Mass spectrometry

Why does the pre-cell mass filter of the Neoma MS/MS MC-ICP-MS revolutionize collision/reaction cell technology?

Collision/reaction cell (CRC) technology enables the separation of elements from their isobaric interferences by means of chemical reactions where the interfering species are either neutralized or reacted to a different product molecule to create a mass separation. This technology has been demonstrated to be successful for simple systems, i.e. where there are a limited number of different elemental and molecular species involved in the chemical reactions inside the CRC. However, for laser ablation analyses, where a whole host of different matrix elements are introduced to the mass spectrometer, the chemistry within the CRC becomes very complex and chemical reactions can even produce new interfering species which can yield to chaotic and unpredictable reactions inside the CRC. To better control the reactions inside the CRC, a pre-cell mass filter is used to preselect a certain mass range of ions to enter the cell. This significantly reduces the complexity of the chemical reactions going on in the CRC and gives much better control on the accuracy of interference removal.

The double Wien filter of the Thermo Scientific™ Neoma™ MS/MS MC-ICP-MS filters out matrix elements based on their mass, limiting the number of elements and molecules entering the CRC. This means that reaction chemistry in the CRC is predictable and the isobaric interferences can be successfully removed. In this SmartNote, we provide details of this revolutionary technology and demonstrate the advantages for a range of different applications.

What is collision/reaction cell technology?

Even at the highest possible mass resolution achievable with MC-ICP-MS, there are some isobaric interferences that cannot be resolved, such as ^{87}Rb and ^{87}Sr. In this case, collision/reaction cell (CRC) technology enables isobaric interferences

such as these to be separated. As the name suggests, ions are introduced into a cell containing a reaction gas. Reaction between the gas and the element of interest (or in some cases the interference) results in a mass separation between the element of interest and its isobaric interference, allowing the isotope ratio to be determined interference-free.

Whilst CRC technology is widely used for determination of trace elemental concentrations, its success is due to the coupling of a pre-cell mass filter with the CRC (see below). By comparison, the only commercially available multicollector CRC-ICP-MS for isotope ratios used a CRC without any pre-cell mass filter. In these cases, MC-CRC-ICP-MS has been demonstrated to measure Ca and K isotopes, free from the Ar and ArH interference[1,2] with some success. The Thermo Scientific™ Proteus™ MS/MS MC-ICP-MS was the first instrumental implementation of coupled pre-cell mass filter technology with CRC on a MC-ICP-MS[3,4], this pioneering innovation has opened the doors to a much wider range of isotope applications[5–7].

What is the reason for having a pre-cell mass filter?

Whilst CRC is a powerful technique, it is reliant on producing predictable reactions in the CRC. For analysis in which samples have been chemically separated, CRC technology coupled with MC-ICP-MS can provide accurate isotope ratios. However, in more complex systems, for example those with significant molecular interferences (e.g. Si in HNO_3), or for laser ablation applications, the large number of matrix elements entering the collision cell can produce unpredictable reaction chemistry, and in some cases can greatly enhance the interferent peak rather than suppressing it (Figure 1, red line)[8].

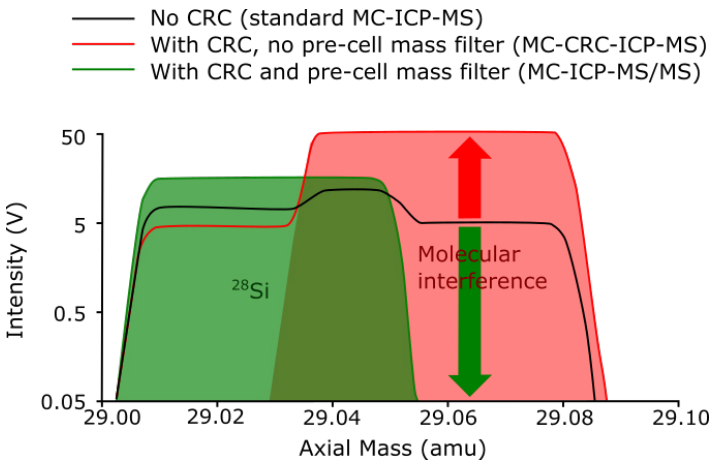

Figure 1. Effect of pre-cell mass filtering on Si in HNO_3. Standard MC-ICP-MS, no CRC shown in black. No pre-cell mass filter, all masses enter CRC (red), resulting in significant increase the molecule interferences and strong peak tailing onto ^{28}Si. With the pre-cell mass filter technology of Neoma MS/MS MC-ICP-MS, only masses around *m/z* 29 enter the CRC, allowing predictable reaction chemistry, completely suppressing the molecular interferences on ^{28}Si (green).

Users familiar with triple quad ICP-MS technology will know that filtering a narrow mass range before the CRC enables better control over the reaction chemistry within the CRC. Neoma MS/MS MC-ICP-MS works on exactly the same principle of filter, react and separate (Figure 2). The pre-cell mass filter of Neoma MS/MS MC-ICP-MS allows effective removal of the sample matrix and the major Argon ion beam, preventing the creation of molecular interferences inside the collision/reaction cell and cleaning up the mass spectra, enabling the analyte to be detected interference-free.

How does pre-cell mass filtering improve CRC chemistry?

The addition of a mass filter in front of the CRC allows the reaction chemistry in the CRC to be controlled. By only allowing ions of a defined mass to enter the CRC, the number of secondary reactions and reactions with molecular interferences is suppressed. For example, in the case of Si in HNO_3, restricting the transmission into the CRC to masses around *m/z* 29 results in successful suppression of the molecular interferent peak on ^{28}Si (Figure 1, green line).

Additionally, pre-cell mass filtering also provides a way to "clean" the mass range of interest so that once reactions have taken place, the user can be confident that the only ions being counted are those of the reaction products (Figure 3).

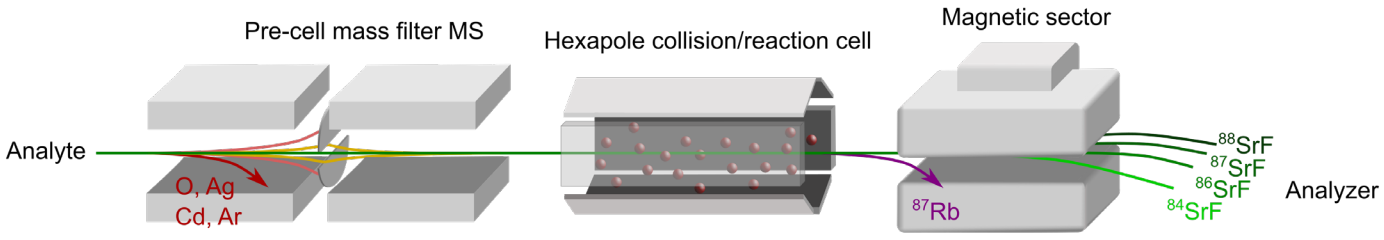

Figure 2. Schematic of the Neoma MS/MS MC-ICP-MS showing the three main components: the pre-cell mass filter for filtering matrix elements (FILTER), the hexapole collision/reaction cell for removing isobaric interferences (REACT) and the magnetic sector for isotopic separation (SEPARATE).

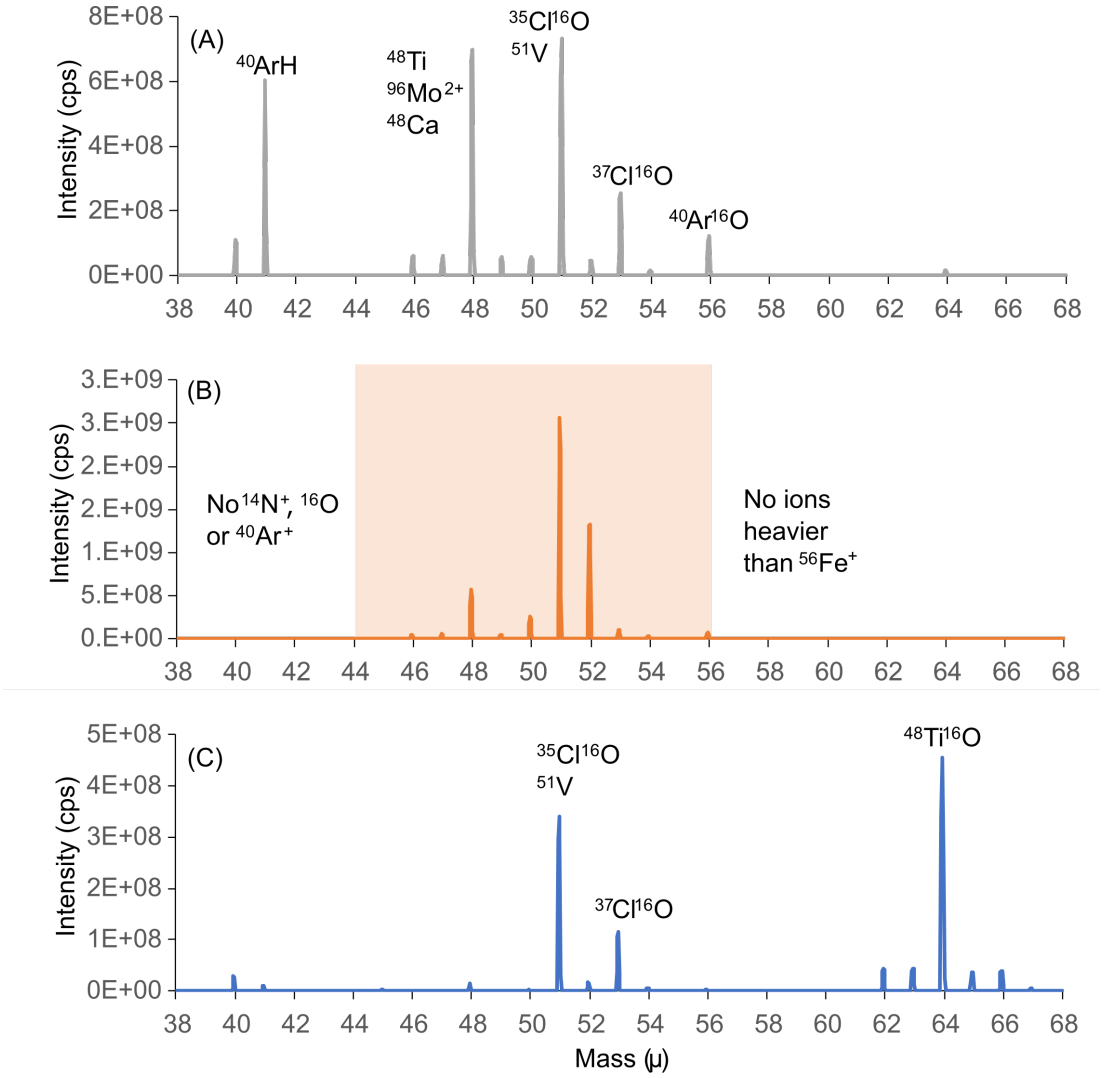

Figure 3. Pre-cell mass filter provides a clean spectra for reaction products. (A) Without pre-cell mass filtering, a number of interferences are observed on the mass range for Ti (*m/z* = 46-50). (B) Pre-cell mass filtering removes all interferences outside the mass range of Ti. (C) The addition of O_2 reaction gas enables separation of Ti from isobaric interferences such as $^{96}Mo^{++}$.

How does the pre-cell mass filter of Neoma MS/MS MC-ICP-MS work?

The Neoma MS/MS MC-ICP-MS has a pre-cell mass filter in the form of a double Wien filter with an inversion lens placed symmetrically between them (Figure 4). The first Wien filter acts to disperse ions based on their *m/z* ratio. Transmission of the mass window of interest is enabled using a selectable slit. The second Wien filter is then used to bring all the transmitted ions back into a single ion beam before entry into the CRC.

By varying the strength of the magnetic field (B field) and the spacing of the selectable slit, the width of the transmitted mass window can be varied. Increasing the B field increases the mass dispersion, thereby reducing the mass range of ions that are transmitted through the selectable slit (Figure 5b).

The advantage of the double Wien filter of the Neoma MS/MS MC-ICP-MS is that there is no compromise in sensitivity and the mass bias characteristic of the combined instrument follows the exponential fractionation law. This is because the double Wien filter is based on sector field technology and static magnetic and electric fields for mass filtering. The high beam energy of the double Wien filter allows for high ion transmission and reduced space charge broadening effects, providing sensitivities as good as (and in cases better) than the previous Thermo Scientific™ Neptune™ MC-ICP-MS. Furthermore, because the two filters are identical and operated with matching electrostatic and magnetic fields, the mass bias behavior is predictable (following exponential mass bias). The accuracy and reproducibility of calculated isotope ratios have been demonstrated for a number of isotopic systems including Fe, Sr, Nd, Hf, Pb and U[8].

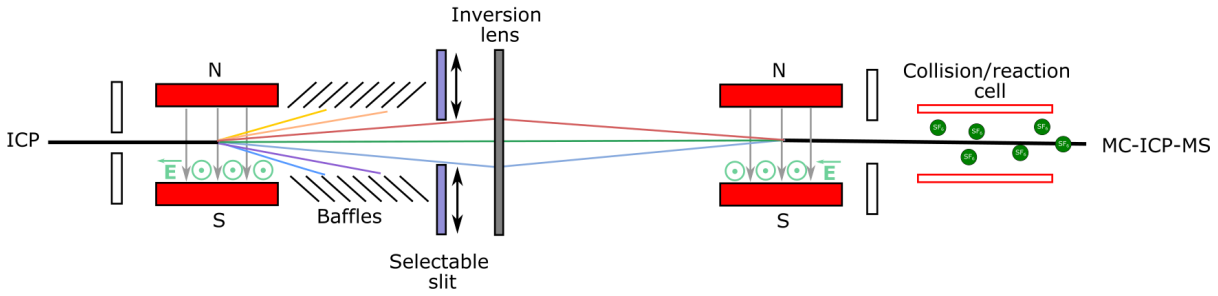

Figure 4. Schematic overview of the ion path within the double Wien filter of the Neoma MS/MS MC-ICP-MS. The ion beam from the ICP passes through the first tunable Wien filter, with a selected *m/z* continuing to travel on the axial plane of the mass spectrometer. All other *m/z* are dispersed along a transverse plane by the filter. An adjustable slit is then used to crop an *m/z* "window" on the transverse plane, which proceeds into the second Wien filter. The second Wien filter applies an equal and opposite dispersion to the first Wien filter to recombine all *m/z* on the axial plane prior to entering the CRC.

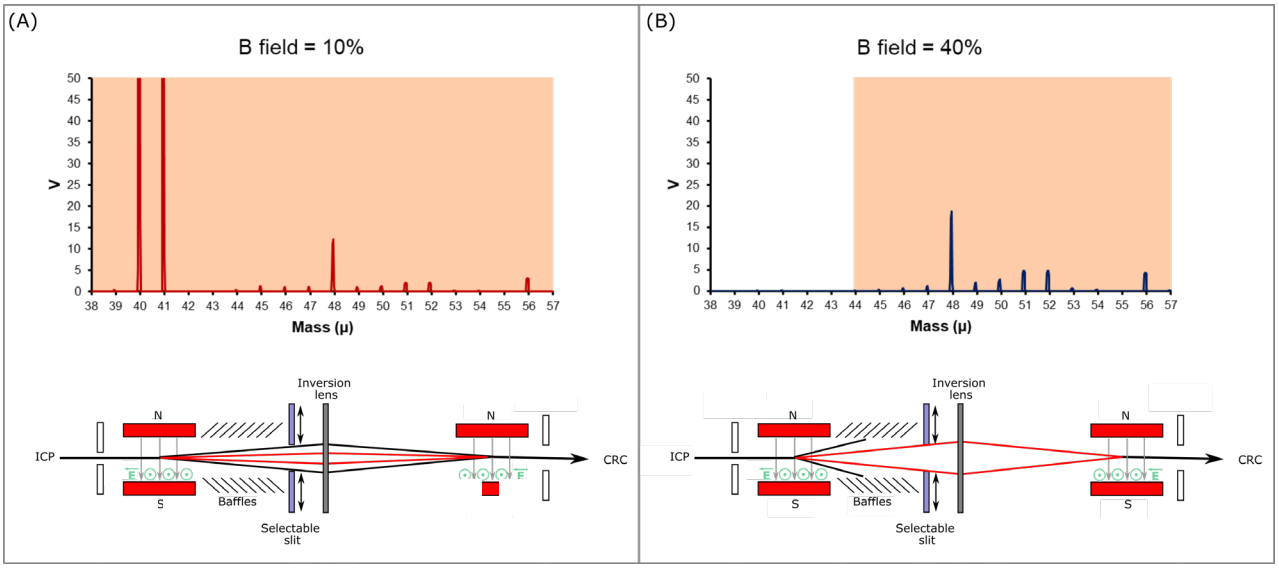

Figure 5. How varying the strength of the B field in the double Wien filter affects the mass range of transmitted ions. (A) With a weak B field, the mass dispersion of ions is reduced, enabling a greater mass range of ions to be transmitted through the selectable slit. (B) Increasing the B field, increases the mass dispersion of ions, meaning that a smaller range of ions are transmitted through the selectable slit. This is how argon and other major ion beams can be selectively removed with the double Wien filter before entering the CRC.

What are the advantages of Neoma MS/MS MC-ICP-MS over traditional CRC-MC-ICP-MS systems?

The major advantage of Neoma MS/MS MC-ICP-MS over traditional CRC-MC-ICP-MS systems is that the reaction chemistry in the CRC can be better controlled and the mass shift reaction is predictable, resulting in the successful removal of isobaric interferences and therefore improved precision of isotope ratios measured on a clean background, in particular if mass shift reactions can be applied. This opens a whole world of new possibilities for using CRC for LA-MC-ICP-MS applications.

One example of these pioneering applications is in-situ Ti isotope measurements. Isobaric interferences from Ca and Cr make in-situ measurements of Ti isotope ratios challenging. Reaction of Ti^+ with O_2 can successfully shift Ti isotope ratio measurements away from interferents in the none mass shifted mass range. The pre-cell mass filter is crucial in this application to clean the mass range (*m/z* 62-66, Figure 3) of mass-shifted TiO and, additionally, cuts ^{40}Ca, ^{40}Ar and $^{40}Ar^{16}O$ ion beams, which would otherwise induce unwanted secondary reactions and space charge broadening.

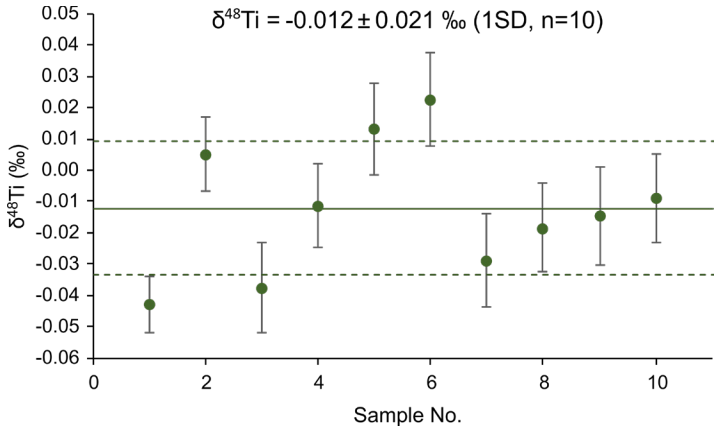

Figure 6. Example of Ti isotope analysis on 1000 ppb Ti solution spiked with Ca, V, Cr and Fe. Oxygen was used in the collision/reaction cell to separate Ti from isobaric interferences. The sample has been measured via standard-sample bracketing (SSB) against itself. Data is mass bias corrected with $^{49}Ti^{16}O/^{47}Ti^{16}O$.

Similarly, for in-situ Rb-Sr dating, ^{87}Sr and ^{87}Rb cannot be resolved. Therefore, the method to separate these isobaric interferences is to introduce a mass separation through reacting Sr with SF_6 gas in the collision/reaction cell. However, it is necessary to filter the mass range around Sr and Rb (79-90 amu) to remove matrix elements that might otherwise isobarically interfere with the reactant SrF (e.g. ^{103}Rh and ^{107}Ag; Figure 7a). By cleaning up the mass spectra, the pre-cell mass filter allows us to be confident that only the reactant (SrF) is being analyzed (Figure 7b).

The Neoma MS/MS MC-ICP-MS isn't only advantageous for *in-situ* analysis, it also revolutionizes traditional isotope measurements. By eliminating isobaric interferences, the Neoma MS/MS MC-ICP-MS enables certain isotope systems, that would be measured in high resolution with tradition MC-ICP-MS, to be measured in low resolution. This is exemplified with potassium isotopes. Measuring at low resolution dramatically increases the transmission of ions and therefore smaller sample sizes can be analyzed by MC-ICP-ICP MS/MS technology. With traditional high resolution, an external reproducibility for K isotope ratios of 0.035 permil 1SD has been reported[9], for samples sizes between 250ppb and 1ppm. By contrast, using He and H in the collision cell to neutralize ArH allows K isotopes to be measured in low resolution, thereby significantly increasing ion transmission and improving counting statistics. It is possible to produce an external reproducibility of 0.03 ‰ for 25 ppb K samples (Figure 8).

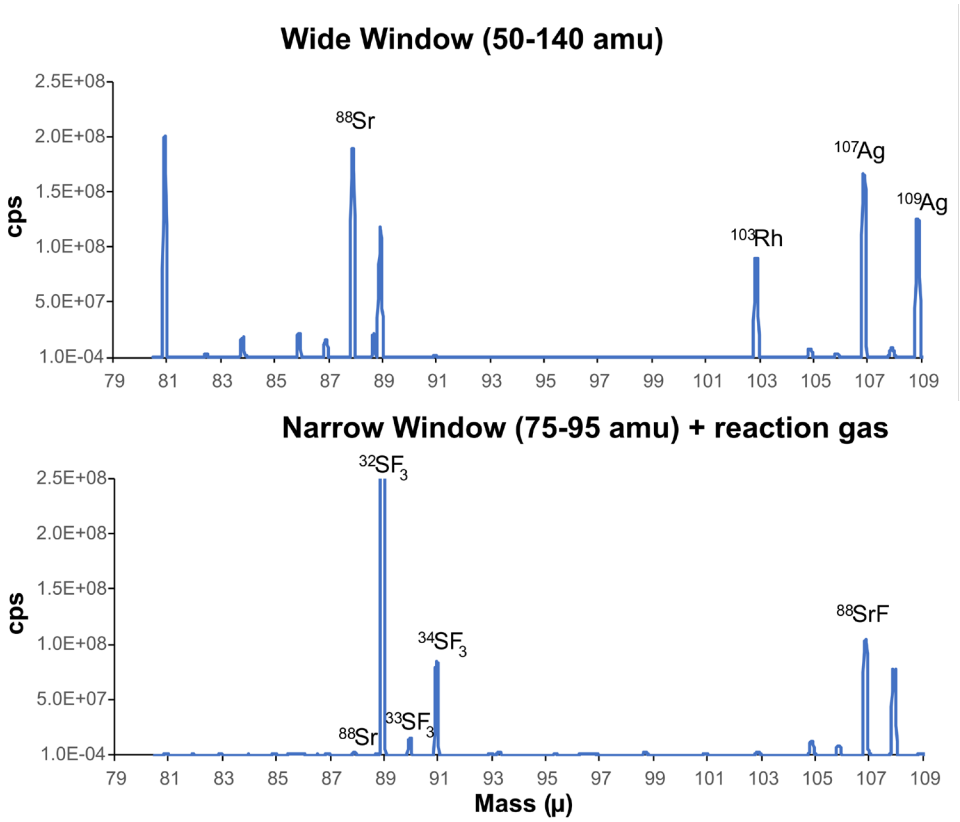

Figure 7. Pre-cell mass filter provides a clean spectra for reaction products for in-situ Rb-Sr dating. (A) Without pre-cell mass filtering, a number of interferences are observed in the mass range for SrF (*m/z* = 103-107). (B) By applying a narrow filter window, matrix elements are removed such that SrF is the only observable mass in the mass range 103-107.

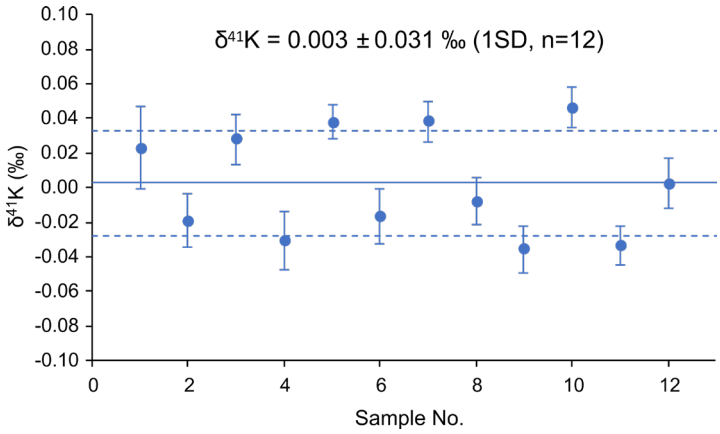

Figure 8. K isotope analysis of 25 ppb SRM 3141a using Neoma MS/MS MC-ICP-MS. Hydrogen and helium were used in the collision/reaction cell to neutralize ArH. The sample has been measured via standard-sample bracketing (SSB) against itself.

The pre-cell mass filter of Neoma MS/MS MC-ICP-MS does not come at the sacrifice of instrument sensitivity. In fact, mass filtering reduces the space-charge effects within the ion beam, resulting the Neoma MS/MS MC-ICP-MS having slightly higher sensitivity than the Neptune MC-ICP-MS for some elements. This can be seen in the Si isotope example (Figure 1). By transmitting only masses around *m/z* 29 (eliminating argon from the ion beam) using the pre-cell mass filter, the sensitivity of Si doubled.

Another striking feature of the Neoma MS/MS MC-ICP-MS is the abundance sensitivity. The removal of abundant ion beams by the pre-cell mass filter means that space-charge effects as well as unwanted scattering effects of the major ion beam species are significantly reduced along the ion path in the multicollector mass analyzer. This results in a dramatic improvement in abundance sensitivity. For IC with RPQ routinely <20ppb at 1 amu U spacing is achieved. This is as good as what can be achieved via Thermal Ionization Mass Spectrometry (TIMS). The excellent abundance sensitivity of Neoma MS/MS MC-ICP-MS benefits applications with significant differences between the major and minor isotope beam, e.g. U-Th dating applications.

Conclusion

- Pre-cell mass filters are essential to reduce the complexity of reactions in the CRC
- Failure to pre-filter a narrow band-pass of ions transmitted into the CRC can in some cases amplify the interferent signal
- Pre-cell mass filters are crucial for cleaning the mass range of mass-shifted reaction products
- The double Wien filter of the Neoma MS/MS MC-ICP-MS allows a selectable range of masses to enter the CRC, opening up new avenues in LA-MC-ICP-MS applications.
- Combining pre-cell mass filtering with CRC technology revolutionizes analysis of some traditional isotope systems, enabling isotopes to be analyzed a low resolution, leading to dramatic improvements in precision.
- The Neoma MS/MS MC-ICP-MS has higher sensitivity and improved abundance sensitivity compared to other commercially available MC-ICP-MS instruments.

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