THE NU ATTOM HIGH RESOLUTION ICP-MS: LONG TERM SIGNAL STABILITY, WET AND DRY PLASMA

INTRODUCTION

Since the commercial introduction of ICP-MS during the 1980's, the technique has evolved into a well-established method for quantitative and semi-quantitative trace and ultra-trace element measurement as well as isotope ratio determination.

For successful use of ICP-MS as an analytical tool, it is essential to transport a sample into the plasma in the most efficient way. Many different approaches are used, all of them having a common aim to convert the sample into a suitable aerosol which is subsequently introduced into the plasma for ionisation. To guarantee reliable and consistent results, the sample introduction needs to be as stable as possible, even during long analytical periods. A number of things can influence the stability of the sample introduction, such as the matrix of the sample and the total dissolved solids content. There are also instrumental factors such as pulsing of the peristaltic pump and variations in nebulisation efficiency.

Traditionally, liquids are analysed by ICP-MS using 'wet plasma' operation, whereby the liquid is aspirated directly into the spray chamber and hence the torch using a concentric nebuliser. An alternative method is to use a heated membrane to extract much of the solvent, this is known as 'dry plasma'.

Figure 1: *Wet plasma sample introduction system consisting of baffled cyclonic spray chamber and microconcentric nebuliser, both manufactured by Glass Expansion.*

Figure 2: *Sample introduction system used for the dry plasma experiment (Cetac Aridus II, left) and autosampler used for all measurements (Cetac ASX112, right).*

Instrumentation

The Attom HR-ICP-MS is a double-focusing single-collector instrument of forward Nier-Johnson geometry which features the unique Attom 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.

To evaluate and compare the signal stability in wet and dry plasma, the results of two unattended long-term stability experiments were performed with the Attom HR-ICP-MS. The first experiment was performed using the standard wet plasma sample introduction system (figure 1) and the second experiment utilised a Cetac Aridus II desolvation unit for dry plasma measurements (figure 2). For both experiments, the respective sample introduction system was connected to a Cetac ASX112 autosampler equipped with a gas displacement rinse station (figure 2).

The standard wet plasma sample introduction system of the Attom is a low volume baffled cyclonic spray chamber with a 200 μl/min microconcentric nebuliser. The spray chamber is peltier cooled to about 5°C and the nebuliser is used in natural aspiration mode under normal operational conditions. The spray chamber is drained by a peristaltic pump.

Experiment

To evaluate the signal stability, two experiments were performed over the course of 4 to 6 hours in low resolution fast peak jumping mode without any user intervention. A rhenium ICP-MS single element standard was used, diluted to three different concentrations; 0.5 pg/g, 1 pg/g and 10 pg/g. Experimental details are given in table 1. The only difference between the wet and dry plasma experiment was the length of the transfer and wash times. The whole sequence was repeated 5 times for wet plasma and 6 times for dry plasma, respectively.

	Wet Plasma		Dry Plasma	
Sample	**Time [s]**	**Replicates**	**Time [s]**	**Replicates**
Blank 1	90	4	120	5
0.5 pg/g Re	90	4	120	5
Wash	*130*		*270*	
Blank 2	90	4	120	5
1 pg/g Re	90	4	120	5
Wash	*130*		*270*	
Blank 3	90	4	120	5
10 pg/g Re	90	4	120	5
Wash	*130*		*270*	
	Total Duration:	4 hours	Total Duration:	6 hours

Table 1: *Details for both experiments.*

The dwell times for ^{185}Re and ^{187}Re were 500 μs each. For isobaric interference correction, ^{188}Os and ^{189}Os were monitored, also with a dwell time of 500 μs each. The peak took about 20 μs. Therefore, the total time for each sweep was around 2 ms. One cycle consisted of 3000 sweeps and each analysis run consisted of 20 cycles. Thus, each analysis run was around 2 minutes long. A dead time correction of 14 ns was applied to signal intensities. The signal intensities of ^{188}Os and ^{189}Os were constant and <10 cps so that isobaric interference correction was not deemed necessary. All data presented here is raw data that is dead time corrected but not blank corrected.

Results and Discussion

Wet plasma: The signal intensities for ^{185}Re and ^{187}Re achieved for the three different concentrations with the standard wet plasma configuration are shown in table 2. The overall signal stability over the course of the 4 hour analytical session can be expressed by the relative standard deviation (RSD%) of the average signal of each concentration. The RSD% is better than 1.8%. Figure 3 depicts the signal variation of the blanks and the different sample concentrations with time. The blank is very low, generally less than <10cps. Slightly elevated blank values can be observed after running the 10ppt solution (<30 cps), but the background generally returns to ~10 cps within the course of the subsequent blank measurement. This behaviour could be improved by choosing slightly longer washout times prior to a new blank measurement. Nevertheless, the blank values always return to <20 cps within the course of the blank measurement.

Dry plasma: The signal intensities obtained with the dry plasma configuration are shown in table 3. The RSD% is better than 2.5%. Figure 4 depicts the signal variation with time. Again, the blank is very low (<20 cps). The washout times were increased slightly for this experiment compared to the wet plasma experiment. However, background values returned quickly to their original levels. After running the 10ppt solution, the next blank measurement is slightly elevated, but within the course of five replicates the background returns to ~ 20cps.

^{185}Re	0.5pg/p Re	1 pg/g Re	10 pg/g Re
Average [cps]	247	491	4827
SD	3.5	4.8	60.5
RSD%	*1.43*	*0.98*	*1.25*

^{187}Re	0.5pg/p Re	1 pg/g Re	10 pg/g Re
Average [cps]	404	803	7918
SD	7.0	9.6	94.6
RSD%	*1.73*	*1.20*	*1.20*

Table 2: *Signal intensities for the wet plasma experiment.*

^{185}Re	0.5pg/p Re	1 pg/g Re	10 pg/g Re
Average [cps]	4388	9321	87443
SD	111	204	1962
RSD%	*2.53*	*2.19*	*2.24*

^{187}Re	0.5pg/p Re	1 pg/g Re	10 pg/g Re
Average [cps]	7300	15514	145962
SD	112	216	1870
RSD%	*1.53*	*1.39*	*1.28*

Table 3: *Signal intensities for the dry plasma experiment.*

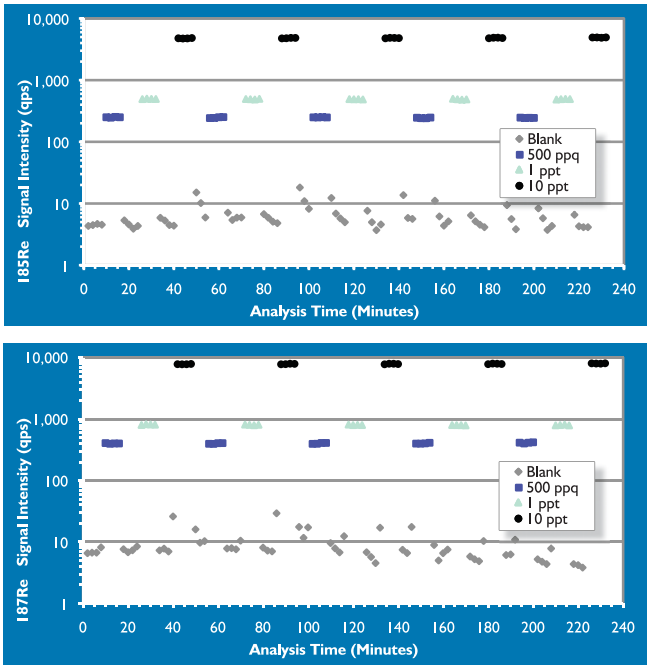

Figure 3: *Data produced by the wet plasma experiment*

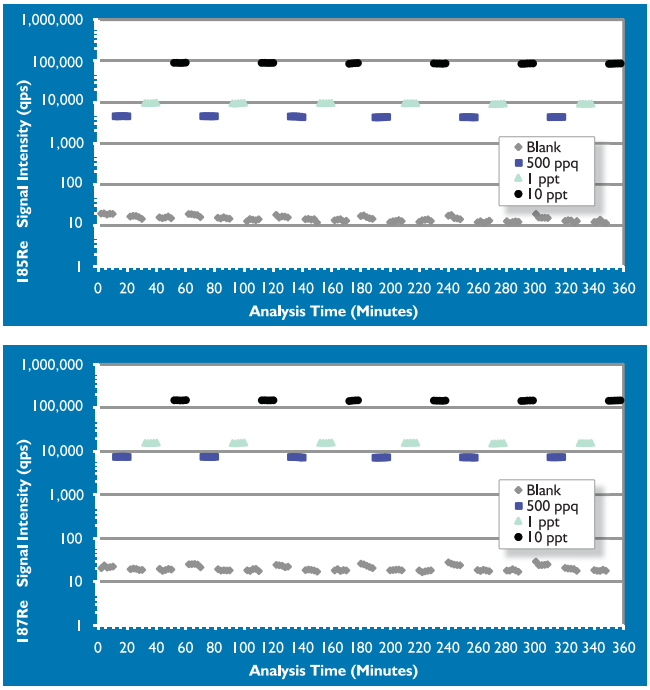

Figure 4: *Data produced by the dry plasma experiment*

Conclusions

Overall signal stabilities for rhenium of <2% and <3% were achieved during long-term analytical sessions of 4 hours in wet plasma and 6 hours in dry plasma respectively, without any user-intervention. This clearly shows the suitability of the instrument for routine applications where instrument stability is a key factor to obtaining reliable and consistent results.