

Inappropriate tail corrections can cause large inaccuracy in isotope ratio determination by MC-ICP-MS

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New generation multicollector ICP mass spectrometers are now being widely used for precise isotope ratio measurements. Different instruments show marked differences in abundance sensitivity, which, if corrected using the conventional thermal ionization mass spectrometry method of half-mass zeroes, result in large inaccuracies in isotope ratios. It is shown that a tail correction based on measurements of mono-isotopic ion beams is essential to obtain isotope ratio accuracy on instruments with poorer abundance sensitivity. This effect can largely explain published artefacts in MC-ICP-MS Pb isotope determination (M. Rehkämper and K. Mezger, *J. Anal. At. Spectrom.*, 2000, **15**, 1451).

Introduction

Multicollector magnetic sector ICP mass spectrometry (MC-ICP-MS) instruments are now a major source of isotope ratio data in the geosciences. Most users and manufacturers of these instruments have extensive experience with isotope ratio determination using thermal ionization mass spectrometry (TIMS), and transfer analytical protocols almost unchanged from TIMS.

A common such protocol is static multicollector isotope ratio measurement. This involves the simultaneous integration of ion beam intensities in several ion beam detectors, usually Faraday cups, and calculation of a set of isotope ratios from these. The measured ion beam intensities must be corrected for the zero offset of each Faraday amplifier, and this is commonly done in TIMS and MC-ICP-MS^{1,2} by taking integrations at ± 0.5 u from the peak mass prior to the static peak measurements. The mean of these half-mass zeroes is then subtracted from the raw peak intensity before ratio calculation. Thus, for a typical protocol for static Sr isotope ratio measurement:

$$\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}} = \frac{I_{87} - 0.5(I_{87.5} + I_{86.5})}{J_{86} - 0.5(J_{86.5} + J_{85})} \quad (1)$$

where I_m and J_m signify the mean signals at mass m for Faraday amplifiers I and J . The calculated ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ is subsequently corrected for Rb isobaric interference and instrumental mass fractionation.

However, this baseline subtraction does more than correct for amplifier offsets. In all magnetic sector mass spectrometers, there is a small contribution to peak intensity, called a tail, from adjacent peaks. This mostly results from ions losing energy by collisions with residual gas molecules in the analyser after passing through the magnetic sector, and is thus, in theory, on the low-mass side of a peak. This tail clearly also must affect the half-mass zeroes, and thus the use of half-mass zeroes is often thought to correct for tail as well. For example, eqn. (1) would correct the ion beam intensity at mass 87 for the amplifier offsets, and for a small component of the 88 ion beam at 87.5 u (Fig. 1).

In reality, the tail profile is concave-up, so a linear interpolation of the profile between 86.5 and 87.5 overestimates the tail at mass 87. Further, the signal at mass 86.5 is a consequence

of a tail from both 87 and 88. The component of the tail from 87 cannot be responsible for the elevated background underneath the peak of 87, and thus again the tail under 87 is overestimated. Finally there may be some tail on the high-mass side of a peak: again, the signal at 87.5 thus includes a component from 87 which cannot actually contribute to the baseline under 87, thus also resulting in overestimation of the tail under 87, while the signal at 86.5 includes a component from 86.

Quantification of tail under a peak

All three problems in using half-mass zero corrections [eqn. (1)] identified above result in overestimation of the tail underneath a given peak. The consequence is that ion beam intensities of minor isotopes are overcorrected for tail. This is true for both TIMS and MC-ICP-MS, but the magnitude of the overcorrection is a function of analyser vacuum, and this may be significantly worse in MC-ICP-MS than TIMS, because the ion source is at atmospheric pressure.

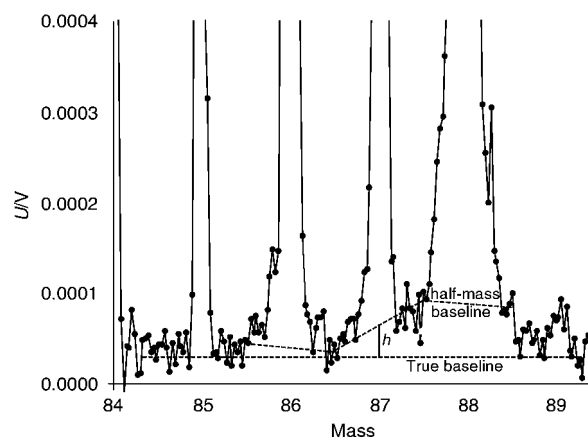


Fig. 1 Scan across Sr mass spectrum of SRM 987 on the Royal Holloway IsoProbe with about 4 V ${}^{88}\text{Sr}$. True baseline is estimated from the signal away from the larger peaks; the line half-mass baseline joins mean signal intensities at half-mass; and h is the additional baseline that would be subtracted from the ion beam at mass 87 if half-mass zeroes were used. Although this would appear visually to be a reasonable estimate of tail, it actually amounts to about 9 ppm of the 88 signal, while the true tail at -1 u is about 3 ppm (see Table 2).

Table 1 Abundance sensitivity specifications for the main TIMS and MC-ICP-MS manufacturers. All abundance sensitivities specified without a retardation filter at 400 mass resolution

Manufacturer	Instrument	Abundance sensitivity	Mass
Micromass (UK) Ltd.	IsoProbe	< 15 ppm	231/ ²³² Th
	Sector TIMS	2 ppm	237/ ²³⁸ U
Nu Instruments	Nu Plasma	< 5 ppm	237/ ²³⁸ U
Thermo Elemental	Axiom MC	< 5 ppm	237/ ²³⁸ U
	P54	< 5 ppm	237/ ²³⁸ U
Thermo-Finnigan	Neptune	1 to 3 ppm	237/ ²³⁸ U
	Triton TI	1 ppm	237/ ²³⁸ U

The magnitude of the tail is commonly measured by the parameter of abundance sensitivity. This is usually expressed in manufacturers' instrument specifications as the proportion of a ²³⁸U ion beam measured at mass 237, and varies from about 1 to 15 ppm (Table 1). The tail, 1 u away from a peak, is expected to decrease with atomic mass as the dispersion increases. However, this parameter does not allow quantification of the tail overcorrection that results from using half-mass zeroes, for which information is needed on the proportion of mass ²³⁸U present at mass 237.5 and also at mass 238.5.

Fig. 2 and Table 2 give the results of very slow scans across the mass spectrum around large ion beams (about 8 V) of ²³⁸U, ²⁰⁹Bi, ¹⁴¹Pr and ⁸⁹Y on the Micromass IsoProbe MC-ICP-MS at Royal Holloway on a single day. Scans on each Faraday detector were used to estimate mean signal intensities at 0.5, 1.5, 2.5, 3.5 and 4.5 u away from the peak, and the reported means and 2SE (standard error) values reflect the range of values observed across the detector array at each mass position. Signal intensities at unit masses were estimated by interpolating the curve of half-masses. For comparison, tail measurements on a Daly electron multiplier around 8 V ²³⁸U ion beams on the Royal Holloway VG354 TIMS are also given. The IsoProbe uses turbomolecular pumps to maintain analyser vacuums of about 2.5×10^{-8} mbar and has a relatively high specified abundance sensitivity of 15 ppm of ²³⁸U at mass 237. Table 2 shows that, at our current analyser vacuum, about 27 ppm of ²³⁸U is present at 237, and about 370 ppm is present at mass 237.5. The slope of the tail is so steep around 237.5 that this value is very dependent on the accuracy of centering the ²³⁸U peak. This steep slope means that half-mass zeroes would grossly overestimate the tail at 237, by about 180 ppm. If half-mass zeroes are used to estimate the baseline at mass 237, this will be inaccurate by 153 ppm of ²³⁸U intensity. In contrast, if it

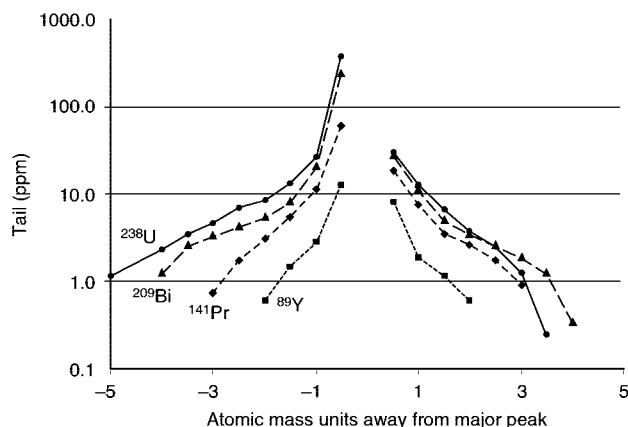


Fig. 2 Tail profiles for ⁸⁹Y, ¹⁴¹Pr, ²⁰⁹Bi and ²³⁸U on the Royal Holloway IsoProbe with analyser vacuum of about 2.5×10^{-8} mbar (data from Table 2). Note the very high tailing at -0.5 u for heavy elements and the strong asymmetry at ± 0.5 u. The four elements were prepared in 2% HNO₃ to give approximately 100 ppb concentration and introduced into the IsoProbe using a Cetac Aridus desolvating nebulizer. Extraction potential was used to achieve about 8 V ion beam, and Aridus Ar sweep gas was tuned for each element. All other machine parameters remained the same. Of these, Ar pressure in the collision cell is the only parameter that can affect abundance sensitivity, and only if grossly detuned.

is assumed that no tail is present beneath 237 (e.g., a baseline correction is made from amplifier offsets with no ion beam in the analyser), then the baseline estimate will be inaccurate by only 27 ppm of ²³⁸U.

Furthermore, there is significant tailing of ²³⁸U at mass 236 (8.5 ± 0.6 ppm), 235, 234 and at 239 and 240 (Fig. 2, Table 2) and thus, for a multi-isotopic element, the half-mass zeroes will be combinations of tails from several peaks. The only way to estimate quantitatively the tail under a peak is to measure the tail profile of a mono-isotopic or near-mono-isotopic element within the mass range of the element of interest, e.g., ²⁰⁹Bi for Pb, ¹⁷⁵Lu for Hf, ¹⁴¹Pr for Nd and ⁸⁹Y for Sr (Fig. 2). The tail under any peak is then the sum of total contributions from peaks up to 4 u away on both sides. So, for example, for ²⁰⁶Pb on a Pb solution doped with Tl to correct for mass bias:

$$^{206}\text{Pb}_{\text{tailcorr}} = ^{206}\text{Pb}_{\text{meas}} - (^{207}\text{Pb} \cdot Z_{-1} + ^{208}\text{Pb} \cdot Z_{-2} + ^{209}\text{Bi} \cdot Z_{-3}) - (^{205}\text{Tl} \cdot Z_1 + ^{204}\text{Pb} \cdot Z_2 + ^{203}\text{Tl} \cdot Z_3) \quad (2)$$

where Z_x is the proportional tail ($+0.00002$ for 20 ppm) at x u

Table 2 Tail profiles across selected mono-isotopic (or near-mono-isotopic) elements on the Royal Holloway IsoProbe MC-ICP-MS and VG354 TIMS. All IsoProbe data measured on one day with analyser vacuum of about 2.5×10^{-8} mbar with about 8 V ⁸⁹Y, ¹⁴¹Pr, ²⁰⁹Bi and ²³⁸U. Quoted tails are means ± 2 SE of tails estimated from slow scans across 4 or more Faraday buckets. TIMS data collected for ²³⁸U (analyser vacuum, approximately 4×10^{-9} mbar) and ⁸⁷Rb spike (analyser vacuum, approximately 2.5×10^{-9} mbar) using the Daly detector

		Atomic mass unit from central peak																	
		-4.5	-4.0	-3.5	-3.0	-2.5	-2.0	-1.5	-1.0	-0.5	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Mass																			
IsoProbe																			
Y	89	tail (ppm)					0.6	1.5	2.9	12.6	8.0	1.9	1.2	0.6					
		2SE					0.5	0.7	0.3	1.7	0.9	0.5	0.8	0.5					
Pr	141	tail (ppm)			0.8	1.7	3.1	5.4	11.4	59.8	18.1	7.4	3.5	2.6	1.7	0.9			
		2SE			1.0	1.1	0.8	0.8	0.8	2.8	0.9	0.6	0.8	0.6	0.6	0.9			
Bi	209	tail (ppm)	1.3	2.6	3.3	4.2	5.5	8.1	21.0	238.0	27.3	11.3	4.9	3.5	2.6	1.9	1.3	0.3	
		2SE	0.5	0.5	0.4	0.7	1.0	0.5	2.4	21.2	1.6	0.4	0.8	0.3	0.2	0.2	0.5	0.5	0.7
U	238	tail (ppm)	1.2	2.3	3.5	4.7	6.8	8.5	13.5	27.0	370.0	30.2	12.6	6.6	3.8	2.5	1.3	0.3	
		2SE	0.3	0.7	1.0	0.7	0.9	0.6	0.6	1.4	35.8	3.5	0.8	1.0	0.4	0.6	0.5	0.5	
TIMS (VG354)																			
U	238	tail (ppm)		1.7		2.7		6.8	11.2	38.6	8.5	4.0	0.6	0.2					
Rb	87	tail (ppm)						0.3	0.7	2.6	1.7	0.5							

away from a mono-isotopic peak. This calculation is conveniently performed in an Excel spreadsheet provided that peak intensities from individual integrations can be transferred to a spreadsheet.

Measurement of the tail profile is not without pitfalls. In principle, it should be possible with a mono-isotopic element to measure simply the intensities observed at unit masses by static multicollection. So, with the Faraday collectors set at unit mass spacing for Pb, it should be possible to measure masses 206, 207, 208, ^{209}Bi , 210, 211 and 212 to determine the tail contributions of ^{209}Bi at ± 1 to ± 3 u. It is, however, not easy on MC-ICP-MS machines to remove totally the blank Pb contributions. Subtraction of signal intensities from a blank solution can help, but it is very difficult to obtain better than 5 ppm reproducibility or accuracy on the ^{209}Bi contribution to the signal at mass 208 using this method. Further, in MC-ICP-MS, there may be small peaks at mass 210 (e.g., BiH^+) and 211 of similar magnitude to the expected tails. There are also potential problems with amplifier crosstalk if approximately 10 μV tail signals are measured simultaneously with an 8 V ion beam.

A peak-jumping procedure can be used instead, taking measurements at half masses away from a large peak. The profile can then be extrapolated to give the contributions at unit masses. However, on the IsoProbe, the curve is very steep at -0.5 u for heavy elements and it is only possible to estimate the tail at -1 u to better than ± 2 ppm by using measurements at -0.7 and -1.3 u as well. For lighter elements, where the baseline slope is less steep at -0.5 u, the tail at -1 u can be estimated to ± 1 ppm or better from these half-mass profiles. A final rapid method of measuring tail profiles is to scan on an ion counting detector. The axial Daly detector on the Royal Holloway IsoProbe is behind a retardation filter, so that tails are insignificant, but we can scan instead on a low-mass channeltron detector which, at its closest, is 6 u at U below axial. After calibration for dispersion and gain, tails derived from channeltron scans are fully consistent with tails measured on Faraday detectors. However, they also demonstrate (at Th and Lu) that tails of about 0.2 ppm are still present at 10 u below the major peak.

Tail values obtained for ^{238}U , ^{209}Bi , ^{141}Pr and ^{89}Y in Table 2 show a near-linear relationship with mass (Fig. 3). The tail profiles show limited variation with time. The mean and 2SD of observed tails at -1 u from ^{209}Bi was 20 ± 3.6 ppm for 7 measurements over 3 months. A change was noted after some work was carried out on the analyser, including baking. Although the magnitude of low-mass tails stayed constant, high-mass tails changed by a factor of 2.

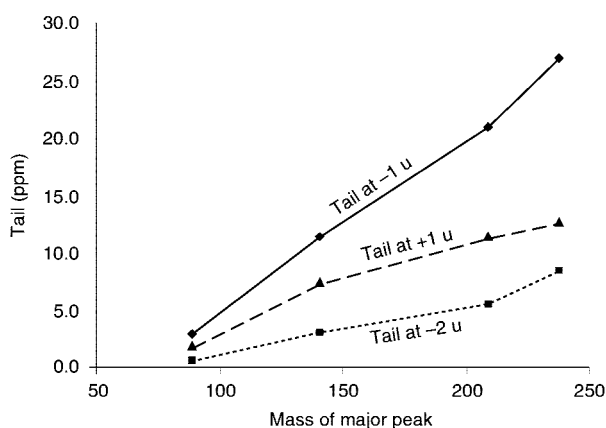


Fig. 3 Tail intensities on the Royal Holloway IsoProbe as a function of mass. Data from Table 2.

Applications of tail profiles on the IsoProbe MC-ICP-MS

Nd

The presence of radiogenic ^{143}Nd between high-abundance isotopes ^{142}Nd and ^{144}Nd means that half-mass zeroes at 142.5 and 143.5 are elevated due to tailing of 142 and 144, and thus ^{143}Nd intensities are too low when corrected using half-mass zeroes. Use of the measured tails of Table 2 instead of half-mass zeroes causes increases of about 0.00002 in both $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$, to give data much closer to TIMS values.³ If no tail correction is used (e.g., baselines measured on a blank solution), measured $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{145}\text{Nd}/^{144}\text{Nd}$ are 0.000014 higher than the true ratios for the tail data of Table 2. In principle, such differences can be corrected using standard analyses, since the tail contribution from the sample Nd onto ^{143}Nd will be proportionally the same as in a standard Nd analysis. However, if Ba, Ce, or Pr in the samples has been inadequately removed by ion-exchange chemistry before analysis, these can contribute significant tails onto the Nd mass spectrum.

Hf

As with Nd, since ^{176}Hf is a low-abundance isotope, the use of half-mass zeroes will lead to values of $^{176}\text{Hf}/^{177}\text{Hf}$ lower than expected. In addition, however, the presence of 0.2 to 1 ppm tails, 5 to 10 u from a peak (seen on channeltron scans) will lead to an underestimate of ion signals at the critical interference monitor of ^{172}Yb , because all the Hf major peaks have a small effect on this mass. No tail correction would lead to an overestimate of the ion signal at ^{172}Yb .

Pb

Rehkämper and Mezger¹ reported a dependence of Tl-normalized Pb isotope ratios on Pb/Tl ratios using an IsoProbe, but no such dependence when using a Nu Instruments MC-ICP-MS. Their IsoProbe data are baseline-corrected using half-mass zeroes while their Nu Plasma data are not. At low Pb/Tl ratios on the IsoProbe, they reported elevated $^{207}\text{Pb}/^{204}\text{Pb}_{\text{RM}}$ which they interpreted to be a result of the half-mass zeroes overcorrecting the ^{204}Pb signal, since at high Tl/Pb, $^{204.5}$ intensity is elevated due to tail from ^{205}Tl . The subscript RM here refers to Tl-normalized Pb isotope ratios as calculated by Rehkämper and Mezger.¹ They also reported increases in $^{208}\text{Pb}/^{206}\text{Pb}_{\text{RM}}$ and $^{207}\text{Pb}/^{204}\text{Pb}_{\text{RM}}$ at high Pb/Tl, which, they showed, followed a mass fractionation trajectory. They did not discuss the possibility that, at high Pb/Tl ratios, the contribution of ^{206}Pb to the ion signal at mass 205.5 results in an over-correction for tail of the ^{205}Tl ion signal, hence lower $^{205}\text{Tl}/^{203}\text{Tl}$ values than real ones, and thus an undercorrection of Pb isotope ratios for mass bias. This would lead to a mass bias relationship between Pb isotope ratios as observed,¹ because at higher Pb/Tl ratios less mass bias correction is made, and hence the normalized Pb ratios would be too high.

The baseline correction method Rehkämper and Mezger¹ used on the Nu Instruments Plasma spectrometer involved using the electrostatic analyser to switch the Pb mass spectrum away from the collectors. This meant that baselines measured were free of any tail contribution, and were equivalent to measuring baselines with the analyser isolation valve closed on the IsoProbe. Thus it is not surprising that their Nu Plasma data show no relationship between $^{208}\text{Pb}/^{206}\text{Pb}_{\text{RM}}$ and Pb/Tl. In fact, their Nu Plasma data were uncorrected for tail, and there should be a slight *negative* correlation between $^{208}\text{Pb}/^{206}\text{Pb}_{\text{RM}}$ and Pb/Tl resulting from no correction of ^{206}Pb tailing onto ^{205}Tl . However, this would be expected to be small at the 2 ppm abundance sensitivity they reported for the Nu Plasma.

Rehkämper and Mezger¹ stressed that the gradient of the $^{208}\text{Pb}/^{206}\text{Pb}_{\text{RM}}$ vs. Pb/Tl curve was the same for different samples, and hence regarded it as a matrix effect, where different Pb/Tl ratios caused changes in the Pb mass bias.

The correlations observed¹ can be quantitatively modelled using the data presented in Table 2. A typical mass bias, as observed on the IsoProbe, was applied using the exponential law to reference “true” Pb isotope ratios for SRM 981, SRM 982 and $^{205}\text{Tl}/^{203}\text{Tl}$ values. Individual ion beam intensities were calculated from these ratios assuming an 8 V ^{208}Pb ion beam and variable mass ratios of Pb/Tl. The tail profile for ^{209}Bi reported in Table 2 was then applied to increment the peak intensities for tail of adjacent peaks, and also to calculate intensities at half-masses. Rehkämper and Mezger¹ used ^{202}Hg to correct for Hg isobaric interference on ^{204}Pb ; in order to model their data it was assumed that there was no real ^{202}Hg signal at mass 202, but a tail from ^{203}Tl resulted in a small positive ion intensity at mass 202. The calculated peak intensities were then corrected for baseline using the calculated half-mass ion beam intensities, in order to mimic the correction method used.¹ Hg correction was then applied to ^{204}Pb ; this involved an increase in ^{204}Pb because the ^{202}Hg is overcorrected for the tail from ^{203}Tl . Finally, the Pb isotope ratios were corrected for exponential mass bias using the reference Tl isotope ratio used initially to calculate the peak intensities.

Results of this modeling are presented in Fig. 4, using the same axis parameters as defined by Rehkämper and Mezger.¹ The same general patterns are observed in Fig. 4 as were reported in Fig. 2 of Rehkämper and Mezger:¹ namely an increase in $^{208}\text{Pb}/^{206}\text{Pb}_{\text{RM}}$ and $^{207}\text{Pb}/^{204}\text{Pb}_{\text{RM}}$ with increasing Pb/Tl and an increase in $^{207}\text{Pb}/^{204}\text{Pb}_{\text{RM}}$ at low Pb/Tl. Further, the magnitudes of the increases predicted were very similar to those observed.¹ This is strong evidence for the correlations between Tl-normalized Pb ratios and Pb/Tl, interpreted as a matrix effect by Rehkämper and Mezger,¹ being in fact a result of the massive overcorrection for tails inherent in using half-mass zeroes. This is supported by the lack of correlation observed¹ on the Nu Plasma, where half-mass zeroes were not used, and the lack of correlation in Royal Holloway IsoProbe data once a tail correction based on ^{209}Bi tail profiles had been made.⁴

The increases in $^{207}\text{Pb}/^{204}\text{Pb}_{\text{RM}}$ at low Pb/Tl observed by Rehkämper and Mezger¹ were interpreted by them to be a result of tailing from ^{205}Tl onto the baseline at 204.5 u. This is fully consistent with the modelling presented in Fig. 4, but, if this interpretation is correct, implies that the Münster IsoProbe

had a similar magnitude of tail at 204.5 u as does the Royal Holloway IsoProbe. This is inconsistent with the 10 ppm abundance sensitivity at 237 from ^{238}U reported for the Münster IsoProbe.¹

Assuming that the effect on $^{207}\text{Pb}/^{204}\text{Pb}_{\text{RM}}$ at low Pb/Tl is due to tail, as proposed here and by Rehkämper and Mezger,¹ then the tail **must** also generate changes in $^{208}\text{Pb}/^{206}\text{Pb}_{\text{RM}}$ of broadly similar magnitude to that reported.¹ Although the modelling predicts substantially different $\Delta^{208}\text{Pb}/^{206}\text{Pb}$ values for SRM 981 and 982 at high Pb/Tl (Fig. 4), contrary to the observations of Rehkämper and Mezger,¹ their reported data are nevertheless bracketed by the model results reported here. The similar behaviour they report might be a fortuitous effect of temporal changes in the tail of the Münster IsoProbe.

These conclusions also require that there is nothing magical about the Pb/Tl ratio of about 12, which Rehkämper and Mezger¹ recommend when using Tl to normalize Pb on the IsoProbe. Clearly, much higher values of Pb/Tl would result in a low Tl ion beam, poor precision on measured $^{205}\text{Tl}/^{203}\text{Tl}$ and unacceptable error magnification on the Tl-normalized Pb isotope ratios. At low Pb/Tl ratios, uncertainty in the proportion of ^{205}Tl contributing to mass 204 is not a significant issue relative to the counting statistics on the ^{204}Pb ion beam. For example, a common Pb sample analysed with 8 V ^{208}Pb and 8 V ^{205}Tl ion beams yields about 60 ppm (2σ) internal precision on $^{204}\text{Pb}/^{206}\text{Pb}$ after fifty 5 s ratios. The uncertainty on the 25 ppm contribution of ^{205}Tl at mass 204 is about 1 ppm (2σ), which propagates to about 20 ppm uncertainty on $^{204}\text{Pb}/^{206}\text{Pb}$.

Pb data reported¹ with a Pb/Tl ratio of about 12 should not be regarded as accurate data because they are still subject to overcorrection of tail through the use of half-mass zeroes. Using the same modelling described earlier, Tl-normalized Pb isotope ratios at Pb/Tl = 12 are reported in Table 3. They differ from the reference values used to calculate them by up to 1100 ppm. These differences may however be reduced by optimising the $^{205}\text{Tl}/^{203}\text{Tl}$ normalizing ratio to obtain the best agreement between the calculated data and the reference values for SRM 981, as was done by Rehkämper and Mezger.¹ A 450 ppm decrease in $^{205}\text{Tl}/^{203}\text{Tl}$ from the value used to calculate the ion beam intensities results in all deviations for SRM 981 being below 200 ppm, but, in order to minimize the deviations for both SRM 981 and SRM 982 (at <350 ppm), a 770 ppm decrease is needed in $^{205}\text{Tl}/^{203}\text{Tl}$. Deviations of up to 350 ppm from reference values were observed¹ when $^{205}\text{Tl}/^{203}\text{Tl}$, optimized using SRM 982, was used to correct

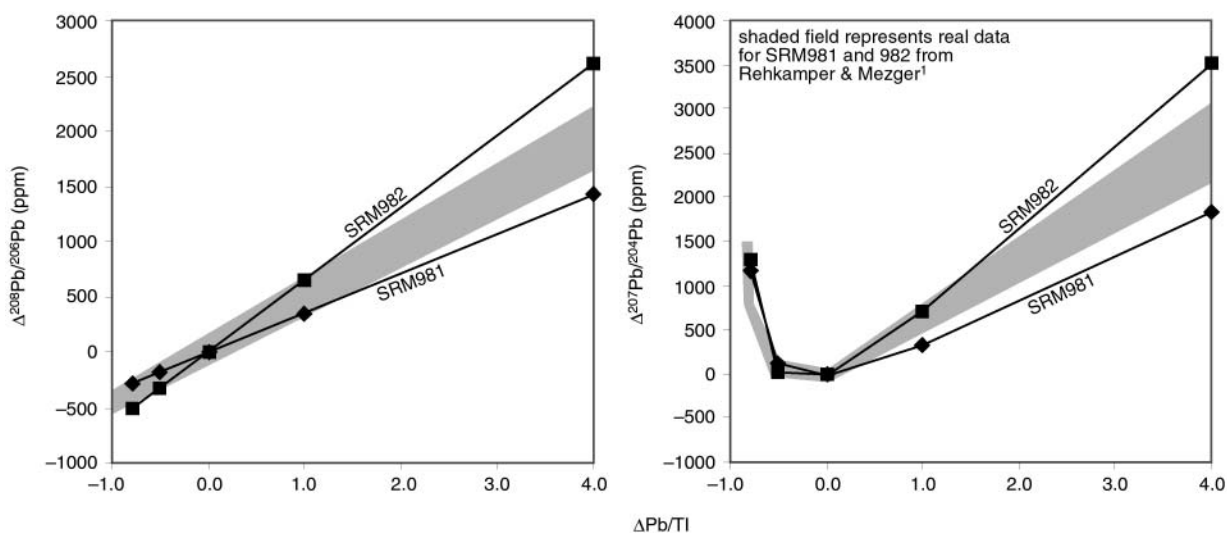


Fig. 4 Deviation in ppm of Tl-normalized Pb isotope ratios from that calculated at Pb/Tl = 12. $\Delta\text{Pb}/\text{Tl} = (\text{Pb}/\text{Tl}_{\text{sample}} - 12)/12$, as defined in ref. 1. Solid lines are expected relationships for SRM 981 and SRM 982 calculated using the ^{209}Bi tail profile in Table 2. Shaded fields are observed data for both standards (ref. 1).

Table 3 Pb isotope ratios for SRM 981 and 982 calculated at Pb/Tl = 12 using half-mass zero baseline correction. Reference values are assumed to be true ratios in order to calculate peak ion beam intensities and their tails onto adjacent peaks and half-masses for Pb/Tl = 12. Calculated values are derived from these after half-mass baseline correction to mimic the data of ref. 1. Normalization is to the same reference $^{205}\text{Tl}/^{203}\text{Tl}$ (2.38983) as used initially to calculate ion intensities at masses 203 and 205

	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
SRM 981 reference	0.059028	0.91464	2.16764
SRM 981 calculated	0.058990	0.91467	2.16861
Difference (ppm)	-646	24	448
SRM 982 reference	0.027210	0.46700	1.00016
SRM 982 calculated	0.027180	0.46707	1.00086
Difference (ppm)	-1109	143	696

SRM 981. The Pb results reported by Rehkämper and Mezger¹ can be corrected for half-mass zeroes and tail, making the assumption that the abundance sensitivity was similar to that of the Royal Holloway IsoProbe. The data produced do not yield improved reproducibility over the reported results, perhaps because of temporal variations in abundance sensitivity, but many other factors can be involved.⁴

Applications of tail profiles to instruments with < 10 ppm abundance sensitivity

It is clear that, on the Micromass IsoProbe at Royal Holloway with 20–30 ppm abundance sensitivity at ^{237}U , it is highly unsatisfactory to use half-mass zeroes to correct for tail virtually throughout the mass spectrum, and it is essential to correct for tail using tail profiles and eqn. (2). To what extent these problems exist on other MC-ICP-MS or TIMS instruments with better abundance sensitivity is unknown.

If the tail at -0.5 u is more than about four times the tail at -1.0 u , the magnitude of over-correction for tail resulting from use of half-mass zeroes will be greater than the error caused by not correcting for tail at all. The ratio of (tail at -0.5 u):(tail at -1.0 u) increases markedly with mass, from 4.4 for Y to 14 at U on the IsoProbe (Table 2), implying that half-mass zeroes become much worse at higher masses. The Royal Holloway TIMS tail data reported in Table 2 would yield half-mass baseline corrections on ^{87}Sr and ^{237}U of almost exactly double the true tail at -1.0 u , so, on this machine, there is no improvement in accuracy in using the half-mass zero correction compared with no tail correction at all. Because tails at -0.5 u are not reported in the literature, it is nearly impossible to judge whether half-mass zero corrections have caused problems on other instruments. However, White *et al.*² used only the higher half-mass zero to correct their Pb data, and these are thus almost certainly overcorrected. The Nu Plasma Pb data of Rehkämper and Mezger¹ use zeroes measured with the Pb ion beam deflected from the collector, and have therefore no correction for tail; at the 2 ppm quoted for the Nu Plasma this would have a significant effect on ^{204}Pb in the presence of about 8 V of ^{205}Tl and imperceptible effects on ^{205}Tl at high Pb/Tl ratios (*ca.* 60).

Conclusions

(1) The common practice of taking baseline measurements at $\pm 0.5\text{ u}$ of peaks during isotope ratio measurements results in overcorrection of the isotopic abundances for peak tailing.

(2) The magnitude of overcorrection is dependent on the abundance sensitivity of the mass spectrometer used and is less, but may still be significant, for lower atomic number elements.

(3) In most cases it is preferable to use no correction for tail (*e.g.*, baseline measurements with no ions in the analyser) than to use half-mass zeroes. The only exception to this is the case of small peaks at relatively large mass separations ($> 1.5\%$) from a single large peak.

(4) On instruments with relatively poor abundance sensitivity, such as the Royal Holloway IsoProbe, accurate isotope ratio determination requires use of the tail profiles most easily measured on mono-isotopic elements in the same mass range as the element of interest. Tail may be significant up to at least 4 amu away from a major peak on Faraday collectors, and even further away using electron multipliers without energy filters. These tail profiles are stable with time provided the analyser vacuum and ion energy spread are stable.

(5) Use of half-mass zeroes on poor abundance sensitivity instruments can give rise to a number of puzzling analytical artefacts:

(i) systematic under-estimation of low-abundance isotopes near large ones, *e.g.*, ^{143}Nd , ^{176}Hf . This inaccuracy can be corrected using isotopic standards.

(ii) unusually low or negative values for interference monitors, *e.g.*, ^{147}Sm in the presence of ^{146}Nd and ^{202}Hg in the presence of ^{203}Tl , resulting in incorrect interference corrections.

(iii) when using doping by another element to correct for mass bias, *e.g.*, Tl for Pb, variations in normalized Pb isotope ratios with Pb/Tl will result. The observations of Rehkämper and Mezger¹ for Pb/Tl can be almost completely accounted for if their IsoProbe has similar abundance sensitivity to the Royal Holloway IsoProbe.

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