High Sensitivity, Fast Scanning, Sector Field ICP-MS – Improving Sensitivity for Laser Ablation with the Jet Interface

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ABSTRACT

The long term trend in laser ablation (LA) coupled to inductively coupled plasma mass spectrometry (ICP-MS) has been to:

•Use smaller spot sizes to increase spatial resolution
•Investigate elements at lower and lower concentrations
•Improve isotope ratio precision.

In order to achieve all of these aims the result has been a need to significantly improve the sensitivity of ICP-MS technology. Sector Field ICP-MS has the potential to deliver significantly higher sensitivity than other mass analyzers. For solution nebulization it has already been shown that the Element XR™ Sector Field ICP-MS, when utilizing a selected sample and skimmer cone geometry together with a high capacity dry interface pump (Jet Interface), improves sensitivity significantly [1], [2], [3].

Here we will demonstrate the sensitivity advantages of Sector Field ICP-MS with the Jet Interface coupled to a modern laser ablation system. We will also show how these sensitivity advantages are bolstered by an extended dynamic range detection system, selectable mass resolution and a high stability magnet and electrostatic analyzer, which enable fast scanning across a wide mass range.

INTRODUCTION

In laser ablation ICP-MS analysis, the choice of which type of ICP-MS to use may not be entirely obvious. High precision isotope ratio analysis, such as epsilon level precision for geochronology, would need to be measured with a multi-collector ICP-MS, such as the Thermo Scientific™ NEPTUNE XT™, but for the majority of applications the precision obtainable with a single collector ICP-MS is sufficient. In the area of single collector ICP-MS we are still left with the choice between a quadrupole-based ICP-MS, such as the Thermo Scientific™ iCAP™ RQ/TQ, and a magnet sector based ICP-MS, the Thermo Scientific™ Element XR™.

The reduced cost, size and complexity of the quadrupole-based ICP-MS make them a popular choice for LA-ICP-MS analysis. However, it has always been known that a magnet sector based ICP-MS enjoys a significant increase in sensitivity: detecting more ions for the same amount of atoms introduced. In laser ablation analysis the amount of sample to be analyzed is often strictly limited. Furthermore, to reduce laser-induced fractionation and to stay within discrete sample zones it is highly desirable to ablate as little sample material as possible. The trend towards higher resolution LA-ICP-MS bio-imaging has also led to a reduction in the amount of sample ablated. These limitations in sample size make the sensitivity of the ICP-MS vital in order to achieve useable limits of quantification and detection (LOQ and LOD).

The Jet Interface option for the Thermo Scientific Element XR HR-ICP-MS greatly increases the sensitivity of fast scanning, sector field ICP-MS, especially for dry plasma. It consists of a high capacity dry interface pump and a companion set of specially designed cones. Here we report the sensitivity (as sample ion yield) of the Element XR when equipped with the Jet Interface option. We then compare this sensitivity to two other ICP-MS for the LA-ICP-MS U-Pb analysis of two common zircon reference materials.

MATERIALS AND METHODS

ICP-MS

Three ICP-MS systems were used:
- NEPTUNE XT (multi collector ICP-MS, with Jet Interface)
- ELEMENT XR (single collector Sector Field ICP-MS), equipped with Jet Interface option
- iCAP TQ (single collector quadrupole based ICP-MS), equipped with high sensitivity cones and insert recommended for laser ablation analysis

The dwell times for ELEMENT XR and iCAP TQ were:

Isotope	^{206}Pb	^{207}Pb	^{208}Pb	^{232}Th	^{235}U	^{238}U
Dwell Time (ms)	26	48	26	26	26	26

ESI™ Apex Omega™ Desolvating Nebulizer System

The dry aerosol generated by a desolvating nebulizer system, similar to a laser ablation aerosol, was used to determine the sensitivity of the Element XR with the Jet Interface option. A 1ppb solution of Li, Fe, Sr, Nd, Hf, Pb and U in 3% HNO_3 was measured 10 times and the amount of solution used weighted. From this the amount of atoms aspirated could be calculated and ratio'ed against the number of ions detected to determine the sample ion yield for each element.

$$sample\ ion\ yield\ (\%) = \frac{number\ of\ ions\ detected}{number\ of\ atoms\ aspirated} x100$$

Sample Reference Materials

The ablated reference materials were:
- NIST SRM® 610
- 2 reference zircons: 91500 and GJ-1

Laser Ablation

The LA system used was a Teledyne Photon Machines Analyte G2™ equipped with a HelEx™ ablation cell.

RESULTS

Sample Ion Yield

As expected for a sector field ICP-MS there was a strong relationship between the isotope mass and the sample ion yield (Figure 1). With the Jet Interface four of the seven elements had sample ion yields greater than 1% (Table 1). For LA-ICP-MS, if we assume a LOD of 5 ions then consequently only 500 atoms of a given isotope would need to be ablated per second to reach this threshold.

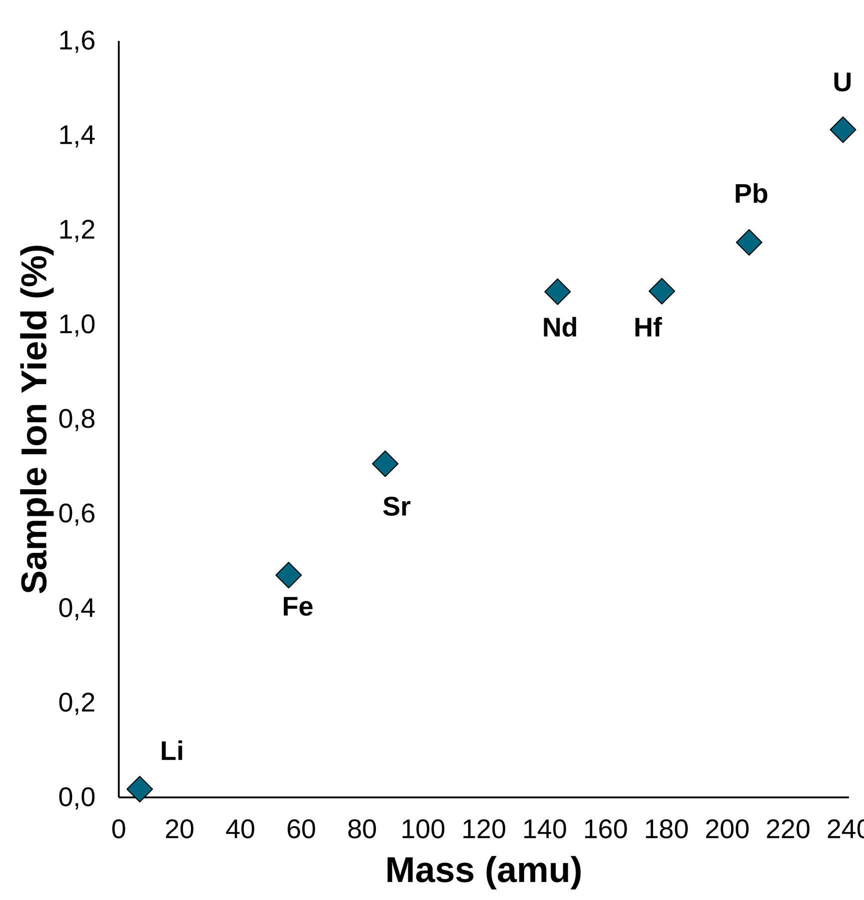
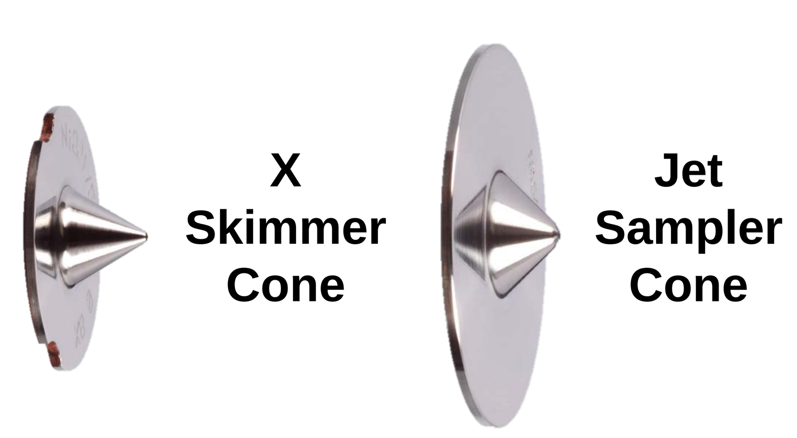


Figure 1. Plot of sample ion yield (%) against mass for seven elements. 1 ppb of each element was aspirated through an Apex Omega desolvating nebulizer system to produce a dry aerosol analogous to a laser ablation aerosol. Due to the mass response of a sector field mass spectrometer the greatest sample ion yields were for the heaviest elements.

Table 1. Sample ion yield (%) for seven elements across the total mass range. 1 ppb of each element was aspirated through an Apex Omega desolvating nebulizer system to produce a dry aerosol analogous to a laser ablation aerosol.

	Li	Fe	Sr	Nd	Hf	Pb	U
Mean	0.018	0.470	0.706	1.070	1.071	1.174	1.412
SD	0.000	0.002	0.003	0.003	0.003	0.004	0.005
RSD (%)	0.48	0.38	0.39	0.24	0.31	0.32	0.34



U-Pb isotopic analysis of two reference zircons: comparison between iCAP TQ, Element XR (Jet Interface) and Neptune XT

The ^{238}U signal for the 91500 reference zircon was used to compare the three LA-ICP-MS systems (Figure 2). The Element XR with the Jet Interface option was 21 times more sensitive than the quadrupole-based ICP-MS (The Neptune XT, also equipped with the Jet Interface and the benefits of multicollection was a further 3.5 times as sensitive).

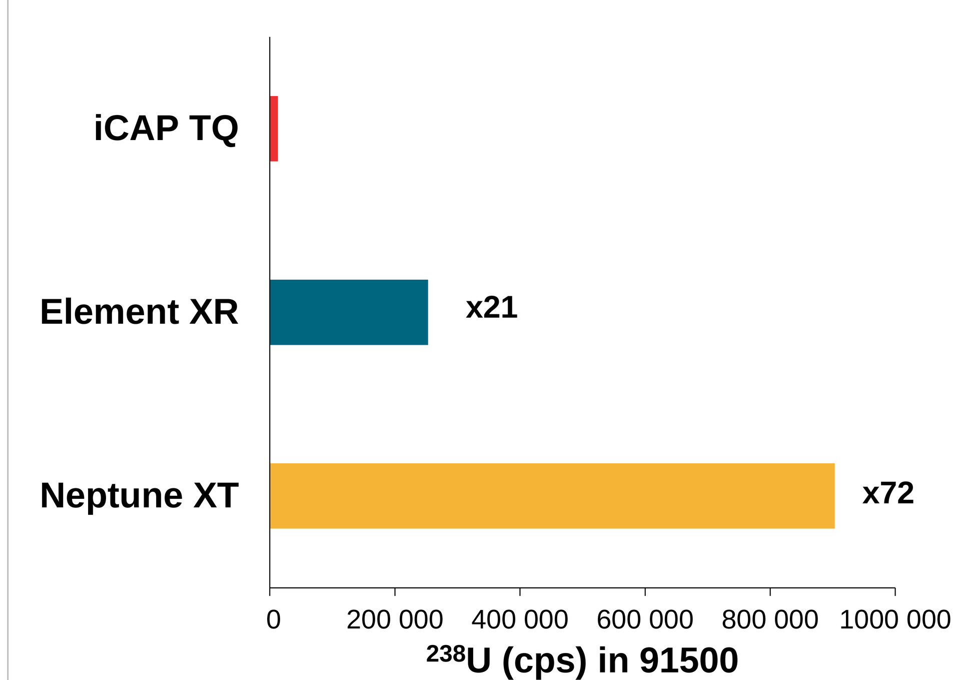


Figure 2. Number of ^{238}U counts per second detected for a 35 µm diameter, 3 J cm^{-2}, 7 Hz repetition rate, 30 second duration ablation of the 91500 reference zircon with three Thermo Scientific ICP-MS in the demo facility in Bremen. The laser ablation system used was the same Teledyne Photon Machines™ Analyte G2™ 193 nm excimer with a HelEx™ ablation cell. Whilst the sensitivity of quadrupole ICP-MS (shown here as tuned in standard mode without CCT mode sensitivity enhancement) is perfectly adequate for this application, the Element XR with the Jet Interface was 21 times more sensitive than the iCAP TQ (high sensitivity interface).

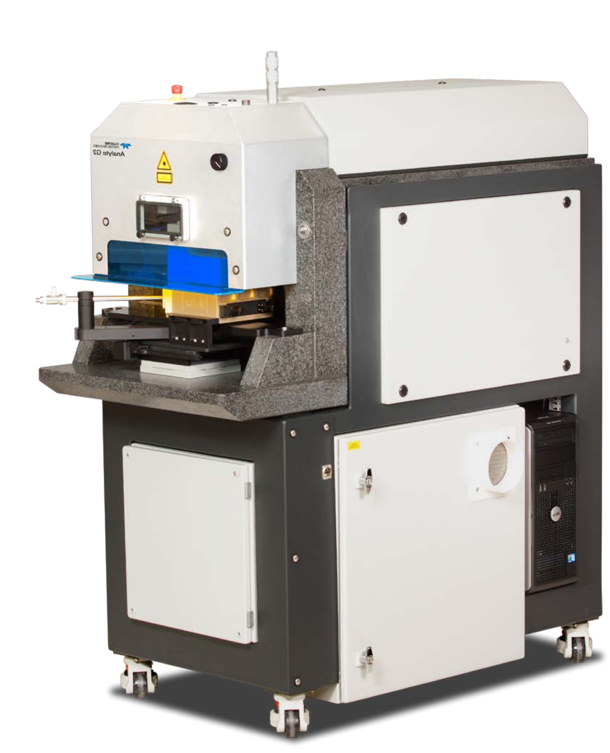
The extra sensitivity of the Element XR would allow a 8 µm spot size to have equivalent counts to a 35 µm spot size on a quadrupole ICP-MS. Just a 2.5 µm spot size with the Element XR would give the same signal as a 35 µm spot size on an ICP-TOF-MS (Table 2).

Table 2. Approximation of spot sizes which would result in equivalent number of counts for LA-ICP-MS.

	Approximate Equivalent Spot Sizes (µm)					
TOF-ICP-MS	10	20	35	50	80	100
Q-ICP-MS	3	6.5	11	16	25	32
SF-ICP-MS (Jet Interface)	0.8	1.5	2.5	3.5	5.5	7.0

The high sensitivity of the Element XR with the Jet Interface is complemented by its high-performance ion detection system which automatically switches between three detection modes to increase the dynamic range by three orders of magnitude over that of a single SEM.

The fast scanning (settling time ≈ 1 ms) electrostatic analyzer of the Element XR can cover a wide mass range: for LA-ICP-MS U-Pb analysis ^{202}Hg to ^{238}U can be measured without changing the settling mass of the magnet. The increased sensitivity from the Jet Interface was demonstrated to result in a twofold reduction in uncertainty on the ^{207}Pb/^{206}Pb ages for the same ablation conditions when compared to the iCAP TQ (Figure 3).



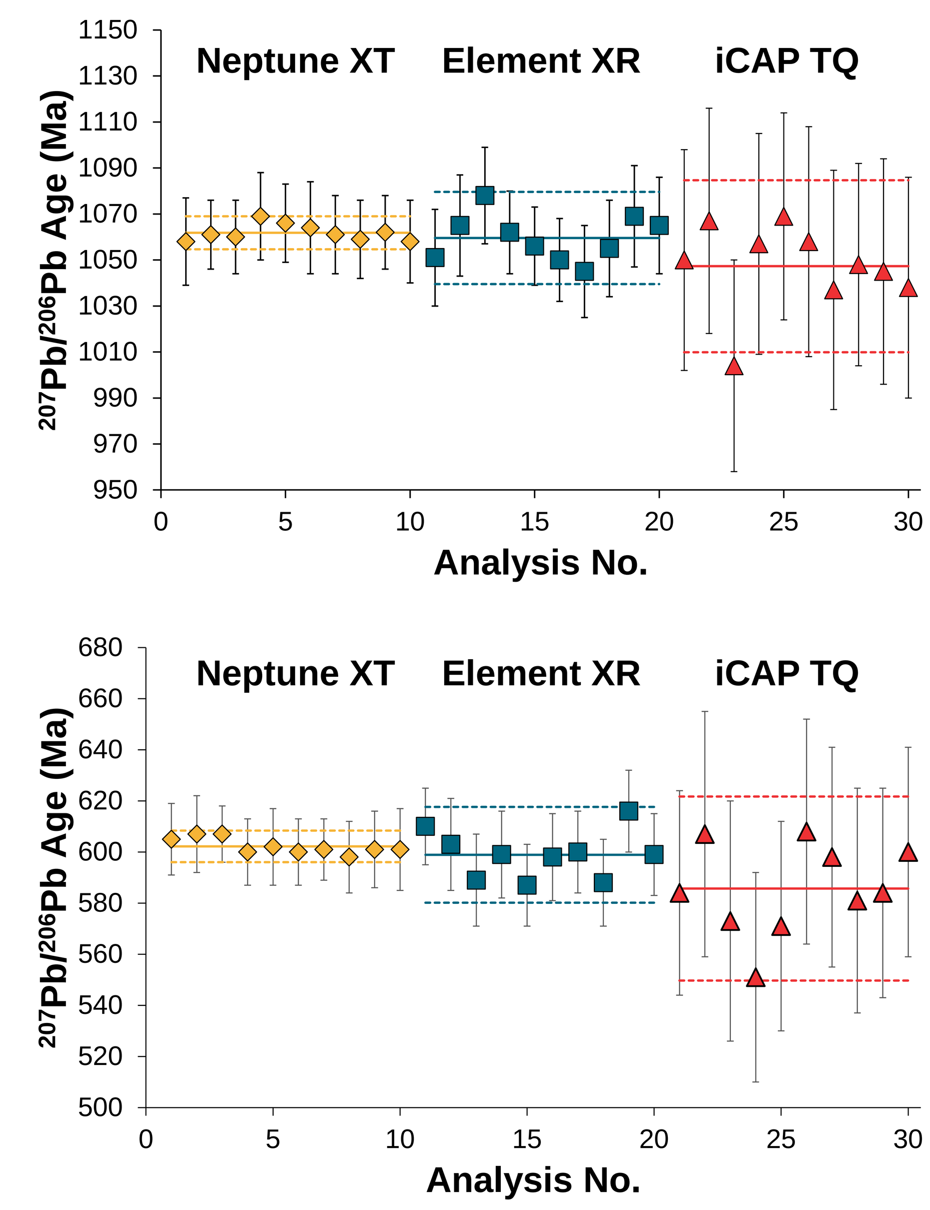


Figure 3. ^{207}Pb/^{206}Pb Age determination for ten replicate 35µm diameter, 3 J cm^{-2} 7 Hz repetition rate, 30 second duration ablations of two common reference zircons. Top: 91500 and Bottom: GJ-1. Internal error bars 2SE, external error bars 2SD. All data processing was carried out in Iolite™ v3.63. For both reference zircons the increased sensitivity of the Element XR with the Jet interface over the iCAP TQ improved the precision and accuracy of the measured age.

CONCLUSIONS

The Jet Interface for the Element XR SF-ICP-MS gives:

- Sample Ion Yield >1% for Nd, Hf, Pb and U.
- Over 20 times LA sensitivity compared to Q-ICP-MS

REFERENCES

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