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Evaluation of deadtime correction for accuracy of isotope ratios determined by quadrupole ICP-MS

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Single and tandem quadrupole ICP-MS instruments are routinely used to determine isotope ratios, such as $^{206}Pb/^{238}U$, $^{207}Pb/^{204}Pb$, and $^{234}U/^{238}U$, while tandem Q-ICP-MS have applications in in-situ $^{176}Lu/^{176}Hf$ and $^{87}Rb/^{87}Sr$ dating. However, there is limited consensus on an approach to mass bias correction, with most using standard-bracketing to correct for both elemental fractionation and mass bias. In tandem Q-ICP-MS $^{87}Sr/^{86}Sr$ analysis, several studies have proposed that the conventional IUPAC approach of using a known $^{88}Sr/^{86}Sr$ ratio for mass bias correction does not yield accurate $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ ratios, instead requiring an additional 'correction factor'. Incorrect detector deadtime has sometimes been implied [1] as one source of inaccurate IUPAC approach mass bias correction of isotope ratios.

Here we present results of a wider investigation into deadtime effects on isotope ratios analysed by tandem Q-ICP-MS. All data were acquired on elemental solution ranging in z from Li to U, with a nominal deadtime of 0 ns on an Agilent 8900 both in no gas and mass shift mode. We confirm the previously proposed increase of deadtime with z (a few ns across the full mass range). However, in detail, this relationship cannot be used for accurate isotope ratio analyses, which require session specific deadtime determinations.

This will be illustrated with Sr-isotope ratio analyses in no gas mode and mass shift mode. We find one consistent deadtime for all analyses modes, but this varies by 1-2 ns over the course of weeks. Accurate $^{87}Sr/^{86}Sr$ ratios were obtained in all modes with the IUPAC mass bias correction from the known $^{88}Sr/^{86}Sr$ ratio with no need for a further 'correction factor'. Accurate $^{84}Sr/^{86}Sr$ ratios were obtained in mass shift mode thanks to the removal of isobaric Kr interferences. Dead time linearity was demonstrated up to 4-6 10^6 cps in pulse count mode, overcoming issues of mixed pulse-count/analogue signals. Collectively, we anticipate that this method will yield more accurate isotope ratio data from Q-ICP-MS and will reduce apparent reverse discordance in U-Pb zircon and erroneous ages in the Rb-Sr dating.

[1] Graczyk et al 2019. Spectrochimica Acta Part B: Atomic Spectroscopy, 153: 10-18.