Laser Ablation with the icpTOF: Sensitive, Simultaneous Analysis of All Isotopes

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icpTOF provides

- Accurate results for even the shortest LA signals
- Fast, simultaneous measurement of all isotopes ensures that small sample features are never missed
- Lower limits of detection, better isotope ratio precision, and higher effective sensitivity for multi-element analysis than QMS-based systems
This study describes the performance and key advantages of the TOFWERK icpTOF mass spectrometer (MS) over quadrupole MS for Laser Ablation (LA) applications.

LA-ICP-MS

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is well established technique for the direct elemental analysis of solid samples. In contrast to liquid-based analysis it offers much higher lateral resolution and requires no sample preparation. Briefly, the sample is placed inside an air-tight chamber and a small volume of the sample is removed (ablated) by a pulsed laser beam. The generated aerosol plume is transferred into the ICP with the flow of helium. Commonly, the sample is either scanned (laser beam is moved across the surface) or ablated on a single spot basis. Signal variations in LA can be as short as a couple of milliseconds arising either from large individual particles or individual laser pulses, provided the cell has fast aerosol washout. Element concentrations are calibrated against certified and closely matrix matched standard reference material (SRM) after correction of LA-ICP-MS signals for differences in ablated mass between the SRM and the sample by normalizing to an element of known concentration (internal standard). If an internal standard is not available, but all elements representing the sample matrix are measured, instrument response can be calibrated from SRM and mass transport can be calculated by a 100% normalization procedure. [1]

Sequential detection in LA-ICP-MS

Sequential mass analyzers based on quadrupole or scanning sector-field technology are used for the majority of LA applications. The user defines a preselected list of isotopes to measure. Isotopes are sequentially measured, one at a time, such that it requires at least a few hundred milliseconds to acquire an entire mass spectrum (cycle) [2]. If aerosol composition or mass changes within the duration of a cycle, sequential detection will bias the result. Even more importantly, the “limited” sample volume is divided (segmented) between all measured isotopes, thereby drastically reducing the effective sensitivity if many isotopes are monitored. In practice, the user has to design the experiment carefully in order to find the best tradeoff between signal duration, the number of measured isotopes, and sensitivity. For these reasons, mass spectrometers which detect all isotopes simultaneously are very attractive for LA-ICP-MS applications, since they do not suffer from this tradeoff and don’t require setting up the measurement list prior to the analysis.

TOFMS in ICP-MS

A time-of-flight (TOF) mass analyzer detects all isotopes simultaneously and has long been proposed as a more suitable detector for LA applications. To date, though, ICP-TOF mass spectrometers have had poor sensitivity and other drawbacks due to imperfections in design and slow acquisition electronics, which are critical components of TOF technology. Also, because of limited linearity, ICP-TOFMS data analysis has required correction procedures for isotope- and element-ratios, ultimately leading to poor quantitative results [3, 4]. As a result of these problems, ICP-TOFMS has struggled to gain wide acceptance as an alternative to well-established quadrupole and sector-field MS.

The data presented in this paper demonstrates that the TOFWERK icpTOF overcomes the problem of sensitivity and provides the linear dynamic range of up to 10⁶.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>iCAP Q</th>
<th>icpTOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP power</td>
<td>1400 W</td>
<td>1450 W</td>
</tr>
<tr>
<td>Nebulizer gas flow rate</td>
<td>0.5 l/min</td>
<td>0.7 l/min</td>
</tr>
<tr>
<td>Ablation/He gas flow rate</td>
<td>1 l/min</td>
<td>1 l/min</td>
</tr>
<tr>
<td>Number of measured isotopes</td>
<td>58</td>
<td>Full mass spectra</td>
</tr>
<tr>
<td>Dwell/integration time</td>
<td>10 ms</td>
<td>30 or 300 ms</td>
</tr>
<tr>
<td>Cycle time (time per readout)</td>
<td>877 ms</td>
<td>30 or 300 ms</td>
</tr>
<tr>
<td>Relative integration time per isotope</td>
<td>1.1 %</td>
<td>100 %</td>
</tr>
</tbody>
</table>

Table 1. Operating conditions of the iCAP Q and icpTOF.

Experimental

Equipment and materials

Experiments were carried out with a Thermo iCAP Q (Thermo, Bremen, Germany) and a TOFWERK icpTOF (TOFWERK, Thun, Switzerland) in order to directly compare performance.

These instruments have the same plasma interface and ion optics, and both were coupled to the NRW213 laser ablation system equipped with the TwoVol2 cell (ESI, Portland, USA). The operating conditions are shown in Table 1. The standard reference material (SRM) NIST610 was used to characterize the figures of merit. LA was performed with 40 µm spot size, at 10 Hz, scanning over NIST610 with 5 µm/s at 7 l/cm² fluence.

Data evaluation

Sensitivity (S_eff(î)) and limits of detection (LOD) were calculated [5] using SRM NIST610 concentrations from ref. [6] and Equations 1-3.

\[
LOD = \frac{1}{S_{eff}} \left[ 3.29 \times \sigma_{eff} + 2.72 \right] \tag{1}
\]

\[
S_{eff}(î) = \frac{t_î}{\sum t_î} \times S(î) \tag{2}
\]

\[
\sigma_{eff}(î) = \frac{t_î}{\sum t_î} \times \sigma(î) \tag{3}
\]

where \(\sigma(î)\) is 1 standard deviation of the background measurement in counts per second (cps), \(S(î)\) is the sensitivity in

* There are some debates in the scientific community whether TOF should be called simultaneous detection system, but quasi-simultaneous instead. TOF does not measure all the ions simultaneously but samples a package of all ions simultaneously. This sampling frequency is much higher than frequency of fluctuations from the source and sample introduction system. To avoid confusions we will use the term “simultaneous” for TOF.
cps/($\mu$g/kg) of the isotope $i$, $t_d(i)$ and $t_{set}(i)$ are the dwell and settling times (applicable for the quadrupole instrument). For the icpTOF $S_{eff} = S$ and $\sigma_{eff} = \sigma$.

The theoretical relative standard deviation (RSD) of isotope ratios was calculated from Equation 4.

$$RSD\% = \sqrt{\frac{1}{I_a} + \frac{1}{I_b}}$$

where $I_a$ and $I_b$ are the total number of counts per integration time (300 ms) of isotopes $a$ and $b$, respectively.

Results

icpTOF linear response

The detector linearity was tested measuring acidified Pt solutions using the standard liquid introduction system of the iCAP Q. Figure 1 demonstrates that the instrument response does not depend on the sample concentration.

![Figure 1. Sensitivity of 195Pt vs Pt concentration in the solution.](image)

Higher accuracy than with sequential MS

Quantification is one of the key advantages of LA-ICP-MS. Element concentrations are commonly calculated from ratios of a target element to internal standard in the sample and in the standard. Ideally, these ratios should represent the sample stoichiometry and should not be biased by laser ablation, plasma or detection processes. Here we will focus only on the effect of the mass analyzer on the ratio accuracy.

As an example of a sample with a high signal variation we ablated NIST610 with 2 Hz laser frequency. Figure 2 shows Sr and U traces and their respective ratios recorded with the icpTOF at a rate of 33 spectra/s (30 ms averaging time). Despite high signal variation, ratios remain stable, as expected for this homogenous standard. The data in Figure 3 simulate the same ratios recorded with a sequential mass analyzer. For this simulation, the icpTOF data, which has continuous time series for all isotopes, was processed following a method similar to standard QMS acquisition: 10 isotopes were sequentially measured for 30 ms each (dwell time) with no quadrupole settling time. This simulation shows that for rapidly changing signal intensities the element ratios are inaccurate due to the scanning effect. This scanning effect can always be minimized by reducing the dwell time and the number of measured isotopes or by stretching the signals. But all of these actions will lead to poorer performance. With the icpTOF laser parameters can be optimized independent of MS settings and even very short transient signals from small inclusions can be accurately quantified.

Higher precisions than with sequential MS

Even if the elemental composition of a sample is homogeneous a sequential scanning MS will be susceptible to multiplicative noise such as fluctuation in sample introduction or plasma flickering, which can skew the measured ratios. The icpTOF simultaneously samples all isotopes every 30 $\mu$s resulting in precisions which approach statistical limits. The precision of isotope ratios with the icpTOF at the operating conditions defined in Table 1 was evaluated from 60 s of the NIST610 signal. Table 2 shows that the measured standard deviations for three selected isotope pairs are very close to the theoretical values.

![Figure 2. Transient signals in counts/integration time of Sr and U and their ratios recorded with the icpTOF during 2 Hz laser ablation of the SRM NIST610 and the example of the mass spectrum recorded at 43.8 s. Element ratios do not change despite significant signal variation. Red box shows the integration window for one laser pulse, which produced 5200 counts.](image)

![Figure 3. Transient signals of Sr and U and their ratios simulated from the icpTOF data shown in Figure 2. Signals are given in both cps (commonly reported by sequential instruments) and effective counts/integration time. Element ratios are inaccurate due to the scanning effect (10 isotopes were scanned in total). Sr and U are detected at different positions on the signal peak which biases the ratios. Red box shows the integration window for the same laser pulse as in Figure 2. Only 1000 counts were effectively detected.](image)
**Improved LODs for multi-isotope analysis**

This section compares the sensitivity and LODs of the icpTOF and the iCAP Q. To establish a fair comparison between the icpTOF and the quadrupole-based instrument we should understand the nature of detection in each.

In the given example, the iCAP Q measured 58 isotopes with 10 ms dwell time and needed 877 ms to go through one cycle. This means that each isotope was effectively measured only 1.1% of the time. The reported counts per second (cps) are extrapolated by the software. For example, a reading of 1000 cps of the ICP-QMS at the current conditions corresponds to only 11 counts really being recorded in 1 second. The icpTOF measures all isotopes simultaneously and continuously meaning that 1000 cps would represent the real number of counts collected in 1 s.

<table>
<thead>
<tr>
<th>Signal ratio</th>
<th>Measured RSD (%)</th>
<th>Theoretical RSD (%)</th>
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</thead>
<tbody>
<tr>
<td>$^{206}\text{Pb}/^{207}\text{Pb}$</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>$^{207}\text{Pb}/^{206}\text{Pb}$</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>$^{107}\text{Ag}/^{109}\text{Ag}$</td>
<td>1.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 2. Measured and theoretical RSDs of signal ratios of selected isotopes in NIST610 analyzed with the icpTOF. A complete mass spectrum was recorded every 30 μs for 60 seconds. Operating conditions are given in Table 1.

**Conclusions**

The icpTOF provides more flexibility for the analysis and in many cases also more information about the sample. No sample features will be missed as all isotopes are measured continuously. If many isotopes are to be analyzed, limits of detection are improved in comparison to quadrupole MS through higher effective sensitivity. Isotope ratios are not biased as in sequential detection and their precision is closed to statistical limits. Using the icpTOF, LA experiments are conducted without predefinition of the isotope list and without linking the optimization of LA conditions to the MS acquisition settings.

Moreover, due to the measurement of all isotopes, the icpTOF provides an opportunity to conduct matrix-independent standardless LA analysis as demonstrated earlier [7].

**References**


**Acknowledgement**

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