Elimination of Aliasing in LA–ICP–MS by Alignment of Laser and Mass Spectrometer

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Significance to JAAS

Laser ablation is an important technique for sampling of solid materials in the Earth and Life sciences. One of the fundamental problems with this technique is aliasing, an unwanted phenomenon which produces misleading signals and comes about due to insufficient sampling by sequential types of mass spectrometers of the periodic signal produced by the laser. We have developed a device that fires the laser in alignment with the measurement cycle of sequential ICP–MS instruments, thus eliminating aliasing, and allowing all quadrupole LA–ICP–MS analysis to be performed at higher spatial resolution by enabling the effective use of fast response ablation cells.

Abstract

Insufficient sampling of periodic signals results in an unwanted phenomenon known as aliasing. When measuring by LA–ICP–MS it is widely observed that aliasing between laser pulse rates and sampling by sequential ICP–MS instruments creates erroneous variations in the measured element concentrations in the sample. Smoothing the sample flow to the ICP–MS can largely eliminate this variation but reduces spatial resolution of the time-resolved signal and is thus detrimental for imaging with the increasingly popular fast response sample cells. We have developed a fire control circuit that fires the laser in alignment with the measurement cycle of the mass spectrometer to lessen or eliminate aliasing. We describe the device and show that with a conventional quadrupole ICP–MS the technique is able to maintain measurement precision when the extent of mixing between individual laser pulses is reduced by an order of magnitude.

Introduction

Laser ablation is a technique for sampling solid materials for analysis by ICP–MS that is well-established in the Earth and Life Sciences[1]. Most laser ablation instruments are equipped with a pulsed laser operating at wavelengths in the deep UV, and are commonly coupled to quadrupole mass spectrometers equipped with a single-detector. The design of the ablation cell, gas flows and ICP torch operating conditions, as well as the length and internal diameter of the transfer tubing between the ablation cell and the torch, collectively determine the response time of the system. Aerosol delivery during laser ablation occurs as a series of asymmetric pulses where the dominant frequency of the signal is determined by the firing rate of the laser, and the amplitude dictated by the response time of the system. An undesirable issue is that these instruments can be operated at conditions that produce aliasing (also called spectral skew[2]) where insufficient sampling of the periodic signal from the sample produces a modified copy (or *alias)* of the signal. The erroneous signal appears at a frequency

determined by the difference between the frequency of the periodic signal from the sample and the frequency of the sampling by the ICP–MS detector. Being well described by signal processing theory[3], aliasing is present whenever a time varying signal is sampled at a frequency below the Nyquist-Shannon sampling limit, being twice the frequency of the periodic intensity variation of the time resolved signal. A number of strategies are employed to mitigate aliasing, with a range of compromises to consider. Measurement of the signal at faster acquisition rates is impractical due to loss of efficiency when using short dwell periods (increased proportion of time the ICP–MS instrument spends setting acquisition parameters for the next analyte), and an increase in signal noise due to poor counting statistics, both of which result in a reduction to the number of masses that can be measured. Signal smoothing is effective at removing aliasing, but doing so diminishes spatial resolution and lowers maximum signal intensity. In practice, since infinite smoothing is not feasible, most users of LA–ICP–MS will be operating instrumentation with some degree of aliasing noise present, though it may be masked by other sources of uncertainty, such as counting statistics. Recent work[4,5,6] highlights a growing interest in low dispersion ablation cells with fast time responses, most notably their use for imaging elemental distributions within samples. Use of these ablation cells with sequential mass spectrometers shows that aliasing is a substantial problem for imaging applications[7] and to date operators have been forced to either accept aliasing in their results or implement workarounds[8,9], such as use of longer dwell times resulting in measurement of fewer masses, or smoothing by firing the laser at a faster repetition rate. These strategies are effective to varying degrees, but reducing the number of masses, or undoing the technical benefits of a fast response ablation cell by firing the laser faster to produce more shots per *sweep* (ICP–MS cycle), undermines the effectiveness of the technique. One definitive solution to avoid aliasing is to use a simultaneous mass spectrometer. Despite instruments utilising different technologies for simultaneous acquisition being available (e.g., Spectro MS[10], TOF MS[11]) their use is currently limited.

The solution that we present here is compatible with all sequential mass spectrometers, but has been developed and tested with a quadrupole ICP–MS instrument. Our approach is based on signal theory and modelling[3] that shows aliasing can be eliminated by maintaining a constant integer ratio between the laser firing period and the mass spectrometer sweep time. To achieve this, a fire control circuit has been designed and implemented that can monitor the mass filter position in real time and fire the laser in alignment with each sweep of the mass filter.

In order to assess the effectiveness of this approach, and to avoid confusion between signal aliasing and variations in sample composition, we have measured lead isotope ratios in homogeneous materials under different conditions and assessed the observed variance of the time resolved signals.

Experimental

Instrumentation

The fire control system was designed to integrate with any quadrupole mass spectrometer by connecting to the high voltage DC signal that drives the mass filter. The HV DC signal voltage varies with the position of the mass filter[12,13] and while the maximum voltage level varies with the size and

design of the quadrupole, most instruments that achieve 1 AMU resolution over the range 7–260 AMU use a maximum voltage of 500–1000 V DC. The quadrupole HV DC signal is intercepted (see Figure 1) using a custom wiring harness and connected to a high impedance (10^9 Ω) voltage divider before passing through a buffering instrumentation amplifier to an ADC. All processing is performed digitally by a microcontroller (ATSAMD51 by Microchip) running custom code which is able to sample the ADC at 10KHz, detect the end of each quadrupole sweep, and process the entire sweep for mass jumps within 2 milliseconds. The microcontroller also generates the triggering pulses which pass through a phase delay unit before triggering the laser to fire. The microcontroller continuously measures each sweep and updates the triggering pattern, thus ensuring that the laser remains aligned to the mass spectrometer, regardless of how much the sweep duration may drift over time. Overall timing jitter with the current design is measured to be ±100μs, but jitter can be reduced if required for mass spectrometers that scan at a faster rate.

The fire control circuit sits between the laser ablation triggering unit and the laser. A bypass line allows signals from the triggering unit to be passed directly to the laser, thus negating the presence of the circuit and allowing the instrumentation to be operated normally. When the fire control circuit is active, the presence of triggering pulses is used to gate the triggering output from the unit, ensuring that the laser ablation instrument can be used without any modification to the software control scheme used by either the laser or ICP–MS instruments.

The microcontroller is connected by serial port to a Windows PC running custom software for control and diagnostics. The software allows the user to specify the pattern of shots to fire in alignment with each sweep of the mass spectrometer. The basic operation fires an integer number of laser shots per sweep, but it is also possible to fire an integer number of laser shots per dwell period, resulting in substantially more sophisticated modes of operation.

To use the fire control device in practice, first the ICP–MS and laser ablation instruments are configured as normal, with laser firing rate chosen to fit the application and dwell times on the ICP–MS are assigned to masses based on the anticipated count rates and the desired measurement frequency. Because the fire-control device will fire the laser an integer number of times per sweep, the user needs to identify the divider value to use that gives the closest repetition rate to what is desired. For example, if wanting to fire at 10 Hz with a 142.1 ms sweep time, the chosen divider is either: 1, resulting in a laser repetition rate of 7.037 Hz; or 2, resulting in a repetition rate of 14.075 Hz. If the user believes that it is advantageous to use a repetition rate closer to 10 Hz, then they can do so by adjusting their ICP–MS sweep time, for example, extending or contracting dwell times by a few ms each.

The phase delay unit is an essential part of the device that allows the phase between aerosol delivery and the ICP–MS sweep to be adjusted. To align aerosol delivery to the start of the sweep, the delay time is set to the difference between the sweep time and the modulo of the aerosol transit time (from ablation site to ICP–MS detector) and the sweep time. In practice, since the transit time is rarely known precisely, the delay time is set empirically by monitoring the intensity of the ICP–MS signals while setting up the method. It is possible to choose a value for the delay such that peak aerosol

delivery arrives at any point in the ICP–MS measurement cycle, for example by aligning measurement of a specific low abundance mass to sit on top of the peak aerosol delivery, or contrarily, by placing a high abundance mass in the trough between aerosol delivery pulses.

During set up the user would run the ICP–MS with their chosen method and configure the fire control device to suit the application. This can be done without firing the laser to inspect the sweep timing and different firing patterns, or with the laser firing to see signal intensities while setting the phase delay. Once the device is configured for use with a specific ICP–MS method it remains in that configuration for the duration of the analytical session.

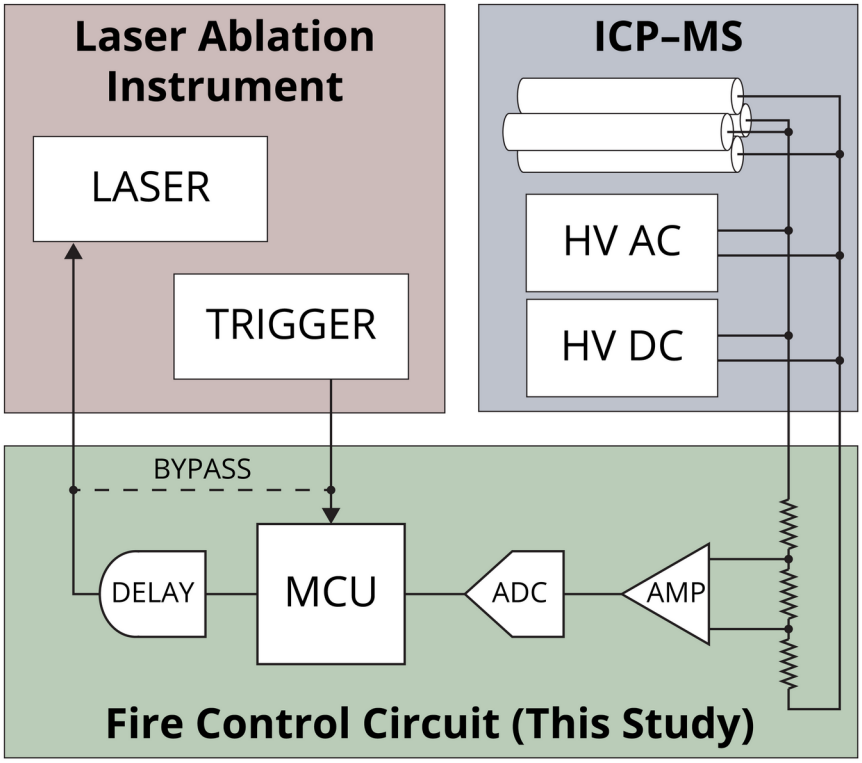

Figure 1: Schematic showing how the fire control circuit interfaces with the laser ablation instrument and ICP–MS. The circuit connects to existing cabling on both instruments.

Testing of the new fire control circuit was performed on a RESOlution laser ablation instrument (Applied Spectra Inc) connected to a 7900 ICP–MS (Agilent Technologies, Inc). The laser ablation instrument features an S155 ablation cell (Laurin Technic Pty Ltd) and an ATLEX ArF 193nm ablation head (ATL Lasertechnik GmbH) with a maximum repetition rate of 300Hz. No modification was made to either instrument, with the fire control system connecting to existing cabling on both systems.

Ablation Cell and Interface Tubing

The S155 ablation cell was configured to provide two different time responses. Configuration “A” uses the standard S155 ablation funnel with 1.5m of 2.7mm ID tubing and a “squid” smoothing device to produce a single-shot washout time of 6s to 1% of peak signal intensity.

Configuration “B” removes the squid smoothing device to produce a single-shot washout time of 0.6s to 1% of peak signal intensity.

The washout time of each configuration was measured on SRM612[14] from NIST with a 40µm spot using a single isotope (^{232}Th) sampled with a 5ms dwell time. Time resolved charts of single shot responses are included in the supplementary information.

Samples

Ablation was performed on SRM612 which is homogeneous for lead content (38.6 µg/g[15]) and lead isotopes[16,17] over 40 µm distances.

A natural galena (PbS) sample from Mt. Murchison was chosen due to its very high (87% g/g) and homogeneous total lead concentration.

All lead isotope ratios and concentrations for these samples have been tabulated in the supplementary material.

Conditions and Methods

Ablation conditions were chosen to match the sample material, with 3.5 J·cm^{-2} used on NIST612 and 2.7 J·cm^{-2} on galena. The spot size was kept constant at 40 µm diameter, while repetition rate varied with the ICP–MS method and is listed in the Results section.

Lead isotopes were measured using two different methods. “PbIso1” has a nominal 200 ms sweep time that was chosen in an attempt to align the sweep time to repetition rates of 5 and 10 Hz. Since the true sweep time was measured to be 199.8 ms, the alignment of one and two shots per sweep equates to repetition rates of 5.01 Hz and 10.02 Hz respectively. The method “PbIso2” extends the sweep time by 2% and serves as a proxy for conditions representing casual misalignment between the laser period and mass spectrometer.

Table 1: ICP–MS methods, showing measured masses, dwell times, and total sweep duration.

Mass	**PbIso1 Dwell Time (ms)**	**PbIso2 Dwell Time (ms)**
202	37	37
204	80	81
206	25	26
207	25	26
208	25	26
Reported Sweep Time	200	204
Measured Sweep Time	199.8	203.8

The total sweep time shown in Table 1 was measured using the fire control circuit presented in this paper, whereas the software (*Mass Hunter*) that controls the mass spectrometer only reports the sweep time rounded to the nearest millisecond.

Results and Discussion

Time Resolved Signals

Assessment of the time resolved signals was made using a single mass (^{232}Th) measured with a 5 ms dwell time. These steady-state time resolved signals (see Figure 2) show that at 5.01 Hz, configuration A produces a signal with no periodic component, while at 5.01 Hz configuration B produces a substantial (±50% peak to peak) periodic signal. Doubling the repetition rate to 10.02 Hz shows that configuration B still produces a significant (±15% peak to peak) periodic signal.

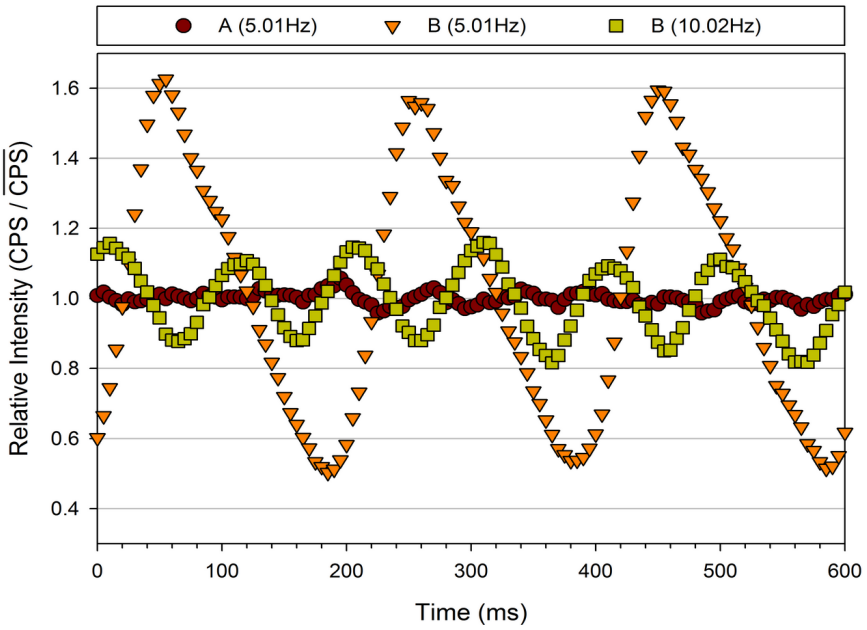

Figure 2: Time resolved signals showing intensity variation over 600 ms, equivalent to three sweeps of the mass spectrometer. Signals were measured on ^{232}Th with a 5 ms dwell time and normalised to the average intensity over the chart period. The plot shows that configuration A provides sufficient smoothing that no periodic variation is observed while configuration B shows ±50% variation when sampled at the same repetition rate. Increasing the repetition rate to 10.02 Hz for configuration B reduces the variation to less than ±15%.

Representative measurements of galena were made at 5.01 Hz with configuration B using the two methods PbIso1 and PbIso2 (see Figure 3a and 3b). It can be seen that changes in signal intensity due to aliasing are present in both ablations. The presence of low frequency aliasing when measuring using PbIso1 is noteworthy since the laser frequency of 5.01 Hz was chosen to align with the sweep time (199.8 ms) which is a strategy employed by other workers[5] with mixed success. One feature of aliasing is that signal aliases adopt lower frequencies as the sampling frequency approaches, but does not match perfectly, an integer multiple of the laser firing period. As shown in Figure 3a the measured change in signal intensity is varying over a time period longer than the ablation. When observed, such signals may not be readily identified as aliasing and can be easily mistaken for down hole fractionation, concentration gradients within the sample or sensitivity drift in the mass spectrometer.

Comparative measurements taken with the fire control circuit enabled show that all aliasing is removed from the signals (Fig. 3c and 3d). In this mode of operation, the laser firing period is fixed to that of the sweep time, and inspection of the time resolved signals shows that signal noise has been reduced to that

of the technique (e.g. counting statistics and flicker noise[18]). The small change in relative signal intensity between the two methods (see Figure 3c and 3d) when the fire control circuit is enabled is due to the mass measurements occurring at different, but constant, parts of the time-varying signal. A side-effect of this mode of operation is that the measured mass ratios can be significantly different to what is physically present in the material. We propose that this phenomenon is fundamentally no different to what already occurs with mass bias, which is trivially corrected for by measuring a reference material with a homogeneous and well-characterised isotopic ratio. This approach is valid provided the fire control circuit always aligns the firing of the laser to the ICP–MS measurement cycle and the aerosol transit time remains constant.

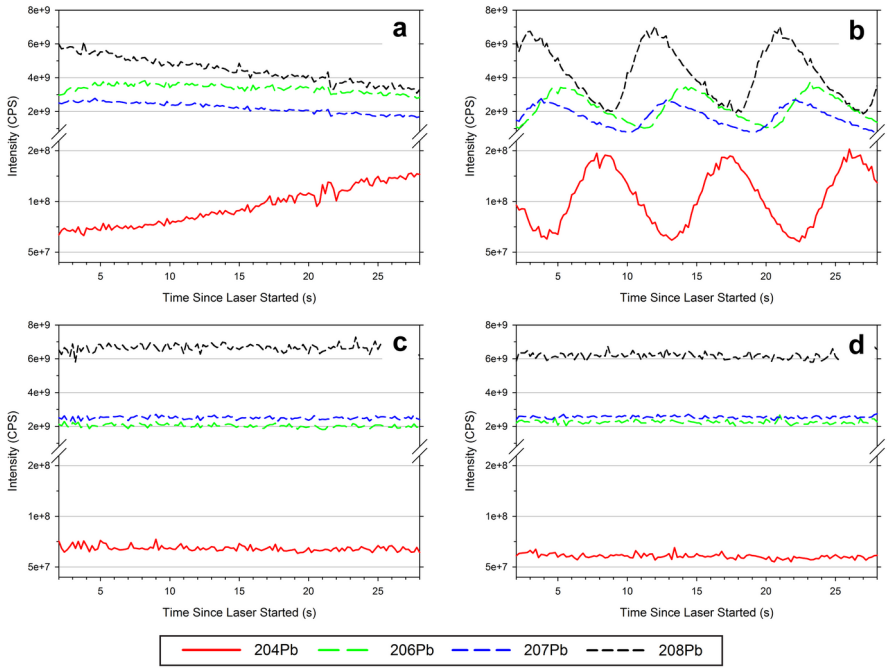

Figure 3: Time resolved signals showing aliasing (a & b) that is entirely removed when the fire control circuit is enabled (c & d). The measured mass ratios with the device enabled do not match the ratios in the sample due to the different masses being measured at different parts of the aerosol delivery pulse. However, the measured ratios are constant and the response can be calibrated using a reference material as is already widely done. a: Free running, PbIso1. b: Free running, PbIso2. c: Fire control enabled, PbIso1. d: Fire control enabled, PbIso2. All: Configuration B, 5.01 Hz, galena, 40 µm spot, 2.7 J·cm^{-2}.

Signal Variance

To quantify the improvement in precision of measuring lead isotope ratios that is achieved by use of the fire control circuit, galena and NIST612 have been ablated using configurations A and B with and without the circuit enabled. The variance reported is the observed standard deviation of the ratio over ≈100 sweeps in 25 s averaged over three replicates. As shown in Figure 4a, the measurement of galena using configuration A establishes the baseline of precision that is possible using a practical degree of smoothing. Using the fire control device reduces the variance considerably, almost to the same level as that achieved by smoothing. The small amount of extra uncertainty when ablating with the device enabled is most likely caused by timing jitter in the operation of the device.

The observed precision of the measurements on NIST612 (Figure 4c) are dominated by counting statistics due to the low abundance of lead in this material, and because of this, the device is able to reduce signal variance to the level limited by counting statistics at all conditions.

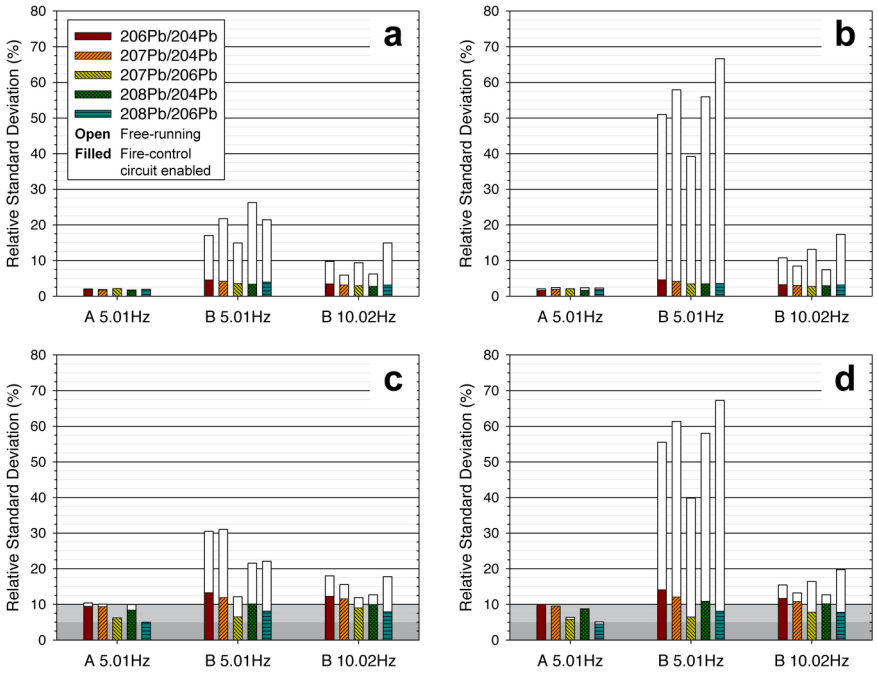

Figure 4: Observed variance of ratios (standard deviation of gas blank subtracted ratios, averaged over three replicates) as measured using two methods, PbIso1 (a & c) and PbIso2 (b & d) on samples galena (a & b) and NIST612 (c & d). Open bars show high variance due to aliasing when free running the laser, while filled bars show reduced variance when the fire control circuit is enabled. Observed variance on galena (a & b) is above the theoretical variance based on counting statistics (not shown) while theoretical variance on SRM612 is at 10% for ratios to ^{204}Pb and 5% for other ratios (shaded regions). Use of the fire control circuit has effectively reduced signal variance to the limit of the technique at all conditions.

Advantages of Using the Fire Control Unit

We propose that the main advantage of using this fire control device is that it allows fast response cells to be used with quadrupole mass spectrometers without any aliasing noise. In turn, the primary advantage of ablating using fast response cells is improved spatial resolution. While of obvious benefit to imaging applications, higher spatial resolution when depth drilling allows for better delineation of phases and identification of inclusions. Due to reduced mixing between phases, integration periods can be extended by bringing them closer to phase boundaries, thus reducing signal error.

While the total mass of aerosol delivered remains the same, use of a faster cell response gives higher peak signal intensities. For the response times presented in this work, configuration B has a peak intensity an order of magnitude greater than that of configuration A. This substantial increase in intensity is most significant for low abundance isotopes and in some cases will be sufficient to raise signals above detection, or conversely, allow ablation to be performed using smaller spot sizes.

If dwell times are reduced commensurate to the response time of the faster cell, then measurement precision is maintained and allows the same analysis to be performed in less overall time, reducing

consumption of resources and cost overheads. The improvement does not scale perfectly due to the reduction in measurement efficiency when the quadrupole is operated using short dwell times because these instruments often have a fixed jumping and settling time of 1–2 ms. Most importantly here, use of the fire control circuit allows operating conditions to be chosen that represent an optimal compromise between acquisition time and measurement precision for a given application.

While it would be incorrect to state that fast response cells are beneficial for all kinds of laser ablation ICP–MS analysis, it is important to note that until now most ablation cell technology has incorporated a degree of signal smoothing by *necessity* and it has simply not been possible to perform a like-for-like assessment of fast response cells due to the presence of aliasing noise.

It is anticipated that the main application of this device will be imaging using fast response ablation cells. Recent work (Šala et al. 2020) with the ARIS system[19] (Teledyne Technologies Inc) explored the use of a high repetition rate (500 Hz) laser as a means of reducing aliasing. Their single mass measurements over the range 100 to 500 Hz were collected using 100 to 20 ms dwell times, which equates to a dosage value of 10 shots per sweep. So while the response time of the system was short, using such a large dosage serves to decrease the effective time response of the system, with a commensurate decrease in resolution of the measurement. Our future work will focus on testing the fire control circuit for imaging applications, including assessment of quantification and image fidelity and resolution when ablating more complicated mixed phase samples. By using fast response ablation cells and reducing the dosage down to one shot per sweep, we anticipate considerable improvement to throughput and resolution while maintaining the same measurement precision achieved by slower ablation cells.

Other future work with this fire control circuit will be to evaluate novel modes of measurement, such as firing a single laser pulse for each analyte, firing multiple laser pulses for a specific analyte in the sweep, or, firing a single laser pulse for each sweep. This last suggestion is particularly intriguing, since alignment of each sweep with the delivery of material originating from a single laser pulse has the potential to transform the sequential mass spectrometer into a simultaneous collection instrument.

Conclusion

We have shown that a fire control circuit that aligns laser repetition rate to ICP–MS sweep time is a practical and effective means of eliminating aliasing from LA–ICP–MS analysis. This new approach maintains measurement precision even when cell response time is reduced by an order of magnitude. As an enabler of low dispersion ablation cells, analysis can now be performed at greater resolution, higher peak signal intensity, and with a reduction in overall analysis time. Further work will explore imaging applications a well as more sophisticated modes of operation such as aligning a single shot with a single sweep which turns the sequential quadrupole instrument into a simultaneous one.

Author contributions

CAN conceived the idea; CAN and NW designed and built the device; LD, PO, and CAN designed and performed the experiments; CAN and LD wrote the manuscript with input from PO, NW, MS, and DS.

Conflicts of interest

The authors declare the following competing financial interest(s): C. Ashley Norris and N. West are employed by Norris Scientific; Norris Scientific has a patent pending on the fire control device described in this manuscript.

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