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Elemental Analysis of Pure Metals and Alloys by Femtosecond Laser Ablation (LA-)ICP-MS

100% normalization function provides accurate quantification without matrix-matched standards

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Introduction

Most ICP-MS applications involve the analysis of liquid samples, but solids and gases can also be measured directly by ICP-MS using suitable accessories. Laser ablation (LA) has been used as a solid sampling accessory since the early days of 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 is now a well-established approach for the direct analysis of the elemental content of a wide range of solid samples (1–4). 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. LA can sample a small area or feature on the sample, giving information on the distribution of elements for mapping and imaging applications. But LA can also be used for bulk analysis, by collecting data while moving the ablation site over a wider area of the sample.

One of the key factors that has limited widespread adoption of LA-ICP-MS for routine quantitative analysis is the challenge of producing reliable, traceable, multi-element, solid calibration standards for the sample types of interest. 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. As a result, LA-ICP-MS analysts often have to use non-matrix-matched calibration standards, which may give errors due to the very different ablation characteristics of the samples compared to the standard.

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 example, opaque materials such as teeth, bone, shell, coral, plastics, and ceramics are often analyzed using a solid-state Nd:YAG laser operating at 266 or 213 nm. On the other hand, transparent glasses and minerals such as quartz are better analyzed using a laser with a lower UV wavelength, such as a 193 nm Excimer laser.

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). 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.

To encourage wider adoption and use of LA-ICP-MS, simple, automated data analysis methodology that corrects for differences in ablation rates between standards and samples would also be beneficial. Agilent ICP-MS MassHunter software (version 5.2 onwards) includes a data correction function that is designed to address this aspect of LA-ICP-MS calibration. Applications that use direct solid sampling—including LA-ICP-MS—often measure all the elements in a sample, including the matrix element or elements. The full elemental coverage 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.

The analytical performance of the ICP-MS MassHunter 100% normalization approach was evaluated by analyzing varied metal reference materials using a femtosecond LA system coupled to an Agilent ICP-MS. The metal alloy and pure metal samples were calibrated against a well-characterized glass standard reference material (SRM), NIST 612 Trace Elements in Glass (NIST, Gaithersburg, US). The 100% normalization function was used to correct for differences in the ablation yield between different sample matrices, i.e., the glass calibration standard and the metal samples in this case. The 100% normalization function enables greater flexibility in calibration strategies, and significantly improves accuracy compared to a conventional approach where a major element is used as an internal standard.

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 (RAIJINα supplied by Seishin Trading Co., Ltd., Kobe, Japan).

Femtosecond laser ablation for LA-ICP-MS

Femtosecond laser ablation has several major benefits compared to conventional LA systems with a nanosecond pulse width. A fs laser can operate using a pulse width of less than 290 fs, which is less than the time scale of heat conduction from the laser beam to the sample. Removing thermal effects during ablation prevents sample heating and melting, so elemental and isotopic fractionation is reduced or eliminated (6–8).

Ablation with a fs pulse duration also gives smaller and more consistent particle size distribution, which means particles are transported more efficiently to the ICP. Because more of the particles are transported to the plasma, redeposition rates are low and sensitivity is high. The smaller and more uniform particles are also easier for the plasma to decompose completely, so fractionation effects in the ICP are also reduced and signal stability is improved. The more consistent ablation and more complete transport and decomposition of the particles improves the accuracy of the analysis, particularly when non-matrix-matched calibration standards are used, as in this study.

Femtosecond lasers are also capable of operating at very high (kHz) pulse repetition rates while maintaining consistent energy density, or fluence, at the sample surface. The high pulse repetition rate gives a smooth signal and increases the yield of ablated material, leading to higher sensitivity.

LA analysis method

Many LA-ICP-MS applications involve studying small features or inclusions in a sample, or the variation in elemental distribution across the sample, for example in imaging applications. These feature and imaging applications are enabled by the laser optics that allow the beam to be focused onto a spot as small as a few microns across. However, LA-ICP-MS can also be used for "bulk" analysis, where the laser ablation site is moved in a line or raster pattern to sample a larger sample area. To avoid errors due to sample inhomogeneity when performing bulk analysis with a small laser spot size, an area of several mm^2 is usually sampled. For this work, the fs LA system was used to ablate an area of 1.5 x 1.5 mm using a raster pattern with a line spacing of 8 µm.

The laser raster pattern was ablated continuously while data was collected, with about 10 raster passes being completed during the data acquisition for each triplicate sample measurement. All target analytes were measured using an integration time of 0.6 s (1 s for Be). For each sample, the analysis was repeated four times at the same site, giving three separate data acquisition measurements (each n=3), preceded by a "preablation" measurement that was not included in the data analysis. A "gas blank" was also measured using the same method as the sample acquisitions, but with the LA energy set at 0%, so no sample ablation occurred.

The sweep gas carrying the ablated material from the LA cell was mixed with the makeup gas of the 8900 ICP-QQQ using a Y-piece connector, and then introduced to the ICP torch. Helium (He) is normally used as the LA carrier gas, as He provides the best ejection and transport of the ablated material, although the benefit may be less significant with fs LA. For this work, a He LA carrier gas supply was not available, so argon was used, giving about a 2x reduction in sensitivity compared to what would have been achieved with He.

The 8900 ICP-QQQ was operated with the ORS[4] collision/reaction cell pressurized with He for all elements, so the acquisition method would also be applicable to an Agilent single quadrupole ICP-MS. He collision mode reduces interferences by using kinetic energy discrimination (KED) to selectively reduce the transmission of polyatomic ions. LA and ICP-QQQ operating conditions are given in Tables 1 and 2, respectively.

Table 1. Laser ablation operating conditions.

Parameter	Setting
Pulse Width (fs)	290
Wavelength (nm)	257
Spot Size (µm)	10
Repetition Rate (kHz)	20
Scan Speed (mm/s)	30*
Fluence (J/cm²)	5 (metals) or 7 (NIST Glass)
Scan Pattern/Line Spacing (µm)	Raster/8
Laser Carrier Gas Flow Rate (L/min)	1.0

* The fast scan speed was enabled by the galvanometer (galvo) mirror beam-scanning feature of the Seishin laser.

Table 2. Agilent 8900 ICP-QQQ operating parameters.

Parameter	Setting
RF Power (W)	1550
Sampling Depth (mm)	8.0
Makeup Gas (L/min)	0.25
Extract 1 Lens (V)	−10
Extract 2 Lens (V)	−180
Omega Bias Lens (V)	−80
Omega Lens (V)*	8.0
Helium Cell Gas Flow Rate (mL/min)	3.0
KED (V)	3.0

* Cu in EB385 was overrange under normal tuning conditions. So, a multi-tune method was used with an extended dynamic range (EDR) tune condition to reduce the Cu signal by a factor of 100 by detuning the Omega Lens voltage

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* (9).

To demonstrate the capability of the 100% normalization approach to provide accurate quantitative results without matrix matched calibration standards, three metal alloy and pure metal certified RMs (CRMs) were measured. The 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, and 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.

Certified and indicative concentrations for all elements (except carbon) with values quoted for each of the three CRMs are summarized in Table 3.

Table 3. Certified concentrations and indicative values (in parentheses) of all elements with certificate values for the three metal CRMs (carbon in NIST 1249 is excluded). Units mg/kg. Blank cells indicate no reference value is provided for that CRM.

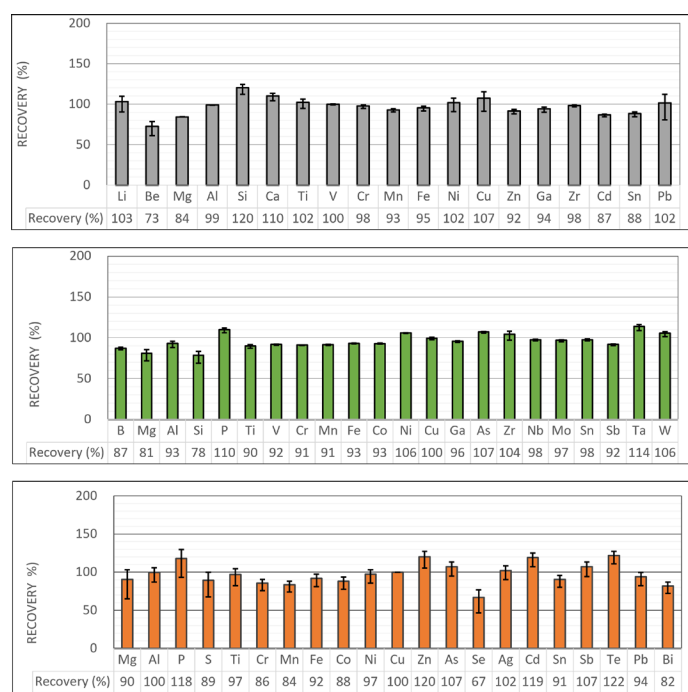| Element	BAM 310 Al/Mg Alloy	NIST 1249 Nickel Alloy	ERM-EB385 Pure Copper
Li	3.66		
Be	1.28		
B		23	
Na	3		
Mg	9940	12	29.1
Al	988,000	5682	28.6
Si	797	1200	(7.2)
P		134	12.9
S		6.4	31.3
Ca	7.3		
Ti	30.1	9590	3.83
V	44.4	338	
Cr	9	184,720	9.81
Mn	30.7	1080	10.1
Fe	705	176,930	45.4
Co		3371	6.93
Ni	24.4	532,900	11.9
Cu	16.9	1402	999,000
Zn	86		57.9
Ga	115.2	19	
As		13	11.4
Se			7.2
Zr	13.5	29	(<7)
Nb		51,960	
Mo		31,120	
Ag			28.6
Cd	23.7		5.8
Sn	23.8	24	18.0
Sb		3.0	19.1
Te			10.0
Ta		27	
W		846	
Pb	34.7		11.3
Bi			5.81

Calibration and data analysis

To enable the use of a glass matrix standard for the accurate quantitative analysis of trace elements in the metal CRM samples, the 100% normalization-calibration function (included in ICP-MS MassHunter from revision 5.2) was used. The 100% normalization function corrects for differences in the mass of material ablated between the calibration standard and the samples and for changes in ablation yield from sample to sample. The normalization function works by first determining the raw concentrations of all measured elements in each sample, calibrated against the standard, NIST 612 Glass in this case. The measured concentrations are then normalized so the sum of all measured elements equals 100%, thus correcting for differences in ablation rates between the sample and calibration standard matrices. For the normalization to provide accurate results, all the major elements in the samples must be included in the analyte list.

In many sample types, the elements are present in their elemental form, so, by default, the raw measured concentration is used for calculation of the normalized concentration for each element. However, if an element is present as a specific compound such as an oxide or fluoride, a compound-specific correction factor can be calculated and applied automatically in ICP-MS MassHunter. For example, if Ca is known to be present as CaO, the measured concentration of elemental Ca can be converted to the actual concentration of CaO present. The compound concentrations are then used in the 100% normalization, giving more accurate calculation of the total content of all elements analyzed. Once the concentrations have been normalized to 100%, the corrected concentrations are converted back to the elemental content for reporting of the ICP-MS results. Setup of the compound correction factors simply requires the user to enter the actual compounds into the 100% normalization calibration table in ICP-MS MassHunter, so the conversion can be applied during the normalization.

Results and discussion

In this work, the 100% normalization function for LA-ICP-MS was used for the analysis of trace elements in three metal alloy and pure metal CRMs, calibrated using NIST 612 Glass. The gas blank (background) signal was subtracted from all sample data. Figure 1 shows the recoveries of the measured concentrations determined in each of the CRMs compared to the certified values, after 100% normalization. Note that different elements are certified in each of the CRMs.

Almost all the recoveries were within 80–120% of the certified values, demonstrating the excellent accuracy that can be achieved using LA-ICP-MS with the 100% normalization function, even without matrix matched calibration standards. The error bars in each graph show ± the standard deviation (SD) of the three triplicate analyses measured sequentially at a single site for each sample. The precision was excellent for most analytes with SDs below 2% for most analytes in BAM 310 Al/Mg Alloy, and below 1% SD for most analytes in NIST 1249 Nickel Alloy. Higher SDs of around 5% were observed for the trace analytes in the ERM-EB385 Cu CRM, where many of the elements are present at single ppm levels in the pure Cu.

Figure 1. Quantitative analysis recoveries for certified elements in metal CRMs using the 100% normalization function with NIST 612 as the calibration standard: BAM 310 Al/Mg Alloy (top), NIST 1249 Nickel Alloy (middle), and ERM-EB385 Pure Copper (bottom). No data is shown for S in NIST 1249 or Si in ERM-EB385, due to low signal-to-noise.

NIST 1249 Ni Alloy SRM contains nearly 1% Ti and only 12 ppm Mg. Ti has a relatively low second ionization potential of 13.557 electron volts (eV), so forms a small proportion of doubly charged ions (M^{++}). Doubly charged ions appear at half their true mass in quadrupole mass spectrometry, as a quadrupole mass filter separates ions based on their mass-to-charge ratio (m/z). This means that doubly charged ions of the main Ti isotope, $^{48}Ti^{++}$, appear at m/z 24, where they overlap the main isotope of magnesium, $^{24}Mg^+$. He KED mode cannot resolve M^{++} interferences effectively, but Agilent ICP-MS systems use high performance, hyperbolic profile quadrupoles, which maintain high ion transmission under high resolution settings (peak width <0.5 u). The quadrupole performance enables an automated narrow peak mode to be employed, allowing the half mass correction function in ICP-MS MassHunter to be applied to correct for M^{++} overlaps. M^{++} correction is most commonly used to correct for doubly charged ion interferences from the rare earth elements and/or barium on Zn, As, and Se (*10*). But the correction algorithm can also be applied to other M^{++} overlaps, including $^{48}Ti^{++}$ on $^{24}Mg^+$ using the correction shown in equation 1.

$$Mc(24) = M(24) - M(24.5) \times 13.6 \qquad \text{Equation 1}$$

Where Mc is the corrected Mg signal (in counts), M is the measured signal, the number in parenthesis is the mass-number, and 13.6 is the ratio of the abundances of the isotopes ^{48}Ti to ^{49}Ti. By measuring the signal for $^{49}Ti^{++}$ at the half-mass position (m/z 24.5), the contribution from $^{48}Ti^{++}$ at m/z 24 can be calculated from the known isotopic abundances.

Applying the mathematical correction to calculate and subtract the contribution from $^{48}Ti^{++}$ on $^{24}Mg^+$ enabled a good recovery result to be obtained for Mg in NIST 1249 Ni Alloy, as shown in Figure 1 (middle plot).

Conclusion

Generating a representative multi-element calibration is one of the biggest challenges for accurate quantitative analysis of solids by LA-ICP-MS. In this work, a new calibration approach using 100% normalization (included in ICP-MS MassHunter from revision 5.2) was used for the accurate analysis of certified elements in metal alloy and pure metal CRMs. The metal CRMs were calibrated against the well characterized—but not matrix matched—standard, NIST 612 Trace Elements in Glass. The analysis was performed using an Agilent 8900 ICP-QQQ operated in helium collision mode for all elements so the acquisition method would also be applicable to an Agilent single quadrupole ICP-MS. The ICP-QQQ was coupled to a femtosecond laser ablation system; the fs ablation also contributed to reducing sample-to-sample differences in the ablation rate.

The LA-ICP-MS method with 100% normalization successfully determined all certified elements (excluding carbon) in three different metal CRMs. 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.

The method outlined in this work represents a new, simple, and effective procedure for the direct, elemental analysis of metals and other solid samples. The normalized calibration method is likely to become a standard procedure for LA-ICP-MS.

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