thermo scientific

APPLICATION NOTE 30824

Long term multi-element signal stability in wet plasma

Authors: L. Bracciali, T. Lindemann, H. Vollstaedt, J. Roberts, Thermo Fisher Scientific, Bremen, Germany

Keywords: HR-ICP-MS, Element XR, Jet Interface, multi-element signal stability

Introduction

A Single Collector ICP-MS instrument measures signal intensities while rapidly repeating mass scans from low to high mass. Signal intensities are measured sequentially at each mass of interest across the scan. Signal stability is therefore critical to ensure accurate and precise results in trace elemental and isotope ratio analysis by Single Collector ICP-MS.

Assuming homogeneity of the sample, signal stability largely relies on the overall performance of the mass spectrometer. For low concentration analytes, good signal stability will result in good detection limits. On the other hand, signal fluctuations (e.g. at the scale of the analytical session) would bias the results by introducing artificial inter-sample variations.

Signal stability can be expressed as Relative Standard Deviation (RSD) of a signal intensity measured over a period of time. It is generally observed that short term stability (e.g. monitored over a period of a few minutes) is better than signal stability monitored over a longer period of time (e.g. tens of minutes or hours).

Here we report signal stability data for a 1 ppb multi-element solution. The data were collected in wet plasma conditions with a Thermo Scientific™ Element XR™ HR-ICP-MS equipped with an optional High Capacity Air-cooled Dry Interface Pump (100 m^3/h pumping speed), replacing in these experiments the standard interface pump of the mass spectrometer.

In a first set of experiments, the HR-ICP-MS was equipped with standard cones (Standard sample cone and H skimmer cone) while in a second set of experiments the Jet sample cone and X skimmer cone were used.

This latter configuration (High Capacity Air-cooled Dry Interface Pump, Jet sample cone and X skimmer cone) corresponds to the optional Jet Interface available for the Element Series HR-ICP-MS. The Jet Interface enables the Element HR-ICP-MS to set a new standard for sensitivity in elemental analysis (Thermo Scientific Application Note 30685).

ThermoFisher SCIENTIFIC

In all experiments, twenty-six isotopes in total were measured in low to high mass resolution mode and the signal stability was monitored for several hours during each experiment. The signal stability was consistent across each experiment. In this Application Note we report data from a representative 2 hour interval from each of the two sets of experiments.

Remarkably, the RSD over 2 hours was < 1.5% for all isotopes in both sets of experiments. For reference, the specified signal stability of the Element Series HR-ICP-MS is < 1% RSD over 10 minutes and < 2% RSD over 1 hour (Thermo Scientific Product Specification PS30436).

Additionally, when the Jet sample cone and X skimmer cone were used, a general improvement of the long term (2 hour) signal stability was observed in the low mass range and in all resolution modes, with most isotopes yielding RSDs < 1%.

Analytical setup and methods

Table 1 details the operating conditions of the Element XR HR-ICP-MS for both sets of experiments. The sample flow was determined gravimetrically and the detection sensitivity reported here was determined on the same multi-element solution used for the experiments. Plasma conditions were tuned to minimize oxide formation. Each replicate sample was measured for 4.3 minutes, with a take-up time of 2 minutes.

Table 1. Operating conditions and acquisition parameters

	First experiment (Standard and H cones)	Second experiment (Jet and X cones)
Sample introduction	Twinnabar™-type quartz cyclonic spray chamber; 200 µL/min MicroMist™ nebulizer, self-aspirating; 2.2 mm I.D. quartz injector tube	
Cones	Standard Ni sample cone and Ni H skimmer cone	Ni Jet sample cone and Ni X skimmer cone
RF power	1250 W	1100 W
Sample gas flow	0.9 l/min	1.1 l/min
Detection mode	Triple	
Sample type	1 ppb multi-element solution from dilution of SPEX CertiPrep™ Multi-element Solutions 2 and 4 in 3% HNO_3	
Sample flow	220 µL/min	190 µL/min
Isotopes monitored	10, 15 and 1 isotopes were respectively measured in LR, MR and HR. Full list and resolution modes in Fig. 3.	
Detection sensitivity in Low Resolution (> 300)	1.3 $*10^6$ cps/ppb ^{115}In	5.5 $*10^6$ cps/ppb ^{115}In
Detection sensitivity in Medium Resolution (R > 4000)	4.4 $*10^4$ cps/ppb ^{56}Fe	3.1 $*10^5$ cps/ppb ^{56}Fe
Detection sensitivity in High Resolution (R > 10000)	1.5 $*10^4$ cps/ppb ^{39}K	9.2 $*10^4$ cps/ppb ^{39}K

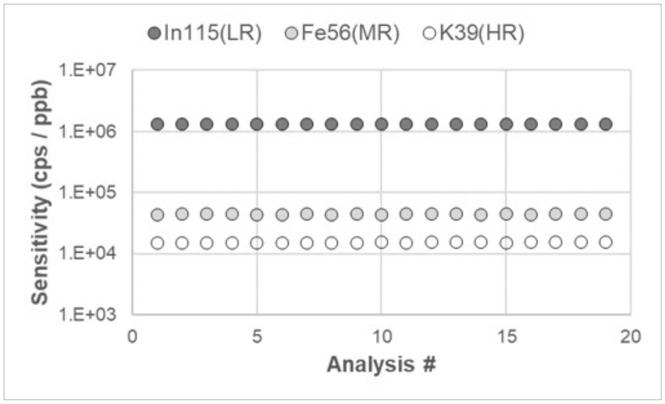

Fig. 1. Sensitivity data for three isotopes measured in different resolution modes with Standard sample cone and H skimmer cone. Total measurement time was 2 hours corresponding to 19 individual analysis. Note the logarithmic scale for the y-axis.

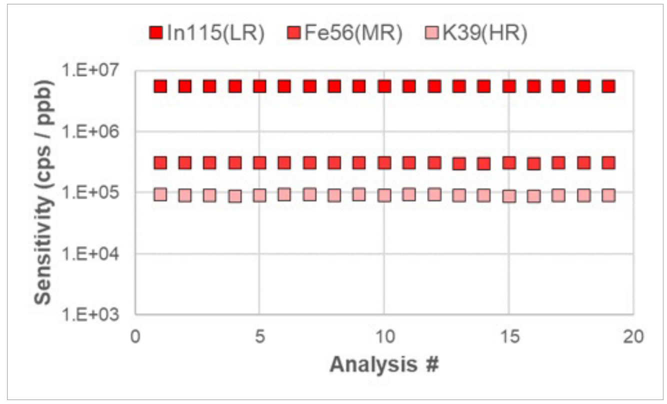

Fig. 2. Sensitivity data for the same isotopes as in Fig. 1 measured with Jet sample cone and X skimmer cone. Total measurement time was 2 hours corresponding to 19 individual analysis. Note the logarithmic scale for the y-axis.

Results: Sensitivity

Two-hour sensitivity data are plotted in Fig. 1 and Fig. 2 for three isotopes, one for each of the mass resolution modes: ^{115}In (LR), ^{56}Fe (MR) and ^{39}K (HR). The increase in sensitivity with the full Jet Interface option (Fig. 2) is remarkable: the sensitivity of ^{115}In measured in LR mode shows a ~4-fold increase, while for ^{56}Fe (MR) and ^{39}K (HR) the sensitivity is respectively ~7 and ~6 times higher in comparison to standard cones (Table 1).

Two-hour average sensitivity for all the twenty-six monitored isotopes is plotted in Fig. 3. Consistent with what was previously reported (Thermo Scientific Application Note 30685), we observed that the increase in sensitivity was more pronounced for the lighter masses relative to the higher end of the mass range (Fig. 3, left panel).

Results: Stability

Two-hour RSD data for all monitored isotopes are plotted in Fig. 4.

In low resolution mode all isotopes monitored during both experiments yielded RSDs < 1.5%, with the majority between 0.4 and 1.0% (Fig. 4, left panel). No significant difference is observed between both analytical set-ups, except a lower stability for Li measured with Standard sample cone and H skimmer cone.

In medium resolution mode all isotopes measured during the first experiment with Standard sample cone and H skimmer cone yielded RSDs between 0.7 and 1.4% (Fig. 4, right panel). For 9 out of 15 isotopes measured in MR we report RSDs ≤ 1.0%.

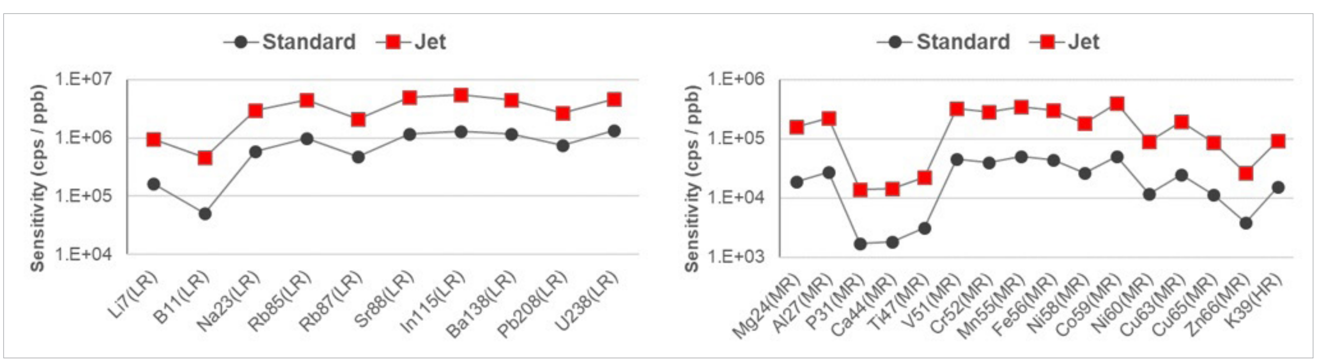

Fig. 3. Average of two-hour sensitivity data for a multi-element 1 ppb solution. Left panel: isotopes measured in LR mode. Right panel: isotopes measured in MR and HR mode. Each datapoint is the average of nineteen measurements.

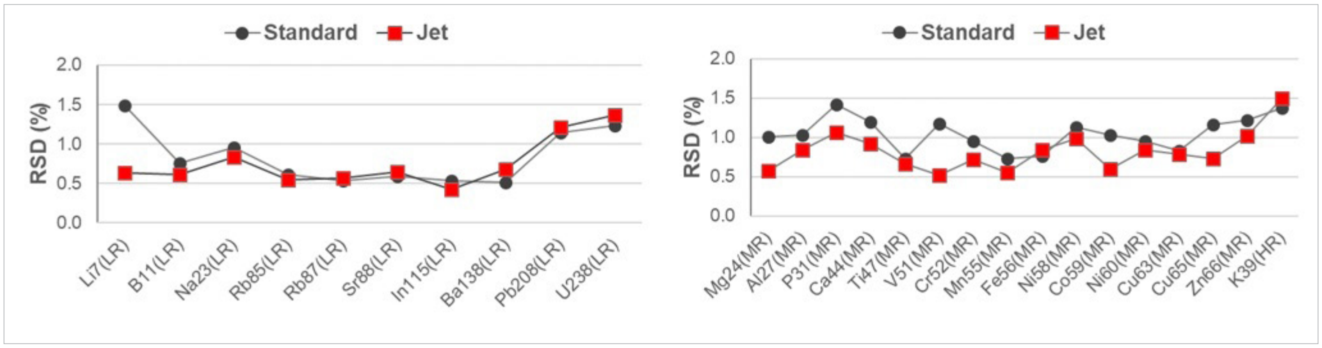

Fig. 4. Two-hour stability data (RSD % determined on the same 19 measurements as in Fig. 3). Left panel: isotopes measured in LR mode. Right panel: isotopes measured in MR and HR mode.

Remarkably, all the isotopes measured in MR (^{24}Mg to ^{66}Zn) with Jet sample cone and X skimmer cone yielded similar or lower RSD values, compared to the first experiment, ranging between 0.5 and 1.1.%.

In high mass resolution mode ^{39}K yielded similar RSDs of 1.4 and 1.5% in both experiments.

The long-term stability of the measurements is also apparent from Fig. 5 where the blank-subtracted intensities of all isotopes are plotted for the 2 hour interval (19 measurements in total).

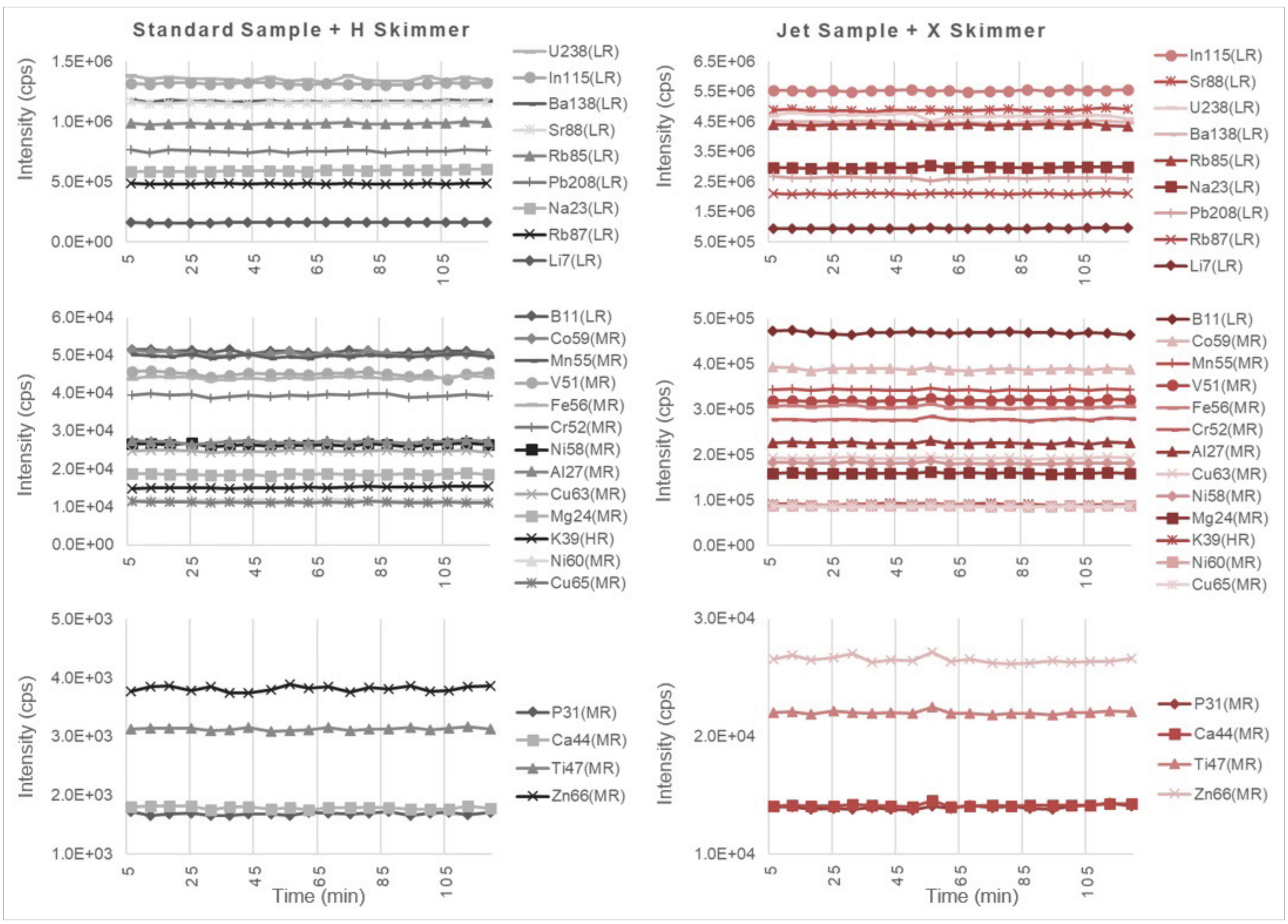

Fig. 5. Two-hour intensity data for all isotopes monitored in the 1 ppb multi-element solution. Left panel: with Standard sample cone and H skimmer cone. Right panel: with Jet sample cone and X skimmer cone. Same data as in Figures 3 and 4.

Overall these results show that:

- The optional Jet Interface significantly increased the sensitivity across the mass range and at all resolution modes (with a four to nine-fold increase, Figures 3 and 5).
- The long term (2 hour) stability of the Element XR HR-ICP-MS in wet plasma conditions (regardless of the cones used, i.e. Standard sample + H skimmer or Jet sample + X skimmer) was consistently lower than 1.5% across the entire mass range. For some elements it was consistently lower than 1%.
- The 2 hour stability of trace element data collected with the Jet sample cone and X skimmer cone was comparable or better (particularly in MR) than the 2 hour stability of data collected with Standard sample cone and H skimmer cone (Fig. 4).
- In wet plasma, the Jet Interface systematically increased the sensitivity across the mass range and in all mass resolution modes (e.g. by ~4-, ~7- and ~6 times respectively for ^{115}In (LR), ^{56}Fe (MR) and ^{39}K (HR)).
- The Jet Interface not only significantly increased the sensitivity of trace elemental analysis in wet plasma conditions, but also reproduced or improved the long term (2 hour) signal stability.
- Remarkably, all isotopes from the low mass range (^{24}Mg to ^{68}Zn) measured for 2 hours in MR with the Jet Interface yielded RSDs between 0.5% and 1.1%.

Conclusions

- The long term (2 hour) stability monitored in several experiments by measuring a suite of 26 isotopes in a 1 ppb multi-element solution with an Element XR HR-ICP-MS in LR, MR and HR was consistently < 1.5% RSD, i.e. better than the specified signal stability for 1 hour (< 2% RSD for 1 ppb In) and comparable or slightly lower than the specified stability for 10 minutes (< 1% RSD for 1 ppb In).

References

1. Thermo Scientific Product Specification PS30436
2. Roberts J. et al., Thermo Scientific Application Note AN 30685: The Jet Interface: improving sensitivity of trace element analysis.

Find out more at **thermofisher.com/HR-ICP-MS**

ThermoFisher SCIENTIFIC