Application Note: 30103

Analysis of Non-Conductive Solid Samples by Laser Ablation Interfaced with Extended Dynamic Range HR-ICP-MS

Julian D. Wills, Meike Hamester, Thermo Fisher Scientific, Bremen, Germany
Masahiro Oishi, TDK Corporation, Material Analysis Center, Technology Group, Japan
Rob Henry, Thermo Fisher Scientific, Boulder, CO, USA

Key Words

- ELEMENT XR
- Ceramics
- Laser Ablation

Introduction

The requirements for the direct elemental analysis of conductive and non-conductive materials in industrial applications may be separated into bulk and small feature analysis. Glow Discharge MS (GD-MS) is the accepted technique for accurate bulk analysis of conductive (and some semi-conductive) matrices and the Thermo Scientific ELEMENT GD will enhance its position as the industry standard[1].

Laser ablation ICP-MS (LA-ICP-MS) is the most appropriate tool for the elemental analysis of non-conductive samples, such as ceramics. The high spatial resolution of the laser (< 10 µm sampling) allows accurate analysis of surface features or individual sites that is not possible with GD-MS. However accurate measurement of the sample matrix elements by LA-ICP-MS has been limited by the saturation of the secondary electron multiplier (SEM) detector.

Extended Dynamic Range with the Thermo Scientific ELEMENT XR

SEMs are limited in their dynamic range to between 8 - 9 orders of magnitude. With the high sen-sitivity of the Thermo Scientific ELEMENT 2 (> 2 Mcps per ng g^{-1} in solution) and low background noise, a 9 order measurable concentration range - from fg g^{-1} to µg g^{-1} in solution mode is possible. While this is sufficient for most applications, multiple dilutions may have to be performed in order to avoid saturation of the detector.

The limited dynamic range is more troublesome with LA-ICP-MS as the sample matrix is an ideal internal standard. Our normal goal is to maximize laser sensitivity for the analysis of ultra-trace elements by using high laser energies, large spot sizes and high ablation rates. However, due to the limited upper dynamic range of the SEM detector system, the highest laser fluxes must be avoided in order to keep the internal standard within the measurable range of the detector system, thereby sacrificing ultimate detection power.

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Implementation of a Combined SEM and Faraday Detection System

A new detection system (Figure 1) has been implemented in the Thermo Scientific ELEMENT XR HR-ICP-MS that is based upon the proven design of the ELEMENT 2. Through the combination of a single Faraday collector with the dual mode SEM, the linear dynamic range of the ELEMENT XR has been increased by an additional three orders of magnitude, to over 10^{12}.

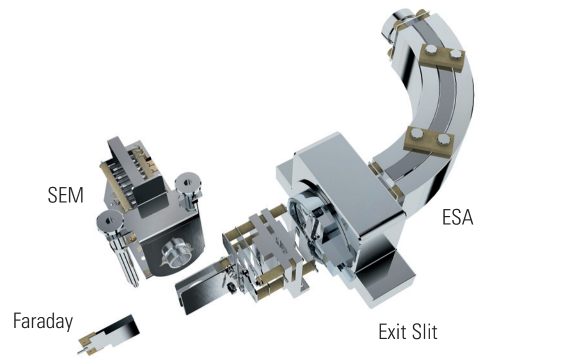

Figure 1: Thermo Scientific ELEMENT XR detection system.

Features of the Thermo Scientific ELEMENT XR detection system:

- Sample times down to 1 ms.
- No decay time required after the measurement of high intensities.
- Automatic switching between SEM (Analog and Counting detection modes) and Faraday with delay times < 1 ms.
- Wide crossover ranges (> 2 orders of magnitude) between different detector modes to allow accurate, automated cross-calibration.
- Dynamic range: 5×10^7 cps - > 1×10^{12} cps (1 ms sample time).

With this increase in dynamic range, any limitation on the upper level of quantification is removed as the maximum measurable concentration achievable with the ELEMENT XR is over 1000 µg g^{-1}.

Determination of Trace Elements in Ceramics

In order to test the applicability of the Thermo Scientific ELEMENT XR's extended dynamic range for the LA-ICP-MS analysis of non-conducting samples, a series of $Ba(Ti_{0.8}Zr_{0.2})O_3$ (barium titanate zirconate, BTZ) ceramic disks (1 cm φ) were prepared with a range of added impurities at known concentrations. BTZ ceramics are of great interest currently as they are lead free and therefore more environmentally friendly than the traditional PTZ (Pb based) ceramics that are currently used in a wide range of piezoelectric applications.

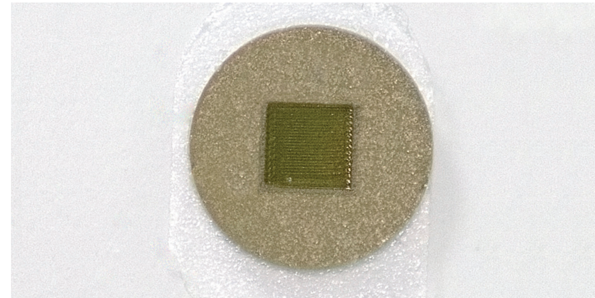

Figure 2: One of the BTZ ceramic disks investigated showing the 300 µm square ablation raster used.

The laser system used was the New Wave Research UP213 AS (switchable aperture focused, aperture imaged) operating at 213 nm. Laser operating parameters are shown in Figure 3.

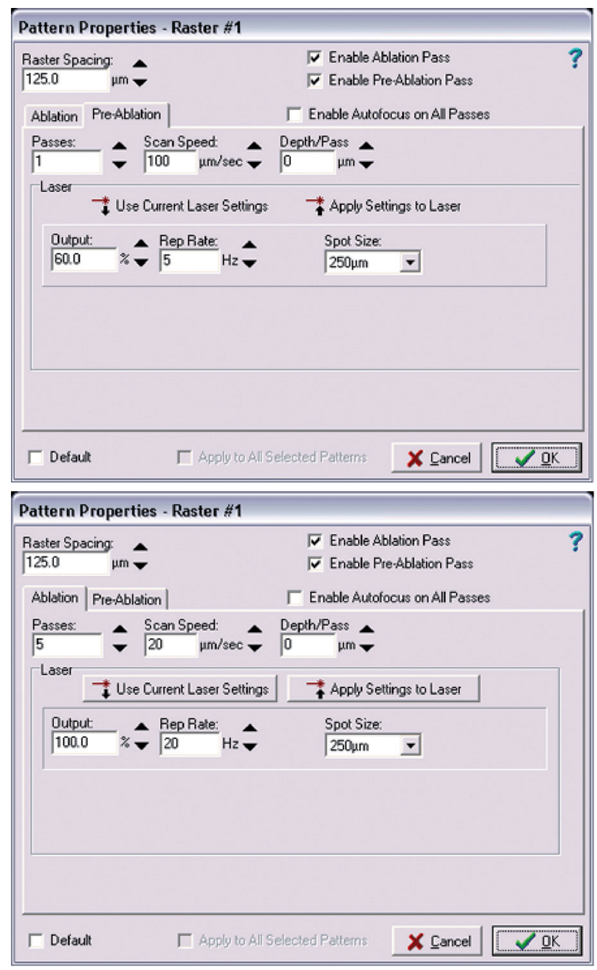

Figure 3: Laser pre-ablation and ablation operating parameters.

The high laser flux parameters used here are necessary due to the low target impurity concentrations in the BTZ ceramic. With the ELEMENT XR as detector in LA-ICP-MS, there is no limit on the maximum laser energy, repetition rate or spot size that can be used. The extended dynamic range (> 12 orders of magnitude) allows for the simultaneous analysis of the sample matrix as internal standard with the Faraday detector and the traces using the dual-mode SEM (Figure 4).

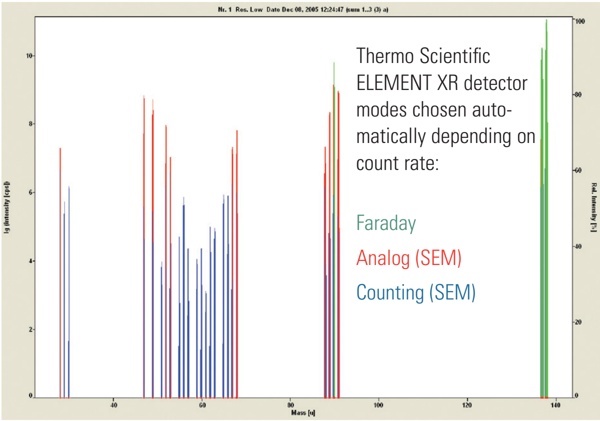

Figure 4: LA-ICP-MS spectrum in BTZ ceramic (logarithmic sensitivity scale). With intelligent, automatic switching between the three detector modes in the Thermo Scientific ELEMENT XR, a dynamic range of 10^{11} is shown for this sample. This allows the simultaneous measurement of the matrix elements (e.g. Ba and Zr) with the Faraday detector and the traces with the counting and analog modes of the SEM.

Identification and Removal of Interferences

Even when using dry plasma, matrix dependent polyatomic interferences exist in LA-ICP-MS and they have to be identified and removed to provide accurate quantification.

The unique ability of high resolution ICP-MS to guarantee accurate quantification, irrespective of the sample matrix, can be seen in the determination of copper in the BTZ ceramic. Figure 5 shows screenshots of both Cu isotopes in Low (R = 300) and Medium (R = 4000) resolution modes.

In complicated matrices, such as the ceramic investigated in this work, only high resolution ICP-MS can identify and remove all polyatomic interferences using a single set of instrument conditions with the speed necessary for laser ablation analyses.

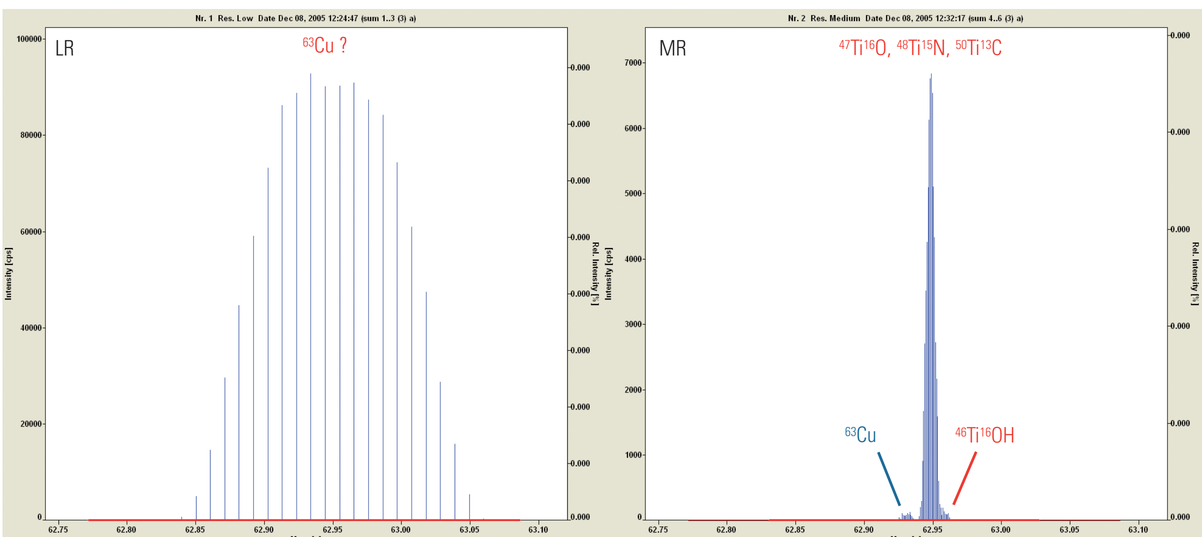

Figure 5a: Low and medium resolution spectra for ^{63}Cu, showing complete separation of the target ^{63}Cu isotope from the matrix induced, Ti-based interferences using Medium Resolution (R = 4000).

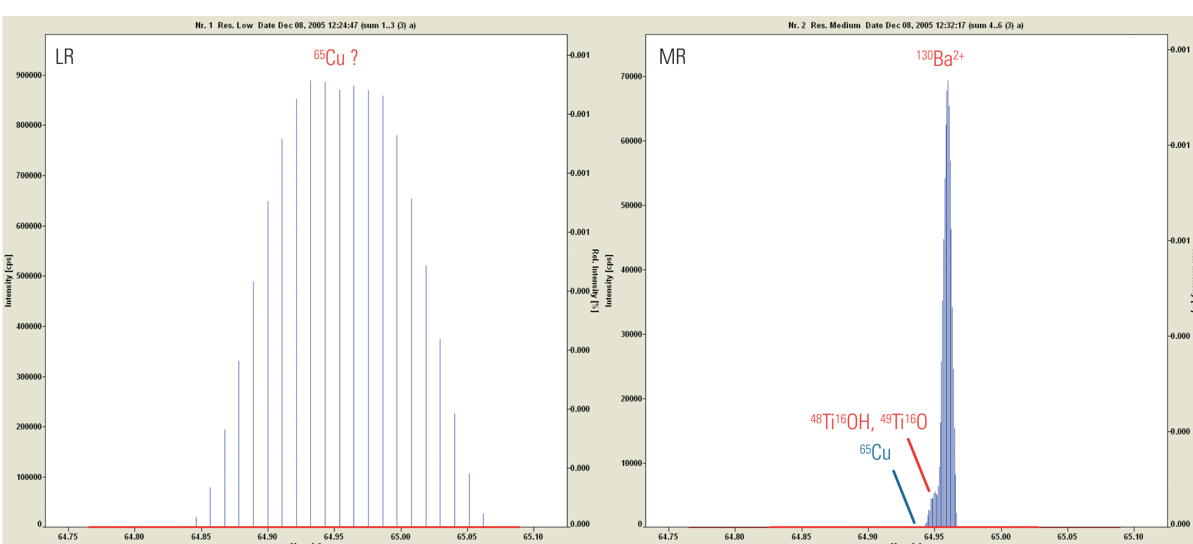

Figure 5b: Low and medium resolution spectra for ^{65}Cu, showing complete separation of the target ^{65}Cu isotope from the matrix induced, Ti and Ba-based interferences using Medium Resolution (R = 4000).

Results

Results from the analysis of four BTZ ($Ba(Ti_{0.8}Zr_{0.2})O_3$) ceramics are shown in Table 1. With the extended dynamic range of the Thermo Scientific ELEMENT XR, the matrix elements can be measured at concentrations > 60% in the solid at the same time as traces with concentrations of 200 ppm.

To test the reproducibility of the LA-ICP-MS analysis of BTZ ceramics, ten sequential repeat analyses were made over the raster pattern shown in Figure 2. The concentration results from these analyses are shown in Figure 6.

Conclusion

The unique combination of a Faraday and SEM detection system in the Thermo Scientific ELEMENT XR has been shown to be the ideal tool for the determination of trace elements in ceramics. The Faraday detector allows the use of optimum high laser fluxes for the measurement of a matrix element as internal standard, while the ultra-trace elements are simultaneously measured using the high sensitivity SEM detector.

References

[1] Thermo Scientific ELEMENT GD Brochure BR30066_E

Ceramic		^{47}Ti	^{51}V	^{52}Cr	^{55}Mn	^{59}Co	^{88}Sr	^{89}Y	^{90}Zr	^{137}Ba
1 (Mn doped)	Average (%)	26.8			0.33		0.019	0.3	9.8	64.9
	%RSD	3.0			1.3		0.4	2.7	0.4	2.8
2 (Cr doped)	Average (%)	23.5		0.29			0.018	0.3	8.7	65.2
	%RSD	3.7		0.5			6.1	6.3	3.2	5.4
3 (Co doped)	Average (%)	25.8				0.30	0.020	0.3	10.1	62.1
	%RSD	0.9				0.6	1.9	4.9	1.1	2.1
4 (V doped)	Average (%)	26.4	0.30				0.021	0.3	10.3	63.2
	%RSD	0.7	1.9				1.1	3.1	2.0	0.0
	Target (%)	25.0	0.30	0.30	0.30	0.30	0.020	0.30	10.0	65.0

Table 1: Results from analysis (n=2) of the four $Ba(Ti_{0.8}Zr_{0.2})O_3$ ceramics (all concentrations reported as % values, no internal standard).

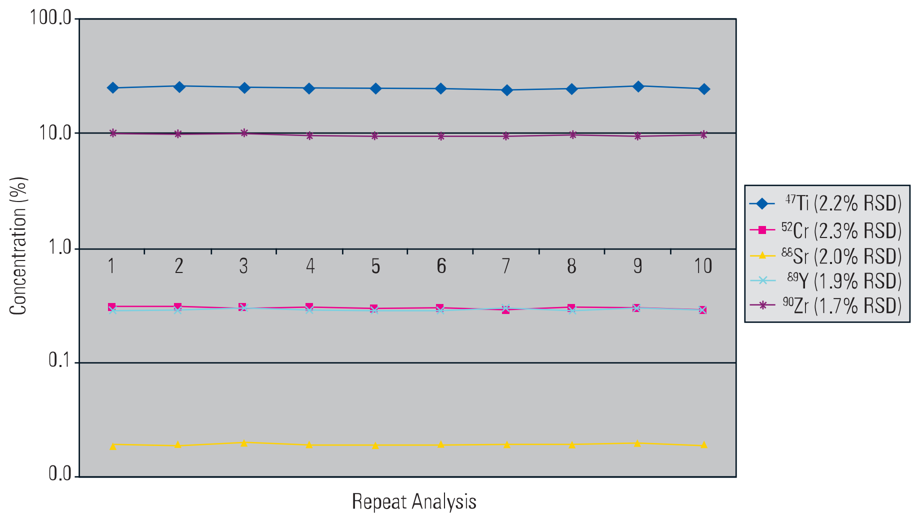

Figure 6: Results from ten repeat analyses of a BTZ ceramic (logarithmic scale). For these measurements, the matrix element Ba (at a concentration of 65%) was used as internal standard.

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