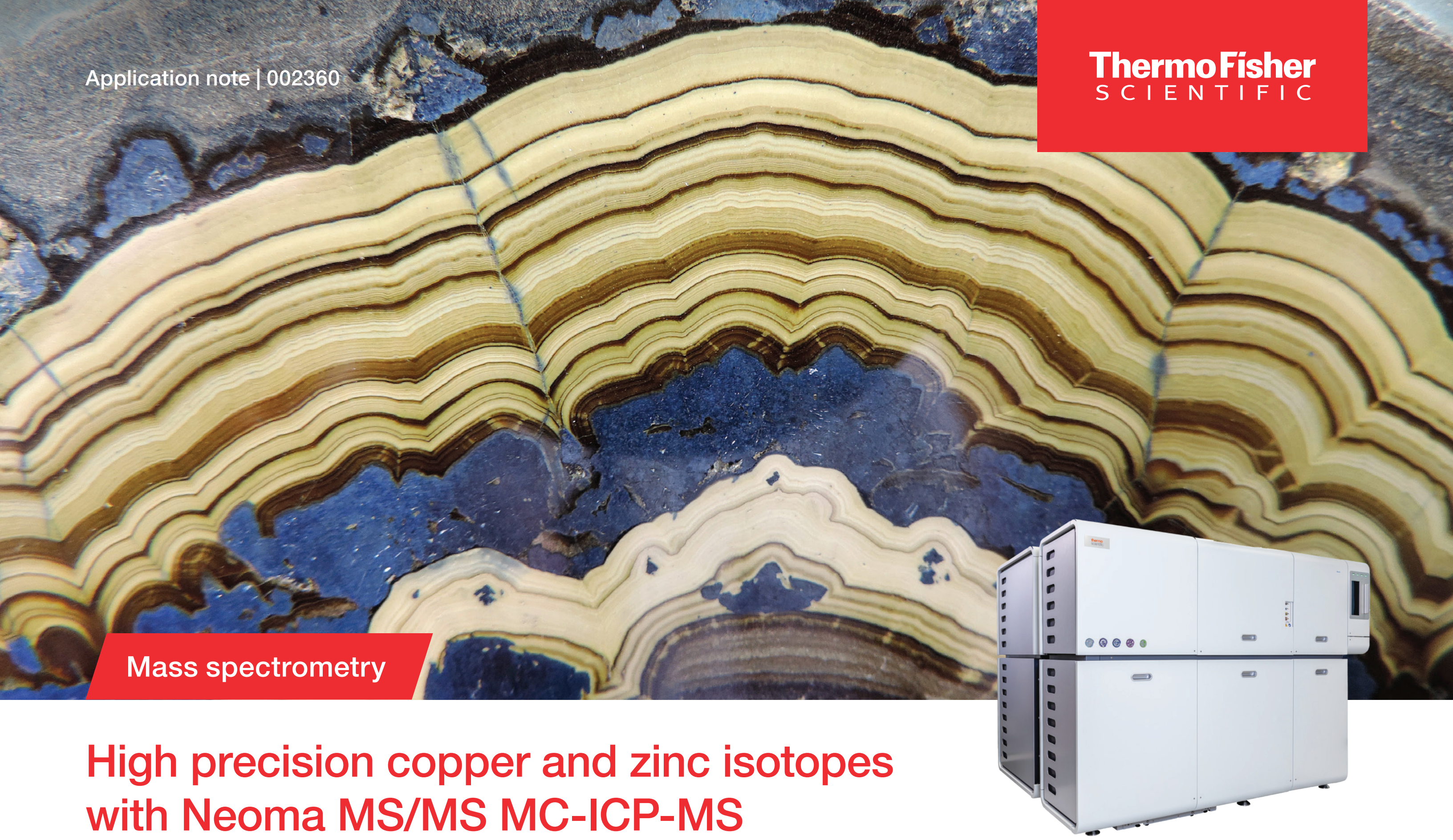
Application note | 002360



Mass spectrometry

High precision copper and zinc isotopes with Neoma MS/MS MC-ICP-MS

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Keywords

MS/MS MC-ICP-MS, Pre-cell mass filter, Copper, Zinc, Mass bias, Neoma

Goal

To demonstrate the ability of Thermo Scientific™ Neoma™ MS/MS MC-ICP-MS to measure copper and zinc isotopes at high precision.

Introduction

Copper and zinc are important metals that exhibit distinct isotopic fractionations as a result of various physical, chemical and biological processes. As a result, copper and zinc isotopes have been widely used in a range of applications, varying from cosmochemistry to medical metallomics. In this application note, we discuss the various application spaces for copper and zinc isotopes and show the capabilities of the Neoma MS/MS MC-ICP-MS for measuring these isotope systems at high precision.

Copper and zinc are important elements for studying metal cycling in the lithosphere, atmosphere, biosphere and hydrosphere. Cu is a siderophile and highly chalcophilic element with moderate volatility. It is the most refractory of the chalcophile elements. As a multivalent element in nature, Cu isotopes respond to changes in redox. Zn is a slightly siderophile and moderately volatile element. It is somewhat lithophile in nature because it often occurs in silicate, forming strong bonds with oxygen. Zinc is not multivalent in nature and thus changes in redox will not fractionate Zn isotopes in a geological context. Within the geosciences discipline, Cu and Zn isotopes have been used to trace planetary formation[1,2], core-mantle differentiation[3], mineralization and chemical weathering[4,5], and biogeochemical cycling[6,7].

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Copper and zinc are also useful tools for studying metal dispersion in the environment. Their isotope ratios have been used as a tracer of anthropogenic Cu and Zn contamination in surface and aquatic environments[8–10]. Trace metals are released by anthropogenic activities (e.g. agriculture, industry, mining, metallurgy, energy production and transport) and dispersed among the different natural compartments such as soil, water and atmosphere. To develop correct environmental management strategies, either for appropriately targeted remediation actions or to maintain emissions at sustainable levels, it is imperative to identify their sources and understand their transport and fate in the environment.

Copper isotope ratios in groundwater have also been used as a mineral exploration vector. Relatively large surface and groundwater $\delta^{65}Cu$ dispersion haloes can exist around mineral deposits[11,12].

Cu and Zn are promising elements in the biomedical field of isotope metallomics because of their small number of functional roles in biology and also because their turnover rate in the body is relatively short. Copper plays a major role in oxidizing iron and controlling electron fluxes, while Zn is a cofactor of hundreds of important enzymes. Cu and Zn isotope ratios have been used to identify multiple cancers and other diseases[13–16].

Methods

Experimental set-up

Here we present 3 analytical runs of Cu and Zn solutions (Table 1). Samples are measured via standard-sample bracketing relative to itself.

The cup configuration for all analytical runs is shown in Table 2.

Table 1. Experimental set-up of three analytical runs for Cu and Zn isotope analysis

Analytical run	1	2	3
Solution	100 ppb Zn and 100 ppb Cu in 3% HNO_3	100 ppb Zn and 100 ppb Cu in 3% HNO_3	1 ppm Zn and 1 ppm Cu in 3% HNO_3
Plasma	Wet	Dry	Wet
Sample introduction system	SIS spray chamber for Neoma MC-ICP-MS	ESI® Apex Omega™ Q desolvating nebulzer system	SIS spray chamber for Neoma MC-ICP-MS
Nebulizer	ESI 100 µL/min microFAST MC™ syringe injection autosampler	ESI 100 µL/min microFAST MC syringe injection autosampler	ESI PFA 100 µL min
Cones	X skimmer Ni cone, Jet sampler Ni cone	X skimmer Ni cone, Jet sampler Ni cone	X skimmer Ni cone, Jet sampler Ni cone
Resolution	Low	Medium	Low
Method	75 cycles of 4 second integration time (5 min total measurement time)	45 cycles of 4 second integration time (3 minute total measurement time)	50 cycles of 8 second integration time (7 min total measurement time)

Table 2. Cup configuration for Cu and Zn isotope analysis

L5	L4	L3	L2	L1	C	H1	H2	H3	H4	H5
^{62}Ni	^{63}Cu	^{64}Zn	^{65}Cu	$^{131}Xe^{++}$	^{66}Zn	^{67}Zn	$^{135}Ba^{++}$	^{68}Zn	$^{138}Ba^{++}$	^{70}Zn
10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω

The instrument settings are shown in Table 3. Note that these experiments could equally have been carried out with the base Neoma MC-ICP-MS (rather than Neoma MS/MS MC-ICP-MS). In all runs, the pre-cell mass filter was in full ion transmission mode and there was no gas within the collision/reaction cell.

Table 3. Instrument settings for 3 analytical runs described in Table 1

Analytical run	1	2	3
RF power [W]	1,200	1,200	1,200
Cool gas [L min^{-1}]	14.0	14.0	14.0
Aux gas [L min^{-1}]	0.798	0.798 (0.8)	0.798
Neb gas [L min^{-1}]	1.057	1.062	1.059
Desolvator settings	–	Ar – 4.6 L/min, N2 – 5 mL/min	–
Wien filter electric field [V]	206.5	213	213
Wien magnetic field [%]	30	30	30
Wien center mass	^{66}Zn	^{66}Zn	^{66}Zn
Pre-filter slit position [%]	95	80	80
CCT entry [V]	-50.5	-50.4	-50.4
CCT bias [V]	-0.1	-0.1	-0.1
RF amplitude [%]	96.8	96.8	96.8
CCT exit 1 [V]	-180	-180	-180
CCT exit 2 [V]	-73.1	-73.1	-73.1
CCT gas	None	None	None

Interference corrections were applied automatically with Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software (Table 4). All isotope ratios were mass bias corrected using $^{66}Zn/^{64}Zn$.

Table 4. Interference corrections applied to each isotope of interest

Isotope of interest	Interferent	Measured interference-free isotope used for correction
^{64}Zn	$^{128}Xe^{2+}$ $^{64}Ni^{+}$	$^{131}Xe^{2+}$ $^{62}Ni^{+}$
^{65}Cu	$^{130}Xe^{2+}$ $^{130}Ba^{2+}$	$^{131}Xe^{2+}$ $^{138}Ba^{2+}$
^{66}Zn	$^{132}Xe^{2+}$	$^{131}Xe^{2+}$
^{68}Zn	$^{136}Xe^{2+}$	$^{131}Xe^{2+}$

Results

Sensitivity

The absolute sensitivity of the Neoma MS/MS MC-ICP-MS is shown in Table 5. In low resolution and wet plasma, the sensitivity for 118–125 V/ppm and 46-48 V/ppm for copper and zinc respectively. For copper, this is almost an order of magnitude higher than sensitivities expressed for other available MC-ICP-MS in the market (ca. 13–34 V/ppm for Cu[17,18]). For zinc, the sensitivity of Neoma MS/MS MC-ICP-MS is a factor of 3 better than other available MC-ICP-MS at low resolution in wet plasma (16 V/ppm)[19].

In dry plasma and medium resolution, the Neoma MS/MS MC-ICP-MS out-performs other available MC-ICP-MS in the market. The sensitivity of Neoma MS/MS MC-ICP-MS for copper in medium resolution was approximately double the sensitivity achieved with other MC-ICP-MS in low resolution (90–100 V/ppm)[20]. For zinc, the sensitivity of Neoma MS/MS MC-ICP-MS in medium resolution was 197 V/ppm, more than an order of magnitude better than other MC-ICP-MS instruments also measuring in medium resolution (17 V/ppm[21]), and more than double what can be achieved in low resolution (70–80 V/ppm[22]).

Table 5. Sensitivity of each analytical run for copper and zinc

Analytical run	1 (Low resolution, wet plasma)	2 (Medium resolution, dry plasma)	3 (Low resolution, wet plasma)
Cu sensitivity (V/ppm)	125	208	118
Zn sensitivity (V/ppm)	48	197	46

Mass bias

Mass bias of Neoma MS/MS MC-ICP-MS follows the exponential law (Figure 1). All samples plot on a straight line in log-log space and the gradient of the slopes match the predicted value based on exponential mass bias law.

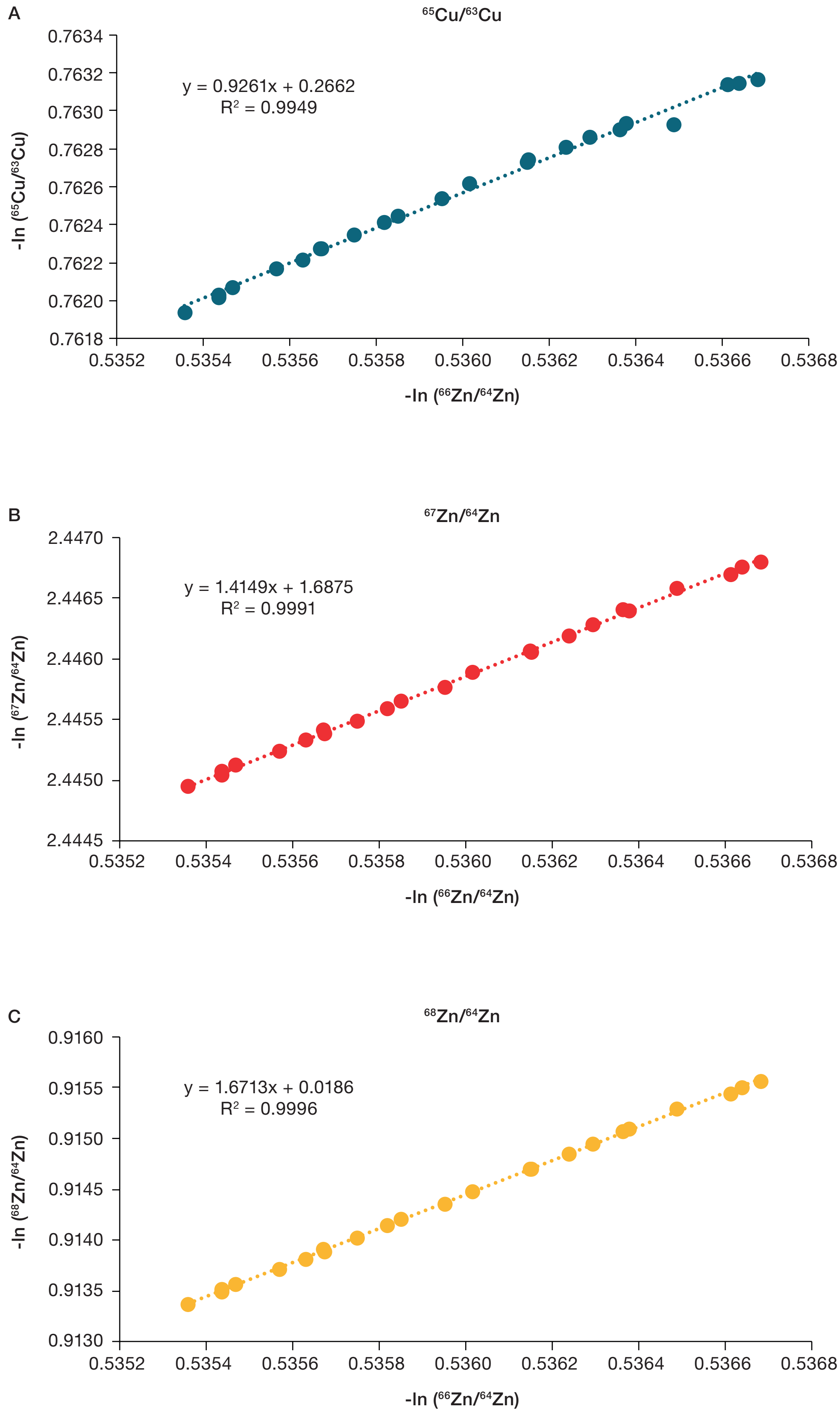

Figure 1. Log-log plots of interference-corrected samples. The expected slopes based on exponential law are (A) 0.9113, (B) 1.4244, and (C) 1.6958.

Cu isotope reproducibility

Replicate measurements of a copper/zinc solution are shown in Figure 2. The performance of Neoma MS/MS MC-ICP-MS is the same under wet plasma in low resolution and dry plasma in medium resolution – this is because the experiments have been set-up such that they produce the same number of total counts across the measurement. Internal precision is similar to external reproducibility in all experiments. At higher concentration (1 ppm Cu/Zn), the external reproducibility was 11.5 ppm (2SD) and 3.45 ppm (2SE).

Zn isotope reproducibility

A similar picture is observed for zinc isotopes, with the external reproducibility of the 1,000 ppb (Analytical run 3) of 17.5 ppm and 22.7 ppm (2SD) for δ^{67}Zn and δ^{68}Zn, respectively (Figure 3). The standard errors are 4.9 ppm and 6.3 ppm (2SE) for δ^{67}Zn and δ^{68}Zn, respectively.

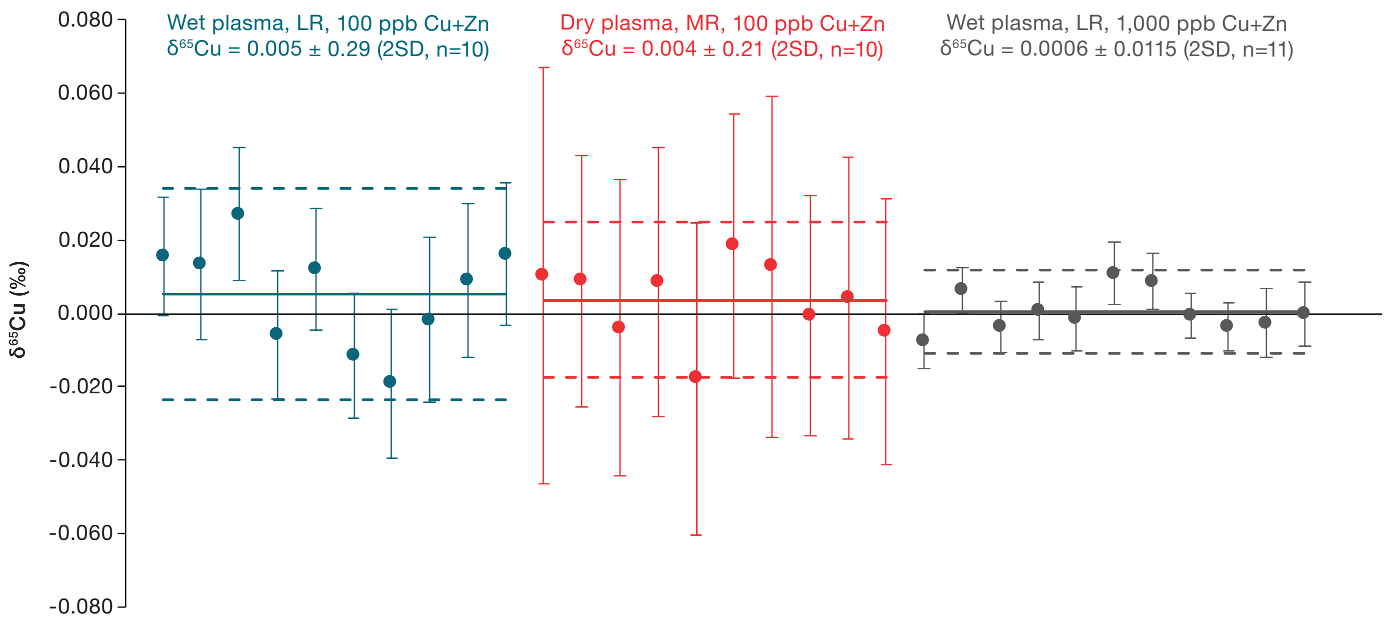

Figure 2. Replicate measurements of copper/zinc solution. δ^{65}Cu has been mass bias corrected using ^{66}Zn/^{64}Zn. (Blue) Analytical run 1 – wet plasma, low resolution, 100 ppb Cu/Zn, (Red) Analytical run 2 – dry plasma, medium resolution, 100 ppb Cu/Zn, (Gray) Analytical run 3 – wet plasma, low resolution, 1,000 ppb Cu/Zn.

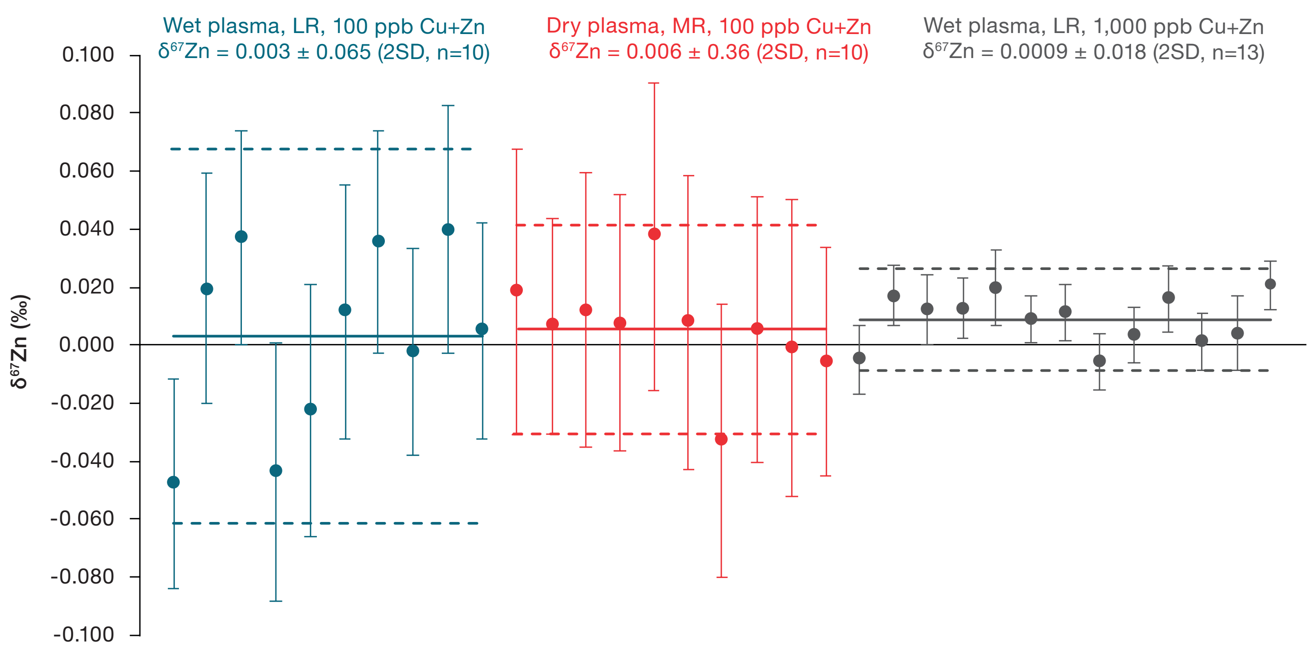

Figure 3. Replicate measurements of copper/zinc solution. δ^{67}Zn and δ^{68}Zn have been mass bias corrected using ^{66}Zn/^{64}Zn. (Blue) Analytical run 1 – wet plasma, low resolution, 100 ppb Cu/Zn, (Red) Analytical run 2 – dry plasma, medium resolution, 100 ppb Cu/Zn, (Gray) Analytical run 3 – wet plasma, low resolution, 1,000 ppb Zn.

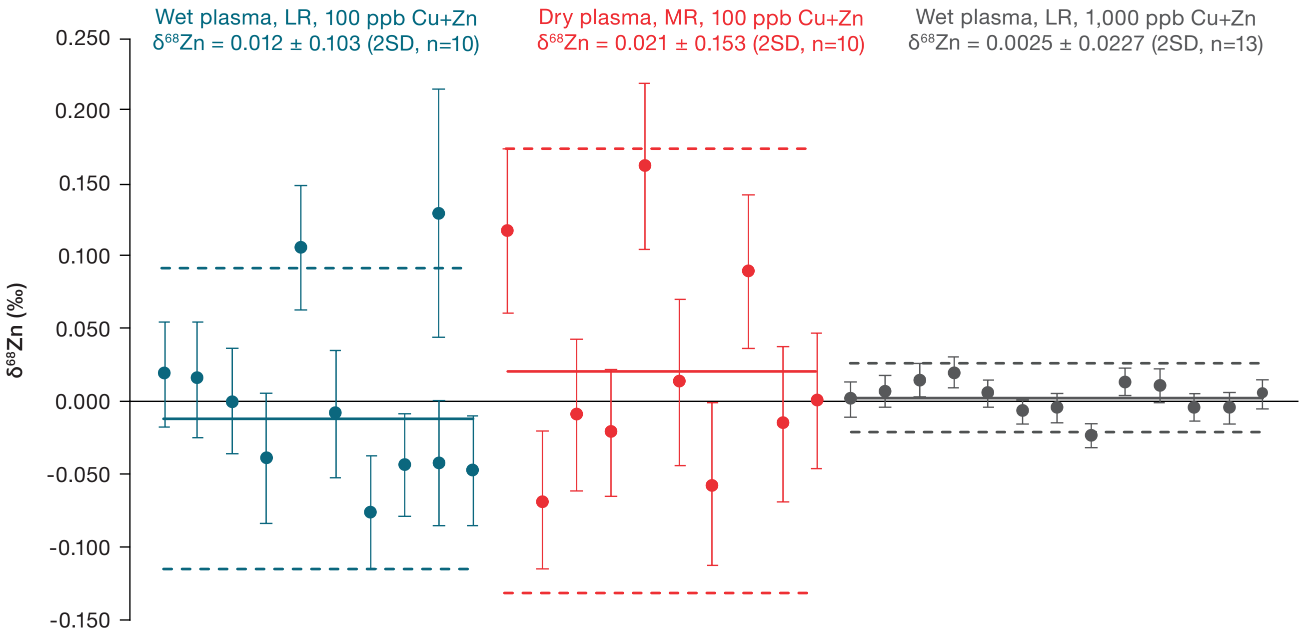

Figure 3 continued. Replicate measurements of copper/zinc solution. $\delta^{67}Zn$ and $\delta^{68}Zn$ have been mass bias corrected using $^{66}Zn/^{64}Zn$. (Blue) Analytical run 1 – wet plasma, low resolution, 100 ppb Cu/Zn, (Red) Analytical run 2 – dry plasma, medium resolution, 100 ppb Cu/Zn, (Gray) Analytical run 3 – wet plasma, low resolution, 1,000 ppb Zn.

Conclusion

Neoma MS/MS MC-ICP-MS in full ion transmission mode can be used to measure copper and zinc isotopes at ppm-level precision. Instrumental sensitivity is more than double that achievable by other MC-ICP-MS instruments available. Mass bias is predictable, following the exponential law. This allows copper and zinc isotopes to be accurately corrected for mass bias, producing accurate as well as high precision isotope data.

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Appendix

A1. Analytical run 1

	MBC		MBC		MBC	
	δ^{65}Cu	2SE	δ^{67}Zn	2SE	δ^{68}Zn	2SE
	0.016	0.016	-0.048	0.036	0.018	0.029
	0.013	0.021	0.019	0.040	0.015	0.022
	0.027	0.018	0.037	0.036	0.000	0.027
	-0.006	0.017	-0.044	0.045	-0.039	0.021
	0.012	0.017	-0.023	0.043	0.106	0.033
	-0.012	0.017	0.012	0.044	-0.008	0.026
	-0.019	0.020	0.035	0.039	-0.077	0.031
	-0.002	0.022	-0.002	0.035	-0.045	0.031
	0.009	0.021	0.040	0.043	-0.042	0.023
	0.016	0.019	0.005	0.038	-0.048	0.028
	δ^{65}Cu	2SE	δ^{67}Zn	2SE	δ^{68}Zn	2SE
Mean	0.005	0.019	0.003	0.040	-0.012	0.027
2SD	0.029	–	0.065	–	0.103	–

A2. Analytical run 2

	MBC		MBC		MBC	
	δ^{65}Cu	2SE	δ^{67}Zn	2SE	δ^{68}Zn	2SE
	0.010	0.057	0.019	0.049	0.118	0.057
	0.009	0.034	0.007	0.037	-0.068	0.047
	-0.004	0.040	0.012	0.047	-0.010	0.052
	0.009	0.037	0.008	0.044	-0.021	0.044
	-0.018	0.043	0.038	0.053	0.162	0.057
	0.018	0.036	0.008	0.051	0.013	0.057
	0.013	0.047	-0.033	0.047	-0.057	0.055
	-0.001	0.033	0.006	0.046	0.089	0.052
	0.004	0.038	-0.001	0.051	-0.016	0.053
	-0.005	0.036	-0.006	0.040	0.000	0.047
	δ^{65}Cu	2SE	δ^{67}Zn	2SE	δ^{68}Zn	2SE
Mean	0.004	0.040	0.006	0.047	0.021	0.052
2SD	0.021	–	0.036	–	0.153	–

A3. Analytical run 3

	MBC		MBC		MBC	
	δ^{65}Cu	2SE	δ^{67}Zn	2SE	δ^{68}Zn	2SE
	-0.0077	0.0075	-0.0048	0.0119	0.0015	0.0122
	0.0063	0.0064	0.0171	0.0102	0.0069	0.0099
	-0.0038	0.0071	0.0122	0.0119	0.0139	0.0114
	0.0007	0.0079	0.0129	0.0104	0.0199	0.0100
	-0.0015	0.0089	0.0197	0.0130	0.0051	0.0095
	0.0109	0.0085	0.0086	0.0086	-0.0072	0.0084
	0.0086	0.0077	0.0113	0.0094	-0.0046	0.0100
	-0.0006	0.0062	-0.0060	0.0097	-0.0235	0.0085
	-0.0039	0.0065	0.0036	0.0098	0.0134	0.0094
	-0.0027	0.0094	0.0159	0.0112	0.0103	0.0119
	-0.0001	0.0087	0.0012	0.0098	-0.0041	0.0092
	–	–	0.0041	0.0129	-0.0044	0.0111
	–	–	0.0206	0.0086	0.0049	0.0104
	δ^{65}Cu	2SE	δ^{67}Zn	2SE	δ^{68}Zn	2SE
Mean	0.0006	0.0077	0.0090	0.0106	0.0025	0.0101
2SD	0.0115	–	0.0175	–	0.0227	–

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