

Introduction

Calibrating LA-ICP-MS

Calibration is a major challenge of LA-ICP-MS analyses. If a matrix-matched calibration standard is available, analysts can accurately determine the concentration of elements of interest in a solid sample in a same manner as for liquid sample analysis.

However, for many applications, there are no well-characterized standards or reference materials that contain all the target elements at known concentrations in a matrix that closely matches the samples.

NIST 61X glass standards can be used as a convenient alternative standard since most elements are doped and the working values are well-characterized in the literature (7).

There are two considerations when using a non-matrix-matched standard for quantitative LA-ICP-MS analysis:

1. The difference of ablation rates between the standard and sample.
2. Elemental fractionation.

The full elemental coverage of a NIST 61X glass standard provides the opportunity to correct the sum of all element concentrations to 100%, giving a simple and reliable way to compensate for variations in ablation yield.

The normalization function in ICP-MS MassHunter software automatically corrects the measured concentrations to give values relative to the sum of all measured elements.

The new function therefore automatically corrects for any differences in ablation rates between standards and samples, while also simplifying the routine analysis of materials of variable composition.

In this study, metal alloy and pure metal samples were analyzed using NIST 612 as the calibration standard.

- A '100% normalization method' was used to correct the differences in ablation rate between the standard and sample.
- A femtosecond laser ablation (fsLA) system was used to reduce elemental fractionation (2-4).

Principles and benefits of LA-ICP-MS

LA-ICP-MS uses a pulsed laser beam to ablate particles and vapor from the surface of a sample, which is held in an enclosed chamber or cell. The ablated material produced by each laser pulse or "shot" is transported to the plasma of the ICP-MS using a carrier gas flow.

- The sample material is decomposed, atomized, and ionized in the plasma in the same way as for liquid sample droplets, and the ions are then extracted into the mass spectrometer for analysis.
- LA-ICP-MS works for conducting and non-conducting materials and is a practical option for samples that are difficult to dissolve or digest, such as acid-resistant ceramics and alloys.
- Eliminating the sample digestion step also saves time and reagents, reduces the potential for errors due to contamination, and avoids the loss of volatile and chemically unstable elements

The sample ablation process

- The amount of sample material ablated during laser sampling—and the size distribution and composition of the particles—is controlled by the interaction of the laser beam with the sample surface.
- This interaction is strongly influenced by the composition of the sample, its surface morphology (for example reflectivity), and the gas present in the ablation chamber.
- The ablation process also depends on the laser wavelength, beam profile, and pulse width, so users often choose a particular type of laser depending on their sample types.
- For some applications, lasers with a shorter, femtosecond (fs) pulse duration have been shown to have potential benefits compared to nanosecond (ns) pulse width lasers (5).

Femtosecond ablation for metals and alloys

- The fs pulses transfer the laser energy without heating and melting the sample, which avoids the elemental and isotopic fractionation that occurs with a longer (ns) pulse.
- Femtosecond ablation therefore gives particles that are more representative of the bulk material, particularly for low melting point and conducting materials such as metals and alloys.
- Femtosecond ablation gives more consistent ablation yield for different materials, enabling the use of calibration materials that are not matrix matched.

Experimental

Instrumentation

An Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) Advanced Applications configuration (#100) was used for the analysis, coupled to a femtosecond LA system (RAIJINa supplied by Seishin Trading Co., Ltd., Hyougo, Japan).

The 100% normalization function of ICP-MS MassHunter software was used to correct differences in ablation rate between the glass standard and metal sample.

The RAIJIN laser ablation system (Figure 1) is the latest fsLA featuring galvano-mirror scanning and a high pulse repetition rate. Both features enable high sensitivity and wide area analysis, compared to conventional LA. Experimental conditions are summarized in Table 1.

Standards and samples

NIST 612 Trace Elements in Glass SRM was used as the standard to calibrate the signal responses for the elements of interest. NIST 612 Glass contains multiple trace elements with certified concentrations of around 40 ppm. However, the NIST 600 series of Glass SRMs have been extensively studied, so updated consensus values have been published for many of the trace elements. In this work, the concentrations used for the NIST 612 calibration standard were based on the values published by Jochum *et al* (1).

Three varied metal matrices were measured as unknown samples against the calibration obtained from the NIST Glass standard. Three metal CRMs were analyzed:

- BAM 310 Al/Mg Alloy (Berlin, Germany)
- NIST 1249 Nickel Alloy
- ERM-EB385 Pure Copper (Sigma Aldrich, Merck).

Where necessary, the samples were cut to fit the LA cell. The samples were cleaned using 1% nitric acid to remove surface contamination, and then analyzed by fs LA-ICP-MS.

Table 1. fsLA-ICP-MS operating conditions.

ICP-QQQ		fsLA	
RF Power (W)	1550	Pulse Width (fs)	290
Sampling Depth (mm)	8.0	Wavelength (nm)	257
Makeup Gas Flow (L/min)	0.25	Spot Size (µm)	10
Extract 1 lens	-10	Repetition Rate (kHz)	20
Extract 2 lens	-180	Scan Speed (µm/s)	30000
OctPole Bias	-18	Scan Pattern	Raster
Cell Gas	He	Fluence (J/cm ²)	5-7
Cell Gas Flow Rate (mL/min)	3.0	LA Cell Gas	Ar
Energy Discrimination (V)	3	Cell Gas Flow (L/min)	1.0

Results and Discussion

Quantitative analysis of metal and alloy CRMs

Figure 2 shows quantitative analysis results of the three metal CRMs. The results show the recovery of the analyte compared to the certified value.

The error bar in the graph shows two times the standard deviation (SD) of three analyses. With a few exceptions, recoveries of 80-120% were achieved by this method.

Half mass correction for ⁴⁸Ti⁺⁺ on ²⁴Mg in NIST 1249 alloy

For the analysis of NIST 1249, half-mass correction (6) was applied for ²⁴Mg since NIST 1249 contains nearly 1% Ti. The following equation was applied to correct the ⁴⁸Ti⁺⁺ interference on ²⁴Mg⁺.

$$M_c(24) = M(24) - M(48) \times 13.6$$

M_c is the corrected signal (counts), M is raw signal (counts), number in parenthesis shows mass-number, and the 13.6 is isotope ratio of ⁴⁸Ti to ⁴⁹Ti. With the mathematical correction, a good recovery of Mg in NIST 1249 alloy was obtained.

Multitune analysis of Cu in the pure copper CRM

In the ERM-EB385 Pure Copper CRM, the signal for ⁶³Cu was so high that the detector over-ranged under normal tuning conditions, so multi-tune was applied.

To lower the sensitivity of the ⁶³Cu signal by a factor of 100, ⁶³Cu was measured using a second ICP-QQQ tune mode. Only the voltage setting of one lens (the Omega-lens) was detuned to achieve the signal reduction.

The 100% normalization method also works for multi-tune, as shown by the excellent recovery of ⁶³Cu in EB385.

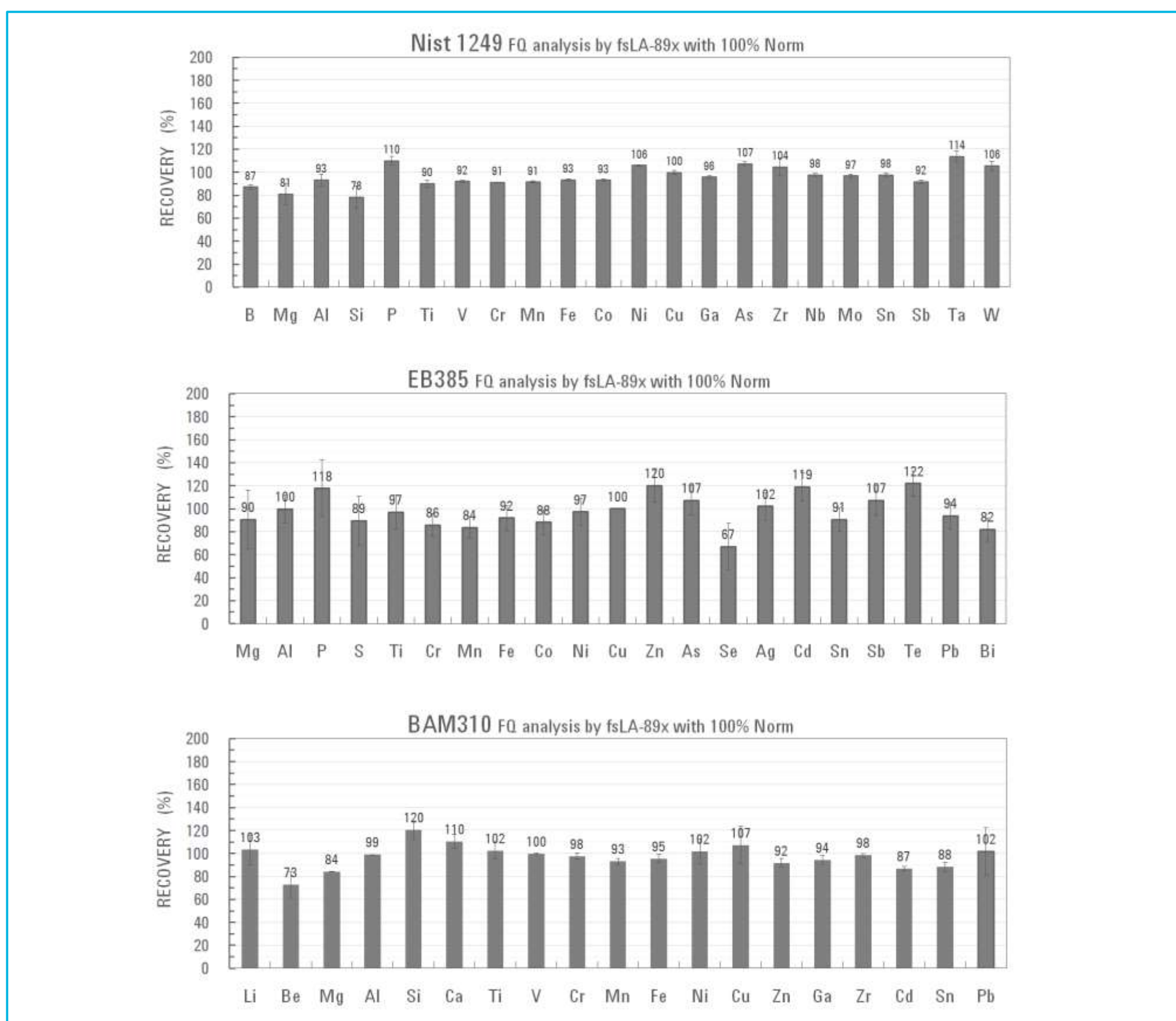


Figure 2. Quantitative analysis recoveries for certified elements in metal CRMs using the 100% normalization function with NIST 612 as the calibration standard.

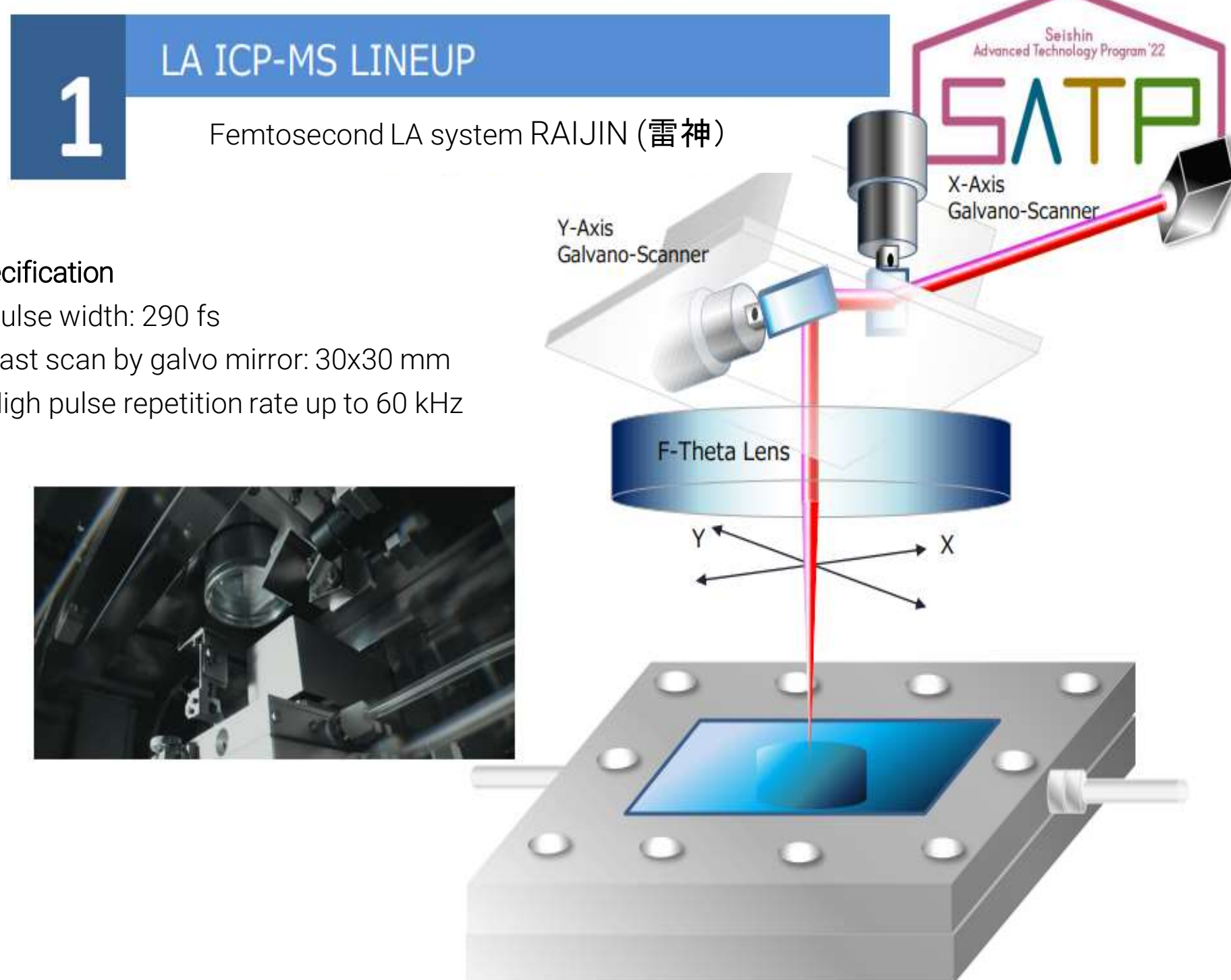


Figure 1. The fast scan speed is enabled by the galvanometer (galvo) mirror beam-scanning feature of the RAIJIN laser (雷神)

Conclusions

Successful LA-ICP-MS analysis using a new normalized calibration method

- The fsLA-ICP-MS method with 100% normalization successfully determined all certified elements (excluding carbon) in three different metal CRMs.
- The metal CRMs were calibrated against the well characterized—but not matrix matched—standard, NIST 612 Trace Elements in Glass.
- High accuracy was achieved, with 80–120% recovery of most elements across a wide range of concentrations from trace (single ppm) level to % level major elements.
- The new 100% normalization function greatly simplifies calibration strategies for LA-ICP-MS applications, addressing the common difficulty of obtaining matrix matched solid calibration standards.

References

1. Jochum, K. P. *et al*, *Geostand Geoanal Res*, 2011, 35, 397–429
2. Koch, J. *et al*, *J. Anal. At. Spectrom.*, 2004, 19, 267–272
3. Gonzalez, J. J. *et al*, *J. Anal. At. Spectrom.*, 2008, 23, 229–234
4. Možná, V. *et al*, *J. Anal. At. Spectrom.*, 2006, 21, 1194–1201
5. Pisonero, J., Günther, D., *Mass Spectrometry Reviews*, 2008, 27, 609–623
6. Kubota, T., Agilent publication 5994-1435EN