High-NAI tuning procedure

In the following text we provide suggestions for a tuning procedure focussing on hot plasma conditions. The principal idea is treating both, ICP and mass spectrometer tuning as separate tasks. The ICP tuning is the primary target, while the mass spectrometer tuning needs to be adjusted to fit to the conditions established in the plasma.

The whole instrumental setup should initially be tuned in the way typically applied for LA-ICP-MS work in the particular lab. The instrument (ICP-MS) should be warmed up for a sufficiently long time (minimum one hour, better several hours) to avoid ongoing drifts while tuning. From our practical experience on different instruments ICP-MS´ perform best if kept running permanently, i.e. plasma is not switched off over night.

After this initial routine tuning test data should be collected, starting with the plasma ions ^{38}Ar and $^{40}Ar_2$, to keep record of the NAI. Now we would continue with ablating NIST-SRM610 or NIST-SRM612, if preferred. This could be done either as a short spot or line analysis using the lab-specific LA parameters. Data should be collected for ThO/Th, and at least one group of elements differing only slightly with respect to mass but strongly with respect to volatility. ^{232}Th and ^{238}U, while convenient because of their almost identical concentrations in the mentioned standards, represent a highly refractory (Th) and an intermediate (moderately refractory) element (U) and may thus not be the most sensitive candidates to test for elemental fractionation. Instead we suggest using ^{209}Bi, ^{232}Th and ^{238}U as this includes a volatile (Bi), too. Other useful groups of elements would be e.g. ^{85}Rb, ^{88}Sr, ^{90}Zr or ^{133}Cs, ^{137}Ba, ^{139}La. Each group contains elements representing volatile, intermediate and refractory behaviour. Any of this “test-groups” would be fine for the tuning and respective data should be recorded together with NAI (i.e. $^{38}Ar/^{40}Ar_2$) and ThO/Th.

To get a better feeling of how sensibly the mentioned parameters (NAI, ThO/Th and “test-group”) respond on changing plasma conditions we suggest to continue with cooling down the plasma before actually tuning for hot conditions. To do so, Ar could be monitored (^{38}Ar or ^{36}Ar, if applicable) while increasing the sample gas flow. Keep on increasing the sample gas flow until the monitored Ar intensity decreases to about 10% of its initial value. Now proceed with tuning the mass spectrometer without any further gas flow adjustments. We suggest optimizing the ion optics for maximum intensity of ^{36}Ar (or ^{38}Ar). After this is done, run test ablations on the standard to find the optimal [X,Y]-position of the torch monitoring an isotope of a refractory element (e.g. Zr, La, Th…) and optimize the balance between He cell gas and admixed Ar, keeping the total sample gas flow about constant. After the torch position is adjusted another round of mass spectrometer tuning is advisable, again optimized the ion optics for maximum Ar intensity.

A different (cooler) plasma state has been established and the mass spectrometer was accordingly tuned. Now test data can be collected for this plasma state. Again, NAI is determined without ablation, ThO/Th and “test-group” data are collected ablating the NIST glass using identical laser conditions as before. ThO/Th and “test-group” data should be plotted vs. NAI to allow for a first comparison of both plasma states. For the “test-group” we suggest plotting the ratios volatile/intermediate and refractory/intermediate or just volatile/refractory for simplicity. The results obtained until this point are illustrated in Figure S1 using the data from our experiment.

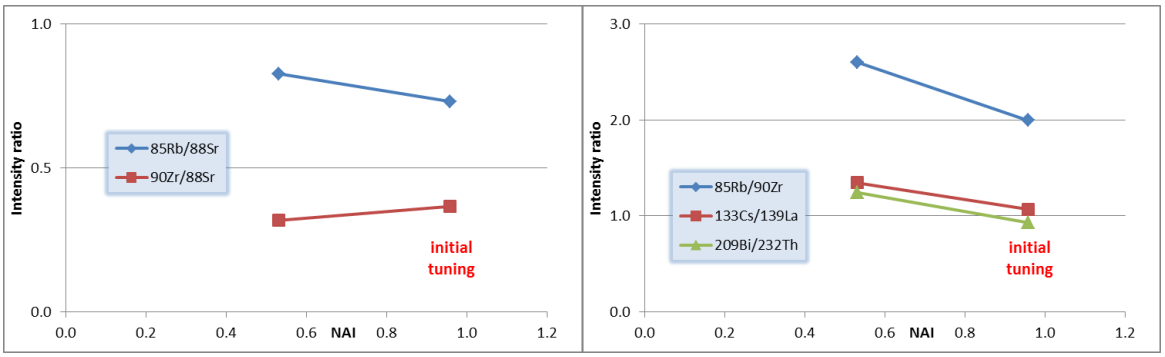

Fig. S1: Examples for "test-group" data after tuning for colder plasma (lower NAI) relative to initial tuning conditions. Left figure: volatile/intermediate (blue) and refractory/intermediate elemental ratios (red). Right figure: volatile/refractory elemental ratios for three different "test-groups".

After this tuning step towards colder plasma conditions (lower NAI) in the following the plasma conditions will be shifted step-wise towards hotter plasma states (higher NAI). Doing this in several steps has the advantage of keeping track with respect to mass spectrometer (ion optics) adjustment more easily. We also prefer to use a high cool gas flow (17.5 l/min) which protects the torch while supporting hot conditions in the plasma core region. In general each tuning step follows the same procedure:

1) Reducing the sample (Ar+He) and auxiliary gas flows, while monitoring the respective Ar ion intensity.
2) Tuning the mass spectrometer (ion optics) for maximum Ar intensity.
3) Ablating the NIST glass for torch [X,Y]-position adjustment monitoring a refractory element. Eventually also fine-tuning the balance between He and Ar in the sample gas for optimal sample transport out of the ablation cell keeping the total flow about constant.
4) Repeating step 2).
5) Collecting data for NAI (without sample ablation) and ThO/Th and "test-group" (ablating the NIST glass).

After several of the described tuning steps a hot plasma state is established and the mass spectrometer is tuned for optimal ion transmission for the particular plasma conditions. The resulting "test-group" data vs. NAI plot (see Figure S2) provides the information if elemental fractionation has stabilised.

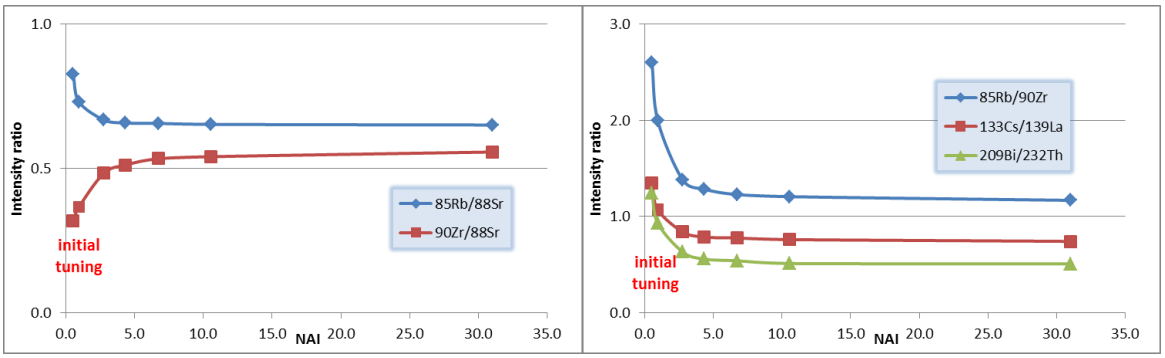

Fig. S2: Examples of "test-group" data vs. NAI after the 6 steps of rounds of gradual plasma/MS tuning. Again the left figure shows an example using volatile/intermediate and refractory/intermediate ratios, while the right figure displays volatile/refractory elemental ratios using the three "test-groups".

As can be seen in Figure S2 the two opposite trends in the left plot clearly show the differences in the elemental behaviour derived from the ratios of volatile to intermediate and refractory to intermediate element of one “test-group”. The right plot highlights the similarities in the behaviour of volatile vs. refractory elements of all three “test-groups”. As described in the main text the elemental fractionation stabilizes under hot plasma conditions (high NAI).

We typically apply a plasma tuning resulting in a NAI of about 30 for our routine analyses. As mentioned in the main text this results in a reduction of sensitivity but has the advantage of hardly over-loading the plasma even if larger sample amounts are introduced.

Once this plasma state is established and accompanied by optimal ion optics tuning the performance can be maintained easily on the long-term. As already mentioned the instrument is kept running over night for optimal long-term stability. Nevertheless, we prefer to apply cooler plasma conditions during nights (and weekends) to reduce the impact of the strong Ar ion beam on apertures and slits. This is done by increasing the sample gas Ar flow (turning down the He to reduce consumption) well above the total sample gas flow applied for hot plasma conditions. The same is done for the auxiliary gas. Monitoring Ar helps finding good settings. The ion optics settings are not modified. On the next day only the gas flows need to be re-established and the plasma needs to stabilise again for some 30 minutes. After very minor tuning of the ion optics the instrument is ready to continue routine operation.