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An investigation into detector dead time variability and mass dependency in quadrupole ICP-MS and implications for isotope ratio accuracy

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Quadrupole inductively-coupled-plasma mass-spectrometers (Q-ICP-MS) are used to analyse enormous numbers of isotope ratios, most prominently ^{206}Pb/^{238}U for age determination. With the advent of reaction-cell equipped tandem Q-ICP-MS (Q-ICP-MS/MS), the scope for isotope ratio determination has grown, especially for β-decay isotope systems (*e.g.*, ^{87}Rb/^{87}Sr). Reaction of unwanted interfering species (*e.g.* ^{204}Hg on ^{204}Pb) has also increased the feasibility of Pb-isotope ratio measurements by Q-ICP-MS. Unlike in sector-field MS isotope ratio analysis where mass bias is corrected *via* a known isotope ratio or with calibrated double or triple-spikes, Q-ICP-MS(/MS) analysts generally apply an 'external correction' with reference to interleaved calibration standard analyses. Despite this protocol, there remains inaccuracies in derived isotope ratios when compared to reference values which are inadequately explained. The aim of this study was to investigate the origin of the inaccuracy in Q-ICP-MS isotope analysis, which has so far received surprisingly little attention. We assessed whether improved detector dead time correction can achieve more accurate isotope results and explored fractionation effects arising from steering ion beams across complex Q-ICP-MS/MS paths. We investigated detector dead time as a function of Z in both single MS and mass-shifted MS/MS mode. We document how dead time varies over time as detectors and electronic components of the ICP-MS age. We show that session specific dead times yield substantially more accurate isotope ratios for mass shifted Sr isotope ratios than when applying a generic dead time. We also provide recommendations for how to incorporate session-specific dead time analyses into an isotope ratio run. Despite the much-improved quality of dead time and conventional mass bias corrected mass shifted Sr isotope ratios, small (up to 4‰) inaccuracies remain. The inaccuracy is systematic and specific for each session. Therefore, it can be corrected with a small bias correction relative to a CRM analysed throughout the session. The origin of the Sr isotope ratio inaccuracy after dead time and conventional mass bias correction remains speculative. Our exploratory analysis suggests that voltages on lenses tuning and directing the ion beams through the MS/MS may be a source of an additional isotope fractionation process (bias) that cannot be fully corrected with conventional mass bias procedures.

1 Introduction

The number of isotope ratio analyses being conducted with quadrupole inductively-coupled-plasma mass-spectrometers (Q-ICP-MS) is rapidly increasing and extending into new research fields, because of their versatility, low detection limits, speed, ease of operation and relative affordability.[1,2] The recent advent of tandem Q-ICP-MS (Q-ICP-MS/MS) has further expanded the scope of available isotope systems that can be investigated because of the ability to minimise or remove isobaric interferences, particularly the ability to perform *in situ* β-minus decay scheme geochronology.[3–5]

It has been recognised for some time that isotope analysis by Q-ICP-MS(/MS) can be inaccurate when using conventional mass bias correction *via* a known constant isotope ratio, instead requiring additional or alternative correction methods, for example *via* standard-sample-standard bracketing.[3,6,7] This is particularly evident in the Q-ICP-MS/MS analysis of ^{87}Sr/^{86}Sr where Bolea-Fernandez and Balcaen[3] proposed that the conventional IUPAC approach of using a known ^{88}Sr/^{86}Sr ratio for mass bias correction does not yield accurate ^{87}Sr/^{86}Sr instead requiring an additional correction (bias) factor.

All isotope analyses by mass spectrometry require correction of the raw data for well-known and understood phenomena including mass bias (*e.g.* ref. 8–11), removal of isobaric interferences[12] and detector dead time.[6,13–21] Both mass bias correction and correction of isobaric interferences have received a great deal of attention in the Q-ICP-MS community. By

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contrast, although detector dead time as a source of inaccuracy in Q-ICP-MS isotope analysis has been well documented,[6,7,17,18,22,23] it has received surprisingly little attention relative to its importance in recent years until now (*e.g.* ref. 15 and 16). Considering session-specific detector dead time correction has not become standard in Q-ICP-MS isotope data reduction. This is at least in part because dead time is not an easily changeable parameter in most modern Q-ICP-MS software. Instead, in most laboratories, dead time is normally set upon installation or detector replacement and not subsequently changed,[17] despite detector aging and the likelihood of being sensitive to laboratory and/or pre-amplifier electronics temperature.[18]

Here we investigated whether detector dead time impacts isotope ratios for elements over a range of atomic numbers (*Z*: Li, Sr, Ce, Pb & U) and across multiple Sr isotope analytical sessions. This allowed us to assess the suitability of an unchanged dead time set upon installation, to assess the constancy of dead time over most of the mass range of the periodic table and to document dead time fluctuations between different analytical sessions.

We show that with a session specific dead time, accuracy and precision of isotope analysis dramatically improve, and we present a straightforward method for obtaining a session specific dead time. However, minor inaccuracy remains in Q-ICP-MS isotope ratio data corrected with the IUPAC method and we explore potential origins of this inaccuracy.

2 Detector dead time

Dead time is a phenomenon that affects any detection system that records discrete events. It reflects the time required for a detector and its associated electronics to reset after recording the impact of an event. For the electron multipliers used in Q-ICP-MS the dead time is corrected using eqn (1):[13,14,20]

$$\mathrm{cc} = \frac{\mathrm{oc}}{(1 - \mathrm{oc}\cdot\tau)} \tag{1}$$

where cc is the dead time corrected count rate and oc is the observed count rate with no dead time correction applied and τ is a dead time correction factor.

Russ and Bazan[22] proposed a straightforward method for calculating τ by analysing $^{238}\mathrm{U}/^{235}\mathrm{U}$ at differing concentrations. They observed that the effect of dead time increased linearly with signal intensity, *i.e.* concentration of the analysed solution. Given that $^{238}\mathrm{U}$ is 138 times more abundant than $^{235}\mathrm{U}$ at a given concentration, the much larger $^{238}\mathrm{U}$ signal is proportionally more affected by dead time than $^{235}\mathrm{U}$. This leads to a linear decrease in the observed dead time uncorrected $^{238}\mathrm{U}/^{235}\mathrm{U}$ with concentration. Russ and Bazan[22] then applied eqn (1) to both the $^{238}\mathrm{U}$ and $^{235}\mathrm{U}$ observed count rates with a τ to achieve a constant $^{238}\mathrm{U}/^{235}\mathrm{U}$ with varying concentration. Of note, as mass bias occurs prior to and unrelated to detection in mass spectrometry it should be corrected for separately and after dead time correction.

This approach to deducing dead time can be generalised for any two masses, where the abundance of M_1 is greater than M_2, as shown in Fig. 1 and the relationship between the observed count rate and τ leads to the linear eqn (2).

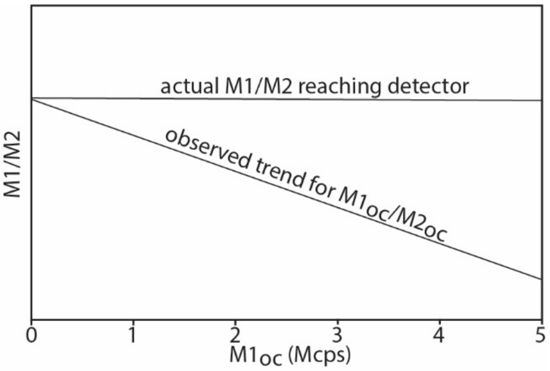

Fig. 1 Plot of the relationship between the ratio of masses M_1 and M_2 observed by a detector affected by dead time and the observed count rate of M_1 where M_1 is the more abundant mass.

$$\frac{M_{1\mathrm{oc}}/(1 - \tau\cdot M_{1\mathrm{oc}})}{M_{2\mathrm{oc}}/(1 - \tau\cdot M_{2\mathrm{oc}})} = m\cdot M_1 + c \tag{2}$$

As the count rate approaches zero the effect of dead time becomes negligible and thus, in eqn (2), the *y* intercept (*c*) is the actual M_1/M_2 reaching the detector. Tau can be deduced by the reasonable assumption that a slope (*m*) of zero results from applying the ideal dead time. Thus, solving for τ the equation can be rearranged as follows:

$$\tau = \frac{c\cdot M_{2\mathrm{oc}} - M_{1\mathrm{oc}}}{M_{1\mathrm{oc}}\cdot M_{2\mathrm{oc}}(c - 1)} \tag{3}$$

Eqn (1) and (2) can be used to calculate the best fit τ for an experiment provided it includes analysis of a suitable isotope pair analysed at different concentrations. When the actual M_1/M_2 reaching the detector has been deduced it is possible to use eqn (3) to calculate τ for individual analyses and thus assess whether τ has varied within an experimental run, as might occur if critical conditions, such as room temperature, change in the laboratory. Once the appropriate dead time has been applied to the data for all isotopes investigated, classic mass bias methods can then be applied to obtain the true isotope ratio, assuming there are no isobaric interferences.

More complex methods of τ correction have been proposed that combine the non-extending dead time (eqn (1)) and extending dead time (*e.g.* ref. 15, 16 and 18). However, for the purpose of this study we use the non-extending dead time eqn (1) initially and then assess whether a combined non-extending dead time and extending dead time correction is required to achieve improved accuracy and precision in the discussion.

3 Dead time effect on isotope ratios over a range of *Z*

Vanhaecke and de Wannemacker[23] demonstrated for Mg and Pb isotope ratio analyses, that dead time did not covary with *Z* for some types of electron multipliers yet was highly dependent on Z for other types. This conclusion was drawn with the analytical precision available at the time. This presumably motivated Q-ICP-MS manufacturers to select electron multipliers with minimal dependent dead time in newer models and/or provide a correction method built within the instrument software for removing Z-dependent dead time artefacts. Thus, there is clearly a need to repeat the experiment of Vanhaecke and de Wannemacker.[23] Here we investigate dead time *via* single quad Q-ICP-MS mode for a wide range of Z (Li, Sr, Ce, Pb & U).

Furthermore, we present a preliminary investigation of the effect on dead time with Z after reaction and mass shift during tandem Q-ICP-MS/MS by investigating mass shifted Sr, Ce and U isotope ratio data.

3.1 Methodology

All analyses were performed in solution mode on an Agilent 8900 Q-ICP-MS/MS housed in Queensland University of Technology's (QUT) Central Analytical Research Facility (CARF) with a nominal τ set to 0 ns and the pulse-analogue cross-over set to 5 Mcps. This instrument had a τ of 41.5 ns set upon installation on mass 135, with a Z-dependent variation of 6 ns over the 0–270 amu mass range. The high pulse-analogue cross-over was used to extend the data array to high count rates where counting statistics and the dead time effect are pronounced. All analytical runs were performed in time-resolved mode where a solution that was directly aspirating into the nebuliser exhibited a continuous increase in the concentration of the element of interest over an approximately thirty-minute period. Only data acquired in pulse mode were considered. Analyses where the less abundant isotope was <0.1 Mcps were discarded to maintain good counting statistics.

Analytical conditions including isotopes analysed and the duty cycle for each of the experiments are provided in SI Table 1. For the tandem Q-ICP-MS/MS, N_2O was used as the reaction gas because of its efficient conversion of Sr^+, Ce^+ and U^+ to SrO^+, CeO^+ and UO^+. Note, the duty cycles for SrO^+, CeO^+ and UO^+ had longer dwell times than those of the other analytical runs (SI Table 1) which gives rise to fewer data points in otherwise similar experimental runs.

Lithium, Ce and U solutions were prepared from ICP-MS 10 $\mu g\ ml^{-1}$ single-component high purity standards from Choice Analytical; with catalogue part numbers and batch numbers provided in SI Table 1. Strontium and Pb solutions were prepared from CARF stock solutions of isotope standards, including National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) 987 (strontium carbonate) and 981 (equal-atom lead isotope standard).

For each experiment, 2 solutions of the target element were prepared by diluting the stock solution using double distilled HNO_3 to achieve[1] 0.5–1.5 Mcps and[2] 6 Mcps on the target M_1 isotope. The high concentration solution[2] was continually added *via* a pipette into the low concentration solution[1] to achieve a continual increase in Mcps over the course of the experiment.

3.2 Results for dead time *via* single Q-ICP-MS mode

For the five isotope ratios investigated, the effect of uncorrected dead time ($\tau = 0$ ns) can clearly be seen as negative trends when plotted *versus* signal intensity (the left panels of Fig. 2). The slopes of the trends for the $\tau = 0$ data correlate with the intensities of both the more (M_1) and the less abundant isotopes (M_2). When M_1/M_2 is high (*e.g.*, $^{238}U/^{235}U$) the slope of the linear regression is comparatively high and when M_1/M_2 is low (*e.g.* $^{207}Pb/^{206}Pb$) the slope is comparatively low. The intercepts of the linear regressions are all different from the accepted isotope ratios because no mass bias correction was applied.

In the right-hand side panels of Fig. 2, dead time corrected data are shown, where τ for each element was calculated using eqn (1) to achieve a slope as close to zero as possible in eqn (2). This can be calculated by plotting the slope from eqn (2) *versus* a range of τ, where the intercept of a regression through the resultant trend gives the ideal τ for the experiment. We then used the covariance of the dead time corrected data to calculate the τ uncertainty following Iso, OIML.[24] The intercepts of the linear regressions through the τ corrected data are indistinguishable to those of the τ uncorrected data. There is a significant variation in τ with Z, with the calculated τ for Li of 7.8 ns lower than that for U (Fig. 3).

The linear regression through the τ values for the different isotope ratios investigated (Fig. 3) indicates a Z-dependent variation of 7.7 ns over the 0–270 amu mass range, slightly higher than that set upon machine installation, albeit with a high uncertainty on the fit.

3.3 Results for dead time *via* tandem Q-ICP-MS/MS mode

The metal-oxide isotope ratios for Sr, Ce and U are shown in Fig. 4. The slopes and intercepts of the trends for the dead time uncorrected data (left panels Fig. 4) are very close to the equivalent single Q-ICP-MS data (left panels Fig. 2) except for U, where the metal-oxide isotope ratio y intercept is lower (136) than that obtained by single Q-ICP-MS.

The calculated τ values for both SrO and CeO are indistinguishable from the equivalent single Q-ICP-MS data. The UO τ is indistinguishable from those of SrO and CeO but slightly lower, outside uncertainty of the single Q-ICP-MS data for U isotopes (Fig. 3).

4 Investigating dead time variation over time with mass shifted Sr isotope tandem Q-ICP-MS/MS data

It has been suggested that dead time experienced by Q-ICP-MS is sufficiently variable to warrant session-specific estimates of $\tau = 0$ for the element of interest (*e.g.* ref. 6 and 7) but this has neither been documented systematically nor tested for tandem Q-ICP-MS on metal-oxide ratio measurements. Here we inspect mass shifted Sr isotope tandem Q-ICP-MS/MS data to investigate the stability of dead time over time and to test whether session specific dead time corrections improve the precision of mass bias corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$. This focus on mass shifted

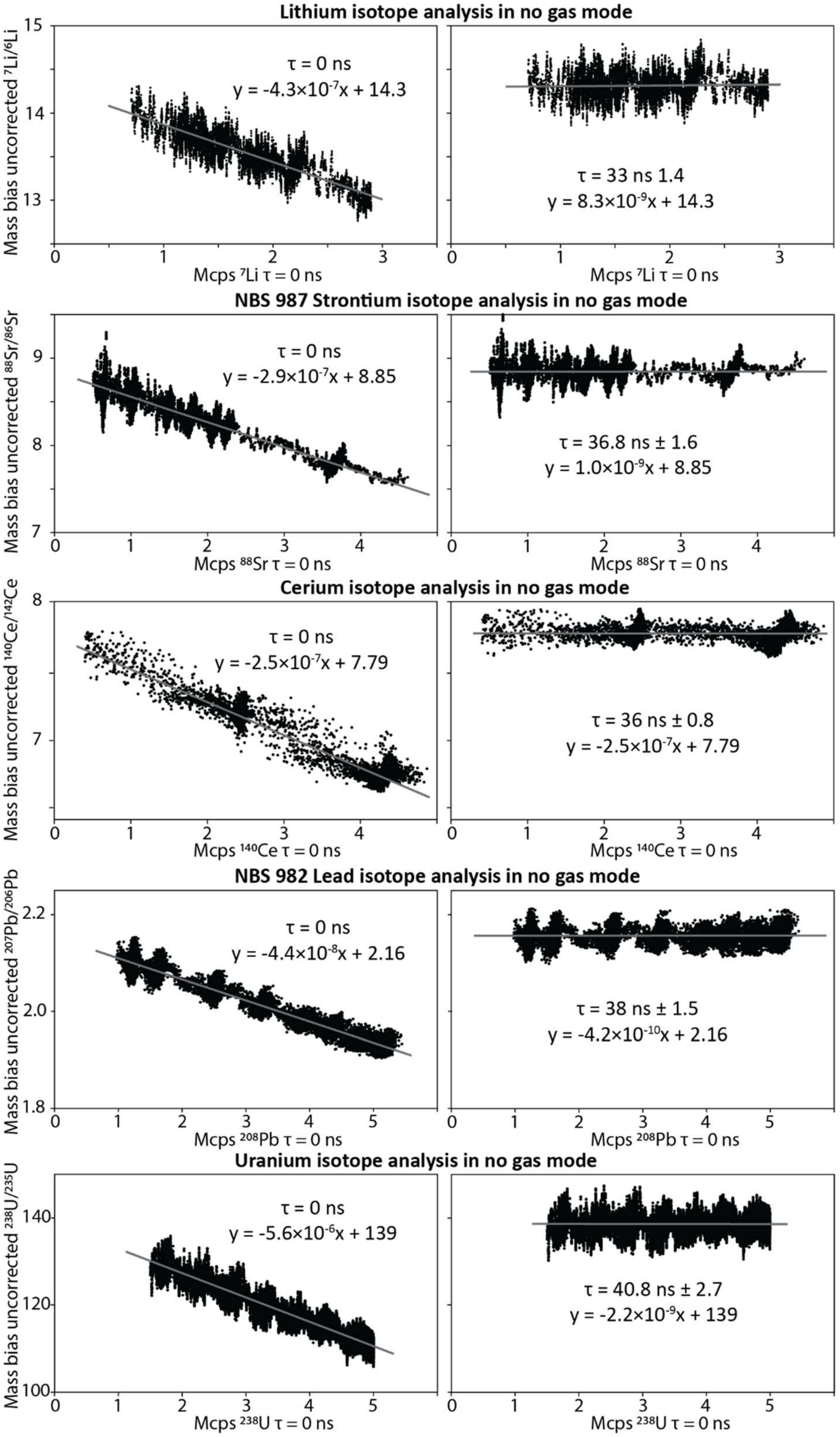

Fig. 2 Plots of single Q-ICP-MS mode data. Signal intensity (Mcps) of the most abundant isotope plotted against mass bias uncorrected isotope ratio. Left-hand panels show $\tau = 0$ while right-hand side panels show dead time corrected intensity ratios to achieve a slope as close to zero as possible.

^{87}Sr/^{86}Sr data is because of the interest in this ratio and because the conventional IUPAC approach of ^{88}Sr^{16}O/^{86}Sr^{16}O mass bias correction of the ^{87}Sr^{16}O/^{86}Sr^{16}O can be applied. A further motivation of the analysis was that a number of studies have applied correction factors to mass shifted Sr isotope data without, however, explaining the physical phenomenon that

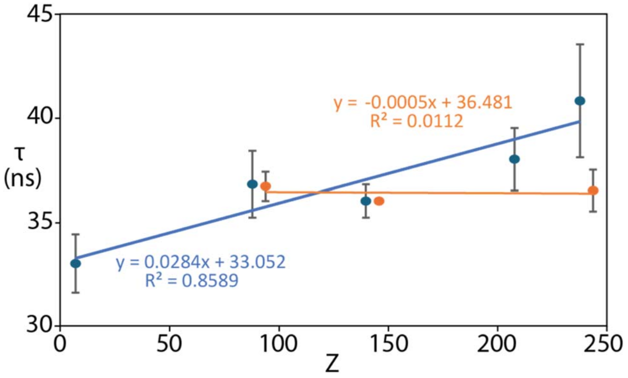

Fig. 3 Plot of mass number (Z) *versus* calculated τ for single Q-ICP-MS mode experiments (blue-coloured symbol) and mass shift Q-ICP-MS/MS mode (orange-coloured symbols).

leads to the requirement for the correction factor (*e.g.* ref. 3). We present data for the certified reference materials (CRMs) that were run with unknowns in Sr isotope tandem Q-ICP-MS/MS experiments (NIST-SRM-987, NIST-SRM 1570a, USGS-AGV2, USGS-BIR-1, USGS-W2). Both data from O_2 or N_2O reaction gas experiments from a five-year period were combined. We chose experiments where there was at least a 0.3 Mcps variation in the $^{88}Sr^{16}O$ between the CRMs allowing for calculation of τ using eqn (2). Four of the experiments include analysis of NIST-SRM-987 at different concentrations specifically to precisely determine session specific dead time.

4.1 Methodology

All analyses were performed in solution mode on an Agilent 8900 Q-ICP-MS/MS coupled to a Teledyne Cetac MVX-7100 Microlitre Workstation autosampler in QUT's CARF. Analytical conditions for each run are presented in SI Table 1. Four experiments used the dead time set at installation of 41 ns. The output data from these experiments were recalculated to a 0 ns dead time using eqn (1), rearranged to solve for the observed counts (oc). Four experiments used a nominal dead time set to 0 ns (SI Table 1).

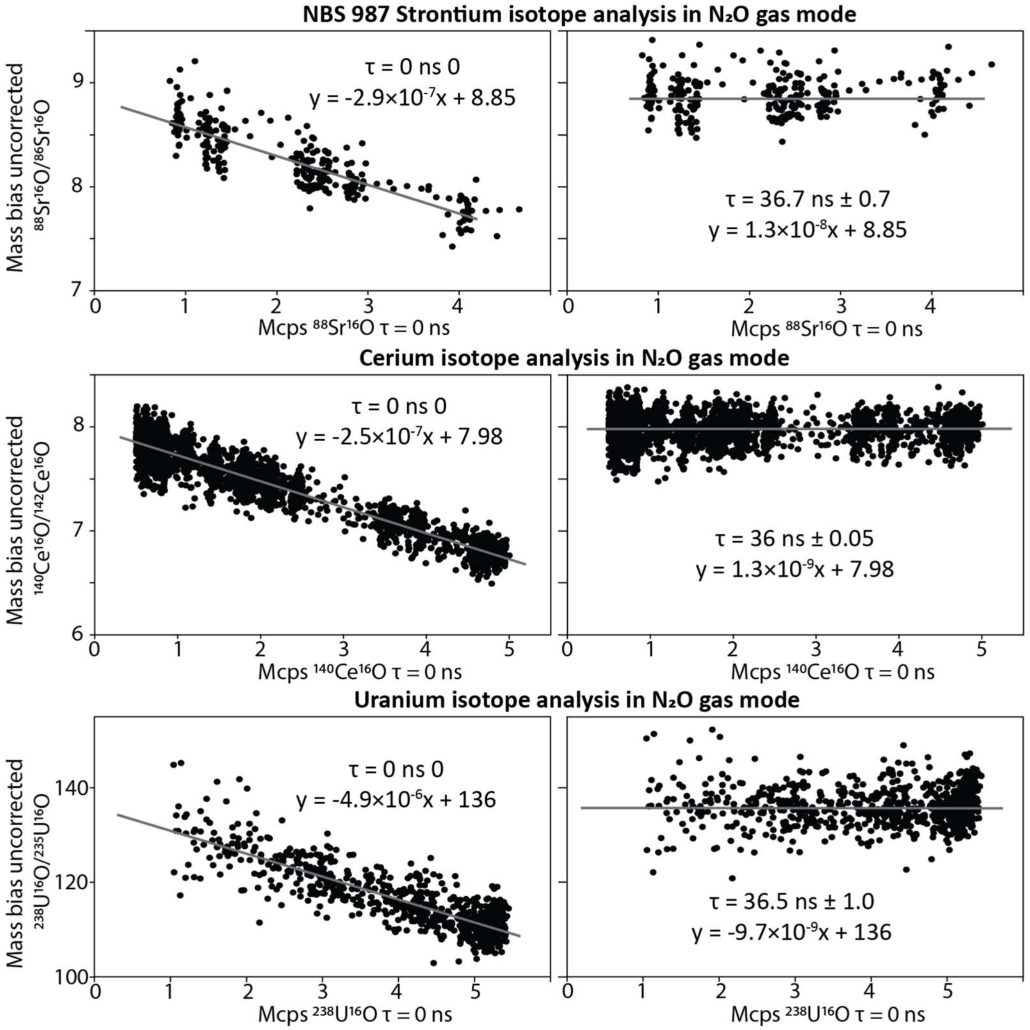

Fig. 4 Plots of tandem Q-ICP-MS/MS mode data. Signal intensity (Mcps) of the most abundant element-oxide mass plotted against mass bias uncorrected isotope ratio. Left-hand panels show $\tau = 0$ while right-hand panels show dead time corrected intensity ratios to achieve a slope as close to zero as possible.

For NIST SRM 1570a 'spinach leaves' ($^{87}Sr/^{86}Sr$ 0.70905 ± 0.00002;[25]) a 50 mg aliquot was dissolved in concentrated double-distilled HNO_3, dried down, and the residue was dissolved in 2% HNO_3 to make stock solutions that could be diluted for analysis.[26]

For the USGS-AGV2, USGS-BIR-1, USGS-W2a rock CRMs, 50 mg aliquots were digested in a milestone bench-top ultrawave single reaction chamber microwave digestion system (Milestone Srl, Sorisole, Italy) following 'Method guideline #1: silicate rocks without resistant minerals'[27] to generate stock solutions.

All CRM dilutions were prepared from previously dissolved stock solutions and diluted to give signals between 0.5 and 4 Mcps on $^{88}Sr^{16}O$. None of the solutions underwent Sr purification. Over the study period, the PA cross-over was set either to 1.5 or 5 Mcps. Only data analysed in pulse mode were included.

As most mass bias in a Q-ICP-MS occurs in the plasma torch, for two of the experiments run on the same day (320 707 – 8 mm

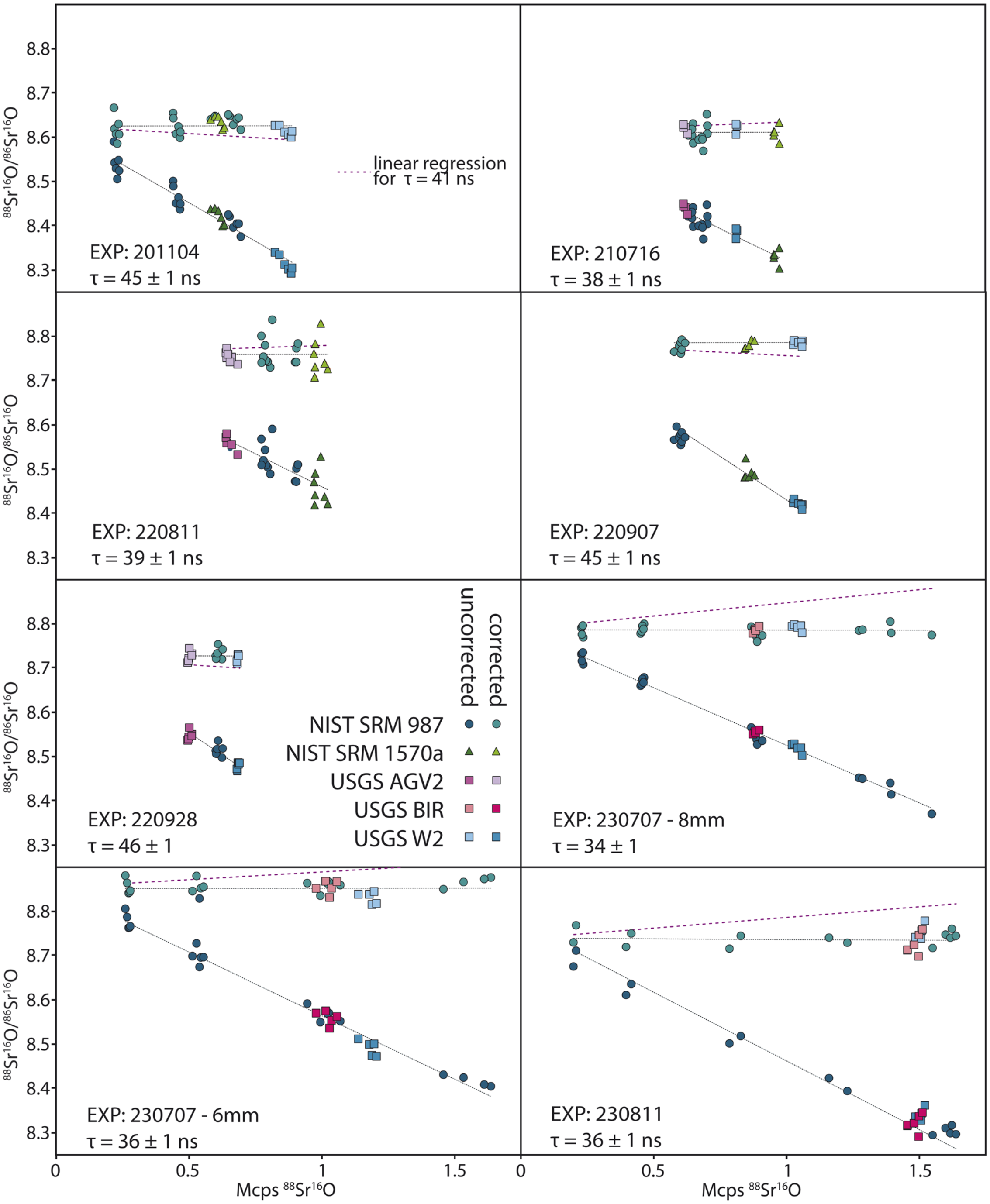

Fig. 5 Plot of $^{88}Sr^{16}O$ intensity (Mcps) *versus* $^{88}Sr^{16}O/^{86}Sr^{16}O$ that is dead time uncorrected ($\tau = 0$) and that has a session specific dead time correction to achieve a linear regression through the data with an effective slope of zero. For comparison, a linear regression defined by the data calculated with the installation set dead time ($\tau = 41.5$ ns) is also shown.

& 320 707 – 6 mm) the distance of the torch to the cones was changed to deliberately vary the mass bias.

4.2 Results: correcting dead time

The dead time effect is clearly visible in the uncorrected $\tau = 0$ $^{88}Sr^{16}O/^{86}Sr^{16}O$ for the experiments shown in Fig. 5 with all datasets showing a negative trend with increasing intensity of the $^{88}Sr^{16}O$ signal. A session specific dead time was calculated for each experiment to achieve a zero slope (-1^{-10} to 1^{-10}) for the dead time corrected $^{88}Sr^{16}O/^{86}Sr^{16}O$ *vs.* Mcps $^{88}Sr^{16}O$ data arrays. A significant range in dead time (35–46 ns) was observed across the experiments, although it is noted that the larger dead time estimates came from datasets with limited spread in $^{88}Sr^{16}O$ intensity. In the two experiments where the distance of the torch to the cones was changed (320 707 – 8 mm & 6 mm) the Mcps $^{88}Sr^{16}O = 0$ intercepts are very different ($^{88}Sr^{16}O/^{86}Sr^{16}O$ of 8.81 and 8.88 respectively). Despite this, the calculated dead times for the two experiments are within uncertainty. Since most of the experiments have different Mcps $^{88}Sr^{16}O = 0$ intercept $^{88}Sr^{16}O/^{86}Sr^{16}O$ ratios, it is likely that dead time and mass bias are not related.

4.3 Assessing accuracy after mass bias correction

The impact of incorrectly set dead time on mass bias corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ is shown in Fig. 6a with a comparison of results derived from the dead time set at installation (41.5 ns) *versus* the session specific dead times (Fig. 6b). For analytical runs where all CRMs were run at $^{88}Sr^{16}O < 1$ Mcps the effect of the incorrect dead time is relatively minor, with the average corrected/accepted $^{87}Sr^{16}O/^{86}Sr^{16}O$ for the CRMs having a standard deviation of 0.06%. This is compared to a standard deviation of 0.05% for the same CRMs when a session specific dead time is applied. They also show similar degrees of deviation from the accepted values.

However, in the experiments where Mcps $^{88}Sr^{16}O$ range from <0.5 to >2 the routine set dead time ($\tau = 41.5$ ns) has a major effect on the mass bias corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ with percentage level deviation from the accepted isotope ratio. In the three experiments where different concentrations of NIST SRM 987 were analysed, yielding a range of $^{88}Sr^{16}O$ signal intensities of 0.3–2 Mcps, different mass bias corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ ratios were obtained. When using the installation set dead time (Fig. 6a) at low Sr concentrations, the sample's internal correction achieves a mass bias corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ relatively close to the accepted values. However, as Mcps $^{88}Sr^{16}O$ increases the mass bias correction leads to increasing over-correction of the $^{87}Sr^{16}O/^{86}Sr^{16}O$ that scales with Mcps $^{88}Sr^{16}O$ (Fig. 6a). The session specific dead time completely removed this effect with all concentration solutions having indistinguishable $^{87}Sr^{16}O/^{86}Sr^{16}O$ (Fig. 6b).

The dead time and mass bias corrected data presented in Fig. 6b include several experiments where all CRMs are within 2SE of the accepted $^{87}Sr/^{86}Sr$ values and others that are not. Despite this, in all experiments the ratio of corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ to accepted $^{87}Sr/^{86}Sr$ for each CRM is within uncertainty of each other. This means that for each of the experiments where the corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ ratios are not within uncertainty of the accepted $^{87}Sr/^{86}Sr$, a systematic cause for inaccuracy is indicated. This systematic deviation allows for an external calibration, whereby one CRM (*e.g.* NIST SRM 987) is used to estimate the residual bias, which can then be applied to the remaining CRMs. With this final correction, the accuracy of CRMs run as unknowns can be estimated (Fig. 7).

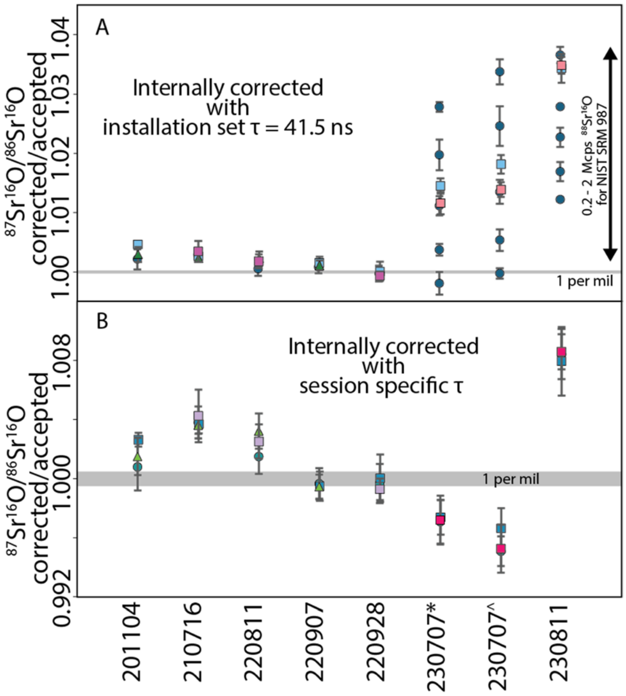

Fig. 6 Plots of mass bias corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$, using an internal correction derived from the $^{88}Sr^{16}O/^{86}Sr^{16}O$, divided by accepted $^{87}Sr/^{86}Sr$ for the CRMs presented in Fig. 5 (same symbols). Panel (A) shows data that were dead time corrected with the fixed τ of 41.5 ns, as set upon installation. For samples with high Mcps for $^{88}Sr^{16}O$ (see Fig. 5) highly inaccurate results are obtained. Panel (B) shows the same data corrected with a session specific dead time (Fig. 5).

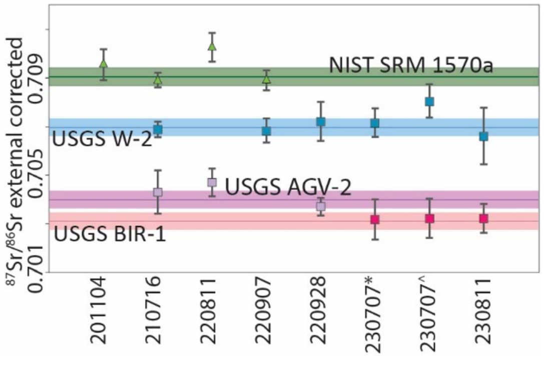

Fig. 7 Plot of session specific dead time corrected, internal mass bias corrected and externally corrected, using NIST SRM987, $^{87}Sr/^{86}Sr$ for four international CRMs. The bands represent the accepted $^{87}Sr/^{86}Sr$ for each of the standards, with the width of the bands corresponding to 1 per mill standard deviation.

5 Investigating the origin of residual inaccuracy after session specific dead time and mass bias correction in mass shifted Sr isotope tandem Q-ICP-MS/MS

The mass bias and session specific dead time corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ ratios (Fig. 6b) vary in accuracy between 0.996 and 1.008 relative to accepted values for the analysed CRMs. Although this residual inaccuracy can be adequately corrected with a bias estimate from one CRM, ideally, the cause of the bias needs to be identified.

A number of physical mechanisms that affect ion beam transmission have the potential to be responsible for residual inaccuracy; these include beam emittance and acceptance, beam matching, energy-dependent transmission and space-charge effects.[28–30]

One of the primary ways of assessing the effect of beam emittance and acceptance and beam matching while tuning a Q-ICP-MS is to investigate peak shapes. Therefore, we first explored peak shapes in Q-ICP-MS as a possible cause of inaccuracy, as it is one obvious difference from the high mass resolution MC-ICP-MS and TIMS, which exhibit flat topped peak shapes. In contrast, due to the lower abundance sensitivity of a Q-ICP-MS the peak shapes have more obvious asymmetry. In addition, during Q-ICP-MS routine auto-tuning, the peak shape is optimised for a wide range of Z, rather than the mass range measured in isotope ratio analysis. This global tuning can lead to asymmetrical peak shapes. In time resolved Q-ICP-MS isotope analysis, as was used in all our experiments, only one data point per peak is acquired. The exact position of Z for analysis is not determined by considering the peak top itself, rather as the half-way point of the shoulders of the peak. With a substantially asymmetric peak, the half-way point may not necessarily sit at the highest point on the peak. Therefore, we reasoned that if the peak shape is not carefully checked prior to an experiment, it could be possible that the analysis point sits slightly off-peak, which could lead to a systematic bias in the resultant isotope ratios. To explore this possibility, a series of experiments was run with deliberately varying the peak shape and symmetry and also varying the number of data points acquired per peak. The data showed no influence on isotope ratio accuracy and they are therefore not presented here.

It is worth noting that our deliberate variation of the peak shape and peak symmetry caused changes in beam emittance and acceptance and beam matching. Although not a systematic test of these factors, the lack of change in isotope ratio with peak shape strongly suggested that the residual inaccuracy is not dominantly caused by varying ion beam emittance and acceptance and beam matching.

Energy-dependent transmission was explored for MC-ICP-MS by Albarède and Albalat.[28] They showed that isotope fractionation caused by energy-dependent transmission was predominantly due to the configuration of the ICP MS cones relative to the plasma torch, was mass dependent and could be corrected for. We argue that because the fundamental architecture of the plasma torch, cones and extraction ion optics is broadly comparable between MC- and Q-ICP-MS, energy-dependent transmission would also be mass dependent in a Q-ICP-MS. Our experiment of varying the torch distance confirms this. By varying the distance of the torch from the cones, ions are extracted from different regions of the plasma, which affects their kinetic energy distribution and thus energy-dependent transmission. As no variation was observed between the dead time and mass bias corrected data for these two experiments, we infer that energy-dependent transmission does not cause the additional bias required to correct the experimental data.

We next reviewed the analytical conditions of each run of the data presented here (SI Table 1) and by Zepeda and Kamber,[31] who manipulated various tune parameters to minimise the BaO interference on Eu to achieve accurate Eu concentration analysis in high Ba samples. From the review, we hypothesised that the extent of ion beam deflection when directed through the offset between the reaction cell and quad 2 could impact accuracy. Therefore, we investigated whether varying the voltages on extract 2, plate deflect, and plate bias could help to elucidate upon the origin of the residual inaccuracy.

For these tests, all analyses were run on the same instrument with analytical conditions for each run presented in SI Table 1. Three sets of experiment were conducted using the analytical conditions of the 220 907 run that gave both precise and accurate dead time corrected and internally corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ (Fig. 6b). In each set, one single parameter (extract 2, plate deflect and plate bias) was varied.

For each experiment three different concentration solutions of NIST SRM 987 were run (15, 30 and 60 ppb), three times each so that dead time could be calculated independently for each run.

5.1 Results of the effect of varying the voltage on extract 2, plate deflect and plate bias

The effect of varying the voltage on extract 2, plate deflect and plate bias on accuracy and sensitivity is shown in Fig. 8. All corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ ratios were offset from the accepted value of NIST SRM 987 by ∼0.8% for extract 2 and plate bias and by 1.4% for plate deflect. The dead time correction for the 3 sets of experiments was indistinguishable within uncertainty (extract 2; 36.65 ± 0.37 ns, plate deflect; 37.1 ± 0.38 ns, and plate bias; 36.5 ± 0.37 ns).

Varying extract 2 voltage produces a linear relationship with sensitivity and within-run precision, with the standard deviation of the corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$ varying from 0.09% to 0.04% as the voltage is lowered from −240 to −160 V (Fig. 8). No variation in precision was observed when varying the voltage on plate deflect or plate bias (Fig. 8).

Neither extract 2 voltage nor plate deflect voltage showed a resolvable relationship with dead time and mass bias corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$. By contrast, a clear negative linear relationship is observed between plate bias voltage and accuracy (Fig. 8). The trend predicts that a plate bias voltage of close to 0 would yield accurate results. However, the signal sensitivity

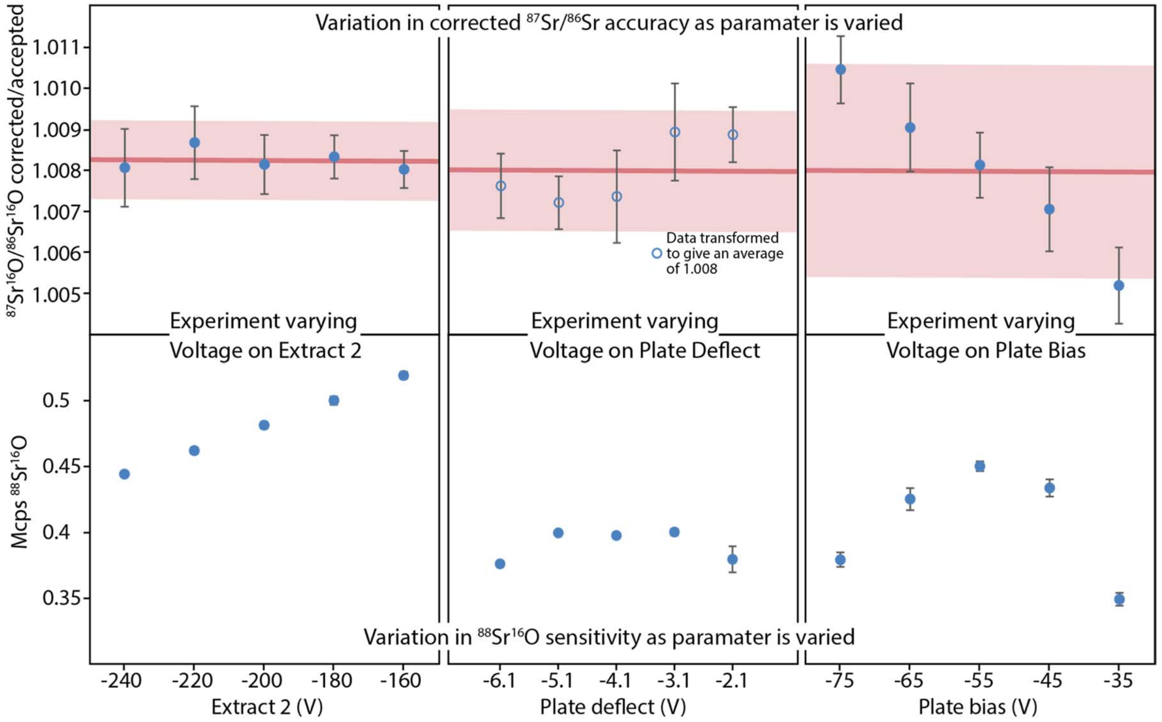

Fig. 8 Plots of (upper panels) session specific dead time corrected and internally mass bias corrected $^{87}Sr^{16}O/^{86}Sr^{16}O$, divided by accepted $^{87}Sr/^{86}Sr$ for NIST SRM 987 and (lower panel) $^{88}Sr^{16}O$ signal intensity for the 15 ppb Sr solution. Each column represents five experimental runs where one parameter was varied (extract 2; left, plate deflect; centre and plate bias; right) and all other parameters remained the same. For the upper central panel, the average $^{87}Sr^{16}O/^{86}Sr^{16}O$ corrected/accepted is 1.014 ± 0.001 and to keep a common scale the data were transformed to give an average of 1.008.

dramatically dropped above −21 V for plate bias and thus using 0 V was not viable.

5.2 Discussion on the residual inaccuracy after session specific dead time and mass bias correction

Both plate deflect and plate bias are lenses controlling the deflection of the ion beam after it leaves the reaction cell and enters the second quadrupole. The experiment on varying voltage on plate bias is a clear demonstration that redirecting the ion beam can affect the accuracy of isotope ratios that cannot be corrected for with classic dead time and mass bias corrections. To understand the nature of the residual isotope fractionation observed here and implicit in the vast majority of published isotope ratio data obtained by Q-ICP-MS, which all had correction factors applied, the underlying physical process needs to be identified. However, the lens architecture of modern Q ICP MS/MS is complex, and tuning is non-unique, and further research may best be conducted by instrument manufacturers.

The plate deflect and plate bias lenses control how the ion beam bends as it travels from the reaction cell into the second quadruple. This bend is required to stop non-charged particles formed in the reaction cell getting to the detector. It is possible that space charge effects, where a build-up of charge causes repulsion of similarly charged ions, could occur due to the high voltage applied to the plate bias.

Importantly, other types of mass spectrometers also employ lens sequences to direct ion beams, including multi-collector ICP-MS (MC-ICP-MS) with collision and reaction cells. It is possible that similar isotope ratio inaccuracies could occur in data derived from such instruments. For example, K isotope ratio measurements by reaction cell MC-ICP-MS recommend analysing solutions of constant K concentration, suggesting that variations in ion signal intensities can also cause inaccuracies in those instruments.[32]

Another possible cause of residual inaccuracy is where strongest space charge effect occurs in the cones between the plasma torch and the extraction optics.[29,30] Yu and Hathorne[30] demonstrated that plasma temperature influences mass bias and that low plasma temperatures lead to mass bias that cannot be internally corrected for. Further investigation of the space charge effect would require further experiments and is beyond the scope of this study.

6 Non-extending *vs.* extending dead time

Here we assess whether a component of residual imprecision in corrected Q-ICP-MS isotope ratios is due to the requirement to correct for both non-extending and extending dead times. All electron multipliers are affected by detector pileup to some degree and this occurs when an event hits the detector before it

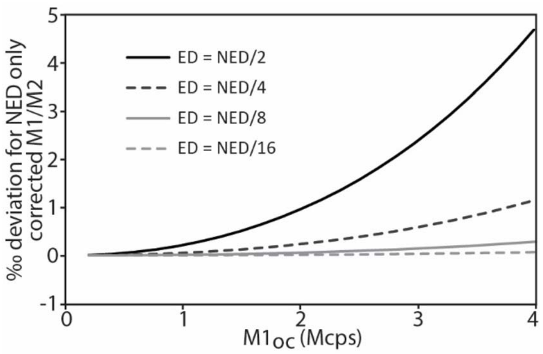

Fig. 9 Plot of the effect on an isotope ratio ($M_1/M_2 = 10$) where both non-extending dead time (40 ns) and extending dead time have a significant impact. The data were calculated with eqn (4) and only corrected for non-extending dead time (eqn (1)).

has had time to reset from a preceding event, causing the dead time period to be extended.[15,16,19,21] The effect of combined non-extending and extending dead time is expressed with the throughput formula (τ_{ne} non-extending dead time; τ_{e} extending dead time):[16]

$$\rightarrow_{\tau_{\text{ne}} > \tau_{\text{e}}} \text{oc} = \frac{\text{cc}}{e^{\text{cc}\tau_{\text{e}}} + \text{cc}(\tau_{\text{ne}} - \tau_{\text{e}})} \tag{4}$$

The formula can be used to assess the impact of extending dead time on an isotope ratio over a range of observed counts. The effect of correcting data that have been affected by non-extending and significantly extending dead times only with eqn (1) is shown in Fig. 9 for $M_1/M_2 = 10$ and $\tau_{\text{ne}} = 40$ ns. There is a clear increase in non-extending dead time corrected M_1/M_2 as the count rate increases, with high extending dead times having a greater deviation. Within the count range of interest to Q-ICP-MS (<2.5 Mpcs) only if the extending dead time is >25% of the non-extending dead time would you expect a resolvable ($\geq 1‰$) effect on isotope ratios analysed with Q-ICP-MS.

We do not see a resolvable positive relationship between the count rate and non-extending dead time and mass bias corrected isotope ratios in our experiments. Therefore, we conclude that the extending dead time is <25% of the non-extending dead time, and thus not the cause of residual imprecision in corrected Q-ICP-MS isotope ratios and does not need to be corrected for. However, in higher precision instruments where an accuracy of $\ll 1‰$ is required, extending dead time may be significant.

7 Conclusions

For reliable isotope ratio measurements on Q-ICP-MS and Q-ICP-MS/MS it is essential to perform appropriate correction for detector dead time and mass bias. Session specific dead time can be corrected for if the experiment includes a CRM analysed at three or more appropriate concentrations for fitting a dead time that provides linearity in the isotope ratios. While results in this manuscript are all from the same instrument, both Ulrich and Kamber[7] and Graczyk *et al.*[6] demonstrated the impact of variable dead time on other Q-ICP-MS instruments. Therefore, we are confident that our session specific dead time approach will improve precision on all Q-ICP-MS instruments.

Our study indicates that there is a positive near-linear relationship between mass number (z) and dead time in single Q-ICP-MS mode, but not in reaction mode; further research is required to test this.

Investigating Sr isotope ratio experiments conducted episodically over 5 years (2020 to 2025) indicates that dead time for a single element can vary by several ns. It is likely that this range relates to ageing ion counters, ageing electronics and changing laboratory conditions such as temperature and humidity.

Session specific dead time and mass bias corrections yield reproducible isotope ratios over a range of element concentrations. However, the corrected isotope data can be systematically moderately inaccurate. Because the inaccuracy is consistent across all analysed CRMs, a simple final bias correction can be applied when one CRM is used as a calibration standard for the purpose of achieving accurate results for the other CRMs and the unknowns.

We started an investigation into the origin of the systematic residual inaccuracy and found that varying the voltage to one of the lenses that deflects the ion beam from the reaction cell through to the second quadrupole affected the degree of systematic inaccuracy. Thus, we conclude that there is an as yet unidentified process that is causing isotope fractionation in Q-ICP-MS/MS and potentially other mass spectrometers that require steering ion beams across complex paths.

We find no evidence for the requirement to correct for both non-extending and extending dead times for Q-ICP-MS isotope ratios measured at precisions of 1 to 2‰. However, for higher precision isotope analysis, extending dead time may be an important factor to obtain more accurate data.

Author contributions

David T. Murphy: conceptualization, methodology, data acquisition and curation, and writing. Balz S. Kamber: conceptualization, methodology, and writing. Naoki Sugiyama: conceptualization, methodology, and writing review. Fred Freyer: conceptualization, methodology, and writing review.

Conflicts of interest

The authors declare that there are no competing personal or financial interests that could have impacted the work reported in this paper.

Data availability

The data for the experiments in Sections 4 and 5 of this study are available within the article and its supplementary information (SI). The data for Section one is available on request from the corresponding author. Supplementary information: Supplementary Table 1: experimental parameters for the analytical conditions for all analytical runs. Supplementary Table 2: the results for all Section 4 experiments, including the workflow for calculating a Session Specific τ. Supplementary Table 3: the results for all Section 5 experiments, including the workflow for calculating a Session Specific τ. See DOI: https://doi.org/10.1039/d5ja00398a.

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