

Laser Ablation Analysis of High Purity Solids Using High Sensitivity Quadrupole ICP-MS

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Introduction

Glow discharge mass spectrometry (GD-MS) is the accepted technique for the routine determination of metals and non-metals in high purity conductive (and semi conductive) materials – see poster F27B on Friday. The versatility of laser ablation coupled to Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) can, in some cases, offer significant advantages in terms of compatibility with non conductive materials; provide more detailed spatial resolution and ease of automation as can be seen in the following selection of applications.

FIGURE 1. Thermo Scientific XSERIES 2 ICP-MS and New Wave UP213 SA (switchable aperture) Laser Ablation system used in these analyses.

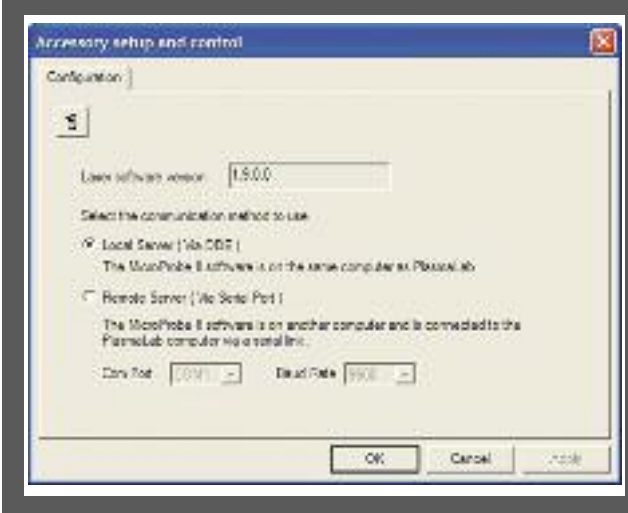


The XSERIES 2 provides a complete LA-ICP-MS solution for routine analysis of high-purity solids when coupled with the New Wave UP series of laser ablation systems.

Hardware integration:

- Additional cabling for triggering between the New Wave laser and the XSERIES 2 is not necessary since all communication is made directly between the two software packages installed on the same PC for a seamless analytical package
- Additional mass flow controller with software controlled gas calibration for different gases (He for laser)
- 'On the fly', in-scan switchable high mass resolution
- Dual monitor support for continuous sample viewing during all analyses
- AI sample and skimmer cones for decreased elemental blanks

FIGURE 2. Screenshot showing the 'handshake' between the Laser Ablation and ICP-MS softwares via DDE control on the same control PC.

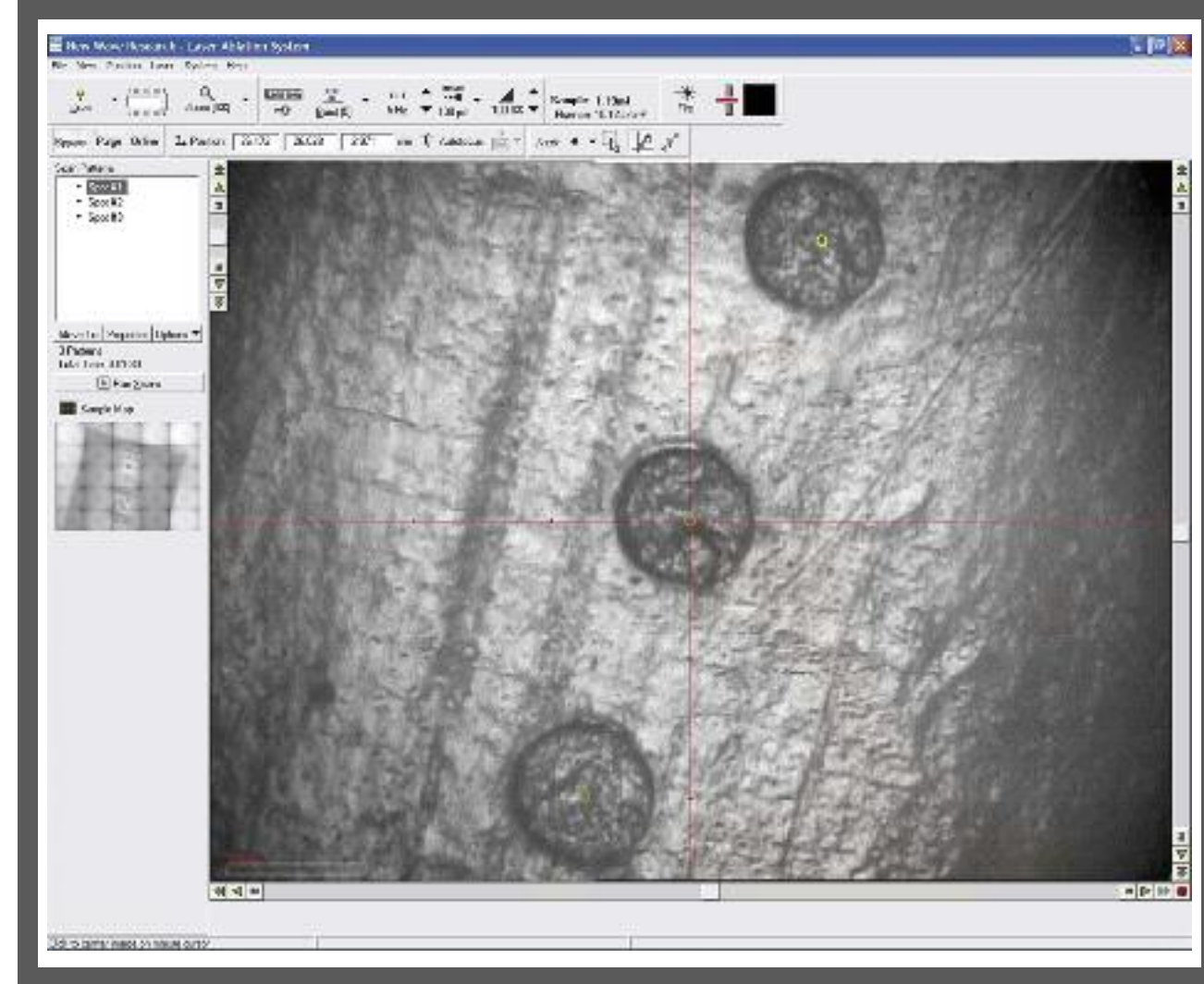


- Optimized skimmer cones for enhanced performance or minimum polyatomic ion formation
- Dual mode introduction system for the addition of wet or dry aerosols simultaneously with the ablated particles for additional application flexibility, for example:
- In-line mass bias correction for isotope ratio studies
- Standard addition for quantification in matrices without reference materials
- Analyze the internal standard (matrix) in high resolution to reduce ion beam on the detector to improve detector lifetimes

Software integration:

- The New Wave and XSERIES 2 PlasmaLab software can be run simultaneously on the same PC
- Sample positions generated in the New Wave software are automatically assigned to analyses in PlasmaLab – no need for the sample list to be defined twice
- Powerful script control in PlasmaLab allows for full flexibility in laser control through shared DDE functionality between the two software platforms
- PlasmaLab contains a complete Time Resolved Analysis (TRA) package in the default installation for a complete range of quantification techniques
- Laser data can be easily exported into dedicated laser data reduction packages such as GLITTER™

FIGURE 3. Screenshot of three ablation sites in polypropylene from the New Wave laser software. The laser scan patterns defined are automatically assigned to analyses in the XSERIES 2 software.



LA-ICP-MS of Polyolefins

Why?	Current technique?
Determination of residuals from catalysts used in production in order to evaluate the catalyst's performance.	Traditional techniques are based around sample dissolution (acid digestion) and subsequent analysis by ICP-AES.

FIGURE 4. Laser parameters used with the New Wave UP213. Sample was moved at a rate of 5 µm/s over a line of 500 µm.



Mg analysis:

- AI sampler and Xs skimmer for maximum sensitivity
- ¹³C as internal standard in high resolution mode to reduce the ion beam on the SEM detector, 25 ms dwell
- ²⁴Mg and ²⁶Mg as analytes in standard resolution, 25 ms dwell

FIGURE 5. Calibration curves for ²⁴Mg and ²⁶Mg in polypropylene standards.

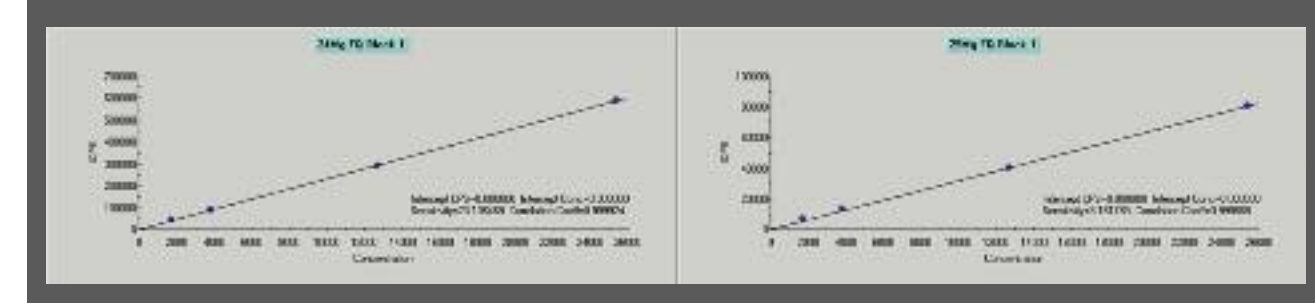
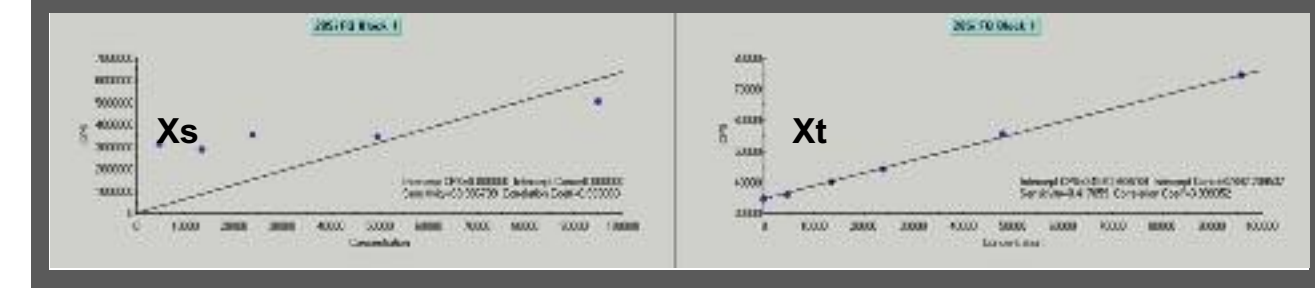


TABLE 1. Concentrations obtained from 3 sites in different polypropylene samples as well as the detection limit (LoD) and background equivalent concentration (BEC) obtained.

	Average (ppm)			% RSD				
	Sample 1	Sample 2	Sample 3	LoD	BEC			
²⁴ Mg	8303	2.9	556	10.1	8397	2.7	0.003	0.031
²⁶ Mg	8502	3.1	768	9.4	8556	3.0	0.013	0.101

FIGURE 6. ²⁸Si calibrations for polypropylene standards comparing the results obtained using the Xs and Xt interfaces.



Si analysis:

- AI sampler and Xt skimmer in order to reduce the ¹²C¹⁶O interference at m/z 28
- ¹³C as internal standard in high resolution mode to reduce the ion beam on the SEM detector, 50 ms dwell
- ²⁸Si as analyte in high resolution, 50 ms dwell

LA-ICP-MS of Ni Alloy

Why?	Current technique?
Ni super alloys are used in high technology industries such as aerospace. Control of both elemental impurities and additives is required.	GD-MS is accepted as the technique of choice for low level (< ppb) trace element analysis in Ni alloys.

- Sample was surface grinded before analysis to give a fresh surface using a grinding machine (Struers LaboPol-2 at 500 rpm, Ni piano 80)
- In order to reduce surface contamination a 5 mm x 5 mm square was ablated using the laser parameters shown in Figure 7.

FIGURE 7. Pre-ablation parameters and fluence with the New Wave UP213. Sample was moved at a rate of 200 µm/s over a 5 mm square.



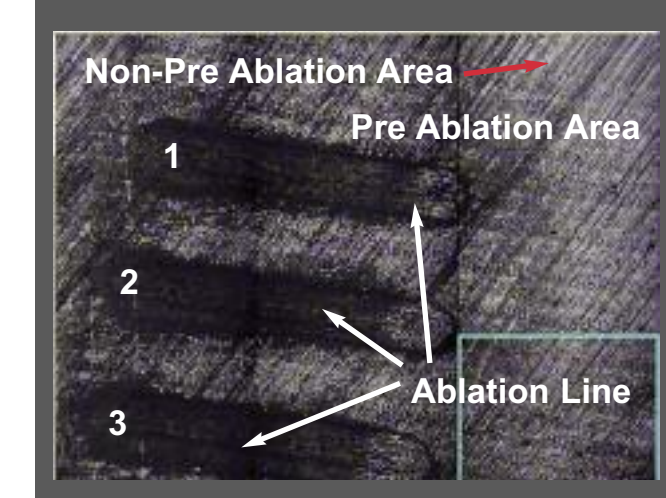
- Sample measurements were made in this 'pre-ablated' area using the laser settings in Figure 8.

FIGURE 8. Laser parameters and fluence with the New Wave UP213. Sample was moved at a rate of 5 µm/s across a 1 mm line.



- BCS (British Chemical Standard) Ni reference materials, CRM 345 and 346a (IN 100 cast Alloy) was used to generate calibration curves for the elements of interest
- 3 x 1 mm laser lines were made in the pre-ablated area of the Standard
- Each line analysis was used as a calibration point in the Fully Quantitative calibration curves

FIGURE 9. Pre-ablation area and 3 ablation lines as made in each sample & standard.



- 3 x 1 mm laser lines were made in the pre-ablated area of the sample
 - Each line analysis was quantified separately in order to assess reproducibility
- The timing and interaction between the New Wave LA and XSERIES 2 ICP-MS is shown in Figure 10 in a Time Resolved Analysis (TRA) display from the XSERIES 2 software.

FIGURE 10. Time Resolved Analysis display from the XSERIES 2 software.

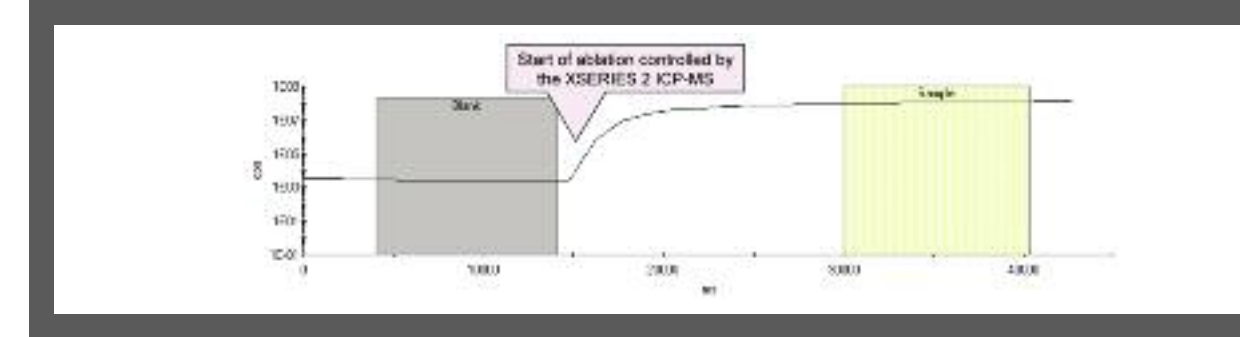


Table 2 shows the concentrations obtained from 3 different sites in the Ni Alloy sample.

TABLE 2. Concentrations from three different sites in the Ni alloy sample.

	Site 1	Site 2	Site 3	Average (%)	% RSD
²⁷ Al (%)	0.561	0.559	0.559	0.560	0.2
⁴⁷ Ti (%)	1.20	1.16	1.16	1.2	2.0
⁵¹ V (%)	0.023	0.023	0.024	0.023	2.5
⁵² Cr (%)	19.4	19.4	19.3	19.3	0.3
⁵⁹ Co (%)	0.137	0.140	0.140	0.139	1.2
⁹⁵ Mo (%)	3.46	3.44	3.57	3.49	1.9
¹⁰⁷ Ag (ppm)	0.165	0.170	0.176	0.170	3.2
¹¹⁸ Sn (ppm)	11.7	12.6	11.1	11.8	6.3
¹²⁵ Te (ppm)	0.363	0.344	0.320	0.342	6.3
²⁰⁸ Pb (ppm)	0.616	0.617	0.584	0.600	3.1
²⁰⁹ Bi (ppm)	0.180	0.140	0.150	0.160	14.4

Conclusions

Coupling the Thermo Scientific XSERIES 2 with laser ablation sample introduction has been shown to provide the sub ppm detection limits required for solid analysis in a wide range of sample types. With this analytical capability more applications will be found for LA-ICP-MS since it does away with the need for lengthy and possibly contaminating sample preparation techniques commonly used.

Acknowledgement

We would like to gratefully acknowledge Basell, Ferrara (www.basell.com) for providing the polyolefin samples analyzed in this presentation.

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