

Optimising the mass spectrometer

The first step in the optimisation aims to increase the spectrometer sensitivity without significantly compromising the oxide and doubly charged ion production rates (Table 1). A common daily sensitivity optimisation can include a torch positioning, minor sample flow adjustment and focus lens voltage adjustment. Additionally, a dead time determination based on the ratio method can be carried out, as well as the triple calibration of the detection system; these steps are compulsory if the inter-dynode voltage of the multiplier was changed. The dead time determination is based on the I^{235}/I^{238} ratio values measured in the counting mode on the NIST SRM 612 glass using different ablation rates (two replicate measurements at a high ablation rate and two replicate measurements at a low ablation rate). Slow rastering of the laser beam helps to obtain stable and constant intensities during such measurements. The triple calibration of the detection system is performed on the Ar^{36} peak using the integral intensities of the slopes and of the central part of the peak for the determination of the counting-analog and the analog-faraday cup intensity transformation coefficients, respectively; it is similar to the standard triple calibration performed during the liquid mode spectrometer optimisation. The second step is the age optimisation. A short test series made of eight analyses is performed. The GJ-1 zircon is analysed four times as an external standard. The Harvard 91500^{1,2} or the Plešovice³ zircons are analysed four times as unknowns (secondary standards). If the mean 206/238 and 207/235 ages of the secondary standard calculated from the eight measurements falls within $\pm 1\%$ of the certified ages (1062.4 and 1065.4 Ma¹; 337.13 Ma³, respectively) without significant discordance, the instrument is considered ready for the analysis of sample zircons. If not, the spectrometer optimisation must be adjusted and a next test series performed. After accurate ages are obtained, sample zircons are measured. One of the secondary standards, the 91500 or the Plešovice (old and young samples, respectively), is used to control the accuracy; it is measured along with the sample zircons during the whole data acquisition shift (1 spot on the secondary standard per 3-5 sample spots).

Table 1. ICPMS optimisation requirements for laser ablation zircon dating (Element XR at the IMG, University of Lausanne)*

La ¹³⁹⁺ cps	2.5-3x10 ⁶
U ²³⁸⁺ cps	4-4.5x10 ⁶
ThO ²⁴⁸⁺ /Th ²³²⁺ , %	0.03-0.15
Ba ¹³⁷⁺⁺ /Ba ¹³⁷⁺ , %	1.5-2.5
U ²³⁸⁺ /Th ²³²⁺ , %	105-115%

*UP-193FX, 75 mm pit size, linear scan, 20 Hz repetition rate, 6 J/cm² energy density.

The Element XR offers ion collection by an electron multiplier in pulse counting or analog mode, as well as by a Faraday cup. We have selected an intensity acquisition protocol that helps minimising the inaccuracies. For U²³⁸, the multiplier is operated only in the analog mode to exclude the influence of systematic errors in the determination of the counting-analog intensity transformation coefficient and the influence of systematic errors in the dead time determination and of the dead time fluctuations during the analytical shift, if there are any (the analog mode has no dead time). The Element XR multiplier operates in the analog mode for intensities $> 5 \times 10^6$ cps. Lead isotopes intensities are lower than the intensity of U²³⁸, at least for zircon ages < 1 Ga that are most common in our laboratory practise. They are lower than 5×10^6 cps for the ablation rates that we usually use, both for the GJ-1 standard, the secondary standards, and the sample zircons. They are measured in the counting mode. The counting-analog transformation coefficient plays no role in the lead intensities computation. Only the dead time related systematic errors could potentially be of concern, especially for intensities amounting to $2-5 \times 10^6$ cps. A better precision at low intensities and a low background are the inherent

advantages of the counting mode. Th^{232} is measured in the triple mode allowing the software chose between the counting, analog or Faraday cup regimes. Th^{232} is measured mainly to enable the calculation of the Th/U ratio of the sample zircons (e.g., to better distinguish the magmatic and the metamorphic growth episodes), where the highest accuracy is no pre-requisite.

Although the mercury and the (Hg-Pb)²⁰⁴ intensities are included in the protocol, we do not apply the Pb²⁰⁴-based common lead correction in the routine practice. The low intensities and the insufficient precision of mono-collector instruments, the presence of heavy rare earth argide and zirconium oxide-based spectral overlaps on masses 201, 202 and 204, as well as the variability of the mercury isotope abundances compromise the quality of such corrections⁴. A more conservative approach based on the cathodoluminescence imaging of sample zircons to avoid zones potentially enriched in common lead during ablation is preferred instead, as well as the compulsory, albeit qualitative, control of the Hg and (Hg-Pb)²⁰⁴ intensities to identify analyses clearly influenced by the presence of common lead.

External accuracy control

The daily optimisation includes the analysis of a secondary standard to ensure that its 206/238 and 207/235 ages fall within $\pm 1\%$ of the certified ages. This action has some analogies in the classical trace element solution nebulisation ICPMS, where several standard solutions with different element concentrations are usually used to obtain the k coefficient from a linear regression of the intensity ratio - concentration ratio data. Similar proceedings are also supported by some trace element software packages for LA-ICPMS (e.g., AMS⁵) and serve to minimise the influence of systematic errors in the standard element concentration values. The same approach is possible in the U-Pb LA-ICPMS zircon dating, provided that the acquisition of only one (or two) measurement for one zircon standard already yields sufficiently precise isotope ratios for this zircon. This was rarely possible in the past, because of the widespread use of low sensitivity quadrupole machines and restricted availability of homogeneous U-enriched zircon standards able to yield relatively stable signals. The introduction of the GJ-1 standard and the tendency to use highly sensitive mono- and multi-collector sector-field ICPMS for zircon dating changes the situation, and the multi-standard age calibration can become a reality. Instead of checking the measured age of a secondary standard, the correlation coefficient of the calibration regression line will have to be checked. However, to control the accuracy of sample ages, it becomes necessary to introduce a standard not participating in the calibration: a secondary standard.

We do not use multiple standard calibrations in our routine practise of the LA-ICPMS dating. Still, we optimise the instrument in the beginning of each analytical shift in a way as to ensure that the secondary standard age is accurate. In some sense, this represents a rudimentary implementation of the multiple standard calibration. It is then doubtful that the age accuracy obtained for the secondary standard during sample measurements directly characterises the age accuracy of the unknown samples. Therefore, we welcome zircon samples already measured by TIMS among the zircons to be dated by LA-ICPMS. We also analyse the Plešovice zircon against the pair GJ-1 / Harvard 91500, or the Harvard 91500 zircon against the pair GJ-1 / Plešovice (primary and secondary standards, respectively). The 206/238 and 207/235 ages accuracy is better than 2 % in all such tests, and is better than 1% in the majority of them. To characterise the accuracy of old ages, we analyse relatively homogeneous zircons with a concordant TIMS age of 1.79 Ga⁶, received from F. Corfu, against the pair GJ-1 / Harvard 91500. The accuracy of the 206/238 and 207/235 ages is always better than 1%.

About the optimisation of the acquisition protocol: ratio-of-the-mean-intensity approach

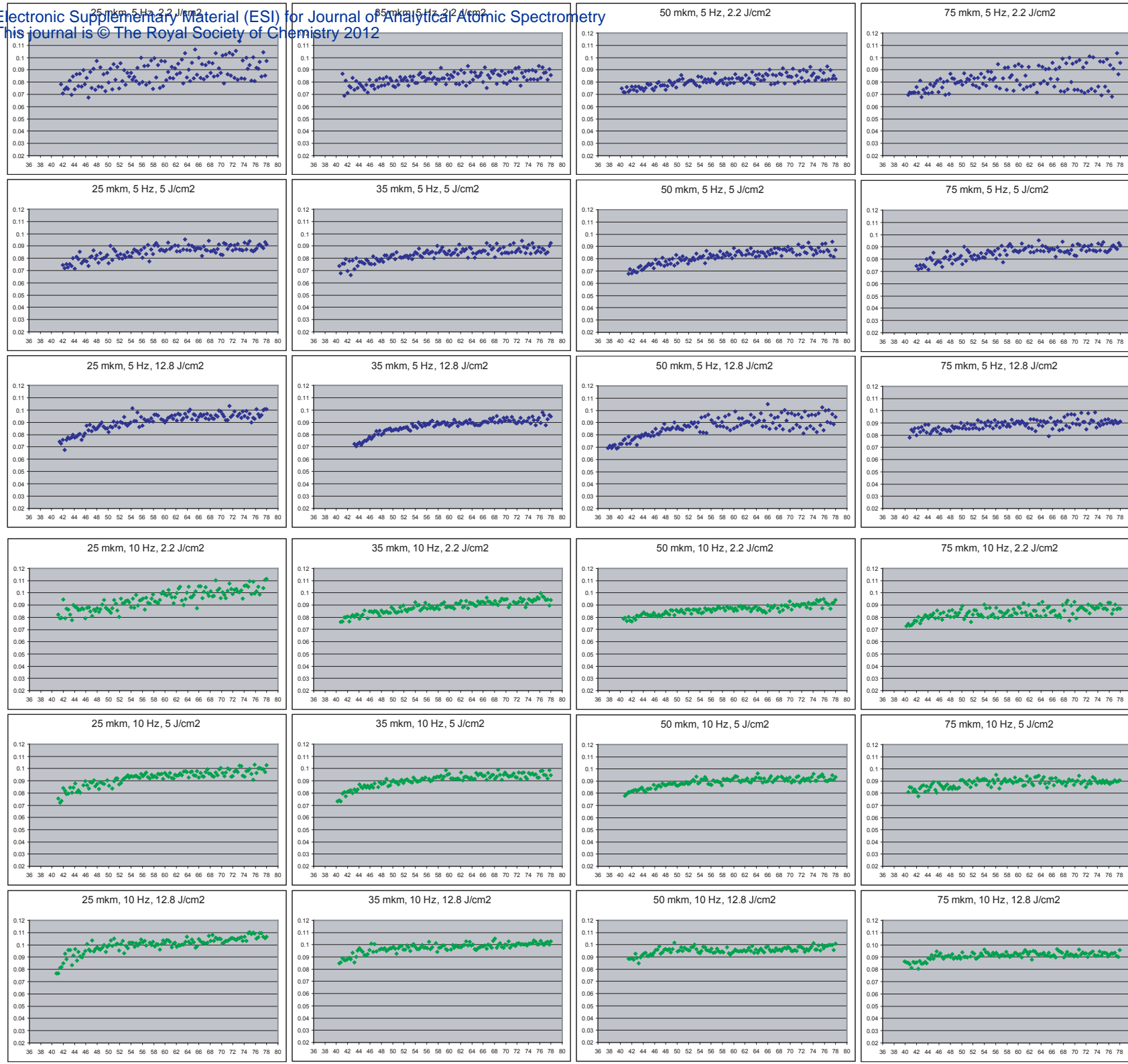
Spot mode LA-ICPMS signals are transient. The uncertainty calculation on such a signal requires its decomposition into segments, each of which could still be considered as sufficiently stable, non-transient. Each of these segments has to include a sufficient number of sweeps to yield representative standard deviations for the individual segments, which are further propagated in quadrature for the whole signal (see section 'the ratio-of-the-mean-intensities approach for a transient signal'). Therefore, the duration of each individual sweep must be short, particularly for signals for zoned zircons with fast varying intensities. This translates in short dwell times per isotope.

References

1. M. Wiedenbeck, P.Allé, F. Corfu, W.L. Griffin, M. Meier, F. Oberli, A.Quadt, J.C. Roddick and W. Spiegel (1995). Three natural zircon standards for U–Th–Pb, Lu–Hf, trace element and REE analyses. *Geostand. Newsl.*, 19, 1-23.
2. B. Schoene, J.L. Crowley, D.C. Condon, M.D. Schmitz and S.A. Bowring (2006). Reassessing the uranium decay constants for geochronology using ID-TIMS U-Pb data. *Geochim. Cosmochim. Acta*, 70, 426-445.
3. J. Sláma, J. Košler, D.J. Condon, J.L. Crowley, A. Gerdes, J.M. Hanchar, M.S.A. Horstwood, G.A. Morris, L. Nasdala, N. Norberg, U.Schaltegger, B. Schoene, M.N. Tubrett and M.J. Whitehouse (2008). Plešovice zircon—a new natural reference material for U–Pb and Hf isotopic microanalysis. *Chem. Geol.*, 249, 1–35.
4. S.E. Jackson, N.J. Pearson, W.L. Griffin and E.A. Belousova (2004). The application of laser ablation-inductively coupled plasma-mass spectrometry to in situ U–Pb zircon geochronology. *Chem. Geol.*, 211, 47–69.
5. S.R. Mutchler, L. Fedele and R.J. Bodnar (2008). Appendix A5: Analysis management system (AMS) for reduction of laser ablation ICP-MS data. In : *Laser Ablation ICP-MS in the Earth Sciences : Current Practices and Outstanding Issues*. Mineralogical Association of Canada, Short Course 40 (Ed. P. Sylvester), 318-327.
6. F. Corfu (2004). U–Pb Age, Setting and Tectonic Significance of the Anorthosite–Mangerite–Charnockite-Granite Suite, Lofoten–Vesterålen, Norway. *J. Petrol.*, 45, 1799-1819.

Fractionation of the I206/I238 ratio as a function of ablation time for pit sizes of 25, 35, 50 and 75 μm , on- sample energy densities of 2.2, 5.0 and 12.8 J/cm^2 and repetition rates of 5 and 10 Hz

GJ-1 standard zircon,
Institute of Mineralogy and Geochemistry,
University of Lausanne



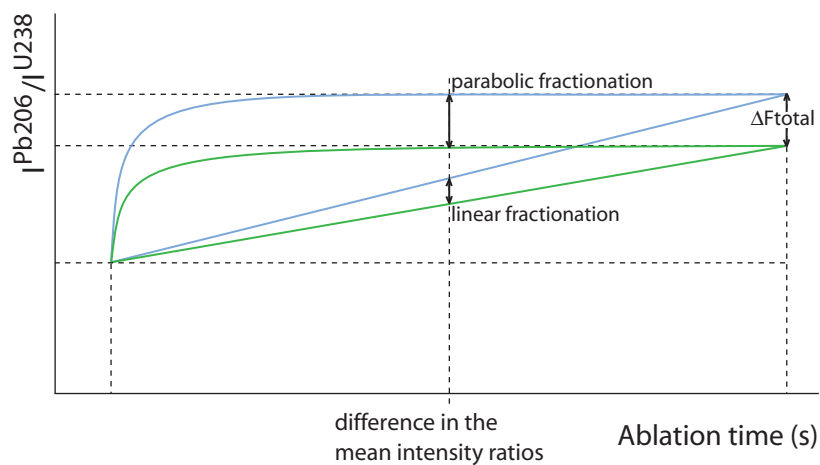


Fig. 5. A schematic plot illustrating the linear and the parabolic fractionation models for two zircons (green and blue colours, respectively). The total amount of fractionation is the same for the both fractionation models, but differs between the zircons. Let us imagine that the ratio-of-the-mean intensities or the mean-of-the-intensity-ratios approach is used for data reduction. The mean I^{206}/I^{238} value lies in the middle of the line in the linear fractionation case and close to the middle of the curve in the parabolic fractionation case, provided the number of sweeps corresponding the beginning of fractionation, where the ratio increases fast, is low compared to the plateau of the curve. Although approximate, this graphical solution shows that the difference between the mean intensity ratios of two different zircons is lower in the case of linear fractionation, even if the total amount of fractionation is the same for both models. If one of the zircons is an external standard, and the other – a sample of unknown age, then the sample age accuracy will be less compromised by fractionation if the latter is linear.