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Correction Strategies for Isotopic Ratios in Overspiked Samples Using the Double Spike Technique

Jian-Ming Zhu,* Wenlong Sun, Thomas M. Johnson, Zhuo Lu, and Decan Tan

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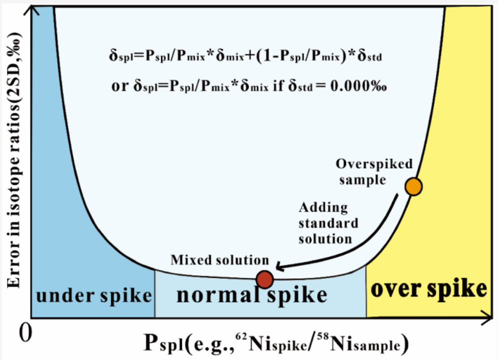
ABSTRACT: The double spike (DS) technique is a highly effective approach for measuring the isotope ratios of many elements. However, it is common for some fraction of the prepared samples to be "overspiked." The usual solution for this problem involves repurifying and reanalyzing the samples to ensure data accuracy. Here, we propose a straightforward mathematical scheme to rectify the isotope ratios of overspiked samples, avoiding repetitive, time-consuming operations. The principle behind this scheme is that adding a standard solution with the certified isotope ratio decreases the overspiked ratio to the normal range. The related theoretical equations and a thorough error propagation model are presented. Taking nickel (Ni) isotopes as an example, we demonstrate how to utilize the spike-to-sample ratios of the overspiked sample and the sample-standard mixture, as well as the spike-subtracted isotope ratios of the mixture ($\delta^{60}Ni_{mix}$), to accurately determine the actual sample isotopes. This method's accuracy and precision (2SD) were evaluated by testing Ni, chromium (Cr), and cadmium (Cd) isotope measurements. Precision consistent with traditional DS measurements can be achieved when the fraction of the added standard solution (f_{std}) is ≤0.60 (60%) in the mixture or when the overspiked multiple is ≤2.5. The added standard solution is recommended to be the same as the standard used to define the delta scale (e.g., $\delta^{60}Ni$ = 0.000‰) to simplify the calculation procedures. This method expands the application of DS from the normal to the overspiked range and can be extended to isotope analyses of many elements where DS is applicable.



■ INTRODUCTION

The double spike (DS) technique, initially proposed by Dodson,[1] has become a routine method for measuring stable isotopes of many elements with extremely high precision. This method, utilized with thermal ionization mass spectrometry (TIMS) and multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), has delivered higher accuracy and precision in analyzing the isotopic compositions of elements such as Pb,[2,3] Ca,[4,5] Fe,[6] Cr,[7−9] Se,[10,11] Mo,[12,13] and more.[14−17] Unlike the sample-standard bracketing (SSB)[18,19] and element doping (ED)[20,21] that have been employed to correct for instrumental mass discrimination, DS not only rectifies any isotopic fractionation that might occur during the chemical purification of samples and measurement but also demonstrates a remarkable tolerance for matrix effects and low yields.[22,23] Additionally, it can ascertain accurate sample concentrations when the amount of DS added is known.[22] Therefore, the DS method is the preferred choice for determining the isotopic composition of elements with ≥ three isotopes.[24] However, the method is inherently challenging in certain aspects, such as selecting double spikes and optimizing the mixing ratio between the double spikes and between the spikes and samples.[3,25−29]

With regard to the issues mentioned above, Galer,[3] Rudge et al.,[26] John[27] and other researchers[9,28,29] have addressed these issues comprehensively and provided a DS toolbox for users.[26,30] Once a DS solution has been created and stored carefully to maintain a constant ratio (e.g., $^{61}Ni_{spike}/^{62}Ni_{spike}$ = 0.901839 in this study), there exists a U- or V-shaped relationship between the uncertainty of theoretical or measured δ values and the ratio of spike (spk) to sample (spl).[26,27,31,32] Usually, the slope of the curve near the optimal ratio is small, and this allows us to obtain accurate isotope ratio determinations with the smallest achievable error propagation across an optimized range of spk/spl ratios (e.g., $^{62}Ni_{spk}/^{58}Ni_{spl}$ = 0.9−1.5 in this study). According to the relationship between the spk/spl ratio and the U-shaped curve of uncertainty, samples with spk/spl ratios across the range where uncertainties are very close to optimal are named "normally spiked."[32] Those higher (spike/sample ratios much higher than the optimal ratio) or lower than the bound of the normal range are defined as "overspiked" or "underspiked."[32] Or, based on the expected precision or observed drift in actual measurements,[33] we can still divide the U-shaped curve into

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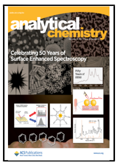

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under, normal, and overspiked regions (Figure 1). Previous studies have primarily focused on applying the DS method within the normal spike range;[3,26−29] overspiked samples have not been discussed in detail.

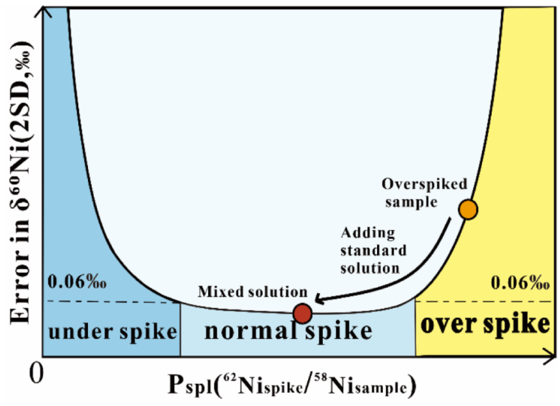

Figure 1. A schematic diagram displaying the normal, under-, and overspiked regions and the principle of overspiked ratio moving to the normal spike ratio after adding a standard solution.

Overspiking and underspiking of samples can occur accidentally due to errors in spike addition or when the sample mass is limited or incorrectly determined during practical operation. Currently, there is no mathematical method to calibrate underspiked samples, except for using a standard solution with the same spk/spl ratio to normalize results,[34] or adding more spike to bring the ratio to the normal range, if the sample yield is 100%. For overspiked samples, similar approaches can also be used for calibration, but the accuracy and precision of the actual calibration are questionable and debatable, often requiring the repurification of a new sample aliquot and further validation. This process wastes time on repetitive work. Here, we propose a new mathematical scheme to accurately extract the isotope ratios of overspiked samples, which efficiently boosts the application of DS from the normal range to include a significant fraction of the overspiked range.

In this method, we add to the overspiked sample solution a certain amount of standard solution with certified isotope ratios; this adjusts the spk/spl ratio to the normal or optimal range. Prior to this adjustment, the spk/spl ratio of the original overspiked sample solution is determined by analyzing some of the solution and applying the normal DS data reduction routine. After the addition of the standard solution, the sample-standard mixture is analyzed to precisely determine the spk/spl ratio of the mixture and the isotopic composition of the spike-subtracted mixture using the normal DS data reduction calculations. Using these three pieces of data, we calculated the sample isotope ratio and its standard deviation (SD) through the isotope binary mixing and error propagation model. The precise proportion of the added standard solution (f_{std}) relative to the sample is determined from the known spk/spl ratio of the overspiked sample and the measured spk/spl ratio of the mixture. The validation of this approach was demonstrated by actual measurements of Ni, Cr, and Cd isotopes. This mathematical scheme improves the effectiveness and efficiency of the DS application, serving as a bridge to the normally spiked range for overspiked samples that typically were discarded previously. Theoretically, this scheme can be extended to more than 33 elements whose isotope ratios can be measured by the DS method.

EXPERIMENTAL DETAILS

The Correction Formula for Overspiked Samples. The DS method can obtain accurate and precise data when the spk/spl ratio, the proportion of DS in a spiked sample,[26] falls within the optimal range and is close to the specific optimal ratio where the analytical uncertainty is minimized.[3,26,27] For example, Ni has four stable isotopes: ^{58}Ni, ^{60}Ni, ^{61}Ni, and ^{62}Ni. ^{61}Ni and ^{62}Ni are generally selected as the double spike isotopes.[35,36] With ^{58}Ni being the most abundant stable Ni isotope in natural samples, the relative amount of spike and sample Ni in a spiked sample is conveniently expressed using the $^{62}Ni_{spk}/^{58}Ni_{spl}$ ratio, which is mathematically determined after the spiked sample is analyzed. The current optimal $^{62}Ni_{spk}/^{58}Ni_{spl}$ range is 0.9−1.5 for the Ni DS in our study (Table S1), slightly narrower than before,[36] and the optimal ratio is still 1.25.[36] When $^{62}Ni_{spk}/^{58}Ni_{spl}$ is >1.5, the sample or standard (std) δ^{60}Ni ($\delta^{60}Ni(‰) = ((^{60}Ni/^{58}Ni)_{sample}/(^{60}Ni/^{58}Ni)_{NIST\ 986} - 1)*1000$) value usually drifts away from the actual value and its precision also becomes increasingly worse with the increase of the $^{62}Ni_{spk}/^{58}Ni_{spl}$ ratio.[36] In this situation, the higher ratio of $^{62}Ni_{spk}/^{58}Ni_{spl}$ can be decreased to the normal range (e.g., 1.25−1.50) by adding a standard solution such as Ni-NIST 986 with a known isotope composition. Then, the ratios of the initial sample $^{62}Ni_{spk}/^{58}Ni_{spl}$ and mixed sample $^{62}Ni_{spk}/^{58}Ni_{mix(spl+std)}$ (after adding the standard solution) can be precisely obtained for each solution using the normal DS measurement and data reduction routine.[10,12,30,37] Thus, the real sample proportion (f_{spl}) in the mixture can be solved in terms of $^{62}Ni_{spk}/^{58}Ni_{spl}$ and $^{62}Ni_{spk}/^{58}Ni_{mix}$, and the sample's isotope composition can also be obtained through the mathematical removal of the added standard Ni using a binary isotope mixing model.[32] The correction formula is listed below:

$$\frac{^{62}Ni_{spk}}{^{58}Ni_{spl}} = P_{spl} \tag{1}$$

$$\frac{^{62}Ni_{spk}}{^{58}Ni_{mix}} = P_{mix} \tag{2}$$

P_{spl} and P_{mix} denote spk/spl ratios of the sample and the mixture of the sample with the added standard solution. Subscripts "std," "spl," "spk," and "mix" represent the standard, sample, spike, and mixed solution or mixture, respectively.

Then, eqs 1 and 2 can be reorganized into eqs 3 and 4 in terms of $f_{spl} + f_{std} = 1$:

$$f_{spl} = \frac{^{58}Ni_{spl}}{^{58}Ni_{mix}} = \frac{^{62}Ni_{spk}/P_{spl}}{^{62}Ni_{spk}/P_{mix}} = \frac{P_{mix}}{P_{spl}} \tag{3}$$

$$f_{std} = 1 - f_{spl} = 1 - \frac{P_{mix}}{P_{spl}} \tag{4}$$

The isotope binary mixing model, as presented in Lu et al.,[32] is expressed as:

$$\delta_{mix} = f_{spl} \times \delta_{spl} + f_{std} \times \delta_{std} \tag{5}$$

where f_{spl} and f_{std} are individually ^{58}Ni molar fractions of the sample and added standard solution in the mixture. Since the

Table 1. Corrected δ^{60}Ni Values of the Overspiked NOD-A-1 and NOD-P-1

		Added NIST 986			Added NIST 3136			Added Alfa Ni		
Sample type	P_{spl}	P_{mix}	f_{std}	δ^{60}Ni(‰)	P_{mix}	f_{std}	δ^{60}Ni(‰)	P_{mix}	f_{std}	δ^{60}Ni(‰)
NOD-A-1	2.3375	1.0855	0.5357	1.034	1.0687	0.5428	1.025	1.0915	0.5331	1.040
2SD (n = 3)	0.0001	0.0008	0.0002	0.049[a]	0.0007	0.0004	0.049[a]	0.0006	0.0003	0.049[a]
	3.1883	0.9991	0.6866	1.008	0.9991	0.6866	1.029	1.0090	0.6835	1.031
2SD (n = 3)	0.0001	0.0005	0.0002	0.077[a]	0.0006	0.0002	0.077[a]	0.0006	0.0002	0.077[a]
Average	**1.028 ± 0.038** (2SD[b], n=6)									
Normal DS	1.020±0.050[36]−1.034 ± 0.059[44]									
NOD-P-1	2.7003	1.2320	0.5437	0.325	1.2097	0.5522	0.311	1.2355	0.5424	0.332
2SD (n = 3)	0.0001	0.0007	0.0003	0.050[a]	0.0004	0.0004	0.051[a]	0.0008	0.0003	0.050[a]
	3.7496	0.9643	0.7428	0.329	0.9616	0.7435	0.349	0.9844	0.7375	0.326
2SD (n = 3)	0.0001	0.0005	0.0001	0.097[a]	0.0006	0.0002	0.097[a]	0.0006	0.0002	0.095[a]
Average	**0.329 ± 0.056** (2SD[b], n = 6)									
Normal DS	0.330 ± 0.050[36]−0.358 ± 0.069[44]									

[a] Uncertainty for sample, derived by error propagation through the mixing equation: $\sigma_{\delta\text{-spl}}$. [b] Actual sample precision (2SD) was calculated by $2SD = \sqrt{(\sigma_{external})^2 + (\sigma_{\delta\text{-spl}})^2}$.[38]

offset between ^{58}Ni molar fraction and Ni molar fraction is negligible within the analytical precision, f_{std} and f_{spl} refer to the Ni standard and sample fraction for the following narrative. δ_{std}, δ_{spl}, and δ_{mix} are the δ^{60}Ni values of the standard, sample, and mixed solution, respectively. Rearranging eq 5 gives:

$$\delta_{spl} = \frac{\delta_{mix}}{f_{spl}} - \frac{f_{std}}{f_{spl}} \times \delta_{std} \tag{6}$$

Substituting for f in eq 6 using eqs 3 and 4, we obtain

$$\delta_{spl} = \frac{P_{spl}}{P_{mix}}\delta_{mix}\left(1 - \frac{P_{spl}}{P_{mix}}\right)\delta_{std} \tag{7}$$

If we select NIST 986 (δ^{60}Ni = 0.000‰, others are similar) as an added standard solution, eq 7 can be simplified as

$$\delta_{spl} = \frac{P_{spl}}{P_{mix}}\delta_{mix} \tag{8}$$

Error Propagation Model (EPM). In eq 7, P_{spl} is consistently larger than P_{mix} for the overspiked samples, and the uncertainty ($\sigma_{\delta\text{-std}}$) of the isotopic composition of the added standard solution can be considered a constant, representing a long-term external reproducibility of 0.020‰ for δ^{60}Ni in this study. Therefore, the calculated δ_{spl} uncertainty primarily depends on the errors related to the P and δ values of the sample and mixed solutions.[32,38] According to Lu et al.,[32] P_{mix} is always within the normal range; then the δ_{spl} error increases nonlinearly when P_{spl} becomes too large. Consequently, we can utilize Monte Carlo simulation and standard error propagation approaches to assess the uncertainty of the sample's δ value derived from eq 7. Sample propagation error ($\sigma_{\delta\text{-spl}}$) can be calculated using eq 9 (details listed in Text S1):

$$\sigma_{\delta\text{-spl}} = \frac{\sqrt{(P_{mix} - P_{spl})^2\sigma_{\delta\text{-std}}^2 + P_{spl}^2\sigma_{\delta\text{-mix}}^2}}{P_{mix}} \tag{9}$$

Where $\sigma_{\delta\text{-std}}$ and $\sigma_{\delta\text{-mix}}$ represent the two standard deviation (2SD) values of the measured standard (here we use long-term reproducibility) and mixed solutions.

Reagents and Materials. The used optima-grade HF, HCl, and HNO_3, bought from Beijing Institute of Chemical Reagents (China), were distilled once using subboiling stills (DST-1500 and −4000, Savillex). A Milli-Q Element system (Millipore, USA) provided ultrapure water with 18.2 MΩ·cm^{-1} resistivity. H_2O_2 (35%, w/w, trace metal grade) was purchased from Alfa Aesar in China. The isotope standards, including NIST 986(Ni), 3108(Cd, lot: 130116), 979(Cr), and plasma standard solutions including NIST 3136 Ni (lot:120619, 10003 μg mL^{-1}), Alfa Ni (lot:595169P, 10000 μg mL^{-1}), BAM-I012 Cd and Spex Cd (Lot: CL8−71CDY, 1000 μg mL^{-1}), NIST 3112a Cr (lot: 030730, 9922 μg mL^{-1}), and Alfa Cr (lot:595169C, 1000 μg mL^{-1}), were acquired from the National Institute of Standards and Technology (NIST, USA), Alfa Aesar, the Federal Institute for Materials Research and Testing, Germany (BAM) and Merck(China), respectively. Six geological reference materials (GRMs) were purchased from the United States Geological Survey (USGS) and one from the Geological Survey of Japan (GSJ). The Fe−Mn nodules NOD-A-1 and NOD-P-1, basalts BHVO-2, dunite DTS-2b, andesite AGV-2, shale SGR-1b, and peridotite JP-1 were determined in this study.

Overspiked Sample Preparation and Mass Spectrometry. Sample decomposition followed procedures presented in Zhu et al.[8] The digested solutions were stored in 1 mL of 10% (v/v) HNO_3. Besides the normal spike samples,[36] all other sample aliquots containing 500 ng Ni were overspiked in terms of the designed $^{62}Ni_{spk}/^{58}Ni_{spl}$ ratio before purification. The chemical separation protocol is given in Wu et al.[36] and listed in Table S2. The total procedural blanks of Ni were below 1.23 ± 0.20 ng (2SD, n = 4). Since only standard solutions were performed for Cd and Cr isotopes, we carried out overspiked measurements without further purification. The normal range is 0.8−6.0 with the optimized ratio of 2.0 for $^{111}Cd_{spk}/^{112}Cd_{spl}$[39] and 0.2−2.0 with an optimum value of 0.35 for $^{54}Cr_{spk}/^{52}Cr_{spl}$,[8] their designed ratios of spk to spl in overspiked samples is expected to be ≥6.0 and ≥2.0, respectively.

The Ni, Cd, and Cr isotopes were determined on the Neptune Plus MC-ICP-MS (ThermoFisher Scientific) at the Isotope Geochemistry Laboratory, China University of Geosciences (Beijing). The instrumental cup configurations and parameters are given in the literature,[8,39,40] and in Table S3. Following previous studies, we employed an improved Aridus II desolvator (Cetac, USA) sample introducing system with an ice chamber to enhance signal sensitivity.[41,42] Ni and Cd isotopes were analyzed in the low-resolution mode at 30 μg L^{-1} and 10 μg L^{-1} during the analytical session, respectively.[36,40] Cr isotopes were performed in high-resolution mode at 25 μg L^{-1}. Each sample was measured three times to achieve better accuracy and precision. The Cr and Cd isotope ratio is expressed as per mil (‰) deviation relative to NIST 979 and 3108,[43] respectively: $\delta^{53}Cr(‰) = ((^{53}Cr/^{52}Cr)_{sample}/(^{53}Cr/^{52}Cr)_{NIST\ 979} - 1) \times 1000$, and $\delta^{114}Cd(‰) = ((^{114}Cd/^{110}Cd)_{sample}/(^{114}Cd/^{110}Cd)_{NIST\ 3108} - 1) \times 1000$.

■ RESULTS AND DISCUSSION

Selection of Added Standard Solutions. Theoretically, for a homogeneous sample solution, its isotope ratio obtained through eqs 7 and 8 should be consistent with the sample's true value when mixed with any standard solution with a certified isotopic ratio. In other words, mixing the sample with any selected standard solution is practically feasible. This hypothesis, which we verified in our studies, can be easily implemented. We utilized overspiked GRM NOD-A-1 ($^{62}Ni_{spk}/^{58}Ni_{spl}$ = 2.3375 and 3.1883) and NOD-P-1 ($^{62}Ni_{spk}/^{58}Ni_{spl}$ = 2.7003 and 3.7496) as samples (Table 1), and the standard solutions, NIST 986, NIST 3136, and Alfa Ni, were added to verify that any isotopic standard can be used. Table 1 shows that the uncertainty of the final δ^{60}Ni values increases with the amount of the standard solution added. Including both the highly overspiked samples and the mildly overspiked samples, the average value of δ^{60}Ni is 1.028 ± 0.038‰ (2SD, n = 6) for NOD-A-1 and 0.329 ± 0.056‰ (2SD, n = 6) for NOD-P-1. All corrected values are highly consistent with the reported data within the uncertainty,[36,40,44] confirming that adding any standard solution is effective. However, it should be noted that the "delta-zero" value of standard NIST 986 can significantly simplify the calculation procedures, as given in eq 8.

Results for overspiked Cd and Cr solutions are given in Table 2. Once again, propagated uncertainties for isotopic compositions determined by the standard addition method for overspiked samples are low, and the results are consistent with published values. This observation strongly suggests that the same approach can be used effectively for many other elements for which the DS method can be applied.

Evaluating Accuracy and Precision. Reference materials are one of the best approaches to evaluate the reliability of methods. Standard solution (Alfa Ni) and GRMs with known isotope ratios, including NOD-A-1, NOD-P-1, AGV-2, BHVO-2, DTS-2b, JP-1,and SGR-1b (Table S4), were analyzed to scrutinize the accuracy and precision of this method. The validation of this method was confirmed through analysis of overspiked solutions of these GRMs, with the range obtained through the DS data reduction routine from 1.4138 (designed initially as 1.60; the actual ratio is 1.4138, but this does not affect the results) to 5.0301 (Table S4). By substituting the $\delta^{60}Ni_{mix}$, P_{mix}, and P_{spl} ratio of an overspiked sample into eq 7 or 8, and 9, the Ni isotope ratio and propagation error of each sample can be obtained. As shown in Figure 2, the obtained δ^{60}Ni values and their precision are consistent with previously reported values[44,45] and our laboratory's long-term reproducibility of Ni isotopes.[36,40,42] Furthermore, validation using Cd and Cr isotopes was also conducted. Our calculated values are −2.117 ± 0.055 (2SD, n = 6, Spex-Cd), −1.313 ± 0.055‰ (2SD, n = 6, BAM-I012) for δ^{114}Cd, and −0.072 ± 0.084‰ (2SD, n = 6, NIST 3102a), −0.001 ± 0.090‰ (2SD, n = 6, Alfa Cr) for δ^{53}Cr (Table 2), respectively. These results remained consistent with the published values,[8,32,38,43,46] or measured data by traditional DS method,[16,39,43] reinforcing the reliability and practicality of this method.

Table 2. Corrected Values of δ^{114}Cd and δ^{53}Cr in the Overspiked Samples

Sample type	P_{spl}	P_{mix}	f_{std}	δ^{114}Cd(‰)	$\sigma_{\delta\text{-spl}}$ (n^{e}= 3)
Spex Cd[a]	6.2333	3.2943	47.15	−2.119	0.042
	5.1597	2.8147	45.45	−2.115	0.040
Average				**−2.117 ± 0.055** (2SD[c], n = 6)	
Normal DS[38]				−2.113	0.041
BAM-I012[a]	7.4791	3.9399	47.32	−1.308	0.042
	6.1735	3.4149	44.69	−1.318	0.040
Average				**−1.313 ± 0.055** (2SD[c], n = 6)	
Normal DS[39,43]				−1.329 ± 0.045 to −1.332 ± 0.043	
	P_{spl}	P_{mix}	f_{std}	δ^{53}Cr/(‰)	$\sigma_{\delta\text{-spl}}$ (n = 3)
NIST 3112a[b]	4.6201	1.2046	73.93	−0.072	0.095
	2.8790	1.0020	65.20	−0.073	0.069
Average				**−0.072 ± 0.084** (2SD[c], n = 6)	
Normal DS[8]				−0.07	0.04
Alfa Cr[b]	3.8326	0.8574	77.63	−0.001	0.106
	2.9605	1.0439	64.74	0.004	0.069
Average				**0.001 ± 0.090** (2SD[c], n = 6)	
Normal DS[d]				−0.011	0.021

[a] Added standard solution is NIST 3108 Cd to all Cd overspiked samples. [b] Added standard solution is NIST 979 Cr to all Cr overspiked samples. [c] Actual sample precision (2SD) was calculated by $2SD = \sqrt{(\sigma_{external})^2 + (\sigma_{\delta\text{-spl}})^2}$.[38] $\sigma_{external}$ is 0.041‰ for δ^{114}Cd[38] and 0.020‰ for δ^{53}Cr.[41] [d] It is determined by the normal DS method in this study. [e] n is the number of independent analyses.

When dealing with overspiked samples, adding a standard solution to a sample can introduce additional errors.[32] It is crucial for us to understand the relationship between the overspiked ratio and propagation error. As stated in the DS-standard addition (SA) method, increasing the standard fraction (f_{std}) in the mixed solution can result in a higher sample error propagation.[32,38] This observation also applies to overspiked samples, in which the higher overspiked ratios encounter more error propagation. In eq 3, the overspiked multiple (P_{spl}/P_{mix}) has a mutual reciprocal relationship with the sample fraction ($1/f_{spl} = P_{spl}/P_{mix}$), implying the higher the overspiked multiples, the smaller the f_{spl} and the larger the propagation error, which is similar to the observation in previous studies.[26,27,32,38] In EPM (eq 9), the $\sigma_{\delta\text{-std}}$ and $\sigma_{\delta\text{-mix}}$ can be assumed to be constants replaced by the long-term reproducibility of Ni isotopes. Since P_{spl} is always greater than the difference of $P_{spl}-P_{mix}$, and P_{mix} should be within the normal range ($^{62}Ni_{spk}/^{58}Ni_{spl}$ = 0.9−1.5),[32] $\sigma_{\delta\text{-spl}}$ should be proportional to the ratio of P_{spl}/P_{mix} or the overspiked multiple. As presented in Figure 3, the propagated error, $\sigma_{\delta\text{-spl}}$, has a nonlinear relationship with P_{spl} but it is linearly proportional to the overspike multiple. That is, the larger the P_{spl} ($^{62}Ni_{spk}/^{58}Ni_{spl}$), the poorer the precision of the samples' corrected data. When P_{spl}/P_{mix} is greater than 2.5 (corresponding to $^{62}Ni_{spk}/^{58}Ni_{spl} \approx 3.0$ in Table S4), the precision of the sample-corrected δ^{60}Ni value is generally >0.060‰, with the maximum reaching 0.125‰ (P_{spl}/P_{mix} = 4.906 at $^{62}Ni_{spk}/^{58}Ni_{spl}$ = 5.0301). On the other hand, when P_{spl}/P_{mix} is less than or equal to 2.5 (corresponding to $^{62}Ni_{spk}/^{58}Ni_{spl} \leq 3.0$), the calculated propagation error is usually ≤0.060‰, consistent with the long-term precision of Ni isotopes obtained by the normal DS method.[36,40,44,45] If high-precision data of

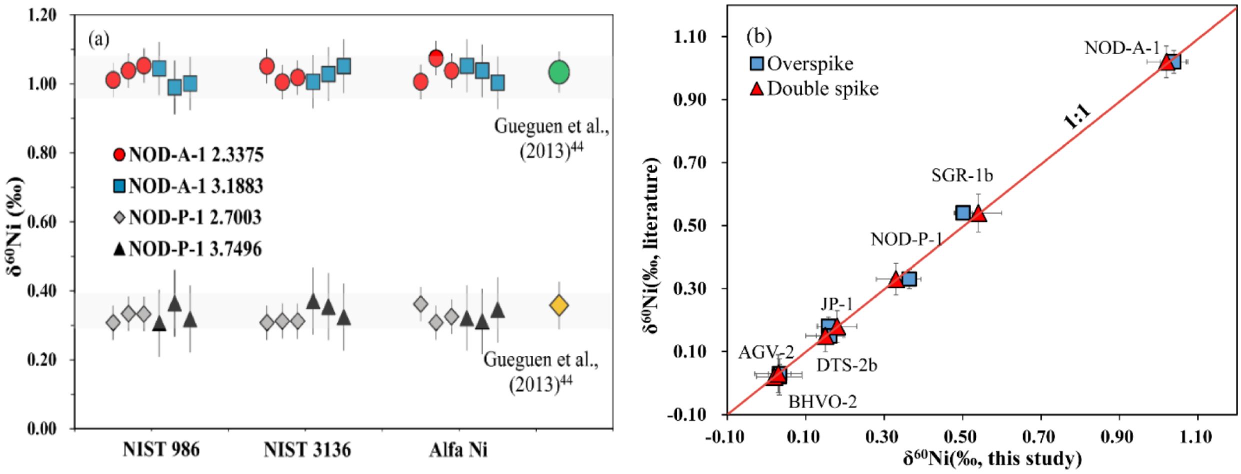

Figure 2. Accuracy comparison of Ni isotope data between the overspiked correction in this study and traditional DS published in previous studies.[36,40,44,45] (a) The corrected δ^{60}Ni values of the overspiked NOD-A-1 and NOD-P-1 by adding different standard solutions. (b) Comparison of δ^{60}Ni values obtained by overspike correction with traditional DS.

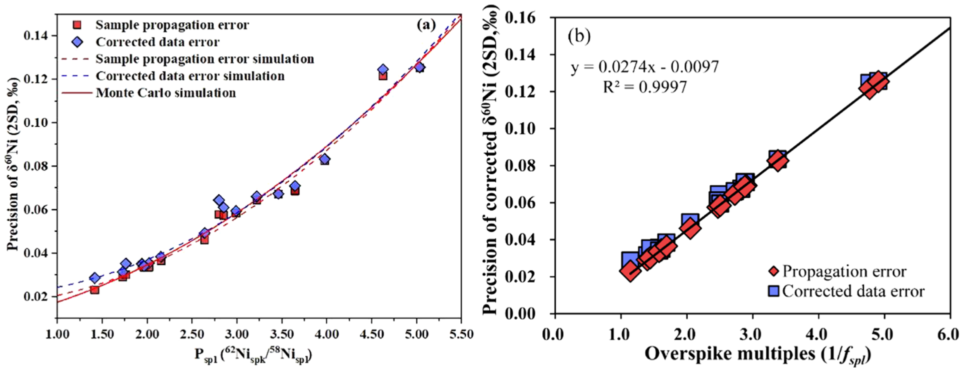

Figure 3. Relationship between overall precision/propagation error($\sigma_{\delta\text{-spl}}$) and P_{spl}/overspike multiples. (a) Overall precision/propagation error vs P_{spl}. (b) Overall precision/propagation error vs overspike multiples ($1/f_{spl} = P_{spl}/P_{mix}$).

≤0.060‰ are expected, then theoretically the ratio of $^{62}Ni_{spk}/^{58}Ni_{spl}$ (P_{spl}) should be ≤3.0 for all overspiked samples. However, when $^{62}Ni_{spk}/^{58}Ni_{spl}$ is ≤3.5, the precision of δ^{60}Ni values is typically less than 0.070‰, still within an acceptable precision range. It is worth noting that although the precision of correcting overspiked samples with $^{62}Ni_{spk}/^{58}Ni_{spl} > 3.0$ deteriorates to a maximum of 0.127‰ (Table S4), the accuracy of the corrected data does not deteriorate and agrees well with the reported values (Figure 2), illustrating that the corrected data still can be as useful as normally spiked determinations.

The Correctable Range of Overspiked Samples. Since the long-term reproducibility of δ^{60}Ni values obtained by traditional DS is generally required to be ≤0.060‰ (2SD),[36,40,44,45] we set 0.060‰ as a critical number for following discussion. As discussed above for eq 9, propagated error predominately depends on the ratio of P_{spl}/P_{mix} and has a positive linear relationship with the overspiked multiples (1−5 times, Figure 3), indicating that we can constrain the correctable range of overspiked samples according to our requirement of precision ≤0.060‰ for Ni or other isotopes. As shown in Table S4, when P_{spl} ($^{62}Ni_{spk}/^{58}Ni_{spl}$) = 5.0301, adding approximately 4 times' sample amount of the standard solution (f_{std} = 79.62% in Table S4) can reduce the P_{spl} value to 1.0253 (overspiked multiple is 4.906 = 5.0301/1.0253), within the currently normal range of 0.9−1.5 for Ni DS on our MC-ICP-MS.[36] The propagated error of the calculated result at this point has reached 0.112‰, exceeding the precision requirement of 0.060‰ for the general Ni isotope measurement. However, when P_{spl} = 2.9872, adding about 1.5 times' sample amount of standard solution (f_{std} = 60.07%) can decrease the P_{spl} value to 1.1927, and the propagated error at this case is only 0.058‰, essentially satisfying the requirement of precision of 0.060‰. This observation suggests that the expected precision can be obtained if the added standard solution fraction (f_{std}) is less than 0.60 (or 60%) in the overspiked samples (Tables 1, 2, and S3). Alternatively, according to the linear equation provided in Figure 3b, the ratio of P_{spl}/P_{mix}, an overspike multiple, cannot exceed 2.50 if we aim for good precision (≤0.060‰). At this point, the sample fraction (f_{spl}) in the mixture is ∼0.40 (1/2.5; ∼40%), and as the f_{spl} increases, the precision will also improve. Therefore, for Ni isotopes, when f_{spl} in the mixture is ≥0.40 (40%) or the proportion of added standard solution (f_{std}) is ≤0.60 (60%), analysis of overspiked samples after adding standard solution can achieve precision similar to that obtained with normally spiked samples. Similar trends were also validated by Cr and Cd isotopes (Table 2), where the precision of the corrected δ^{53}Cr and δ^{114}Cd values is ≤0.060‰ when the f_{spl} is ≥0.40 or the f_{std} is ≤0.60. These results reveal a common observation that good precision can be obtained for overspiked samples when the added standard solution (f_{std}) is no more than 0.60 (60%) of the mixture.

The Application to the Actual Overspiked Samples. When using the DS method, the overspiked samples occur commonly due to careless operations or inaccurate sample concentration. This work presents a new mathematical correction scheme for overspiked samples, which eliminates the procedures of sample reprocessing and saves time. For instance, two overspiked samples were found in the first round of our recent experiments of Ni isotope measurement; their respective ratios of $^{62}Ni_{spk}/^{58}Ni_{spl}$ were 2.1046 and 1.6430. After addition of an appropriate amount of standard solution NIST 986, their $^{62}Ni_{spk}/^{58}Ni_{mix}$ ratios were decreased to 1.3066 (f_{std} = 37.92%) and 1.2727 (f_{std} = 22.54%) in the subsequent tests, falling within the normal range. According to eq 8, using P_{spl} ($^{62}Ni_{spk}/^{58}Ni_{spl}$), P_{mix} ($^{62}Ni_{spk}/^{58}Ni_{mix}$), and $\delta^{60}Ni_{mix}$ ratios obtained by DS data reduction routine, and EPM model, their $\delta^{60}Ni$ values were corrected from −0.044‰ and −0.340‰ to be 0.106 ± 0.06‰ and −0.278 ± 0.06‰, respectively. This correction removes the need to either analyze standard solutions that are overspiked to match the overspiked sample(s) or start over and process new samples through the purification treatment. As shown above, in practical use, this method achieves the required precision (≤0.060‰) when the overspiked multiples are less than 2.50 or $f_{std} \leq 0.60$. Furthermore, a similar observation was confirmed by Cr and Cd isotopes (Table 2), and it also applies to other elements, for which DS can be employed. Additionally, these cases also indicate that to avoid the risk of underspiked samples that cannot be corrected currently, we should add a little more DS to samples to maintain the normal range, such as setting $^{62}Ni_{spk}/^{58}Ni_{spl} = 1.35$ ($1.50 \geq {}^{62}Ni_{spk}/^{58}Ni_{spl} \geq 1.25$) rather than the optimized ratio 1.25 that we used before to save DS. Even if this leads to a little more frequent occurrence of overspiked samples, those can be corrected by adding a standard solution in the later analytical sessions.

■ CONCLUSIONS

This work proposes an innovative method for accurately correcting isotopic ratios in overspiked samples when using the DS technique. The related theoretical equations and an error propagation model were presented thoroughly. According to the provided equations, using P_{spl}, P_{mix}, and δ_{mix} ratios obtained from the normal DS data reduction and the related EPM, we can obtain accurate isotope ratios of overspiked samples by a binary mixing model and estimate their precision. To demonstrate its effectiveness, we take an example of Ni isotopes to discuss issues related to standard solution selection, the correctable range of overspiked samples, and routinely achieved accuracy and precision through the analysis of seven GRMs. The results show that selecting an isotope standard solution with a "delta-zero" value (e.g., NIST 986) can simplify the calculated procedures, and the precision (≤0.06‰, 2SD) is acceptable when the fraction of the added standard in the mixture, f_{std}, is below 0.60 (or ≤60%) or the overspiked multiple is ≤2.5. All corrected $\delta^{60}Ni$ values for seven overspiked GRMs match the published data. Furthermore, the successful application of this approach to Cr and Cd isotopes suggests its potential for broader application to many other elements, which can be analyzed using DS. By addressing previous limitations of DS, the proposed method expands the application of DS from the ordinary to overspiked range, significantly enhancing its versatility and reliability, improving lab efficiency, and avoiding the consumption of additional masses of precious samples in those cases where overspiking occurs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.4c04391.

The detailed uncertainty calculation (Text S1), Ni DS information (Table S1), chemical purification scheme of Ni (Table S2), instrumental parameters (Table S3), and the corrected $\delta^{60}Ni$ values of the overspiked reference materials in this study (Table S4) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jian-Ming Zhu − *State Key Laboratory of Geological Processes and Mineral Resources, and Frontiers Science Center for Deep-time Digital Earth, China University of Geosciences (Beijing), Beijing 100083, China;* orcid.org/0000-0003-4977-6072; Phone: 86-010-82322832; Email: jmzhu@cugb.edu.cn

Authors

Wenlong Sun − *State Key Laboratory of Geological Processes and Mineral Resources, and Frontiers Science Center for Deep-time Digital Earth, China University of Geosciences (Beijing), Beijing 100083, China*

Thomas M. Johnson − *Department of Geology, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States;* orcid.org/0000-0003-1620-1408

Zhuo Lu − *State Key Laboratory of Geological Processes and Mineral Resources, and Frontiers Science Center for Deep-time Digital Earth, China University of Geosciences (Beijing), Beijing 100083, China*

Decan Tan − *State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China;* orcid.org/0000-0002-3224-7599

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.analchem.4c04391

Author Contributions

J.-M.Z. conceptualized the research objectives, conceived the methodology and experiments, guaranteed funding and supervision. J.-M.Z. and T.M.J did manuscript writing, review, and editing. W.L.S. and J.-M.Z. conducted experiments and data processing. Z.L., J.-M.Z., and D.C.T deduced the formula and visualized data. All authors contributed to the discussion and revision of the manuscript.

Notes

The authors declare no competing financial interest.

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