ATTOM®

HR ICP-MS

APPLICATION NOTE **AN04**

THE ATTOM HIGH RESOLUTION ICP-MS: ION COUNTING LINEARITY

INTRODUCTION

Modern high resolution ICP-MS (HR-ICP-MS) instruments offer a number of performance differentiators compared to more widely-used quadrupole ICP-MS instruments. Better sensitivity, superior detection limits and faster scan speeds all offer distinct advantages in addition to the more obvious advantage of higher resolution analysis.

The dynamic range and detector linearity of mass spectrometers of this type can be important for a number of applications. Without a suitably broad dynamic range it is not possible to quantify trace elements in the presence of more abundant (matrix) elements. Typically, an ion counting detector is used for the quantitation of low abundance elements / isotopes, though such detectors are saturated by relatively small ion beams limiting their dynamic range. Additionally, they do not always respond in a linear fashion. This can be especially problematic when measuring isotope ratios, wherein the isotope ratio can vary with the concentration of the element(s) in the sample if the ion counter is not linear.

We report a series of measurements designed to quantify the linearity of the ion counting detector of the Attom HR-ICP-MS, the latest instrument of its kind.

Instrumentation

The Attom is a double-focusing, high-resolution magnetic sector mass spectrometer. 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, and its electrostatic scanning capability has the widest range in its class (40%). Furthermore, the continuously variable high resolution means that sufficient resolution for isobaric separation can be selected with minimum compromise in sensitivity.

Equipment

The linearity of the Attom's ion counting detector was assessed by analysis of the uranium standard CRM U500 in dry plasma mode. Concentrations of the solutions were selected so that a range of count rates between <1000 cps and >2 Mcps on the different U isotopes were achieved. Total U concentrations used were 50 pg/g, 100 pg/g and 200 pg/g. Four replicates of each concentration were measured in the following sequence 50 pg/g, 200 pg/g and 100 pg/g. All analyses were performed in fast peak jumping mode.

The dwell times for ^{235}U and ^{238}U were 200 μs. Dwell time for ^{234}U, ^{236}U, m/z 237 and m/z 239 were 400 μs. Peak jumps were made at 20 μs. Therefore, the total time for one sweep was around 2 ms. One cycle consisted of 2000 sweeps. Each run consisted of 100 cycles and thus, each run was around 7 minutes long. A deadtime correction of 15.5 ns was applied to signal intensities.

Tailing from ^{238}U was measured at m/z 237 and m/z 239. With the retardation filter on, the tail from ^{238}U onto m/z 237 was around 8 ppm and the tail from ^{238}U onto m/z 239 was around 20 ppm. Due to the equal abundance of ^{235}U and ^{238}U, these were subtracted from ^{234}U and ^{236}U peaks to correct for ^{235}U tailing.

The ^{235}U/^{238}U ratio was used for internal mass bias correction using the certified value of the standard of 0.999700 and the exponential correction law. Accuracies of the ^{234}U/^{238}U and ^{236}U/^{238}U ratios were calculated using the certified values of 0.010422 and 0.001519, respectively. This data can be seen in Table 1.

A second set of samples was also analysed, in this case using wet plasma operation. For this set of analyses, solution concentrations were selected to achieve a range of count rates between <1000 cps and 4.5 Mcps on the different U isotopes. Concentrations used were between 500 pg/g and 8,000 pg/g. Three replicates of each concentration were measured in fast peak jumping mode.

Dwell times for all isotopes were 200 μs. Peak jumps were made at 20 μs. Therefore, the total time for one sweep was around 2 ms. One cycle consisted of 1000 sweeps. Each run consisted of 70 cycles and thus, each run was around 3 minutes long. Deadtime correction and tailing were accounted for as per the first dataset.

Accuracies of the ^{234}U/^{238}U and ^{236}U/^{238}U ratios were calculated using the certified values as mentioned above. This data can be seen in Table 2.

Discussion

The data shown in Table 1 indicates that the Attom produces accurate and precise isotope ratios using its fast peak jumping mode. All ion beams were analysed using the ion counting detector. The isotope ratios do not vary with solution concentration, and the 234U/238U and 236U/238U values are within 0.15% and 0.04% of the certified values respectively.

Furthermore, the data shown in Table 2 shows that when more concentrated ion beams are used (up to 4.5 Mcps) there is no loss in either accuracy or precision of the measurements. The recommended maximum count rate of the Attom's ion counting detector is 2Mcps. However, these results indicate that linearity is achieved even with more intense ion beams than the specified count rate limit.

Conclusions

The Attom is a high resolution ICP-MS that is ideal for the most demanding ICP-MS requirements where sensitivity, precision, and speed of analysis are paramount. Isotope ratios can be measured for ion beams of a few hundred cps to >4 Mcps with no loss in either accuracy or precision, indicating that the ion counting detector is linear across a wide range of sample concentrations.

Table 1: Count rates and isotope ratios as measured on the Attom using NBS U500 at a variety of concentrations (dry plasma)

^{234}U (cps)	^{235}U (cps)	^{236}U (cps)	^{238}U (cps)	$^{234}U/^{238}U$	2SE	$^{236}U/^{238}U$	2SE	Conc. (pg/g)
5345	513867	788	520974	0.010455	3.20E-05	0.001528	1.20E-05	50
20977	2017488	3092	2041056	0.010428	1.60E-05	0.001521	5.10E-06	200
9265	891642	1358	900041	0.010411	2.30E-05	0.001519	8.40E-06	100
5264	506688	768	513215	0.010435	3.00E-05	0.001515	1.20E-05	50
21690	2083790	3173	2105072	0.01044	1.50E-05	0.001521	5.20E-06	200
8971	863373	1317	871612	0.01044	2.30E-05	0.001523	8.90E-06	100
5445	523637	794	529429	0.010439	3.40E-05	0.001519	1.10E-05	50
20762	1995291	3055	2018284	0.010434	1.50E-05	0.001524	5.60E-06	200
9266	890254	1361	901564	0.010435	2.20E-05	0.001521	9.10E-06	100
4615	444921	679	453501	0.010428	3.30E-05	0.001513	1.20E-05	50
16672	1605488	2458	1644452	0.010458	1.70E-05	0.001517	6.40E-06	200
7625	736839	1127	756677	0.010452	2.80E-05	0.001513	9.40E-06	100
			Mean	**0.010438**		**0.00152**		
			SD	1.31E-05		4.56E-06		
			RSD%	**0.125**		**0.3**		
			Accuracy%	**0.15**		**0.04**		

Table 2 : Count rates and isotope ratios as measured on the Attom using NBS U500 at a variety of concentrations (wet plasma)

^{234}U (cps)	^{235}U (cps)	^{236}U (cps)	^{238}U (cps)	$^{234}U/^{238}U$	2SE	$^{236}U/^{238}U$	2SE	Conc. (pg/g)
2995	287990	459	290785	0.010376	6.10E-05	0.001532	2.70E-05	500
5968	574920	925	580574	0.01035	6.60E-05	0.001556	2.10E-05	1000
12004	1151781	1835	1162977	0.010397	2.90E-05	0.001538	1.40E-05	2000
23693	2270812	3598	2291426	0.010406	2.60E-05	0.001526	1.20E-05	4000
41979	4033844	6372	4072390	0.010389	2.30E-05	0.001525	7.50E-06	7000
47299	4549946	7170	4592796	0.010371	1.90E-05	0.001524	7.70E-06	8000
2992	284562	459	286898	0.010421	7.30E-05	0.001524	2.70E-05	500
5901	566024	916	571202	0.010382	5.80E-05	0.001549	2.00E-05	1000
11775	1131694	1810	1142594	0.010373	3.40E-05	0.00154	1.40E-05	2000
23609	2265614	3605	2285725	0.01039	3.10E-05	0.001533	1.00E-05	4000
41361	3981371	6347	4019623	0.010364	2.20E-05	0.001543	7.60E-06	7000
46839	4493771	7103	4538556	0.010395	1.80E-05	0.001526	8.40E-06	8000
2937	281150	454	284019	0.010364	7.10E-05	0.001522	3.30E-05	500
5787	554270	897	558926	0.010378	6.20E-05	0.001543	2.10E-05	1000
11667	1120793	1784	1131548	0.010368	3.80E-05	0.001532	1.70E-05	2000
23549	2251992	3560	2272046	0.010436	2.70E-05	0.001526	1.10E-05	4000
40564	3901134	6149	3934048	0.010371	2.10E-05	0.001526	7.70E-06	7000
46879	4503358	7165	4545844	0.010394	2.10E-05	0.001537	7.50E-06	8000
			Mean	**0.010385**		**0.001534**		
			SD	2.13E-05		9.72E-06		
			RSD%	**0.205**		**0.634**		
			Accuracy%	**-0.36**		**0.96**		