

ICP-oTOFMS

TECHNICAL NOTES

The advantages of time-of-flight mass spectrometry for elemental analysis



ICP-oTOFMS



Introduction

ICP-MS is a powerful technique that provides almost complete elemental and isotopic analysis for a diverse range of samples. Since the release of the first commercial ICP-MS instrument in the early 1980's, the technique has gained wide acceptance in a vast range of disciplines including the analysis of environmental, biological, nuclear, geological and industrial samples.

Until now the most common commercially available ICP-MS instruments have utilised quadrupole mass analysers. A diagram of a typical quadrupole mass analyser is shown in Figure 1. DC and RF voltages are applied to each pair of rods and for a given set of DC and RF voltages, ions of a particular mass to charge (m/z) ratio will have a path through the rods and strike the ion detector. For multi-element analysis, the applied voltages may be changed continuously to obtain the mass spectrum or rapidly changed between discrete values (peak hopping) for the selected masses of interest.

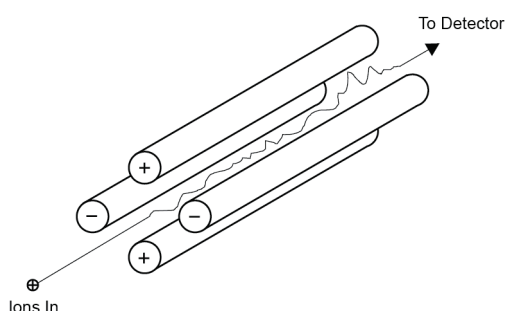


Figure 1: General schematic of a quadrupole mass spectrometer

The nature of a quadrupole based instrument means they can be considered as scanning mass spectrometers. This characteristic of the quadrupole mass spectrometer has serious limitations for elemental analysis due to its slow sequential nature. The speed limitation of quadrupole based ICP-MS instrumentation is responsible for a number of weaknesses of the technique including limited precision at high speed and for a large number of elements, low sample throughput for full mass range analysis and limited capability in handling transient samples for multi-element analysis.

Table 1 details some of the major strengths and weakness of currently available commercial ICP-MS instrumentation based on quadrupole technology.

Strengths of ICP-MS	Weaknesses of ICP-MS
Sub ppt detection limits	Speed of spectral acquisition
Wide dynamic range: typically 10^{-7}	Limited precision at high speed
Wide elemental coverage	Limited precision for isotopic ratios
Isotopic information	Multi-element transient signal capability
Reasonable precision: typically <5%	High cost per analysis

Table 1: Strengths and weaknesses of currently available commercial quadrupole ICP-MS instruments

The GBC OptiMass 9500/9600 ICP Time-of-Flight Mass Spectrometer overcomes many of the major limitations associated with scanning quadrupole based ICP-MS instrumentation. This new ICP-MS incorporates an orthogonal acceleration time-of-flight mass spectrometer (oaTOFMS). A general schematic of an ICP-oaTOFMS is shown in Figure 2. In a time-of-flight mass analyser, all ions that contribute to the mass spectrum are accelerated into a flight tube at the same time, and the mass is related to the time taken to reach the ion detector. The relationship between

mass and time is:

$$t = K \times \sqrt{M}$$

Where t is the time taken to reach the detector, K is a constant and M is the mass. A schematic of the OptiMass 9500/9600 ICP Time of Flight Mass Spectrometer is shown in Figure 3.

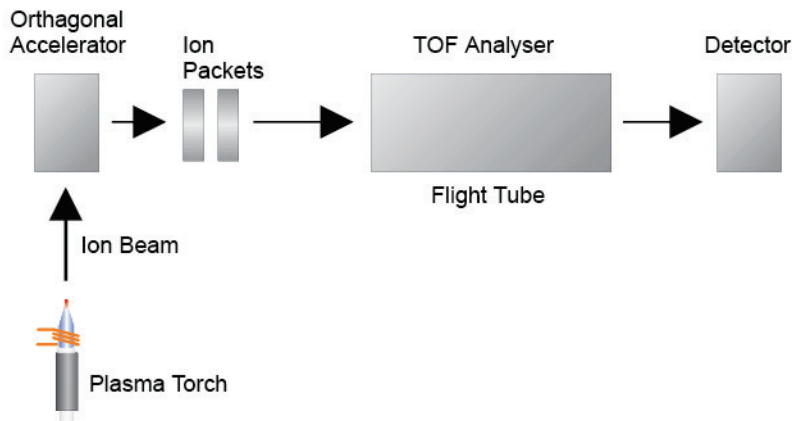


Figure 2: Schematic of an orthogonal acceleration time-of-flight mass analyser

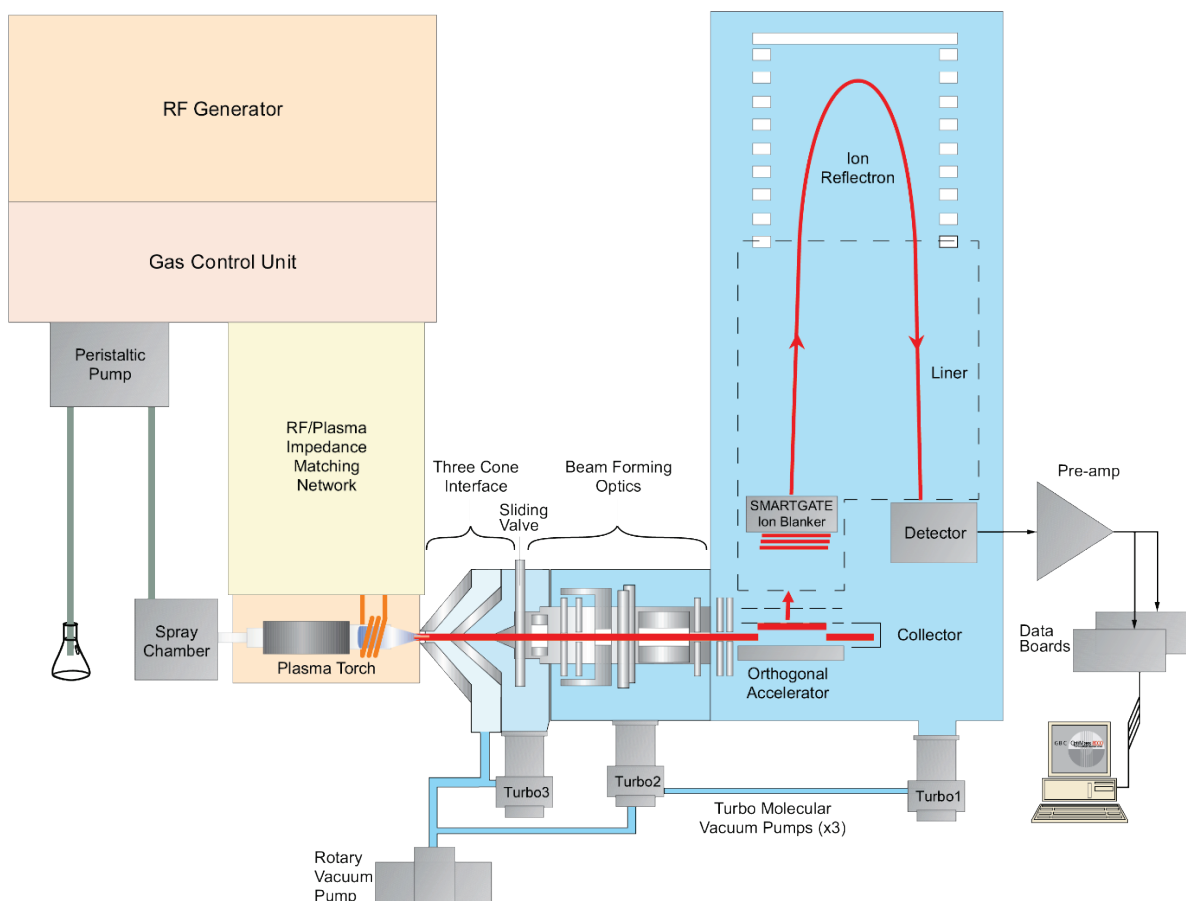


Figure 3: Schematic of the OptiMass 9500/9600 (octopole collision cell not shown) ICP time-of-flight mass spectrometer

The true advantage of a time-of-flight mass spectrometer is high speed and simultaneous sampling mass analysis. The entire mass spectrum can be collected in less than 30 μ s, which equates to 30,000 full mass spectra per second. Whilst the entire mass spectrum is collected in less than 30 μ s, all ions detected during this time are sampled from the source simultaneously,

i.e., there is no time skew between masses during plasma sampling. This high rate of spectral acquisition and simultaneous sampling, inherently overcomes a majority of the limitations of a quadrupole based spectrometer and ultimately leads to higher sample throughput, improved precision at high speeds and for ratio analysis, and provides true multi-element transient analysis.

No compromise on detection limits or precision for full mass range analysis

The fact that only a single mass channel can be measured at any one time with a quadrupole instrument means there is always a compromise that needs to be made between mass range, detection limits, precision of the result, and the measurement time. If the required analysis is at detection limit levels or requires high precision, either the number of masses measured must be limited or the overall measurement time must be increased.

Whereas, if a large number of elements must be determined in a sample and sample volume is limited or speed of analysis is an issue, the achievable detection limit and precision of the result must be sacrificed.

The OptiMass 9500/9600 does not suffer from this compromise. As all masses are measured simultaneously, the required measurement time, achievable detection limits and precision of the result remain the same regardless of the number of masses that need to be measured.

The no compromise speed advantage of the OptiMass 9500/9600 compared to a typical quadrupole based instrument is clearly shown in Figure 4. This figure is a plot of equivalent concentration of the analyte giving 10:1 signal-to-noise ratio versus number of elements measured for an 0.1 s measurement time, for the OptiMass 9500/9600 and a typical quadrupole instrument. For 30 elements, a typical quadrupole can only achieve lower working limits of the order of several parts per billion, whereas for the OptiMass 9500/9600, the lower working limit is tens of parts per trillion, regardless of the number of elements measured.

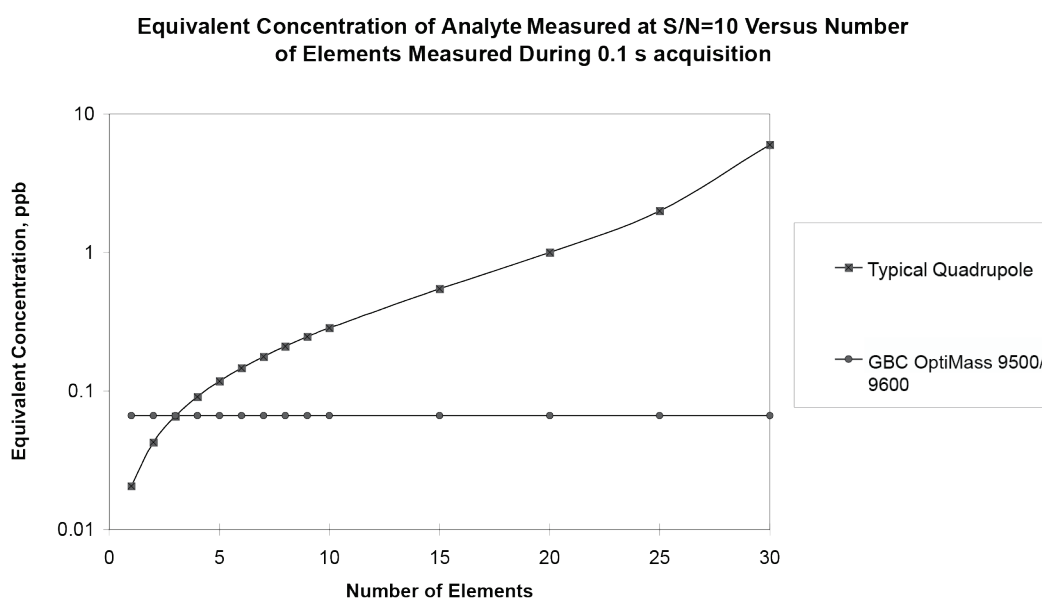


Figure 4: Effect of the number of elements measured in an 0.1 s acquisition time on the lower working limit for the OptiMass 9500/9600 and a typical quadrupole instrument

Higher sample throughput even at detection limit levels

Detection limits equivalent to those achievable with a quadrupole instrument can be achieved with the OptiMass 9500/9600 on the entire elemental mass range within 10 seconds. A typical quadrupole instrument will take 2 to 3 minutes to achieve ppt detection limits for multiple

elements. The high speed of the OptiMass 9500/9600 allows higher sample throughput at detection limit levels with the use of conventional sample introduction systems, and can routinely achieve a sampling rate of two samples per minute for the entire elemental mass spectrum.

The high sample throughput of the OptiMass 9500/9600 compared to a typical quadrupole is shown in Figure 5. This is a plot of sample throughput versus the number of elements measured given a 10 s measurement time for the OptiMass 9500/9600 and a 3 s measurement time for the typical quadrupole instrument. These measurement times are indicative of those required in order to measure at levels approaching the lower working limit.

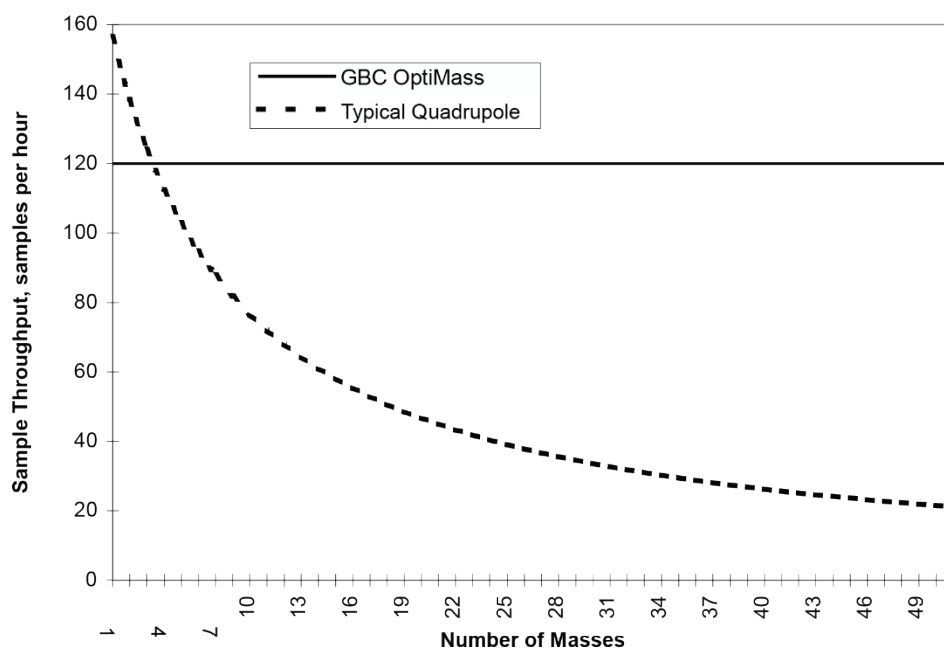


Figure 5: Effect of the number of elements measured on a sample throughput for the OptiMass 9500/9600 and a typical quadrupole instrument

Table 2 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 2: Typical detection limits achieved simultaneously from a 10 s acquisition with the OptiMass 9500/9600

Simultaneous mass analysis yields improved precision for ratioing methods

The most dominant source of imprecision and drift in ICP-MS arises from sample introduction and low frequency plasma noise. The use of ratio methods, such as internal standardisation or isotopic ratios, is used to overcome these instabilities. The ability of a quadrupole-based system to adequately compensate for these fluctuations is limited by the scanning nature of a quadrupole instrument. In order to effectively use ratioing methods to compensate for sample introduction and plasma noise and to achieve high precision, the isotopes being measured need to be sampled and measured simultaneously. The scanning nature of a quadrupole prevents the simultaneous measurement of isotopes, whereas the time-of-flight mass analyser of the OptiMass

9500/9600 offers the advantage of simultaneous determination. A quadrupole based ICP-MS is not only limited in precision due to the non-simultaneous sampling from the plasma, but is restricted to a single isotopic pair in order to achieve reasonable precision. The OptiMass 9500/9600, due to simultaneous sampling, can achieve precision which approaches the statistical limit for any number of isotopic pairs. Table 3 lists typical ratio precisions for a range of isotopes based on a single 10 s acquisition.

Ratio	Precision %	Statistical Limit %
$^6\text{Li}/^7\text{Li}$	1.12	1.11
$^{100}\text{Ru}/^{102}\text{Ru}$	0.9	0.83
$^{101}\text{Ru}/^{102}\text{Ru}$	0.92	0.80
$^{110}\text{Cd}/^{113}\text{Cd}$	1.09	1.07
$^{135}\text{Ba}/^{137}\text{Ba}$	1.06	1.01
$^{206}\text{Pb}/^{207}\text{Pb}$	0.71	0.60
$^{206}\text{Pb}/^{208}\text{Pb}$	0.56	0.52

Table 3: Typical ratio precision achieved simultaneously from a 10 s acquisition

Full mass range data always available

Prior to analysis, the user has to select the masses they wish to analyse with a quadrupole based system, and this limits the amount of spectral information available for a given sample. This is particularly true when the instrument is used in peak hopping mode. This lack of spectral information can potentially lead to erroneous results if one of the analyte masses is effected by interference. Even if the user has the experience to recognise that interference has affected the result, the analysis would need to be repeated with additional masses selected to correct for the interference.

On the other hand, the OptiMass 9500/9600 provides full mass range coverage with full profiles and so complete spectral information is available for every sample measured. The availability of the entire elemental mass range can be a great asset in the deconvolution of spectral interferences and also means that a sample should never need to be analysed twice. As there is no need to perform “peak hopping” with the OptiMass 9500/9600, full peak shape is measured at all times which allows peak shape analysis.

Multi-element transient capability

The simultaneous nature of the OptiMass 9500/9600 is also ideally suited for the analysis of transient signals as the entire mass range can be measured in less than 30 ms. This high speed data collection enables transient signals generated from, for example, single shot laser ablation (LA), electrothermal vaporisation (ETV), gas chromatography (GC), liquid chromatography (LC) or flow injection, to be sampled 30,000 times per second and fifty integrated full mass spectra to be displayed per second. Separation techniques such as GC and LC in combination with the OptiMass 9500/9600 offer great potential for speciation studies.

There are significant advantages to be gained by coupling a laser ablation system to the OptiMass 9500/9600. Not only can full elemental coverage be obtained from each single laser pulse allowing direct multi-element analysis with spatial resolution in solid samples, but noise introduced from fluctuations in the laser signal can be significantly reduced by using ratio techniques. A quadrupole-based system is limited in the number of masses that can be measured from transient signals preventing full elemental coverage and limiting the use of ratioing techniques.

Coupling the OptiMass 9500/9600 to an electrothermal vaporisation system can potentially overcome some of the isobaric interferences that are prevalent in quadrupole based ICP-MS. The temperature dimension of ETV and the high spectral acquisition speed can be used to overcome atomic overlaps by resolving them in the temperature domain, and the use of an ETV can greatly reduce the effect of solvent derived molecular interferences. Quadrupole based systems are limited in this regard due to the limited number of masses that can be measured within the transient signal time period.

Figure 6 demonstrates the multi-element capability of the OptiMass 9500/9600 interfaced to an ETV system.

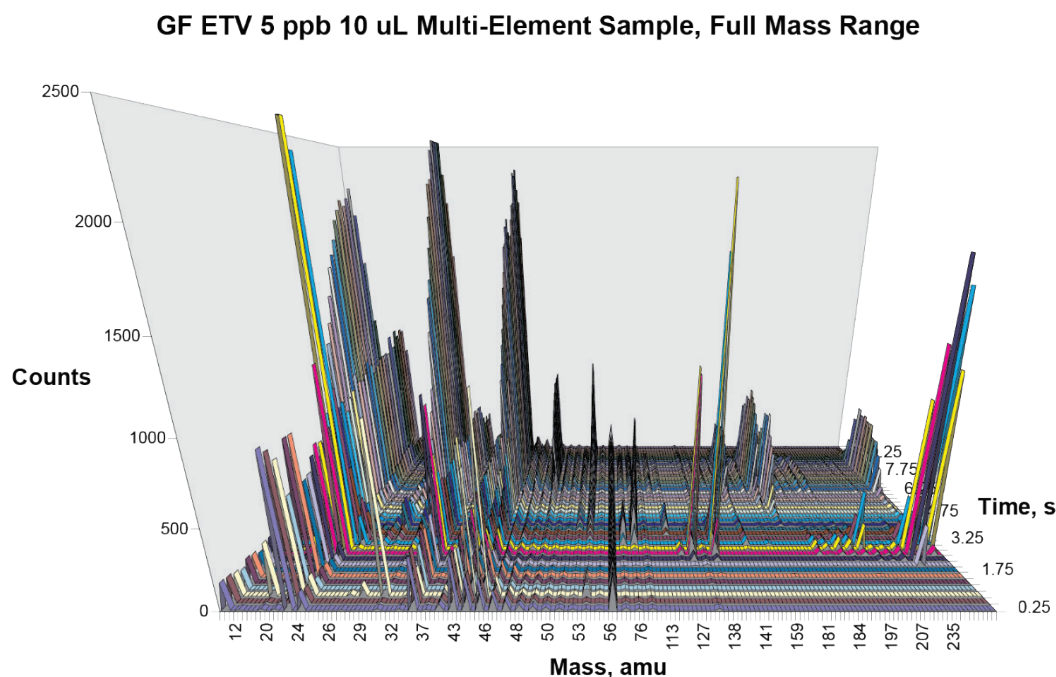


Figure 6: Full elemental mass range, transient data from an ETV system coupled to the OptiMass 9500/9600

Conclusion

Whilst, ICP-MS is a well-established technique in a diverse range of applications, there are still a number of significant weaknesses which arise from the scanning nature of traditional quadrupole based ICP-MS. The OptiMass 9500/9600 through its time-of-flight mass analyser provides both high speed and simultaneous mass analysis, which overcomes most of these limitations.

The GBC OptiMass 9500/9600 offers a range of features and user benefits that quadrupole-based instruments cannot offer. These include:

- Simultaneous measurement of the entire elemental mass spectrum; 30,000 full mass spectra per second.
- High sample throughput with determination of the entire mass range.
- Multi-element transient analysis; sampling rate of 30,000 full mass spectra per second; display rate of 50 integrated full mass spectra per second.
- Simultaneous internal standardisation.
- Simultaneous isotope ratios for all elements with better than 0.1%RSD.