Introduction to Laser Ablation ICP-MS for the Analysis of Forensic Samples

Application Note

Forensic Toxicology

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Abstract

Forensic scientists require reliable methodologies capable of determining the origin of inorganic materials found at the scene of a crime. Due to the great variety, shape, and size of forensic material, there is a need for a flexible analytical tool capable of analyzing the trace element content of solid samples directly. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) enables identification and comparison of physical evidence, discriminating elemental and isotopic differences at the part per billion (ppb) level. In contrast to aqueous analysis, where significant amounts of material need to be destroyed in the analytical process, LA-ICP-MS is a micro-destructive technique. Often the total volume of sample ablated with this technique is <1 µg; sustaining the essential integrity of the original evidence, which may be extremely small, and enabling further measurements to corroborate the results.

Introduction

Today's quadrupole ICP mass spectrometers enable the analysis of elements across the periodic table at very high scanning speeds and with very low detec-tion limits. Typically samples are introduced into an ICP-MS by aspirating a solution of the sample.

Often liquid samples require little preparation, but without a solid sampling accessory, solid samples need to be dissolved. This process is time consuming and often requires the use of acid dissolution reagents and additional sample preparation apparatus. Adding hazardous chemicals, such as hydrofluoric acid to dissolve the sample, can give rise to matrix-based interferences forming in the plasma. Hazardous chemicals are also a potential source of contamination. In contrast, combining ICP-MS with the direct solid-sample introduction technique of laser ablation (LA) requires minimal sample preparation. LA-ICP-MS provides an excellent and relatively nondestructive technique for elemental analysis of forensic samples that are difficult to digest, or where small fragments or inclusions must be analyzed. LA-ICP-MS is particularly amenable to time-resolved analysis (TRA); enabling direct comparison of samples in three dimensions. Combining such flexible data handling capabilities with *in-situ* solid sampling enhances discriminating power; strengthening the analyst's ability to determine the similarities and differences within large data sets.

LA-ICP-MS

LA-ICP-MS is widely used to determine elements directly in solid samples with minimal sample preparation. It is a highly sensitive multi-element technique with a wide analytical dynamic range from the part per trillion (ppt) to the part per million (ppm) level in the solid. For this study, a Merchantek UP-213 (New Wave Research. Inc, USA) LA system was coupled to an Agilent 7500s ICP-MS. A schematic of the LA system is shown in Figure 1.

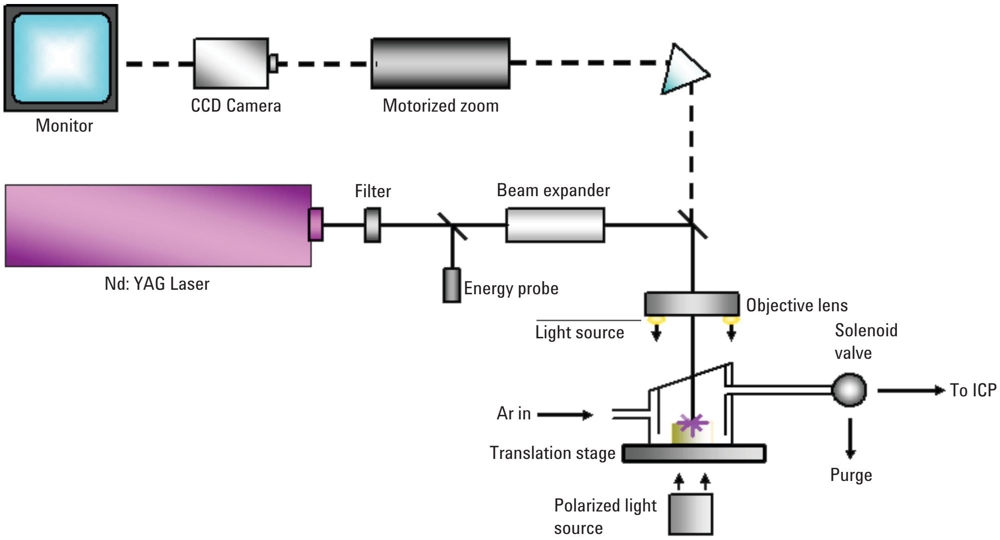

Figure 1. Schematic of Nd: YAG LA system (5th harmonic - 213 nm) for ICP-MS.

The sample surface is irradiated with deep-UV (213 nm) output from a frequency-quintupled Nd:YAG (neodymium doped yttrium aluminum garnet crystal) laser. The high-intensity pulsed ultraviolet (UV) beam is focused onto the sample surface in an ablation chamber or cell, which is purged with argon. The UV beam diameter can be accurately set by 12 software-controlled apertures to produce variable "spot" sizes from <5 µm to 300 µm depending on the application. The high-power, short-wavelength 213-nm laser couples directly with the sample matrix, with high absorption efficiency, reducing or eliminating plasma induced fractionation. The resultant laser-induced aerosol is then transported to the ICP in an argon carrier gas stream where it is decomposed, atomized and ionized, before extraction into the mass spectrometer vacuum system for analysis. Calibration is typically undertaken using a well-characterized synthetic solid material, such as NIST 612 Trace Elements in Glass or other suitable solid standard reference material (SRM).

Sample Analysis Using LA-ICP-MS

Generally, the ICP-MS is optimized by tuning the system during continuous ablation of a suitable SRM; examples of reference materials for glass and tape are given in Table 1. The Agilent ICP-MS can be optimized automatically using the AutoTune function of the Agilent ChemStation software. Often, tuning parameters for LA analysis are similar to those used for solution analysis. Tune parameters can be saved in a separate file for recall at a later date. If a SRM is available for the matrix being analyzed, it can be used to generate semi-quantitative response factors which are automatically stored in the ChemStation software. The sample can then be analyzed using a matrix element as the internal standard (IS). If an SRM is analyzed, the concentration of the IS is given and quantification is straightforward. However, for unknown samples, typical IS 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 it is ideal to match the matrix of the standard to the sample, good semiquantitative data can be obtained for a wide range of matrices using a single set of response factors. This is because of the uniform response of the 7500 Series 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.

Table 1. Details of Forensic Standard Reference Materials

	Glass	Tape
Standard	NIST SRM 612: 50/µg/g nominal trace element concentration	BCR SRM 680: Trace elements in polyethylene
Matrix elements	Si (SiO_2), Na (Na_2O), Ca (CaO), Al (Al_2O_3)	
Source	National Institute of Standards and Technology, USA	Institute for Reference Materials and Measurements, Geel, Belgium

Software Controlled Operation

The LA software can be fully integrated into the Agilent ICP-MS ChemStation software for ease of setup and operation of the LA and ICP-MS. All laser parameters (for example, laser energy, frequency, purge valve position, sample viewing, stage positioning, and ablation pattern) can be controlled via the ICP-MS ChemStation PC. A high-magnification video system enables a full color, high-resolution image of the sample to be viewed directly on the ICP-MS monitor in real time, see Figure 2. The computer-controlled zoom feature and electronically-generated cross hairs aid sample positioning and can also be used to measure the size of any inclusions directly on the screen. Laser parameters can then be set accordingly, and during data acquisition, the laser power meter reading can be monitored on screen.

Forensic Applications

It is the task of the forensic analyst to generate evidence based on trace elemental fingerprinting that can prove or disprove the source of the material. As a consequence, forensic materials presented for analysis by LA-ICP-MS could be anything from strands of hair to fibers of clothing.

For example, the glass used in the headlights and windows of automobiles is often unique to a manufacturer, and the elemental profile can be used to identify the marque, brand, or even year of manufacture of the vehicle. Trace element content offers far better discrimination than the traditional refractive index (RI) method. LA-ICP-MS provides a fast and simple means of characterizing glass fragments found on clothing or at the location of an accident, without time-consuming sample preparation. Although the major and minor elemental composition of these glasses are very similar, and therefore are difficult or impossible to discriminate using traditional methods of characterization, these glasses may have trace elemental signatures (Figure 3) which enable accurate evaluation of differences by LA-ICP-MS.

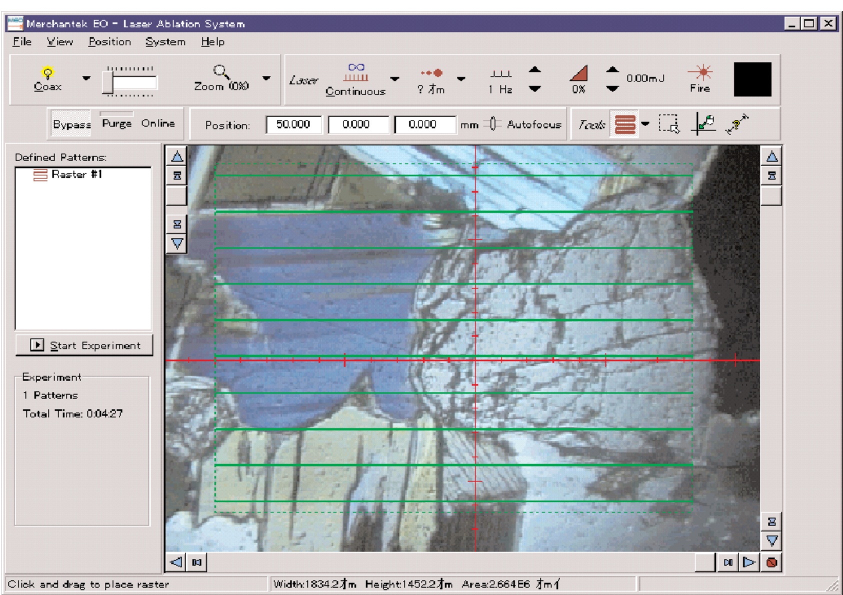

Figure 2. Screen capture showing a full color, high-resolution image of the sample.

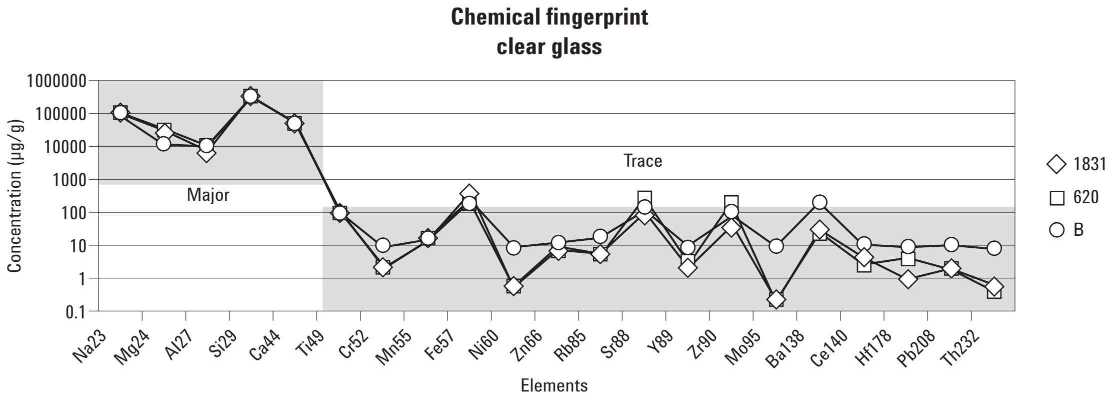

Figure 3. Elemental signature of clear glass.
The major elemental composition of these three glasses is similar (Na, Al, Si and Ca) while the trace elemental composition ≤100 μg/g (Cr, Ni, Rb, Sr, Y, Zr, Mo, Ba, Ce, Hf, Pb, Th) displays significant differences. Mg is an exception and at high concentration is often used as a discriminating element.

LA-ICP-MS can also be applied to other samples such as identifying inks on documents, or element profiles of other crime debris, including multi-layer paints, coatings on glass, bulk polymers, plastic bags, tape, and automobile parts. Figure 4 illustrates a sample of ballpoint pen ink after analysis using LA-ICP-MS. The ablated portion of the ink is clearly visible on the right side of the photograph.

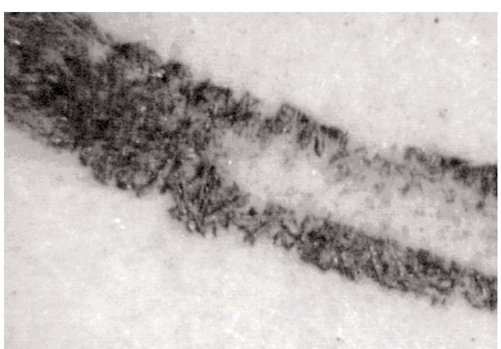

Figure 4. Magnified photograph of ballpoint pen ink sample after LA-ICP-MS sampling.

Data Manipulation

The data generated from LA-ICP-MS can be manipulated in real-time to enable the user to view the results of an analysis within seconds of data acquisition. Various optional software packages are available including:

- Glitter™ data reduction software
  Macquarie University - GEMOC [1]

GLITTER is an acronym for GEMOC Laser ICP-MS Total Trace Element Reduction. In addition to real-time on-line data reduction, GLITTER features a variety of plotting options, linked graphics and analysis tables, for simple presentation of the results. The ability to visualize results can aid users of forensic evidence in their understanding of the data.

- TriPlot Ternary plotting software
  Todd Thompson Software [2]

TriPlot produces a triangular plot of three variables that are plotted on the left, right and bottom sides of an equilateral triangle. Ternary plots are an effective way to discriminate subtle differences in sample populations, especially when multiple data point display is desirable as shown in the example in Figure 5.

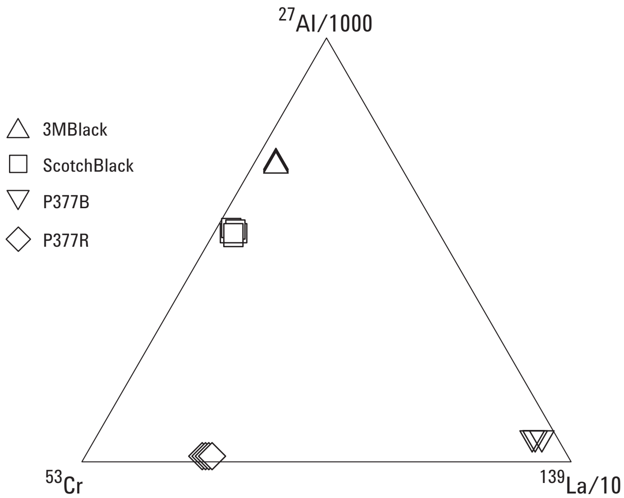

Figure 5. Ternary plot of adhesive tape data (integrated counts per second).

Conclusions

LA-ICP-MS is an effective tool for the analysis of a wide variety of forensic samples. This technique is particularly effective in overcoming the limitations associated with very small sample types or samples composed of chemically inert materials. The definitive "fingerprint" produced by LA-ICP-MS based on elemental and isotopic ratio data is used to qualify or disqualify the source of physical evidence. Often a clear visual representation of the data is produced using a suitable plotting program making it easier to discriminate samples.

Reference

1. Glitter™ data reduction software, Macquarie University - GEMOC http://www.es.mq.edu.au/GEMOC

2. TriPlot Ternary plotting sofware, Todd Thompson Software www.home.earthlink.net/~baedke/triplot

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Printed in the USA
September 9, 2004
5989-1565EN

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