THE NU ATTOM HIGH RESOLUTION ICP-MS: FASTSCAN ION OPTICS FOR RAPID ISOTOPE RATIO MEASUREMENTS

INTRODUCTION

The ICP-MS technique has become a powerful tool for a growing range of organic and inorganic applications including isotope ratio measurements. Compared to quadrupole ICP-MS, magnetic sector instruments (multi- or single-collector) offer higher sensitivity and better signal-to-noise ratios as well as flat-topped peak profiles that yield much better isotope ratio precisions.

A common feature in all types of ICP-MS instruments is the mass discrimination effect, i.e. ions of different mass-to-charge ratios are transmitted with different efficiencies. Many factors such as ionisation, ion optics, mass separation and ion detection contribute to the overall discrimination effect.

It has been shown for the ICP that space charge effects in the ion beam at the interface region (especially after the skimmer orifice) and ion optics region are dominant. In order to achieve accurate results with any ICP-MS, this mass discrimination effect needs to be carefully evaluated and subsequently corrected for using certified reference materials.

Multi-collector instruments are generally operated at a constant magnetic field with simultaneous collection of multiple ion beams in different detectors. Single-collector instruments have to detect the masses of interest sequentially over a limited mass range for isotope ratio measurement. The accepted wisdom is that the change between masses of interest can be achieved either by changing the magnetic field strength or by reducing the acceleration voltage while applying a constant magnetic field. The latter can be the source of additional mass discrimination due to changing the ion energy.

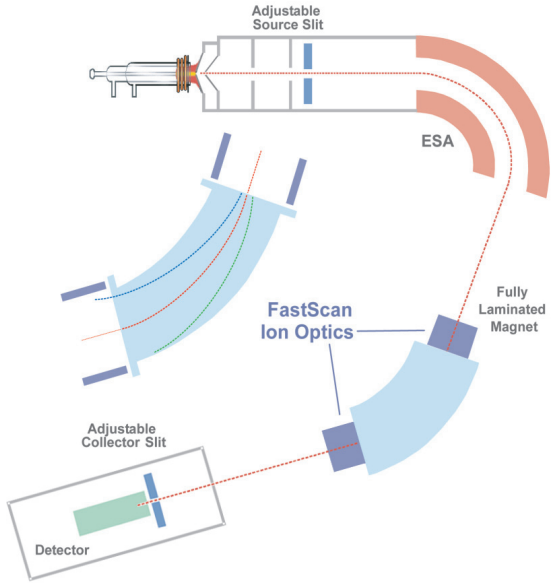

Figure 1: *Attom instrument schematic detailing the FastScan Ion Optics. A change of the ion beam flight path when entering the magnet achieves rapid change of mass across a 40% relative mass range without changing the magnetic field.*

Instrumentation

The Attom HR-ICP-MS is a double-focusing single-collector instrument of forward Nier-Johnson geometry which features the unique FastScan Ion Optics. The instrument is entirely purpose designed and built to provide the best performance and reliability coupled with flexibility and ease-of-use for precise and accurate elemental and isotope ratio analysis. A unique detector system gives the Attom a large dynamic range. Furthermore, the continuously variable high resolution means that sufficient resolution for isobaric separation can be selected with minimum compromise in sensitivity.

The instrument can also be used to rapidly scan/jump between isotopes of interest over a 40% relative mass range without the necessity to change the magnetic field or acceleration voltage (Figure 1). For this mode the magnet is parked in the middle of the mass range of selected isotopes (known as 'park mass'). Acceleration voltage, ESA voltage and ion optics used for beam focusing are kept constant during the acquisition. Only the FastScan Ion Optics located at the entrance and exit of the magnet are varied, being used to rapidly deflect the selected isotopes sequentially onto the magnet park mass for data acquisition.

Depending on which isotopes are selected for the analysis, the park mass will be different, typically about half way between the extremes of the isotope range to be measured. As an example, if

analysing all Pb isotopes the magnet will be set to ~206 amu and if analysing all Pb isotopes and ^{238}U the magnet will be set to ~219 amu (see Figure 2). In each of these examples the setup will need different FastScan Ion Optics settings to deflect the selected isotopes onto the magnet park position and hence the detector.

Experiment

Some types of single-collector ICP-MS instrument achieve peak jumping by varying the ion energy. However, studies have reported variations in the mass discrimination effect depending on the ratio analysed when using this method. Furthermore, applying internal mass discrimination correction either by using an isotope pair of the same or a different/neighbouring element can lead to ambiguous results *(Quétel et al. (2000), J Anal Chem, 368: 148-155)*.

In order to evaluate whether the design of the FastScan Ion Optic induces additional mass discrimination effects, Tl and Pb isotope ratio measurements have been performed using different scan range setups.

A solution consisting of 1 ppb CRM NBS981 and 300 ppt elemental thallium standard was used for Tl and Pb isotope ratio measurements in fast peak jumping mode in low resolution. These concentrations yielded ~500,000 cps for ^{208}Pb and ~215,000 cps for ^{205}Tl. All runs were performed with 4000 sweeps and 25 cycles using the same solution under the same instrument conditions over a course of 4 hours. A peak centre on ^{205}Tl was performed at the start of each run. ^{202}Hg was measured for isobaric interference correction on ^{204}Pb.

Discussion

Three different methods (Group A, B, C) were set up in order to acquire Tl and Pb isotope ratio data with different scan ranges. Park mass and dwell time settings for each of the methods are detailed in the tables on the following page (see Tables 1, 2 and 3 for the different settings). The datasets for each individual group consist of 10 replicates which represent approximately one hour (see Table 4). A 2% HNO_3 blank solution was run before analysing each group.

The data evaluation and comparison was done on raw data. The results for raw $^{205}Tl/^{203}Tl$ and $^{207}Pb/^{206}Pb$ isotope ratios are shown here (see Figure 3 and Table 5).

Group A data represent a relative scan range of 3%, Group B of 19% and Group C of 39%, with 40% being the maximum scan range achievable with the FastScan Ion Optics. The raw $^{205}Tl/^{203}Tl$ and $^{207}Pb/^{206}Pb$ isotope ratios are plotted with 2 sigma error bars and they overlap within error (see Figure 3). No drift of the isotope ratios or variations depending on the scan range can be observed.

For the internal mass discrimination correction a $^{205}Tl/^{203}Tl$ ratio of 2.3875 was used to correct the $^{207}Pb/^{206}Pb$ ratio. The average $^{207}Pb/^{206}Pb$ of each group with external precision (n=10) is shown in Table 4. It highlights that the accuracy is generally better than 0.1% and is within error.

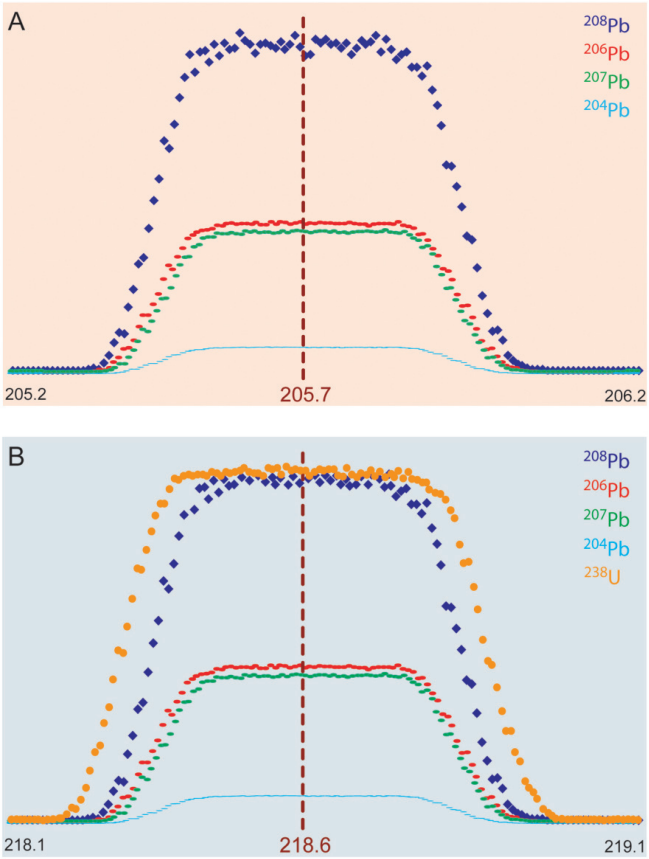

Figure 2: *Peak coincidences of Pb isotopes deflected to two different magnet park positions (see text for details).*

A: Magnet park position is 205.7 if only ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb are selected for analysis.

B: Magnet park position is 218.6 if ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb plus ^{238}U are selected for analysis.

These two examples will need different FastScan Ion Optics settings to deflect the selected isotopes to the two different magnet park positions for analysis.

Conclusions

These results show that there is no additional mass discrimination effect introduced by using the Attom FastScan Ion Optics to deflect different ion beams sequentially into the detector for isotope ratio measurements. Furthermore, it shows that an isotope pair of the same or a neighbouring element can be used for internal mass discrimination correction purposes. It is possible to achieve accurate results which are independent of the scan range.

GROUP A	^{202}Hg	^{203}Tl	^{204}Pb	^{205}Tl	^{206}Pb	^{207}Pb	^{208}Pb
Park Mass (amu)	204.561						
Dwell Time (μs)	600	300	600	300	300	300	300

GROUP B	^{202}Hg	^{203}Tl	^{204}Pb	^{205}Tl	^{206}Pb	^{207}Pb	^{208}Pb	^{238}U
Park Mass (amu)	217.478							
Dwell Time (μs)	600	300	600	300	300	300	300	250

GROUP C	^{150}Sm	^{202}Hg	^{203}Tl	^{204}Pb	^{205}Tl	^{206}Pb	^{207}Pb	^{208}Pb
Park Mass (amu)	174.869							
Dwell Time (μs)	250	600	300	600	300	300	300	300

Tables 1,2 and 3: *Analysis Parameters for Group A (Table 1), Group B (Table 2) and Group C (Table 3). The tables detail the isotopes analysed, the magnet park mass and the dwell time per isotope.*

Corrected Isotope Ratio	External Precision (n=10)		
	GROUP A	GROUP B	GROUP C
^{207}Pb/^{206}Pb	0.915643	0.914974	0.915095
%RSD	0.10	0.06	0.08
Accuracy %	0.098	0.024	0.038

Table 4: *Average ^{207}Pb/^{206}Pb ratios of each analysis group corrected for mass discrimination using ^{205}Tl/^{203}Tl = 2.3875.*

	GROUP A				GROUP B				GROUP C			
Run #	205/203 Raw	2 Stderr	207/206 Raw	2 Stderr	205/203 Raw	2 Stderr	207/206 Raw	2 Stderr	205/203 Raw	2 Stderr	207/206 Raw	2 Stderr
1	2.410218	3.51E-03	0.918756	7.23E-04	2.407614	3.90E-03	0.919693	9.93E-04	2.409583	3.17E-03	0.918354	9.06E-04
2	2.406590	3.54E-03	0.920123	9.97E-04	2.408626	4.16E-03	0.918845	1.08E-03	2.409130	4.05E-03	0.919362	8.49E-04
3	2.409012	3.79E-03	0.918705	9.85E-04	2.409659	2.49E-03	0.919061	7.88E-04	2.410306	2.92E-03	0.920002	9.00E-04
4	2.403042	3.23E-03	0.919271	7.67E-04	2.409683	2.15E-03	0.918781	9.89E-04	2.407417	4.02E-03	0.919823	7.84E-04
5	2.406390	2.77E-03	0.920195	7.65E-04	2.404853	2.70E-03	0.918131	8.49E-04	2.413723	3.53E-03	0.918698	1.25E-03
6	2.410032	2.85E-03	0.918973	1.25E-03	2.409320	2.82E-03	0.919780	1.08E-03	2.407760	3.53E-03	0.918644	9.43E-04
7	2.405412	3.37E-03	0.919824	1.26E-03	2.408498	3.27E-03	0.919206	8.85E-04	2.405252	2.95E-03	0.919474	1.04E-03
8	2.405569	3.33E-03	0.920280	8.45E-04	2.409760	2.67E-03	0.918619	1.07E-03	2.407175	2.77E-03	0.918696	8.49E-04
9	2.408258	3.11E-03	0.919119	1.12E-03	2.411967	2.71E-03	0.918311	1.04E-03	2.410232	4.84E-03	0.919798	6.70E-04
10	2.408340	4.07E-03	0.917977	9.98E-04	2.405048	2.53E-03	0.918801	1.05E-03	2.407833	3.59E-03	0.918993	1.06E-03
Average	2.407286		0.919322		2.408503		0.918923		2.408841		0.919184	
Stdev	0.002284		0.000764		0.002187		0.000534		0.002319		0.000583	
%RSD	0.09		0.08		0.09		0.06		0.10		0.06	

Table 5: *Analysis results for individual runs of each group. Raw ratios of ^{205}Tl/^{203}Tl and ^{207}Pb/^{206}Pb are shown with internal and external precision. Data are corrected for detector dead time of 14ns.*

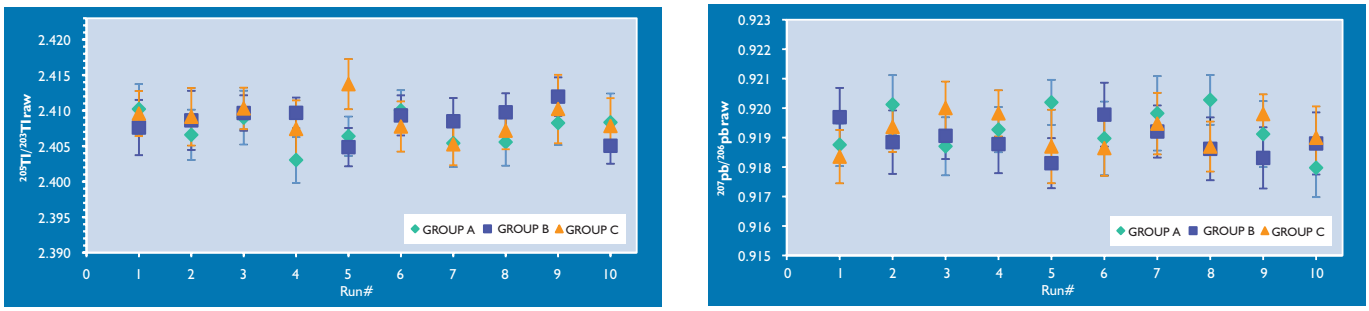

Figure 3: *Raw ratios of ^{205}Tl/^{203}Tl and ^{207}Pb/^{206}Pb of each group are plotted for comparison. The error bars are 2 sigma.*