ICP-oTOFMS
TECHNICAL NOTES

The advantages of orthogonal acceleration in ICP time-of-flight mass spectrometry

ICP-oTOFMS

Introduction

In recent times, there has been a large amount of interest in time-of-flight mass spectrometry for elemental analysis, in particular ICP-MS, due to the advent of suitable high speed data processing electronics. Time-of-flight mass spectrometry offers significant advantages for ICP-MS analysis due to the high rate of spectral acquisition and simultaneous sampling of the ion source. The use of a time-of-flight mass analyser provides 30,000 full mass spectra per second, high rate of sample throughput, simultaneous sampling from the plasma for high precision isotopic ratio analysis, and true multi-element transient analysis.

There are two general geometries, with a variety of different approaches, which can be used to modulate the continuous ion beam from the plasma source, namely orthogonal acceleration and on-axis acceleration. The principle of orthogonal acceleration is to apply an accelerating potential orthogonally to the primary continuous ion beam from the plasma source. This is shown schematically in Figure 1. The on-axis geometry involves modulation of the ion beam and the extraction and accelerating potentials are applied axially or co-axially to the beam. This is shown schematically in Figure 2.

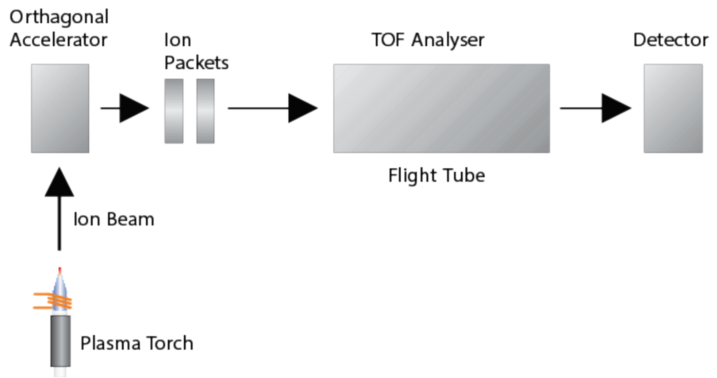

Figure 1: Schematic of an orthogonal acceleration time-of-flight mass analyser

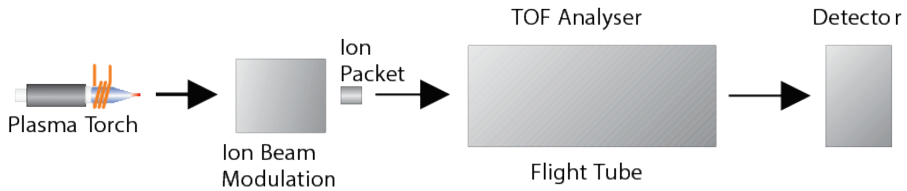

Figure 2: Schematic of an on-axis acceleration time-of-flight mass analyser

OptiMass 9500/9600 ICP orthogonal acceleration time-of-flight mass spectrometer

The OptiMass 9500/9600 incorporates an orthogonal acceleration time-of-flight mass spectrometer and a general schematic of the instrument is given in Figure 3. The continuous ion beam is chopped by an orthogonal accelerator. A push out pulse supply is coupled to the accelerator for providing repetitive push-out voltages at a frequency of 30 kHz. The ion packets that are sliced out of the beam then travel within the field free space towards the SMARTGATE ion blanker. Orthogonal accelerator parameters are set to enable temporal-spatial focussing at the SMARTGATE ion blanker, so that iso-mass ion packets are resolved in time. Any ion packets of unwanted species are ejected from the direction of travel by supplying pulsed voltages onto the deflection plates of the SMARTGATE. The ions to be measured are let through SMARTGATE and travel further down the field free space, to enter the ion reflectron. The ion reflectron increases the resolution of the mass spectrometer by means of temporal-energy focussing. After reflection, the ions travel within the field free space towards the discrete-dynode detector.

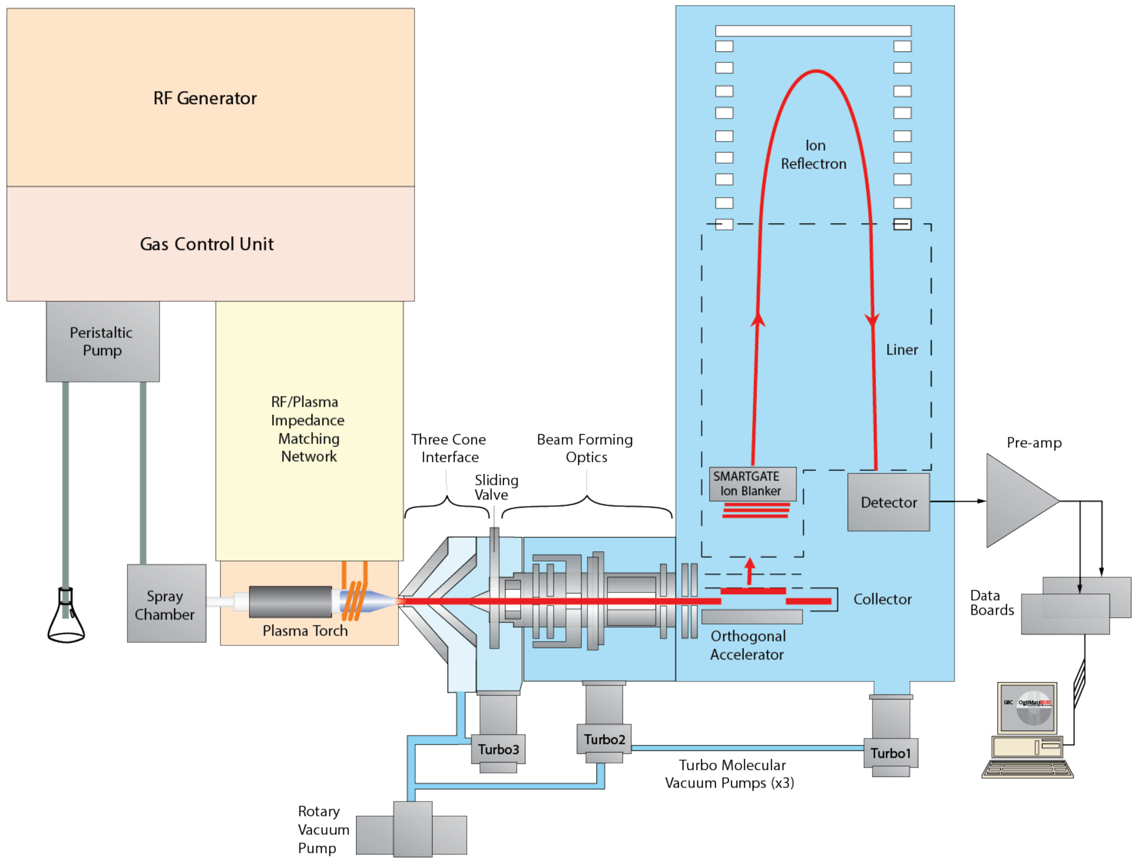

Figure 3: Schematic of the OptiMass 9500/9600 (octopole collision cell not shown) ICP time-of-flight mass spectrometer

Orthogonal acceleration provides superior resolution

In comparison to other acceleration geometries used in elemental time-of-flight mass spectrometry, the OptiMass 9500/9600 orthogonal acceleration geometry ultimately leads to superior resolution. As the energy spread is about three orders of magnitude lower in the time-of-flight direction for an oaTOFMS in comparison to an on-axis system, aberrations acquired in the initial stages of acceleration are much lower. As a result the orthogonal acceleration scheme provides superior resolution at the first spatial focus point and the detector.

The orthogonal acceleration time-of-flight analyser of the OptiMass 9500/9600 is able to provide resolution of at least 1800 at mass 238. Figures 4 and 5 show the typical resolution of the OptiMass 9500/9600 at masses 205 and 238.

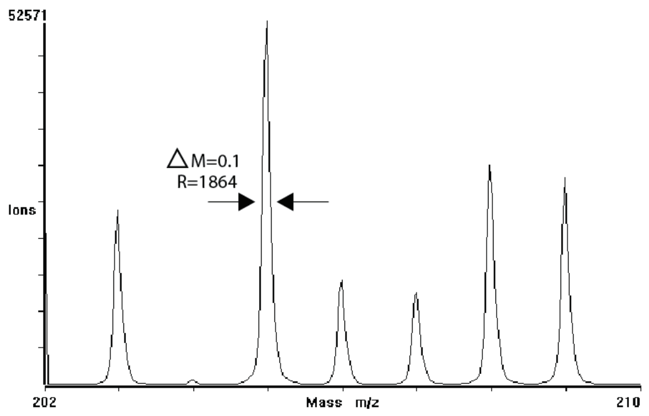

Figure 4: Typical resolution of the OptiMass 9500/9600 at mass 205

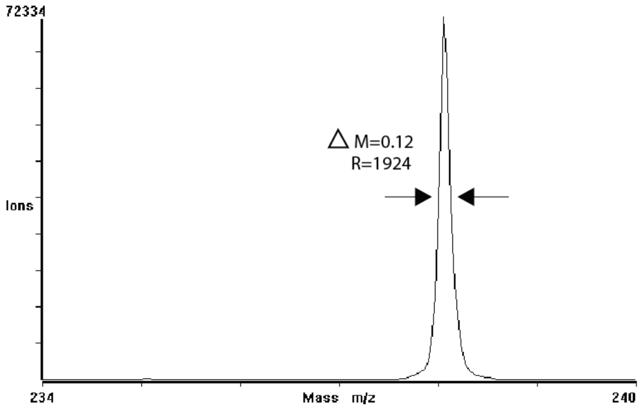

Figure 5: Typical resolution of the OptiMass 9500/9600 at mass 238

As the orthogonal acceleration scheme utilises an ion beam of a much lower energy spread in the time-of-flight direction, the higher order spatial focussing will also provide better peak shapes and greater abundance sensitivity.

SMARTGATE provides superior resolution for unwanted ion species rejection

Resolution at the point of spatial focus is very important as this determines the effectiveness of ion blanking. The OptiMass 9500/9600 has superior mass resolution at the spatial focus point when compared to the on-axis geometry.

Figures 6–8 shows the effectiveness of the SMARTGATE ion blanking system of the OptiMass 9500/9600. Figure 6 is a full mass range scan without ion blanking, whilst Figure 7 shows the effective elimination of Ar to approximately 2 ppb equivalent with the SMARTGATE ion blanker. The data in Figure 8 shows the elimination of 10 ppm sodium at mass 23 whilst allowing measurement of masses 24, 25 and 26 of Mg at sub-ppb level.

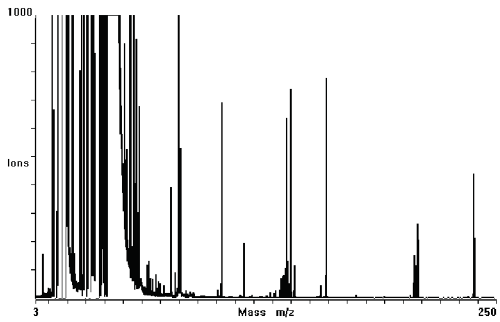

Figure 6: Full mass range scan with SMARTGATE off

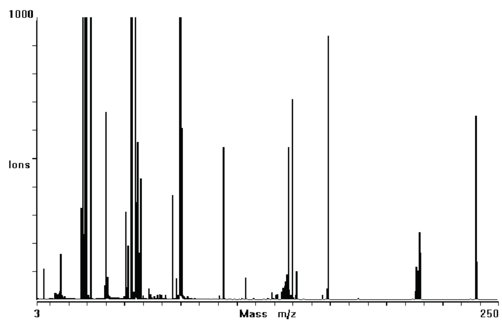

Figure 7: Full mass range scan with SMARTGATE off on showing the effective elimination of Ar species, Ar is eliminated approximately 2 ppb level

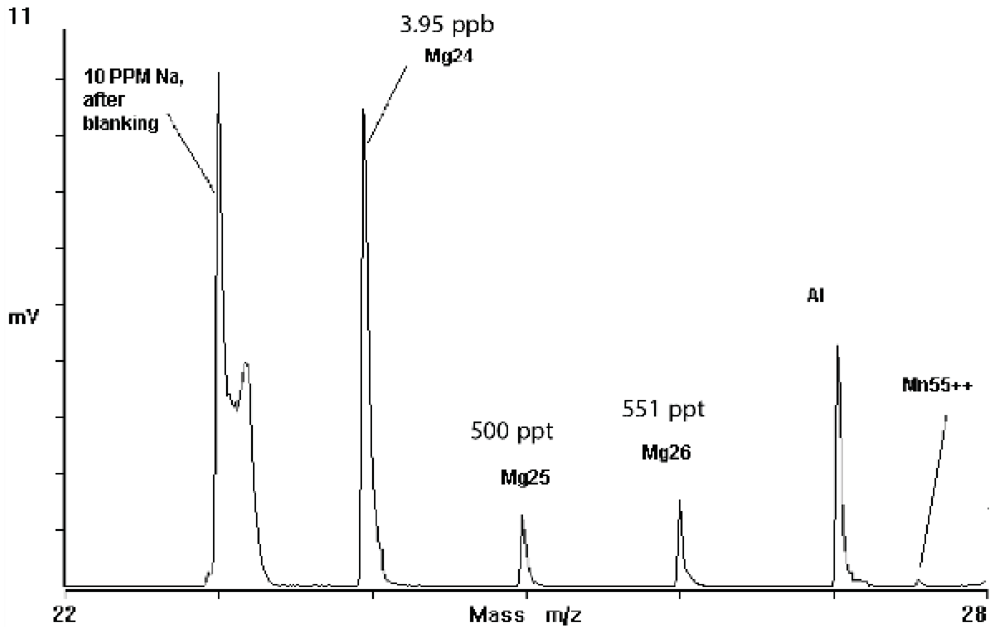

Figure 8: Effective elimination of 10 ppm Na at mass 23 whilst allowing measurement of Mg at sub-ppb level

Orthogonal acceleration reduces space charge effects

The beam forming optics of the OptiMass 9500/9600 utilise high voltages (up to –1500 V) to minimise space charge effects caused by highly abundant argon ions present in the continuous ion beam extracted from the plasma. The high duty cycle of the orthogonal acceleration scheme is achieved by extracting a long portion of the continuous ion beam for time-of-flight analysis. To achieve a similar duty cycle, the on-axis geometry has to operate at much lower voltages and effectively trap the ions between the grids at an energy of just several volts. Space charge effects caused by high Ar + current are much more severe in this case, broadening the ion packets in the spatial focus point, effecting resolution and the mass response.

Orthogonal acceleration provides lower background levels and superior detection limits

As discussed previously the OptiMass 9500/9600 delivers a high duty cycle and thus the on-axis acceleration system suffers from high background levels induced by the abundance of neutral species entering the analyser. In the orthogonal acceleration geometry, neutral species are prevented from entering the analyser and contributing to the background. This typically lowers the contribution of the background level to only 1–3 counts per second across all mass channels. This reduced background in combination with the high duty cycle of the OptiMass 9500/9600 patented orthogonal acceleration time-of-flight analyser ultimately provides superior detection limits when compared to the on-axis geometry.

Table 1 lists the typical detection limits for a range of elements achieved simultaneously from a 10 s acquisition with the OptiMass 9500/9600.

Element	**Detection Limit (ng/L)**
V, Mn, Co, Rb, Sr, Y, Zr, Nb, Rh, Ag, In, Sc, Ba, Ce, Tb, Ho, Ta, Pb, Bi, U	<1 ng/L
Li, Mg, Al, Ti, Cu, Ga, Mo, Pr, Nd, Re, Pt, Au	<10 ng/L

Table 1: Typical detection limits achieved simultaneously from 10 s acquisition with the OptiMass 9500/9600

Conclusion

ICP Time-of-Flight Mass Spectrometry offers significant benefits due to the high speed of spectral acquisition and simultaneous sampling of the plasma source. There are two typical geometries employed in a time-of-flight mass analyser and of these the orthogonal acceleration geometry offers significant advantages over the on-axis geometry. These include:

- Superior resolution; at least 1800 at mass=238.
- Higher abundance sensitivity as a result of superior resolution.
- Unit mass resolution for rejection of unwanted species with the SMARTGATE ion blanker.
- Lower background levels and high duty cycle for superior detection limits.

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