# Quantitative analysis of high purity metals using laser ablation coupled to an Agilent 7900 ICP-MS
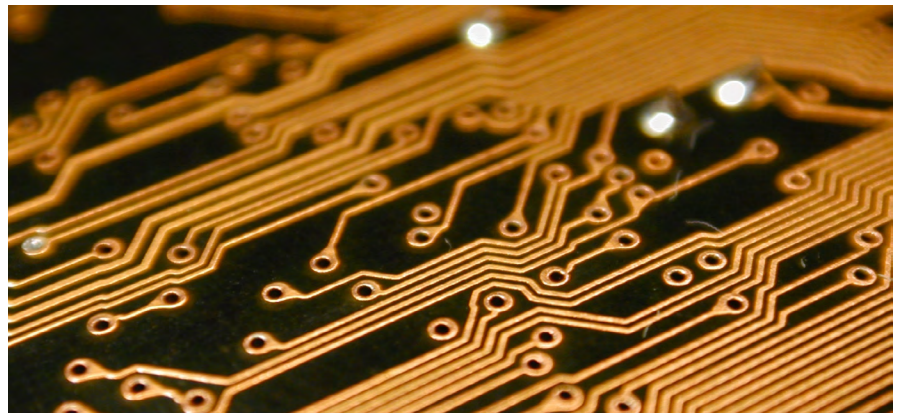
## Application note

Metals Analysis & Production

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## Introduction

Laser Ablation-ICP-MS (LA-ICP-MS) is used for the elemental analysis of solid samples and powders, including geological materials, ceramics, biological tissue and forensic samples. In this study, two calibration strategies (matrix matching and non-matrix matching) were used for the quantitative analysis of high purity metals. Since solid samples can be analyzed directly using LA-ICP-MS, minimal sample preparation is required compared to standard liquid sample introduction. This reduces the risk of analyte loss and eliminates the introduction of contaminants by avoiding the dissolution process. However, accurate quantitative analysis can be problematic for LA-ICP-MS analysis, due to lack of solid calibration standards. Preparing calibration standards for the analysis of solids is more difficult than for liquid sample analysis, and matrix-matched solid calibration standards that contain the analytes at suitable concentrations are rarely available. In a few cases, such as the metals industry, well-characterized, matrix-matched standards may already be available, since established analytical techniques such as Arc/Spark or Glow Discharge (GD) Optical Emission Spectroscopy (OES) utilize solid standards.

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An alternative approach is to calibrate using existing solid certified reference materials (CRMs). For the best accuracy, the physical properties and major element composition of the CRMs should be similar to the samples, but such matrix-matched CRMs are often not available. CRMs of a different composition (non-matrix matched standards) can be used, but differences in ablation yield and elemental fractionation during the ablation process between the CRM and the sample may cause a significant error in quantification. A number of studies have focused on elemental fractionation [1-4], but few have reported on the accuracy that is achievable in quantitative analysis using LA-ICP-MS [5]. The goal of this note is to describe a method for quantitative LA-ICP-MS analysis, with good accuracy and precision, using both matrix matched and non-matrix matched calibration strategies.

## Experimental

### Laser ablation system
A NWR213 (ESI, California, USA) deep UV Nd:YAG laser with a wavelength of 213 nm and pulse duration time of 4 ns was used. It is equipped with two volume ablation cell which ensures high transport efficiency and fast washout of the aerosol irrespective of the position of the sample in the cell. The NWR213 is one of the most widely used LA systems for LA-ICP-MS due to its favorable cost-to-performance ratio. According to the literature [1-3], LA systems that use a short wavelength and narrow pulse duration can minimize thermal effects during the ablation process, and hence reduce elemental fractionation. The aerosol produced by the LA system is carried in a helium gas flow from the ablation cell, mixed with argon (carrier gas of the ICP-MS), and delivered to the spray chamber of the ICP-MS where extra-large particles are removed before entering the plasma torch. The removal of the larger particles of ablated material is important, as they may lead to incomplete particle decomposition and signal fluctuation [6].

For the calibration standards, a single line scan was applied since the homogeneity was known. As the homogeneity of the samples was unknown, five lines per sample were ablated and analyzed. Three replicate measurements were made for each line, and the average and relative standard deviation was calculated for each sample. Each line scan was about 700 μm long, using a 200 μm diameter ablation spot and a

10 μm/s scan rate. Pre-ablation of the calibration standards and samples was carried out using the same operating conditions in order to remove any potential contamination on the surface. LA operating conditions are summarized in Table 1.

### ICP-MS
An Agilent 7900 ICP-MS was used, with MassHunter 4.2 (MH4.2) software. As mentioned above, the output of the LA cell was mixed with the argon carrier gas, and then connected directly to the spray chamber of the ICP-MS at the nebulizer port (the nebulizer was removed). Hydrogen cell gas was used in the 7900 Octopole Reaction System (ORS[4]) collision/reaction cell, to remove argide spectral interferences such as $ArAr^+$, $ArO^+$ and $CuAr^+$, which are more problematic interferences under laser ablation (dry plasma) conditions than the oxide interferences typically encountered in solution mode. The ICP-MS was optimized by monitoring the signal from National Institute Standard and Technology (NIST) SRM 612 Trace Elements in Glass, and the carrier gas flow rate was optimized by maximizing the $Th^+$ signal, while keeping the oxide ratio $ThO^+/Th^+$ at 0.3%. ICP-MS operating conditions are given in Table 1.

**Table 1.** LA-ICP-MS operating parameters

| ICP-MS parameter | Unit | Value |
|---|---|---|
| RF power | W | 1550 |
| Sampling depth | mm | 8 |
| Carrier gas flow rate | L/min | 1.15 |
| Makeup gas flow rate | L/min | 0.0 |
| Extraction 1 lens | V | -15 |
| Extraction 2 lens | V | -180 |
| KED | V | 3 |
| $H_2$ cell gas flow rate | mL/min | 3.8 |
| Data acquisition mode | | spectrum |
| Integration time | s/mass | 1 |
| Number of sweeps | | 50 |
| Replicates per line | | 3 |
| **LA parameter** | **Unit** | **Value** |
| Fluence | J/cm² | 3 |
| Spot size | μm | 200 |
| Scan pattern | | line |
| Scan rate | μm/s | 10 |
| Pre-ablation | | on |
| Warm-up time | s | 10 |
| On delay time | s | 20 |

Using the MassHunter plug-in developed by ESI, the LA system was controlled directly from the ICP-MS MassHunter 4.2 software for fully integrated sample analysis. The scan-pattern is set up in the LA system and then loaded into MassHunter, where the run is controlled using the software plug-in, as illustrated in Figure 1. The first four entries (COPPERSPEC 001 to COPPERSPEC 100) are the calibration standards and the remaining entries, EB385 (BAM-M385) and BAM 383b are samples. Since the use of a spray chamber delays the signal response by several seconds, the "on delay time" parameter was set to 20 s with an LA "warm-up time" of 10 s. Consequently, data acquisition started 10 s after the start of the pattern scan routine, ensuring that the signal had stabilized before the measurement started.
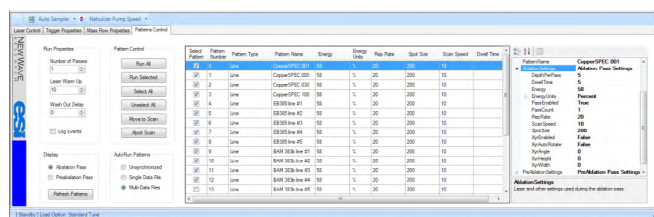


**Figure 1.** LA pattern list displayed in ICP-MS MassHunter

### Sample and standards
Copper CRMs, European Reference Material EB-385 (formally known as BAM-M385) and BAM-M383b, an aluminum CRM BAM-310 and a steel CRM D191-2 were purchased from BAM Federal Institute Material Research and Testing (Berlin, Germany). Each CRM was cut to a suitable size using a wire saw. Any contamination on the cut surface was removed using 30% $HNO_3$. Standards originally developed for DC-Arc spectrometry, COPPERSPEC 001, 005, 030 and 100 purchased from CopperSpec Inc (Utah, US), were used as calibration standards in this study. NIST 612 was used to tune and calibrate the LA-ICP-MS system.

## Results and discussion

### Matrix matched calibration
Four solid COPPERSPEC standards, 001, 005, 030 and 100, which are spiked with 11 elements at 0.1, 0.5, 3, and 10 ppm respectively, were used for the matrix-matched calibration. Two copper CRMs, BAM-M385 and BAM-M383b were analyzed as unknown samples against the spiked copper calibration standards. $^{65}Cu$ was used as the internal standard (ISTD) to correct for any variation in the LA system, ablation yield, and signal suppression/drift of the ICP-MS. Representative calibration curves for three elements (As, Se and Ag) demonstrate good linearity, as shown in Figure 2.
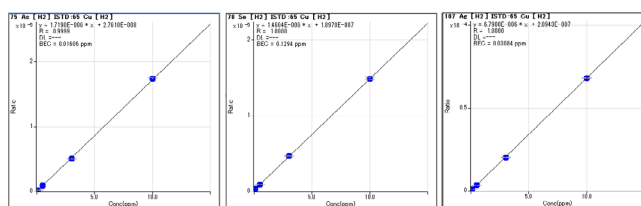


**Figure 2.** Calibration curves for As, Se and Ag using COPPERSPEC copper matrix standards

The lowest standard of 0.1 ppm was analyzed nine times to determine the Method Detection Limit (MDL), which was calculated as three times the standard deviation of the nine analyses. Table 2 summarizes the correlation coefficient of the calibration curve, sensitivity, background equivalent concentration (BEC) and MDL of the 11 spiked elements.

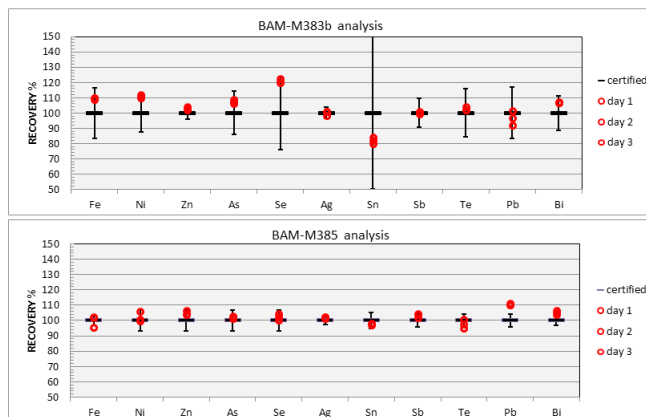**Table 2.** Performance characteristics of the LA-ICP-MS method

| Element | Mass | R | Sensitivity cps/ppm | BEC ppb | MDL ppb |
|---------|------|--------|---------------------|---------|---------|
| Fe | 56 | 0.9991 | 10,500 | 104 | 21 |
| Ni | 60 | 0.9997 | 500 | 9 | 25 |
| Zn | 68 | 0.9992 | 1,400 | 24 | 18 |
| As | 75 | 0.9999 | 1,000 | 16 | 18 |
| Se | 78 | 1.0000 | 770 | 129 | 17 |
| Ag | 107 | 1.0000 | 4,100 | 31 | 12 |
| Sn | 118 | 1.0000 | 6,300 | 22 | 11 |
| Sb | 121 | 1.0000 | 6,700 | 17 | 9 |
| Te | 125 | 1.0000 | 490 | 3 | 21 |
| Pb | 208 | 1.0000 | 10,000 | 13 | 11 |
| Bi | 209 | 1.0000 | 16,700 | 2 | 6 |

Table 3 shows the measured results (average±standard deviation of five separate ablation lines) and certified concentrations for the 11 calibrated elements in the two copper CRMs. The measured concentrations are in good agreement with the certified values; all within ± 10% deviation or uncertainty (given error range) of the CRMs.

The same analysis was repeated on three different days, with good reproducibility. Figure 3 shows the % recovery of the measured average concentrations compared to the certified value on the three days. The results for BAM-M383b have higher variability due to the much lower concentrations of trace elements in this CRM (single- or sub-mg/kg (ppm) for most elements), but the data show that the LA-ICP-MS method is suitable for quantitative analysis of trace elements at the low ppm level in solid copper, with accuracy typically better than ± 10%.



**Figure 3.** Recovery of calibrated (spiked) elements on three different days

**Non-matrix matched calibration**

In many LA-ICP-MS applications, known or certified standards are not available and cannot easily be synthesized. In these cases, a non-matrix matched calibration can be used, based on a common, commercially available, and well-characterized CRM, such as NIST 612 Trace Elements in Glass [7, 8]. Three different metal CRMs were analyzed by LA-ICP-MS using NIST 612 as a non-matrix matched calibration standard to assess the accuracy of the method. BAM-M385 (pure copper), CRM-191-2 (dynamosteel) and BAM-310 (98.5% Al, 1% Mg) were analyzed as samples, and trace element concentrations were calculated against a semi-quantitative calibration, using NIST 612 as the semi-quant standard. Cu, Fe and Al were used as internal standards in analysis of BAM-M385, CRM-191-2 and BAM-310, respectively. Certified concentrations of elements in NIST 612, BAM-M385, CRM-191-2 and BAM-310 are summarized in Table 4.

**Table 3.** Measured (average of 5 ablation lines) and certified concentrations of representative elements in two copper CRMs: BAM-M383b and BAM-M385

| Elements | BAM-M383b | | BAM-M385 | |
|---|---|---|---|---|
| | Certified mg/kg | Measured mg/kg | Certified mg/kg | Measured mg/kg |
| Fe | 3.60 ± 0.60 | 3.92 ± 0.13 | 45.4 ± 1.4 | 43.5 ± 0.1 |
| Ni | 1.43 ± 0.18 | 1.59 ± 0.02 | 11.9 ± 0.8 | 12.0 ± 0.1 |
| Zn | 9.30 ± 0.40 | 9.69 ± 0.15 | 57.9 ± 4.0 | 61.6 ± 0.4 |
| As | 2.80 ± 0.40 | 3.05 ± 0.16 | 11.4 ± 0.8 | 11.7 ± 0.3 |
| Se | 1.17 ± 0.28 | 1.43 ± 0.13 | 7.20 ± 0.50 | 7.37 ± 0.64 |
| Ag | 10.60 ± 0.40 | 10.72 ± 0.36 | 28.6 ± 0.8 | 29.2 ± 0.4 |
| Sn | 0.80 ± 0.40 | 0.66 ± 0.04 | 18.0 ± 0.9 | 17.6 ± 0.5 |
| Sb | 1.69 ± 0.16 | 1.71 ± 0.13 | 19.9 ± 0.8 | 20.8 ± 0.6 |
| Te | 5.70 ± 0.90 | 5.94 ± 0.69 | 10.0 ± 0.4 | 10.1 ± 0.4 |
| Pb | 1.01 ± 0.17 | 1.03 ± 0.09 | 11.3 ± 0.5 | 12.6 ± 0.4 |
| Bi | 1.85 ± 0.21 | 1.98 ± 0.21 | 5.81 ± 0.17 | 6.18 ± 0.22 |

**Table 4.** Certified concentrations of elements in four CRMs. The underlined values for NIST 612 represent consensus values for non-certified elements.

| Element | NIST 612 mg/kg | BAM 385 mg/kg | CRM 191-2 mg/kg | BAM 310 mg/kg |
|---|---|---|---|---|
| Mg | <u>61</u> | 29.1 ± 1.3 | | 9,940 ± 150 |
| Al | *10,584 | 28.6 ± 2.5 | 9,850 ± 60 | ISTD |
| Si | *327,225 | (7.2 ± 1.5) | 32,670 ± 120 | 797 ± 12 |
| Ti | 50.1 ± 0.8 | 3.83 ± 0.17 | 24 ± 2 | 30.1 ± 1.1 |
| Cr | <u>37</u> | 9.81 ± 0.2 | 314 ± 6 | 9.0 ± 1.2 |
| Mn | 39.6 ± 0.8 | 10.1 ± 0.2 | 1,334 ± 19 | 30.7 ± 1.1 |
| Fe | 51 ± 2 | 45.4 ± 1.4 | ISTD | 705 ± 12 |
| Co | 35.5 ± 1.2 | 6.93 ± 0.15 | | |
| Ni | 38.8 ± 0.2 | 11.9 ± 0.8 | 224 ± 4 | 24.4 ± 1.4 |
| Cu | 37.7 ± 0.9 | ISTD | 165 ± 3 | 16.9 ± 0.9 |
| Zn | <u>37.9</u> | 57.9 ± 4.0 | | 86 ± 4 |
| As | <u>33</u> | 11.4 ± 0.8 | 18 ± 3 | |
| Se | <u>15.2</u> | 7.2 ± 0.5 | | |
| Ag | 22.0 ± 0.3 | 28.6 ± 0.8 | | |
| Cd | <u>28</u> | 5.8 ± 0.3 | | 23.7 ± 0.7 |
| Sn | <u>38</u> | 18.0 ± 0.9 | 50 ± 5 | 23.8 ± 0.8 |
| Sb | <u>38</u> | 19.9 ± 0.8 | | |
| Pb | 38.57 ± 0.2 | 11.3 ± 0.5 | | 34.7 ± 2.5 |
| Bi | <u>29.8</u> | 5.81 ± 0.17 | | |

*information value

The substrate metal of each CRM was used as the ISTD to correct for differences in the ablation rate between the standard (NIST 612) and samples (metal CRMs), and to correct any system variation during the analysis. It is usually not practical to find multi-element ISTDs at low, middle and high mass in solid standards so mass dependent drift and signal suppression may lead to more significant errors in the quantified values of high mass and low mass elements in LA-ICP-MS.

The same LA and ICP-MS conditions that were used for the matrix-matched calibration method were used (Table 1). Five lines (about 700 μm length) per sample were measured and concentrations of elements in the sample were determined using semi-quant data analysis mode. The data was background corrected using a background signal acquired using the same acquisition method and laser settings, but with a LA fluence (energy density) of 0 J/cm, so no sample ablation occurred.

Figure 4 shows the semi-quant results for 19 elements as % recovery relative to the certified value. The five separate results from each of the five individual line analyses are represented by circles. The rectangle and the error bar are the average and the standard deviation of the five-line analysis, respectively. The standard deviation for some elements such as Mg, Ti and Se in BAM-M385 was high, possibly indicating some inhomogeneity of the incorporation of these elements in the metal matrix, and illustrating the requirement of averaging multi-line analysis (as used in this method). The standard deviation of most of the other elements was low, indicating homogeneous distribution in the sample.
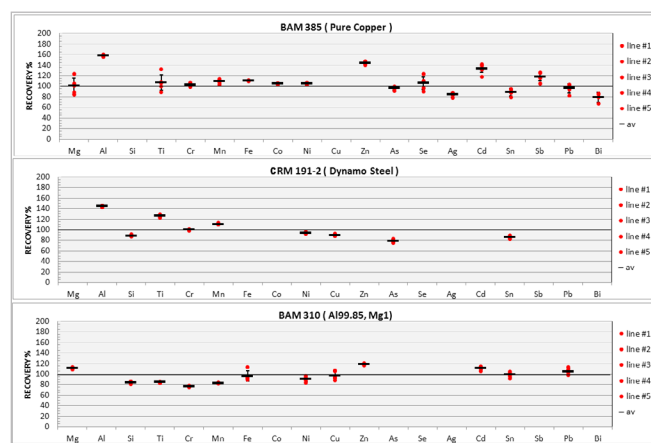


**Figure 4.** Results for 19 elements as % recovery to the certified value

The average recoveries of all elements fall within 50% of the certified value, with the exception of Al (158%) in BAM-M385. Recoveries weren't improved using helium collision cell mode or higher temperature plasma conditions (argon carrier gas flow was reduced to 1.05 L/min.), so the high recoveries are unlikely to be caused by spectral interferences from polyatomic ions. Elemental fractionation during the LA process is a more likely explanation. The accuracy of the results using non-matrix matched semi-quant calibration is poorer than with matrix-matched calibration, but the method is simple, can be applied to a variety of materials, and is a useful approach when matched calibration standards are not available, and when lower accuracy is acceptable, as with screening analysis.

## Conclusions

Two calibration strategies for the analysis of high purity metals by LA-ICP-MS were evaluated in terms of accuracy. The use of matrix-matched copper calibration standards allowed accurate analysis of trace elements in copper CRMs within ± 10% of the certified values. However, in many applications of LA-ICP-MS, known or certified standards are not available and cannot easily be made. The accuracy of the results obtained using non-matrix matching calibration, based on one of the most common commercially available CRMs, NIST 612, was mostly within ± 50%, indicating that this approach may be useful depending on the objectives of the analysis.

It is anticipated that the accuracy of non-matrix matched calibration will improve as the hardware develops, in which case, LA-ICP-MS will become an even more attractive technique for a wide range of applications.

## References

1. J. Gonzales et al, *J. Anal. At. Spectrom.*, 2002, 17. 1108-1113

2. B. Wagner, A. Nowak, E. Bulska, K. Hametner and D. Gunther, *Anal. Bioanal. Chem.*, 2012, 402, 1667-1677

3. R.E. Russo, X.L.Mao, O.V. Borisov and Haichen Liu, *J. Anal. At. Spectrom.*, 2000, 15, 1115-1120

4. P. K. Diwakar et al, *J. Anal. At. Spectrom.*, 2014, 29, 339-346

5. V. Mozna, J. Pisonero, M. Hola, V. Kanicky and D. Gunther, *J. Anal. At. Spectrom.*, 2006, 21, 1194-1201

6. J. Koch, A. von Bohlen, R. Hergenroder and K. Niemax, *J. Anal. At. Spectrom.*, 2004, 19, 267-272

7. N.J.G Pearce. et al, J*ournal of Geostandards and Geoanalysis,* 1997, 21, 115-141

8. M. Guillong et al, *J. Anal. At. Spectrom.*, 2008, 23, 1581-1589

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