nu plasma II

MULTI COLLECTOR
ICP-MS

APPLICATION NOTE **AN22**

CAPABILITY IN RESOLVING ANALYTE PEAKS FROM INTERFERENCES FOR PRECISE AND ACCURATE ISOTOPIC MEASUREMENTS

INTRODUCTION

Multi-collector ICP-MS (MC-ICP-MS) instruments are capable of determining isotope ratios with high levels of precision and accuracy and have been widely used in Earth Sciences and the Nuclear industry since the early nineties. One potential problem with the MC-ICP-MS however, is that the plasma source can generate molecular species that cause interferences on the mass spectrum of some elements. Depending on the levels of these interferences, they can become problematic in the accurate determination of the isotopic ratios of these elements. Early methods had been developed to lower these interferences to an insignificant level, such as careful design of the plasma interface region or by utilising desolvation sample introduction systems. An alternative solution, available on the Nu Plasma II is utilising its high resolution features.

In mass spectrometry, resolution is a measure of the ability to distinguish between two peaks of different mass-to-charge ratio (m/z) in a mass spectrum. High Resolution Multi-Collector ICP-MS instruments require flat topped peaks for high precision measurements where the resolution is limited to ~3000 (10% Valley). It is possible to achieve higher resolutions with flat topped peaks however only when a much larger geometry instrument such as the Nu Plasma1700 is used. In this Technical Note, examples of the different resolution techniques (*Pseudo High* and *High* Resolution) will be demonstrated for Fe and Si using the Nu Plasma II MC-ICP-MS, illustrating the ability of the instrument to distinguish between two peaks of different m/z in a mass spectrum.

Nu Plasma II

Instrumentation

The Nu Plasma II is a double focussing magnetic sector instrument that is fitted with 16 Faraday detectors and up to 6 ion-counting detectors to allow multiple isotope systems to be studied. The instrument is an evolution of the Nu Plasma HR, and represents the latest generation of MC-ICP-MS.

Nu Plasma II has an approximate standard low resolution of 300 (10% valley definition, detailed in a later paragraph). At this resolution, the instrument produces the flat-top peaks that are essential for precise isotopic measurements while maintaining optimal sensitivity.

The *Pseudo High* resolution capabilities of Nu Plasma II are achieved by simultaneous application of two sets of adjustable slits as shown in Fig 1: A source defining slit (Fig. 1a), which has 3 selectable width settings of 0.3 mm, 50 μm and 30 μm and an alpha slit (Fig. 1b) which is adjustable from 7 mm down to 0 mm through the Nu Plasma II software.

A unique feature of the Nu Plasma II is the ability to provide *High* resolution of peaks by the adjustment of collector masks (Fig. 1c) that are positioned in front of a few specifically chosen collectors and are adjustable to reduce the collector slit width.

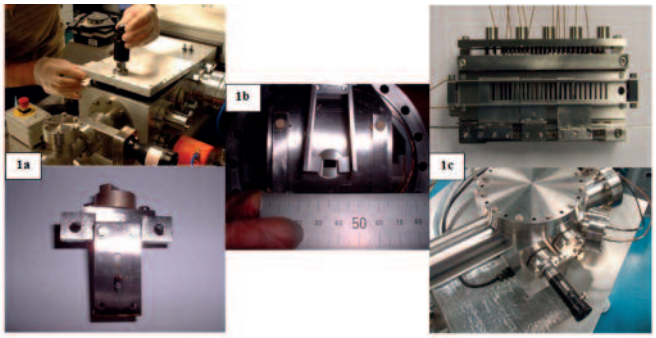


Fig. 1: Photos of the source slit (1a), alpha slit (1b) and collector slits (1c).

Discussion

There are many different ways of defining resolution: three of them being the peak width definition, the 10% valley definition and the peak edge definition.

1) The peak width definition: For a single peak made up of singly charged ions at mass M in a mass spectrum, the resolution may be expressed as $M/\Delta M$, where ΔM is the width of the peak at a height that is a specified fraction of the maximum peak height. It is recommended that one of the three values 50%, 5%, or 0.5% is used.

2) The 10% valley definition: Let two peaks of equal height in a mass spectrum at masses M and M-ΔM be separated by a valley that at its lowest point is just 10% of the height of either peak. For similar peaks at a mass exceeding M, let the height of the valley at its lowest point be more (by any amount) than 10% of either peak height, the resolution (10% valley definition) is M/ΔM. For an isolated symmetrical peak, recorded with a system that is linear in the range between 5% and 10% levels of the peak, the 10% valley definition is technically equivalent to the 5% peak width definition. It is important to report the method used to determine resolution when reporting its value. The Nu Plasma II offers two types of high resolution capability: *Pseudo High* resolution and *High* resolution.

3) The peak edge definition: The peak edge resolving power is often measured at peak heights of 5% and 95% ($RP_{edge\ 5,95\%}$) and is a measure of the definition of the beam at the source slit, independent of the collector slit. It is possible to have an edge resolving power significantly in excess of the peak width or 10% valley resolution.

Pseudo High Resolution

The *Pseudo High* resolution method partially resolves peaks, leaving a flat-topped section of resolved peak on each isotope for isotopic ratio measurements. This technique works as long as the interferences are all on the same side of the peak and the collector coincidence can then be set so that the interferences do not enter the collector at the measured masses.

The *Pseudo High* resolution method is achieved by reducing the width of the source defining slit, using a selectable slit mechanism and then reducing the width of the alpha slit located before the ESA to enhance the peak shape by reducing any image aberration. Utilising the 50 μm source defining slit allows resolving powers of up to 8000 ($RP_{edge\ 5,95\%}$) to be obtained, with a sensitivity reduction of a factor of 10. Utilising the 30 μm source slit allows resolving powers of up to 10000+ ($RP_{edge\ 5,95\%}$), with a sensitivity reduction of a factor of 15-20.

While using the *Pseudo High* resolution technique, the tails from the interfering peaks are the most significant influence on data quality. Care in method development should be taken to ensure that the peak shapes are sufficiently tuned to minimise any residual interference from the tails if the interfering isotope signal level is significant relative to the target isotope.

In MC-ICP-MS the lighter elements are often plagued by molecular isobaric interferences. Iron has several argon based interferences, e.g., $^{38}Ar^{16}O^+$ and $^{40}Ar^{14}N^+$ on ^{54}Fe, $^{40}Ar^{16}O^+$ on ^{56}Fe, $^{40}Ar^{16}O^1H^+$ on ^{57}Fe and $^{40}Ar^{18}O^+$ on ^{58}Fe. The resolutions required to resolve ^{54}Fe, ^{56}Fe, ^{57}Fe, and ^{58}Fe from their respective interferences are calculated by *Resolution = Mass/ΔMass* and are shown in Table 1.

In *Pseudo High* resolution mode, slightly more analyte peak flat can be obtained compared to the *High* resolution mode (see later in this note). All interferences are on the high mass side of the peak as is seen in Fig. 2a, therefore the *Pseudo High* resolution mode is normally chosen for Fe analysis. Once the peak shapes similar to that shown in Fig. 2 are obtained, the magnet position is set to the plateau position indicated in Fig. 2b ready for analysis. The Nu Plasma II utilises a special peak location utility program to select this mass position for automated sample analysis when using the *Pseudo High* resolution method.

Table 1: ^{54}Fe, ^{56}Fe, ^{57}Fe, ^{58}Fe, and the highest resolutions required for their respective interferences.

Analyte	Interference requiring the highest resolution	Resolution (10% valley) required
^{54}Fe	$^{38}Ar^{16}O^+$	2991
^{56}Fe	$^{40}Ar^{16}O^+$	2502
^{57}Fe	$^{38}Ar^{19}F^+$	2212
^{58}Fe	$^{40}Ar^{18}O^+$	2050

Fig. 2a: Iron isotopes resolved from their respective interferences in the *Pseudo High* resolution mode using the 50 μm source defining slit.

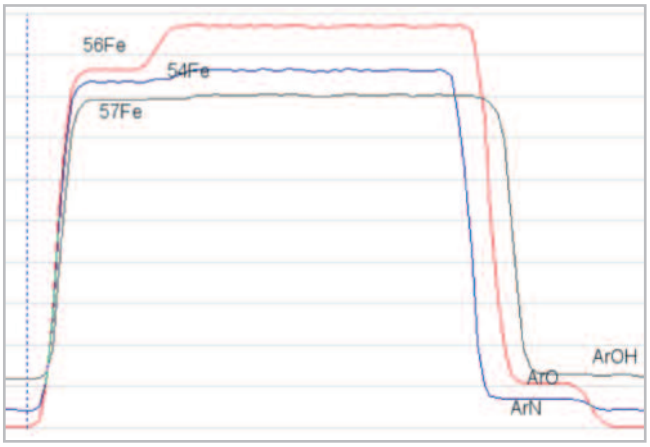
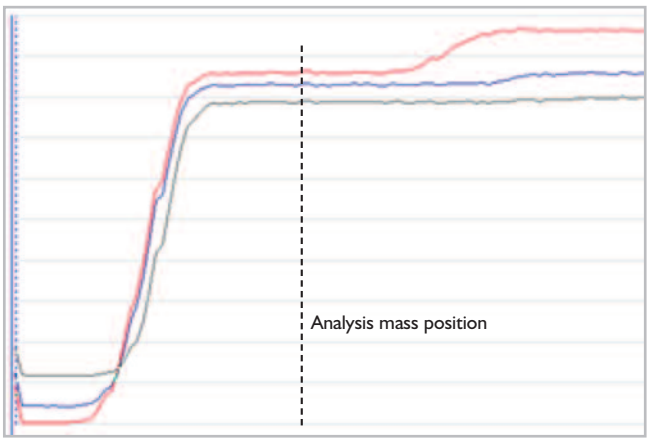


Fig. 2b: Close up of the iron isotopes resolved from their respective interferences in the *Pseudo High* resolution mode.



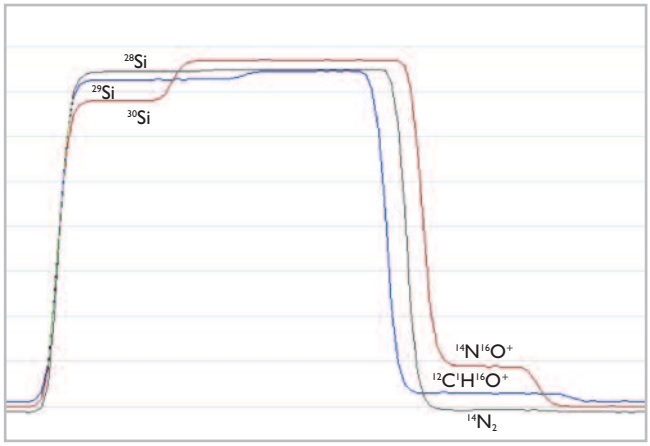
Like Fe, the resolutions required to resolve Si isotopes from their respective interferences are also calculated by *Resolution = Mass/ΔMass*. From Table 2, ^{28}Si requires the highest resolution and will therefore dictate which slit setting is needed.

Table 2: Si isotopes and the highest resolutions required for their respective interferences.

Analyte	Interference requiring the highest resolution	Resolution (10% valley) required
^{28}Si	$^{12}C^{16}O^+$	1555
^{29}Si	$^{12}C^{1}H^{16}O^+$	1104
^{30}Si	$^{14}N^{16}O^+$	1238

Similar to Fe, *Pseudo High* resolution mode can also be used for Si analysis. Peak shapes obtained for Si are shown in Fig. 3, using the 50 μm source defining slit.

Fig. 3: Silicon isotopes resolved from their respective interferences in the *Pseudo High* resolution mode using the 50 μm source defining slit.



High Resolution

The unique design of the Nu Plasma II fixed collector system also makes it possible to obtain full resolution from interferences (*High* resolution) by changing the collector slit widths, without having to replace collectors. This method allows the user to observe the complete resolution of interfering peaks from analyte peaks and is necessary for applications when interferences appear on both low and high mass sides of the analyte. The peak flat width obtained in *High* resolution mode is generally slightly narrower, but does not reduce the sensitivity any further compared to the *Pseudo High* resolution mode. Using the *High* resolution method, resolutions (10% valley) of up to 3000 can be achieved.

The *High* resolution method is achieved by reducing the widths of source defining slit, alpha slit and the collector slits using adjustable collector masks. There are three sets of collector masks fitted within the Nu Plasma II collector array, one for the high mass collectors, one for the low mass collectors and one for the central collectors. The variable collector slit mechanism allows the reduction of selected collector slit widths, while maintaining flat-top peaks as seen in Fig. 4 and Fig. 5.

Fig. 4: Iron isotopes separated from their respective interferences with ^{54}Fe and ^{56}Fe fully resolved using the adjustable collector masks with ^{57}Fe maintained in *Pseudo High* resolution. Resolution approximately 3000 (10% valley), 9000 ($RP_{edge\ 5,95\%}$).

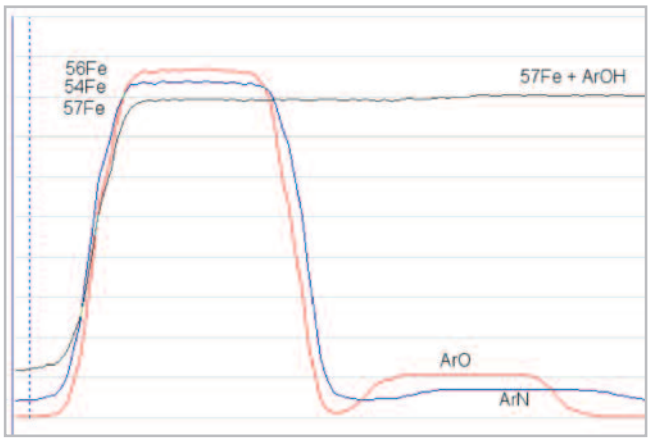
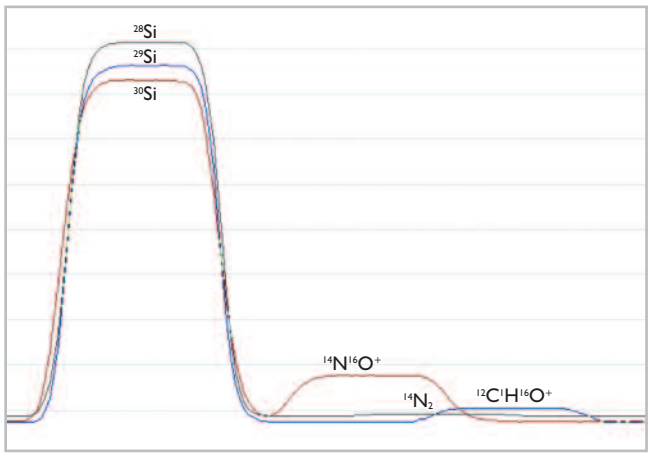


Fig. 5: Silicon isotopes separated from their respective interferences with ^{28}Si, ^{29}Si and ^{30}Si fully resolved using the adjustable collector masks. Resolution approximately 3000 (10% valley), 9000 ($RP_{edge\ 5,95\%}$).



Conclusion

The Nu Plasma II is able to achieve high mass resolving power across the entire multi-collector array. This high resolving power results in the separation of analyte peaks from polyatomic interferences, providing an interference free, flat-top peak area for precise and accurate isotopic measurements.

High resolutions are achieved by reducing the widths of the source defining slit, alpha slit and where necessary, the collector slits. The unique adjustable collector mask design of the Nu Plasma II instrument makes it possible to change the collector slit widths without having to replace collectors, in order to obtain *High* resolution to fully resolve analyte and interference peaks.