Semiquantitative Analysis of Glass by Laser Ablation ICP-MS

Application Note

Chemical

Don Potter

Abstract

The 4500 inductively coupled plasma mass spectrometer (ICP-MS) was fitted with the LSX-100 Laser Sampling System (CETAC Technologies, Omaha, NE), enabling the direct analysis of solids by laser ablation ICP-MS (LA-ICP-MS). This application note describes the use of this system to provide rapid semiquantitative analysis on a certified glass standard. The accuracy of the concentration data generated was excellent, and detection limits obtained were in the 10's of ppb range, demonstrating the high sensitivity of the system when used for multielement analysis. No sample preparation was required, and the sample analysis time, including sample loading was approximately three minutes.

Agilent Technologies
Innovating the HP Way

System Description

The LSX 100 is a benchtop laser sampling system designed for the 4500 ICP-MS. It features a Nd:YAG laser operating at 266nm (UV light). A schematic diagram of the laser ablation system is given in Fig. 1. The laser employed in the LSX-100 operates in Q-switched TM_{00} mode, producing a highly collimated beam (<0.8mrad divergence) and true Gaussian beam energy profile. As a result, laser crater diameters <10um can be routinely achieved. Sample analysis can be performed either at a single spot, or in a computer controlled line or grid pattern.
Sample preparation is normally not required; the sample is simply placed in the sample cell, which is purged with argon. The sample cell is made from a high density polymer, with a removable quartz top window. The sample is viewed though the same objective lens used to focus the laser, and the image captured by a color CCD camera.

The sample is illuminated either from above, by an annular light source built into the objective lens mount, or from below through cross polarizers. The polarized light source enables easy identification of individual grains in mineral thin sections. The image is focused by adjusting the motorized z stage as the sample image is viewed in the ChemStation software. A motorized zoom lens adjusts the image magnification from x20 to x200 so that the area of interest can easily be identified. Electronically generated cross hairs enable accurate sample positioning prior to ablation. The laser is fired, either in single shot or continuous mode and the beam focused onto the surface via the objective lens. The focused beam ablates the sample surface, forming a sample aerosol which is swept directly into the ICP using argon carrier gas. The system is fully safety interlocked, disabling the laser whenever the sample door is opened, or any services are lost.

The LSX-100 can ablate virtually any solid sample, including non-conducting and transparent materials. Sample changeover takes about 2 minutes; as the laser door is opened, a purge valve re-directs the argon gas flow to prevent the plasma being extinguished, and after the sample has been changed, automatically purges the cell with argon before re-directing the gas flow to the ICP. The Agilent Technologies laser software, written specifically for the LSX-100, gives the operator complete control of the entire LA-ICP-MS system from a single control window, and uniquely synchronizes the data acquisition system with the laser ablation program.

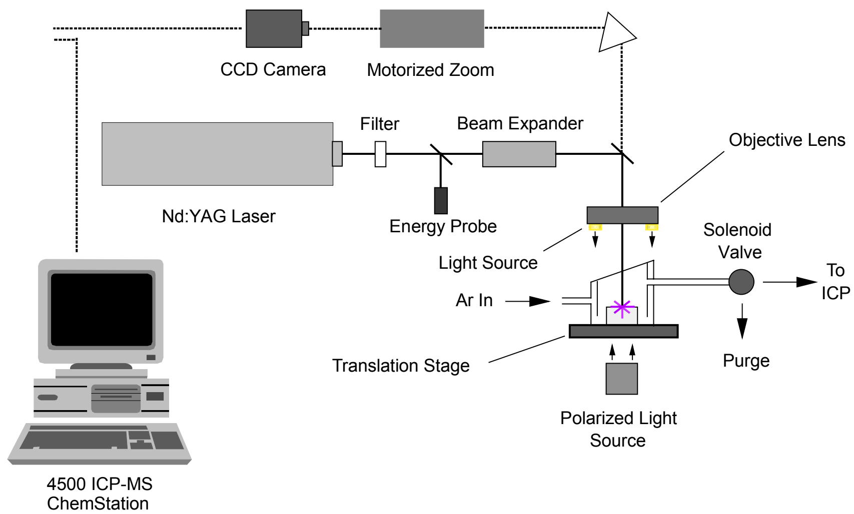

Fig 1.
Schematic diagram of the LSX-100 and Agilent ChemStation system

Complete Software Control

The Agilent laser software is integrated seamlessly into the 4500 ICP-MS ChemStation, ensuring complete compatibility. The Agilent laser software controls the sampling stage, enabling pre-programmed ablation patterns to be performed during acquisition. The Agilent laser software also controls laser energy, frequency, purge valve position, image magnification and sample illumination. The Agilent software is unique in that it enables the LSX-100 to communicate with the ICP-MS, automatically starting data acquisition following a user-selectable delay time after the laser raster program begins. The 4500 ICP-MS user also has the benefit of viewing the sample image directly in the ChemStation software; an on board video overlay card places a full color high resolution live video image in a window in the ChemStation saving the bench space taken up by a conventional CRT.

The sample image also has electronically generated cross hairs for easy sample positioning, and dynamically variable scale bars, which adjust automatically as the zoom magnification is changed. This is extremely useful for geological feature analysis, since it allows the user to measure the size of viewed inclusions directly on the screen, and set appropriate laser parameters prior to ablation.

4500 ICP-MS	
RF power	1300W
Interface	Nickel
Sampling depth	8 mm
Plasma gas	16 L/min
Auxiliary gas	1.0 L/min
Carrier gas	1. 5 L/min
Integration time/mass	0.25 sec/mass
Points per peak	6
LSX-100	
Mode	Q-switched
Laser power	1.5mJ TEM_{oo}
Defocus	0.1mm
Repetition rate	20Hz
Laser scan rate	0.5mm/sec

Table 1.
Instrument Parameters
Integration time 0.25 sec/mass, 6 points\peak. Data calculated using 3 x std. deviation of the gas blank (10 reps).

B	70
V	2
Mn	40
Co	4
Ni	10
Cu	30
Sr	1
Ba	1
Dy	3
Er	3
Th	2
U	0.5

Table 2.
3 Sigma Detection Limits (ppb) Calculated Using NIST 612

Advantages of UV Laser Ablation

There are several benefits to the use of UV laser ablation with ICP-MS, rather than the earlier IR laser systems. Firstly, UV light couples much more efficiently with solids than IR light, allowing efficient, direct ablation even with transparent solids such as glasses. This means sensitivity is enhanced, even when using low power. And since the laser light couples more efficiently, a much finer aerosol is produced (typically ~20-100um particle diameter), containing virtually no large particles which could otherwise be trapped out in the transfer lines and switching valve. This in turn leads to very low memory effects within the system. The larger sample particles generated by the IR lasers also tend not to be completely decomposed by the plasma, which can lead to interface blockage in severe cases, especially when ablating loosely bound powders or soils. In tests using this system, the finer aerosol generated by the UV laser enabled the continuous ablation of loose powders for 2 hours with no sign of interface cone blockage.

Sample Analysis

The 4500 ICP-MS was optimized by tuning the system during the continuous ablation of a certified glass standard - NIST 612 (NIST, Gaithersburg, MD), which contains impurities at low ppm levels. The continuous signal produced enabled system optimization to be easily and quickly checked. Tuning parameters in general were very similar to solution analysis, with some small changes in extraction lens voltage noted. The tune parameters were stored in a separate laser tune file for recall at a later date. NIST 612 was also used to generate semiquantitative response factors, which were automatically stored in the ChemStation software. Another sample of NIST 612 was then re-analyzed and semiquantitative data generated for 24 elements, which had recommended

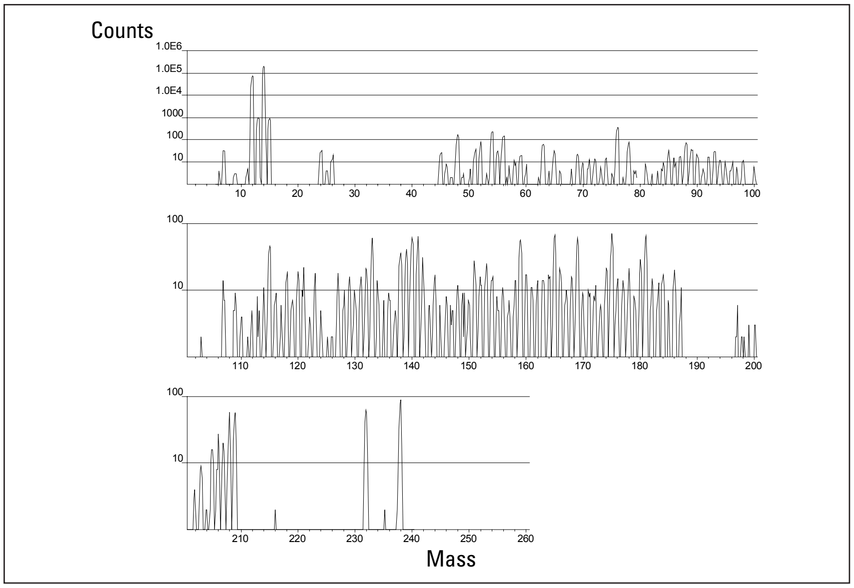

Fig 2.
NIST 612 - full mass range spectra

values supplied by NIST. Since this glass sample is relatively homogeneous, analysis was performed by rastering the laser across the surface of the sample while continuously firing the laser, giving rise to a constant, steady state signal. The resulting crater was approx. 30um in diameter. The laser was defocused by 0.1mm, enhancing signal intensity, and the line ablated in the sample surface was approximately 25um across. Data was acquired across the full mass range for 60 seconds. As described, the 4500 ICP-MS data acquisition system was automatically synchronized with the start of the laser ablation program by the ChemStation. Operational parameters for both the LSX-100 and 4500 ICP-MS are given in Table 1.

Six points per peak were chosen, to give spectral information in addition to semiquantitative information. Detection limits could be improved by selecting one or three points around the top of the peak, but even using six points across the peak, detection limits were still in the low ppb range, due to the excellent signal to noise ratio of the 4500 ICP-MS. Detection limits (3 sigma) for a range of elements certified in NIST 612 are given in Table 2, using the gas blank as a background. Spectra obtained from NIST 612 glass is shown in Figs. 2 & 3, The spectra is shown in log scale to highlight the low random background of the 4500 ICP-MS - typically 2cps. Fig. 2 shows the full mass range scanned- Group 1&2 elements, transition metals, REEs and actinides can clearly be seen. The data was acquired in auto acquisition mode - major elements such as Si and Na were automatically identified by the ChemStation software and skipped to protect the detector. This spectra also demonstrates the uniform response across the mass range - an important feature for multielement analysis. NIST 612 contains 24 spiked elements generally in the 30-50ppm range - other than the C and N peaks shown at low mass in Fig 2, elemental response is relatively flat across the entire mass range. This is due to the 4500 ICP-MS's unique ion lens system, which

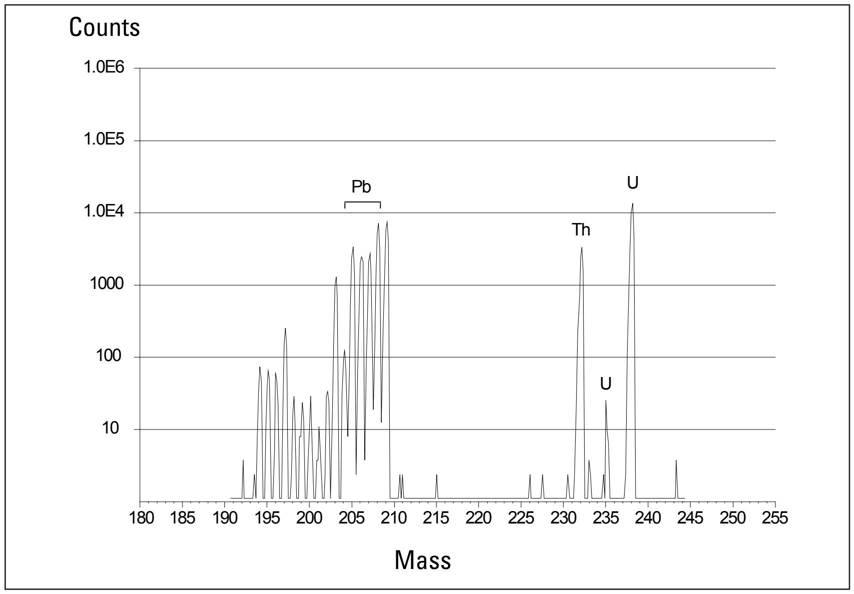

Fig 3.
NIST 612 - High mass range spectra

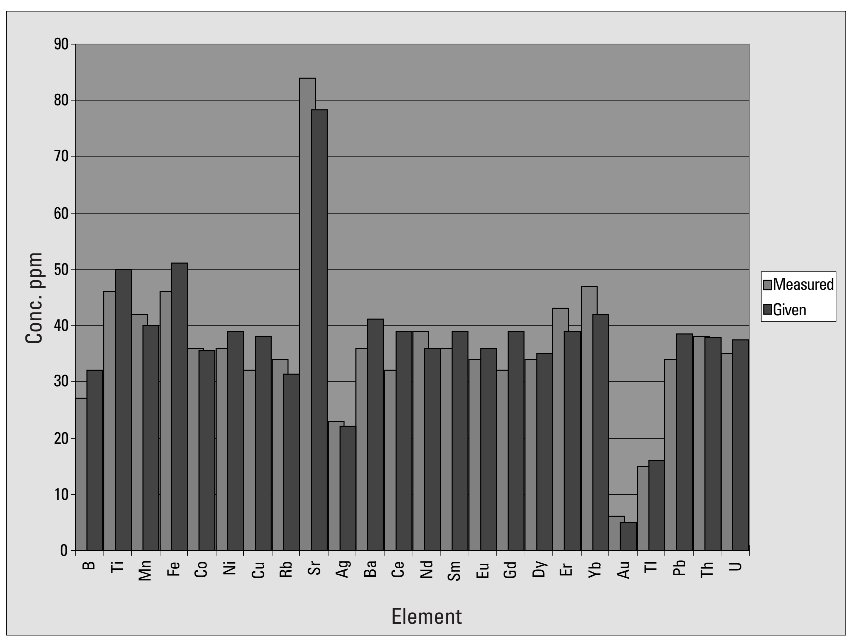

Fig 4.
Semiquantitative data obtained for NIST 612

efficiently focuses ions at all masses, virtually eliminating bias in mass response. The practical benefit of this feature is that essentially uniform detection limits can be achieved at all masses. To further demonstrate the sensitivity of the 4500 ICP-MS, an additional 60 second scan was performed over the mass range 190-245 amu of Fig. 3 shows an expanded view of the high mass region (log scale). Pb, Th and U were present at concentrations between 37-39 ppm, and the high sensitivity available from a 60 second acquisition is clearly apparent. Also of note is the virtually insignificant random background which enables low ppb detection limits (in the solid) to be obtained using this system.

After the generation of response factors, a task which is automatically performed by the software, a second piece of NIST 612 glass was analyzed, using La as the internal standard, and excellent agreement with the given values was obtained from the semiquantitative results. The data is shown in tabular form in Fig. 4. Note - the concentration scale is linear, with typical accuracy in the range +\-0-8%. Quantitation in this case was straightforward, since the concentration of La was given, but for unknown samples, a matrix element can be used as the internal standard to obtain semiquantitative data. Typical internal standard examples include the use of ^{13}C in polymer analysis, and minor matrix isotopes in materials such as ceramics, stainless steel and borosilicate glass, where the stoichiometry of the sample is known. While in this case the matrix of the sample was the same as the standard used to generate the response factors, good semiquantitative data can be obtained for a wide range of matrices using a single set of response factors. This is due to the uniform response of the 4500 ICP-MS across the mass range, and the fine aerosol generated by the UV laser, which is more completely decomposed in the plasma, reducing matrix effects.

The LSX-100, in combination with the 4500 ICP-MS, is a fast, highly sensitive tool for direct elemental analysis in virtually any solid. Multi element semiquantitative data can be generated in approximately 3 minutes with little or no sample preparation.

Don Potter is a Business Development Manager at Agilent Technologies, Inc., Manchester, UK

Visit our website at
http:/www.agilent.com/chem/icpms

Printed 4/2000
Publication number 5965-3033E

Agilent Technologies
Innovating the HP Way