TOFpilot – An Integrated Control Software for the icpTOF that Enables High-Speed, High-Resolution, Multi-Element Laser Ablation Imaging in Real Time

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Introduction

Trace element imaging at the micrometer-scale using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become an important tool in geological, biological, and medical studies (e.g., Ubide et al., 2015; Van Malderen et al., 2017; Becker et al. 2007). Recent advances in laser ablation setups, including fast-washout ablation cells, have paved the way for rapid, high-resolution imaging (Gundlach-Graham et al., 2015; Burger et al., 2015). These faster laser sampling methods are especially efficient when combined with fast, multi-element mass analyzers, such as time-of-flight mass spectrometers (TOFMS) that allow for the detection of single laser pulses while recording the full mass spectrum simultaneously (e.g., Gundlach-Graham and Günther, 2016).

A limitation of such laser ablation imaging experiments, however, is that they are recorded essentially "blindly," because images only become visible after elaborate offline post-processing has been performed. This poses the risk of losing valuable analytical time and precious sample material. Here, we introduce TOFpilot – an integrated control software for the TOFWERK icpTOF and a laser ablation system – which enables the display of laser ablation images in real-time during the data acquisition process.

Analytical Setup

The icpTOF (TOFWERK AG, Thun, Switzerland) is an ICP-MS based on the iCAP RQ (Thermo Scientific, Bremen, Germany) equipped with a time-of-flight mass analyzer (Figure 1). The icpTOF can be coupled to different laser ablation systems for sample introduction. To date, the integrated control via TOFpilot has has been demonstrated with the NWR213 (Electro Scientific Industries – ESI) and the Analyte G2 (Teledyne CETAC Technologies) laser ablation systems.

Precise triggering was used in laser ablation imaging experiments to enable spot-resolved, single-pixel synchronization (Figure 2) (Bussweiler et al., 2017). For each laser pulse, a trigger signal is sent from the laser to the data acquisition PC to synchronize laser pulses, and to add timing information to the recorded signal. The trigger timing needs to be corrected for the delay between the laser firing and the arrival of the signal at the detector (= aerosol transfer delay). This delay is sample-specific and further depends on the ablation parameters, e.g., fluence and spot size, and, therefore, needs to be tuned before each experiment. If the aerosol transfer delay is larger than the difference between individual laser pulses, trigger signals would get lost in a simple “wait for next trigger” scheme. Therefore, the TOFpilot software features a hardware-based trigger delay function which shifts the timing not only of individual triggers, but of entire trains of triggers (Figure 3).

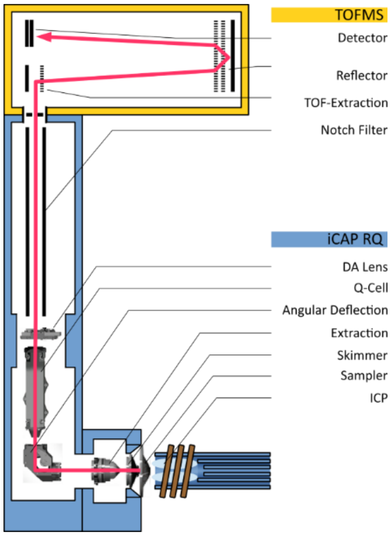

Figure 1 Schematic of the icpTOF. The primary ion beam (red arrow) travels from the ICP interface (blue frame) into the extraction zone of the TOFMS (yellow frame). From there, packets of ions are accelerated orthogonally into the field-free flight drift region at a frequency of 33 kHz. Gaining equal energy from this acceleration, different ions travel at different speeds related to their mass-to-charge ratio, with lighter ions travelling faster than heavier ions. The intensities of all mass-to-charge ratios (times of flight) are recorded at the detector, yielding a complete mass spectrum for each ion packet.

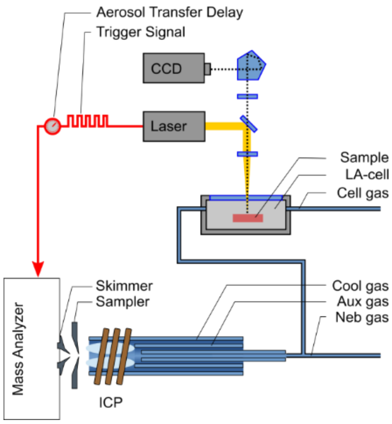

Figure 2 Schematic of precise triggering. Based on synchronized communication between the laser ablation system and the icpTOF (via a TTL cable) a trigger pulse is sent with every laser shot to start the data acquisition at the icpTOF. The delay time between ablation and detection (aerosol transfer delay) depends on the sample material and on the conditions within the ablation cell and must be calibrated prior to analysis.

In the example discussed here (imaging of a garnet crystal), the icpTOF was coupled to the Analyte G2 excimer laser (193 nm) equipped with a HelEx II cell and an Aerosol Rapid Introduction System (ARIS) (Teledyne CETAC Technologies). The fast washout achieved with this cell results in sharp ablation signals with low aerosol dispersion (<20 s signal width, ~10 ms at FWHM) which allows the laser to be fired at repetition rates of up to 100 Hz with minimal overlap of neighboring laser pulses (Figure 3). The advantage of this precisely triggered, spot-resolved approach is that there is no

Figure 3 Aerosol Transfer Delay Module in TOFpilot. The signal from a single laser pulse is shown (<20 ms). The delay can be shifted so that it is within the integration window accounting for pulse-to-pulse jitter.

smearing of pixels and no distortion of the final image.

TOFpilot Workflow

The TOFpilot software operates on a module-based workflow allowing for great user flexibility. The user can set up a sequence of separate items, e.g., from plasma startup and tuning (manual or automated), over data acquisition and display (e.g., laser ablation imaging), to basic data processing and export. Here, the “Laser Ablation Imaging Module” for real-time, multi-element imaging is described.

In the laser software, the user selects the desired laser ablation parameters, e.g., fluence, repetition rate, and spot size. The user then draws the image area of desired size and shape as a raster of side-by-side laser spots. Ideally, the laser spots should have a square shape to provide complete coverage of the image area.

On the icpTOF PC, the TOFpilot software will download all image data, e.g., x, y-coordinates and laser ablation parameters, and re-create a grid from the image coordinates. TOFpilot will then start the ablation and fill the grid with data from the icpTOF – pixel-by-pixel and line-by-line – thereby enabling real-time imaging. Since each pixel contains a full mass spectrum resulting from a single laser shot, the user can scroll through a drop-down menu of different isotopes and inspect the respective image. Furthermore, different display settings, such as color palette and gamma, can be selected during the construction of the image. The finished multi-element image can be exported for data post-processing.

Figure 4 shows the TOFpilot “Laser Ablation Imaging Module” as applied to a garnet crystal. Here, tuning of the aerosol transfer delay and measuring of the signal width determined that imaging could be

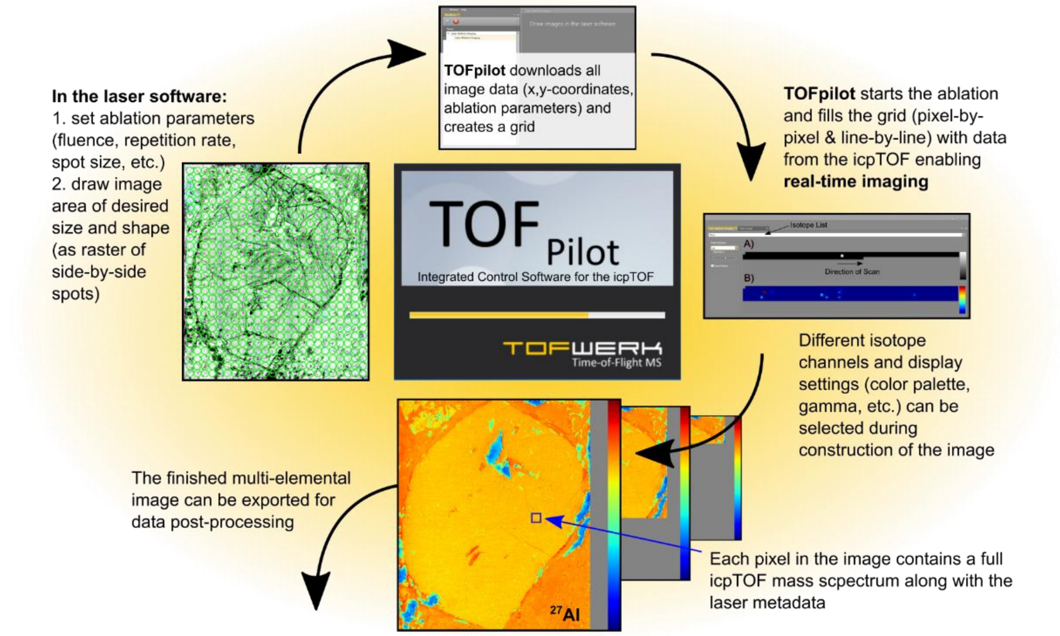

Figure 4 Workflow diagram for the Laser Ablation Imaging Module in TOFpilot. In this example, a 6 mm by 7 mm garnet crystal was imaged. The multi-element image was recorded at a laser repetition rate of 100 Hz, spot size of 20 µm, fluence of 3 J/cm2, and Dosage 1 (laser shots per pixel). Here only the 27Al image is shown. The entire range of elements was recorded simultaneously in ~55 min.

performed at 100 Hz with minimal overlap of neighboring pixels (Figure 3). Acquisition of the 6.1 mm by 7.3 mm multi-element image took less than one hour.

Summary and Outlook

The TOFpilot software greatly simplifies the workflow for the user by integrating the control over the laser ablation system and the icpTOF. Precise triggering enables real-time display of multi-element images, thereby reducing the risks associated with recording images “blindly”. Moreover, TOFpilot operates on a module-basis which allows the user to set up different workflow sequences. In the future, TOFpilot will provide the option to guide the user through the entire analytical session, i.e., from plasma startup and tuning, over data acquisition and display, to processing and export of (quantitative) data.

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