

IsoSpike: Improved Double-Spike Inversion Software

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The double-spike approach for correction of instrumental mass bias in mass spectrometry data is well established. However, there is very little consistency within the scientific community in terms of double-spike data reduction. Double-spike solutions require computer calculation, using either geometric or algebraic approaches, and are often performed using spreadsheet calculations that vary from group to group and between isotope systems. Here, we present *IsoSpike*, a generalised computer procedure for the processing of double-spike mass spectrometry data, built as an add-on for the *Iolite* data-reduction package (www.iolite.org.au). Use of this software permits visualisation of mass spectrometry data in a time window, and rigorous treatment and screening of data. Additionally, *IsoSpike* uses an integration-by-integration approach where the double-spike calculations are performed on every integration within an analysis, providing straightforward quantification of uncertainties on double-spike-corrected isotope ratios. The advantages of this approach over traditional methods are discussed here. Platinum stable isotope data are presented as an example data set, although the procedure is applicable to any double-spike system. *IsoSpike* is freely available from www.isospike.org.

Keywords: double-spike, isotopes, MC-ICP-MS, TIMS, data reduction software.

L'approche du double spike pour la correction du biais de masse instrumental des données de spectrométrie de masse est bien établie. Cependant, il y a très peu de cohérence au sein de la communauté scientifique en termes de réduction des données double spike. Les solutions double spike nécessitent du calcul par ordinateur, en utilisant des approches géométriques ou algébriques, et sont souvent réalisées en utilisant des feuilles de calcul qui varient d'un groupe à l'autre et en fonction des systèmes isotopiques. Nous présentons ici IsoSpike, une procédure informatique généralisée pour le traitement des données de spectrométrie de masse double spike, construite comme une extension pour le package de réduction de données Iolite (www.iolite.org.au). L'utilisation de ce logiciel permet la visualisation des données de spectrométrie de masse dans une fenêtre de temps ainsi que le traitement rigoureux et le filtrage des données. En outre, IsoSpike utilise une approche de type intégration par intégration où les calculs double spike sont effectués sur chaque intégration dans une analyse, permettant une quantification simple des incertitudes sur les rapports isotopiques corrigés par double spike. Les avantages de cette approche par rapport aux méthodes traditionnelles sont discutés. Les données d'isotopes stables du platine sont présentées comme un exemple d'ensemble de données, bien que le procédé soit applicable à n'importe quel système double spike. IsoSpike est disponible gratuitement depuis www.isospike.org.

Mots-clés : double spike, isotopes, MC-ICP-MS, TIMS, logiciel de réduction de données.

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Isotope geochemistry has played a vital part in the study of Earth. Radiometric dating has provided information on the age of the Earth, while radiogenic and stable isotopic tracers

have been used to delineate processes occurring in the mantle and crust as well as the ocean and atmosphere. One of the limiting factors in the accuracy of results in isotope

geochemistry, however, is the effect of instrumental mass bias. Instrumental mass bias is an analytical effect whereby high atomic number or low atomic number ions may be preferentially detected for different reasons depending on the instrumentation, potentially occurring during evaporation, ionisation or transmission. Instrumental mass bias occurs in both inductively coupled plasma-mass spectrometry (ICP-MS) and thermal ionisation mass spectrometry (TIMS), but in an opposite sense, in that ions of higher mass are preferentially detected in ICP-MS as compared with TIMS. Although there exists a variety of means to correct for mass bias, all are empirical, and it is commonly accepted that the double-spike (DS) method (Dodson 1963) is the most precise and accurate where no invariant pair of isotopes are available for mass bias correction or the stable isotopic composition of the sample is being measured (Woodhead and Hergt 1997, Anbar 2004). The advantages of the DS approach have been known since the 1960s (e.g., Compston and Oversby 1969) although at the time, calculations for a single result took more than 15 min (Dodson 1970) and the equations to describe mass bias were typically linear. In the intervening period, more complex equations have been developed to describe mass bias effects (for a summary, see Maréchal *et al.* 1999) and the use of computers has become essential.

While virtually all laboratories producing DS data employ the same algebraic or geometric approaches to the DS correction, there is very little consistency in their implementation. DS data reduction is often performed in complicated spreadsheets, which vary between isotope systems and groups. We aim to provide a generalised, easy to use and freely available tool that is applicable to any double-spike system, and which will provide greater consistency in the data-reduction process. We present *IsoSpike*, a software tool that can perform many thousands of double-spike inversions per second on a modern personal computer, allowing the analyst to calculate mass bias corrected ratios on an integration-by-integration basis within an analysis. This approach also provides a straightforward method for quantification of measurement repeatability, which have previously been estimated by linear uncertainty propagation (Rudge *et al.* 2009), Monte Carlo simulation (Fantle and Bullen 2009, John 2012) or a least-squares approach (Powell *et al.* 1998). We provide examples of data reduction using this approach with the platinum stable isotope system.

The double-spike technique

Various methods are available for the correction of instrumental mass bias in isotope measurements. Reference material (RM) bracketing is one of the most commonly used, whereby analyses of unknowns are bracketed with measure-

ments of a reference material (calibrator) of known composition, and the difference between the measured and reference ratios for the RM is used to determine the instrumental mass bias. The disadvantage of this method is that it requires many additional analyses of RMs to be made, which is time-consuming and often assumes that changes in mass bias are linear between bracketing calibrators. For some radiogenic isotope systems, mass bias can be determined within the analysis of the unknown by assuming that some ratio is invariant in nature (e.g., two stable non-radiogenic isotopes). Alternatively, in some cases, a sample may be doped with another element that exhibits similar mass bias behaviour and has a well-constrained isotope ratio (e.g., Tl in Pb isotope work; Longerich *et al.* 1987, Woodhead 2002, Baker *et al.* 2004), which is then be used to perform the same correction.

The double-spike technique is a variation on 'internal correction' methods, whereby the presence of an invariant ratio is simulated by doping the sample with a solution that is enriched in two isotopes of the element in a known ratio, the so-called double-spike. The fundamentals of the DS approach have been well documented (Dodson 1963, 1970, Compston and Oversby 1969, Hamelin *et al.* 1985, Powell *et al.* 1998, Galer 1999, Johnson and Beard 1999, Rudge *et al.* 2009), and the technique has been used extensively in a range of isotopic systems – most notably Pb, but also S, Ca, Cr, Zn, Fe, Mo, Cd, Ba and Os, and using both ICP-MS and TIMS. In practice, it is impossible to produce a 100% pure DS (i.e., the spike will include both the enriched isotopes and a contribution from the naturally occurring isotopes), and the relative contributions of the spike and sample in the mixture must be taken into account. Mathematical solutions to this problem have been developed, and the sample contribution can be resolved from the spike contribution. With knowledge of the composition of the double-spike, it is therefore possible to calculate the instrumental mass bias from mass spectrometry data and thus derive the natural fractionation of the sample.

The double-spike equations used here are derived by combining exponential mass bias laws describing the instrumental and natural isotopic fractionation, and a mixing relationship between the double-spike and the sample (a thorough treatment of the mathematics is provided in Rudge *et al.* 2009). The result is the following set of non-linear simultaneous equations:

$$F_i(\lambda, \alpha, \beta, n, m, T) = \lambda T_i + (1 - \lambda) n_i e^{-\alpha P_i} - m_i e^{-\beta P_i} = 0 \quad (1)$$

where the subscript *i* refers to the *i*th isotopic ratio of the sample; *P* is the natural logarithm of the ratio of atomic masses; *m* and *n* refer to the measured compositions of the

sample-spike mixture and unspiked sample, respectively; T represents the isotopic composition of the double-spike; λ is related to the proportion in which the sample and double-spike are mixed; α and β are the natural and instrumental mass fractionation factors, respectively. The double-spike inversion takes the values n , m and T for inputs, which are used for the solution of the equation above for the unknowns λ , α and β . Three isotope ratios are required to solve these equations, and thus, the double-spike approach is limited to elements with four or more isotopes.

When the double-spike technique was first used, the equations involved were necessarily simplified to a linear form (Compston and Oversby 1969, Dodson 1970). Since then, complex methods for the computation of double-spike corrections have been developed utilising both algebraic (Albarède and Beard 2004, Rudge *et al.* 2009) and geometric (Russell 1971, Galer 1999, Johnson and Beard 1999, Siebert *et al.* 2001, Markey *et al.* 2003) approaches.

The DS method poses several additional advantages over some of the other methods described above. For stable isotope systems where mass-dependent fractionation is being studied, DS-corrected isotope ratios can be obtained from a single analysis (Rudge *et al.* 2009). Additionally, the DS can potentially correct for any mass-dependent effects to the sample after addition of the DS. Thus, if the addition of the DS to the sample is performed prior to chemical separation of the element, the DS will also correct for any mass-dependent fractionation such as might occur as a result of incomplete yields during chemical separation (Albarède and Beard 2004, Rudge *et al.* 2009).

Software

The DS procedure presented here is called *IsoSpike* and is freely available from www.isospike.org. *IsoSpike* was built as an add-on module for the non-commercial software package *lolite* (Paton *et al.* 2011), which is available from www.iolite.org.au. *lolite* is a data-reduction package for visualisation and processing of mass spectrometric data, which itself runs within the data analysis package Igor Pro (available from www.wavemetrics.com; see Paton *et al.* (2011) for further details). Here, we provide an example using the platinum isotope system, although *IsoSpike* is applicable to any isotope system suitable for the DS method. The *lolite* platform is capable of directly handling data from a variety of different mass spectrometers using the same data-reduction steps and can reduce large data sets quickly and easily, making it ideal for this purpose.

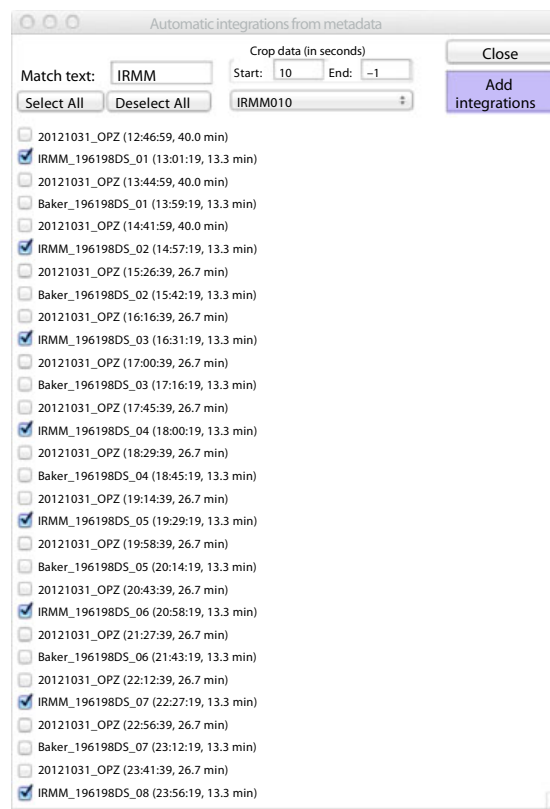


Figure 1. Automatic integration selection window in *lolite*. Text strings can be used to quickly select groups of samples.

Data-reduction process

Once data are imported into *lolite*, they are displayed in a window versus time. The user can then manually select integration periods for each sample/reference material–DS mixture or use an automated process within *lolite* to do so (Figure 1). A relevant Data Reduction Scheme (DRS) is then selected and run (e.g., the Pt_DS DRS, which has been written for Pt isotopes and is used in the example files). The DRS performs the initial processing steps of baseline subtraction and the calculation of raw isotope ratios, which are then used as inputs for *IsoSpike*. *IsoSpike* can be called from within the DRS or run manually to perform the DS calculations.

IsoSpike employs the algebraic method and terminology of Rudge *et al.* (2009). The required DS parameters are the measured isotopic composition of the sample–DS mixture (m), the measured isotopic composition of the unspiked natural sample or the composition of a reference material (n), the isotopic composition of the DS (T) and the natural logarithm of the ratio of the isotopic masses (P ; Equation 1).

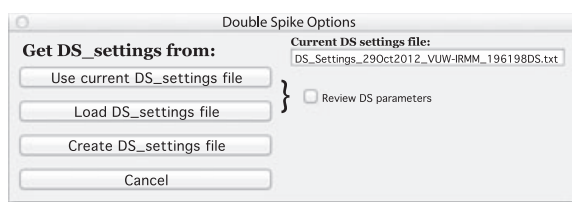


Figure 2. *IsoSpike* options window where the user can select how the double-spike parameters are determined. Settings can be stored in a plain text file, which can be loaded from the options menu or created through a guided process.

These parameters can be input manually or loaded from a saved settings file. In the first instance, a user would typically go through the process of creating a DS settings file (Figure 2). This process is guided by the software, and *IsoSpike* contains a database of IUPAC-recommended isotopic masses (Berglund and Wieser 2011) with an interface for the user to select which isotopes are used in the DS inversion, and the required mass ratios can be calculated automatically. Thus, to change to a new isotope system, the only information that must be input manually is the DS composition and, depending on the application, the composition of a reference material.

Once all the parameters have been loaded, *IsoSpike* performs the DS inversion to solve for three unknowns: the

sample-spike mixing proportion, λ , and the fractionation factors α and β (Equation 1). Several iterative methods are available for finding roots of non-linear equations; *IsoSpike* employs the FindRoots function in Igor Pro, which uses the Jenkins–Traub algorithm (Jenkins and Traub 1975). *IsoSpike* performs these calculations on a integration-by-integration basis, allowing outlier rejection and calculation of statistics to be performed directly on calculated results (Figure 3). This procedure is capable of rapidly reducing a typical analytical session worth of data in a few seconds on a modern personal computer.

The integration-by-integration method employed here is compared with a commonly used method in which DS calculations are performed on means of the three DS ratios for each analysis, which is hereafter referred to as the means-of-ratios approach. In mean-of-ratios methods, uncertainties cannot be quantified directly but can be estimated by one of several available methods (Monte Carlo simulation, linear error propagation, least squares). By performing the DS calculations on each integration within an analysis, *IsoSpike* permits direct quantification of uncertainties. The potential advantages of this approach are discussed below.

Unspiked run

In general, the double-spike method involves an additional measurement of each sample without the DS added, the so-called unspiked run. In isotope systems where mass-

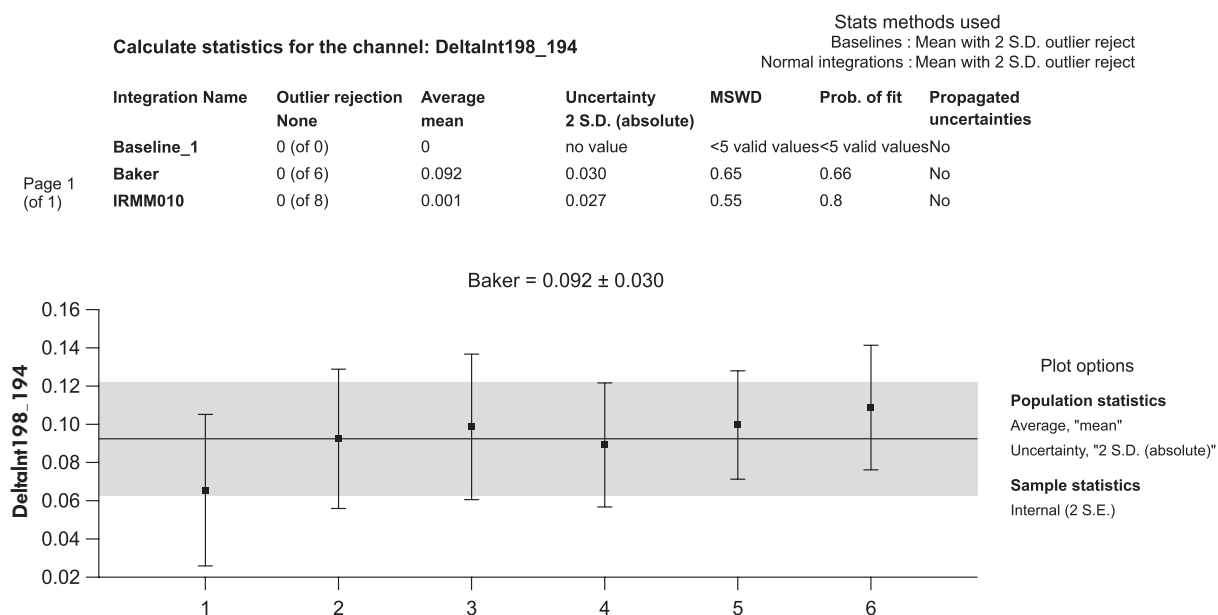


Figure 3. *Iolite* report window with processed double-spike-corrected Pt stable isotope data. Error bars reflect the measurement repeatability (2SE), which is based on the distribution of the results of the double-spike inversion from each measurement integration within each analysis.

dependent isotopic fractionation is being studied, it is possible to compute DS-corrected isotope ratios from a single, spiked, measurement using the value of an isotopic RM for the natural 'unspiked' composition, and DS-corrected ratios are then expressed relative to that RM. IsoSpike can operate in either of these modes, although the preprocessing in the DRS is slightly different. Where an unspiked run is measured, the method employs a fitted spline in *Iolite* so that the measured isotopic composition of the unspiked sample exists in the same time interval as the spiked run. Where no unspiked run is required, the standard composition is defined in the DS settings file.

Materials and analytical methods

The materials and methods for Pt isotope measurements are described in detail in Creech *et al.* (2013). A short outline is also provided here.

Chemicals and standard solutions

Optima™ grade nitric (HNO₃) and hydrochloric (HCl) acids were used as supplied without further purification. Acid dilutions were performed with ultrapure (> 18 MΩ cm) water. All sample handling and preparation was performed in a class-100 ultra-clean laboratory at Victoria University of Wellington, New Zealand.

The Pt isotope reference material IRMM-010 was purchased from the Institute for Reference Materials and Measurements, Belgium (Wolff Briche *et al.* 2002). The reference material was supplied in the form of Pt wire segments, which were cleaned prior to digestion by sequentially rinsing in ultrapure water, analytical grade methanol and dilute (5% v/v) HNO₃. The IRMM-010 material was carefully weighed and then digested in *aqua regia* (HCl:HNO₃ prepared in a volume ratio of 3:1) in a Savillex™ Teflon beaker. The IRMM-010 Pt solution was evaporated to dryness, refluxed with concentrated HNO₃, evaporated to dryness and finally redissolved in 20% v/v HCl. Measurements of a Pt ICP-MS in-house reference solution (J.T. Baker 1000 µg ml⁻¹ in 20% v/v HCl, Lot# H44N77) are also included for comparison, which has been shown to have a small but reproducible offset from IRMM-010 (Creech *et al.* 2013).

The Pt double-spike used for the isotopic determinations was prepared using two single isotope spikes (¹⁹⁶Pt and ¹⁹⁸Pt) obtained from the Oak Ridge National Laboratory, USA. Full details of the design and calibration of the double spike are given in Creech *et al.* (2013). Solutions of IRMM-010 and the reference solution of J.T. Baker were spiked

immediately prior to MC-ICP-MS measurement, spiking in optimal proportions as calculated using the *Double Spike Toolbox* of Rudge *et al.* (2009).

Analytical methods

Platinum isotope measurements were taken using a Nu Plasma HR MC-ICP-MS (Nu Instruments) at Victoria University of Wellington, New Zealand. The MC-ICP-MS was operated in low-resolution mode, with a mass resolution of ~ 1840 (M/ΔM; peak edge width from 5 to 95% full peak height). A Nu Instruments DSN-100 desolvation nebuliser system with an ESI PFA micro-flow nebuliser was used for Pt solution introduction to the mass spectrometer. Measurements were typically made on 0.5 mol l⁻¹ HCl solutions with 60 ng ml⁻¹ of Pt from the sample, with an almost equivalent contribution from DS Pt. The sample uptake rate was ca. 80 µl min⁻¹, and the sensitivity of the instrument was typically ca. 280 V per µg ml⁻¹ total Pt under these conditions. Peak centring was performed at the start of each session and monitored throughout. Each individual analysis comprised 100 × 8 s integrations, corresponding to 13.3 min of data acquisition, and consumed ca. 80 ng of natural Pt. Baselines were obtained by measuring on-peak for 100 × 8 s integrations prior to each analysis. A washout time of ca. 30 min was applied between analyses and baseline measurements. Using this approach, background levels were typically << 1 mV on all Pt isotopes.

Results are reported using δ¹⁹⁸Pt notation, representing the per mil deviation of the ¹⁹⁸Pt/¹⁹⁴Pt ratio from the same ratio for the IRMM-010 Pt isotope RM:

$$\delta^{198}\text{Pt} = \left[\frac{\frac{^{198}\text{Pt}}{^{194}\text{Pt}}_{\text{sample}}}{\frac{^{198}\text{Pt}}{^{194}\text{Pt}}_{\text{IRMM-010}}} - 1 \right] \times 10^3 \quad (2)$$

Results and discussion

The integration-by-integration processing of data within *IsoSpike* presents several advantages over traditional DS data-reduction approaches using means-of-ratios and modelled uncertainty estimates. The differences between *IsoSpike* and traditional methods are explored below.

DS-corrected ratios

The integration-by-integration inversion approach used in *IsoSpike* was compared with data corrected from means-of-ratios from each analysis by performing the DS calculations on the same data using both methods. Means-of-ratios results were calculated using the same procedure in

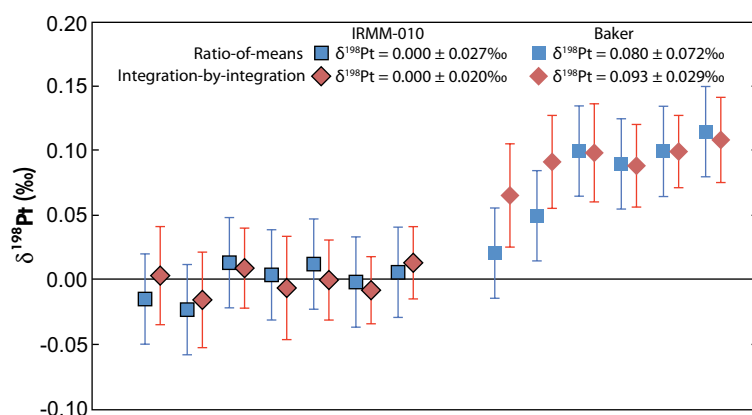


Figure 4. Double-spike (DS)-corrected Pt stable isotope data for IRMM-010 and the Baker Pt reference solution. DS correction was performed both on mean ratios for each analysis and by integration-by-integration correction of every integration. Error bars reflect either estimated 2SE uncertainties determined using the linear error propagation function in the Double Spike Toolbox (Rudge *et al.* 2009) for mean ratios data, or observed 2SE uncertainties for integration-by-integration corrected data.

IsoSpike, but instead using the means-of-ratios for each analysis for inputs. Uncertainties on means-of-ratios data were determined using the linear uncertainty propagation routine (ERRORESTIMATE) within the *Double Spike Toolbox* of Rudge *et al.* (2009).

The mean DS-corrected $\delta^{198}\text{Pt}$ values for each analysis were generally within ca. 5% (relative) between the two methods (Figure 4, Table 1). However, the integration-by-integration method resulted in decreased scatter between analyses, resulting in a slight apparent improvement in precision, as shown by the 2s values of the analyses (Figure 4, Table 1). This subtle difference observed between the two methods may be attributable to small changes in instrumental mass bias within the analysis, which are not effectively accounted for by the means-of-ratios method.

Estimation of measurement repeatability

Previous DS studies have estimated measurement uncertainties on DS-corrected ratios using Monte Carlo simulations (Fantle and Bullen 2009, John 2012), linear uncertainty propagation (Hamelin *et al.* 1985, Rudge *et al.* 2009) or a least-squares approach (Powell *et al.* 1998). These uncertainties are generated from theoretical considerations and modelled probability distributions for the inputs to the DS equations and take into account factors such as amplifier noise and counting statistics. However, those methods typically do not take the variance in measured ratios as an input, and the estimated measurement repeatability is essentially invariant for a given DS mixture.

Table 1. Representative Pt stable isotope data for IRMM-010 and the in-house reference solution of Baker from one analytical session, where DS calculations were performed using the means-of-ratios and integration-by-integration approaches

	Means-of-ratios $\delta^{198}\text{Pt}$ (‰)	Integration-by-integration $\delta^{198}\text{Pt}$ (‰)
IRMM-010		
1	-0.014 ± 0.035	0.004 ± 0.038
2	-0.022 ± 0.035	-0.015 ± 0.037
3	0.014 ± 0.035	0.010 ± 0.031
4	0.004 ± 0.035	-0.006 ± 0.040
5	0.013 ± 0.035	0.000 ± 0.031
6	-0.001 ± 0.035	-0.007 ± 0.026
7	0.006 ± 0.035	0.014 ± 0.028
Mean	0.000 ± 0.027	0.000 ± 0.020
Reference solution (of J.T. Baker)		
1	0.021 ± 0.035	0.066 ± 0.040
2	0.050 ± 0.035	0.092 ± 0.036
3	0.100 ± 0.035	0.099 ± 0.038
4	0.090 ± 0.035	0.089 ± 0.032
5	0.100 ± 0.035	0.100 ± 0.028
6	0.115 ± 0.035	0.109 ± 0.033
Mean	0.080 ± 0.072	0.093 ± 0.029

Uncertainties for the means-of-ratios approach were calculated using the linear error propagation routine in the *Double Spike Toolbox* of Rudge *et al.* (2009), using the double-spike (DS) composition and proportion given in Creech *et al.* (2013), and α and β values calculated from the means-of-ratios DS calculations. Measurement repeatability for the integration-by-integration approach reflects the 2SE of DS-corrected ratios. Errors on the means reflect the 2s of the values making up the mean.

Table 2.
Double-spike-corrected Pt stable isotope results for the reference solution of Baker using different spline types for the IRMM reference material and baselines

Spline type		Baker Pt reference solution $\delta^{198}\text{Pt}$ (‰)
Baseline	Reference material	
Average_mean	Average_mean	0.090 ± 0.051
LinearFit	LinearFit	0.093 ± 0.032
LinearInterpolation	LinearInterpolation	0.088 ± 0.034
StepForward	Average_mean	0.087 ± 0.043
StepForward	LinearFit	0.090 ± 0.030
StepForward	LinearInterpolation	0.087 ± 0.034
StepForward	SmoothAuto	0.090 ± 0.030
Smooth_auto	Average_mean	0.089 ± 0.044
Smooth_auto	LinearFit	0.092 ± 0.031
Smooth_auto	LinearInterpolation	0.089 ± 0.035
Smooth_auto	SmoothAuto	0.092 ± 0.031
LinearInterpolation	Average_mean	0.088 ± 0.044
LinearInterpolation	LinearFit	0.091 ± 0.030
LinearInterpolation	LinearInterpolation	0.088 ± 0.034
LinearInterpolation	SmoothAuto	0.091 ± 0.030

Uncertainties are 2s of six analyses of the reference solution of Baker.

Since *IsoSpike* calculates DS-corrected ratios for every time slice within an analysis, calculation of statistics to be performed directly on calculated results provide a direct assessment of measurement repeatability (i.e., the 2SE of DS-corrected ratios). As these are based on real measurements, they inherently incorporate all sources of measurement uncertainty. As with other methods, *IsoSpike* does not include uncertainty in the DS composition or the reference material composition, although these are considered to be fixed and do not change during the course of a mass spectrometer run (e.g., Rudge *et al.* 2009). Variations in measured ratios are propagated through to DS-corrected ratios, and the 2SE of an analysis provides a realistic assessment of the quality of the analysis. As the time interval for each analysis that is used in calculations can be adjusted in *Iolite*, it is possible for the analyst to adjust the time interval to see how the resultant uncertainty on the DS-corrected result changes due to counting statistics. This allows the ideal sample measurement time for a given required level of precision to be determined. Additionally, by allowing the analyst to see each result, outliers may be manually identified and removed where justified. Alternatively, *Iolite* can remove outliers from the final result based on points that are greater than 3s or 2s from the mean. Similarly, no outlier rejection may also be selected.

Use of splines

In stable isotope studies, isotope fractionations are usually expressed as a relative difference in some ratio

between the sample and a reference material, as for example in δ notation (i.e., Equation 2). It is common practice to make measurements of the RM during a mass spectrometer session, which measurements of unknowns are normalised to. In spreadsheet data-reduction routines, this is generally done by either taking the average composition for the RM measured during the session or interpolating between measurements. *Iolite* uses splines to interpolate RM and baseline compositions between measurements, and a number of different spline fitting modes are available (e.g., averages, linear interpolation, smoothed cubic fitting), and their features are discussed in detail in Paton *et al.* (2011). Splines that use averages or linear interpolations are equivalent to the methods typically employed in spreadsheet data reduction, while the more sophisticated spline types may provide more accurate estimates of changing baseline or RM compositions over time.

The effect of using different spline types for DS data with *IsoSpike* was investigated by reprocessing data for the Pt reference solution of Baker (Figure 4 and Table 1) with some of the available spline types. The results are shown in Table 2. Combinations using an *average_mean* spline for reference materials resulted in an enlarged measurement uncertainty budget as they do not account for any drift in RM values. Other spline combinations can affect the precision by ca. 10%. While the effect on this example data set is relatively minor, this might not be the case for all applications. For example, in applications where baseline corrections are

larger, the choice of baseline interpolation may have a greater effect than that in the example presented here. Our aim here is simply to highlight that the choice of method of interpolation may have an impact on the final result. This choice lies with the analyst and should (ideally) represent an empirical best fit to processes occurring within the mass spectrometer. The interpolation method in *lolite* can easily be changed to examine this effect.

Coherency and applicability

One of the main advantages of the method presented here is the coherency of the data reduction and uncertainty estimation process. Reduction in DS data from a typical mass spectrometer session could be completed in < 1 min, from importing raw data to outputting finished DS-corrected results. This included a rigorous estimate of the measurement repeatability that might otherwise be undertaken as a separate step or by applying a fixed precision to all analyses. The ability of *lolite* to handle raw data files from a variety of mass spectrometers means that there is very little manual handling involved, removing the potential for operator error. At the same time, many functions within *lolite* are open source, including all DRS, statistical functions and *IsoSpike* itself, providing complete transparency (and, if required, modification) of the data-reduction process. *IsoSpike* was designed to be quickly and easily extended to new DS isotope systems, even by users with limited experience with *lolite*. The example files shown here are also available for download and provide a template for those wishing to proceed further.

Conclusions

The *IsoSpike* software for correction of DS data presented here provides a complete and intuitive data-reduction process that can be applied to any DS system and is freely available for use by others. Data reduction is straightforward and fast and provides rigorous estimates of measurement repeatability and possible improvements in reproducibility. The integration-by-integration approach of *IsoSpike* provides, at least, a faster and more consistent approach, and possibly a more accurate way to process DS data than commonly employed methods. Combined with the capabilities built into *lolite* such as data visualisation and exporting, this combination has the potential to be useful to the double-spike community.

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