Elemental "Fingerprinting" for QC and Forensic Applications: Now a Reality with Prodigy's Spectral Subtraction and Advanced Qualitative Analysis Capabilities

INTRODUCTION

One of the promises of array detector ICP systems has been the capability to measure all elements in an unknown sample. Sometimes referred to as elemental fingerprinting, this capability can be extremely powerful for QC and/or forensic applications. In order to take advantage of this capability, the ICP employed must provide full wavelength coverage as well as the spectral data handling tools needed to do the "fingerprinting". This technical bulletin will demonstrate some of the elemental fingerprinting capabilities of the Prodigy ICP.

Imagine for a moment that you are a forensic scientist working for the FBI. You are attempting to determine if several seemingly unrelated crimes might be linked. In this instance the FBI forensic chemistry lab needs to determine if bullet lead fragments from different crime scenes can be linked to a single perpetrator. This is an analytical challenge which is ideal for elemental fingerprinting. This technical bulletin will show how the wavelength coverage and the spectral data handling capabilities of the Prodigy ICP make it possible to fingerprint bullet lead.

Figure 1. The Prodigy ICP

EXPERIMENTAL

For this work, samples were introduced into the plasma using a laser ablation solid sampling device rather than dissolving them and using conventional solution nebulization. For some applications, the lasers ability to directly vaporize a small quantity (between 5 to 1000 μg) of the sample in question can simplify the sample handling process and help to preserve samples for future investigative work. In this case a New Wave Research Macro 266 laser ablation system was interfaced to the Teledyne Leeman Labs Prodigy ICP. Pictures of the Prodigy and New Wave laser system are shown in Figures 1 and 2. Figure 3 shows the lead fragments mounted in the laser cell. The white material in the photograph is a removable adhesive used to hold the fragments in position in the cell.

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Figure 2. Prodigy ICP and New Wave Research Macro 266 Laser

Figure 3. Photograph of lead fragments mounted in a laser cell.

Operating conditions for the laser system and the ICP are listed in Table 1 below.

ICP Operating Conditions

RF Power	1.1 kW
Viewing Configuration	Axial
Plasma Gas	20 L/min
Auxiliary Gas	0 L/min
Carrier Gas	0.44 L/min (Argon)
Laser Cell Gas	0.54 L/min (Helium

Laser Operating Conditions

Aperature	610um x 610 um square Defocused V-knob 1.2 marks (~ 800 μm)
Power	4.4J/cm2 (60% power – in focus) ~3.3J/cm2 final
Frequency	10Hz
Scan Speed	150 μm/sec
Line Length	2000μm with Multiple passes

Table 1. Instrument Operating Conditions

Prodigy's large format programmable array detector and long focal length optical system make it the only commercially available ICP to offer simultaneous full wavelength coverage between 165 to 1100nm. Further, Prodigy's data system is capable of displaying and manipulating the entire spectrum at the users command. The ability to perform spectral additions and/or subtractions combined with the ability to do spectral fingerprint calculations on the resulting spectrum are very powerful in forensic and/or product quality applications. Here's how it all works.

RESULTS AND DISCUSSIONS

The first step in this experimental work was to acquire the full ICP spectrum for the bullet fragments in question. An identical spectrum was then acquired for a high purity lead blank. A spectral subtraction of the blank from each of the fragments was then performed using Prodigy's Spectroscopy Toolbox. The net result is the elemental fingerprint for each fragment. A spectrum from an unknown lead sample and a high purity lead blank are shown in Figures 4 and 5 below. The resulting elemental fingerprint is shown in Figure 6.

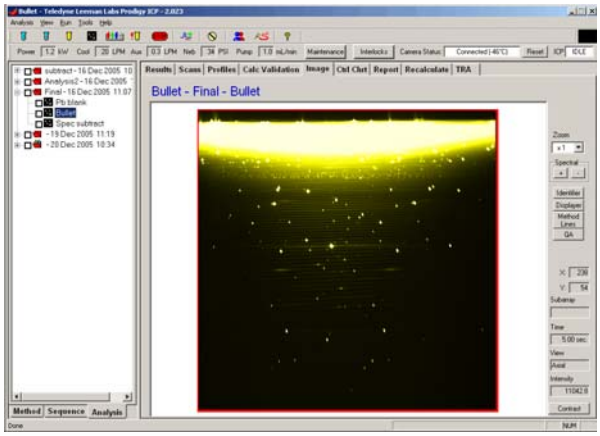

Figure 4. Spectrum of unknown Lead Fragment 1.

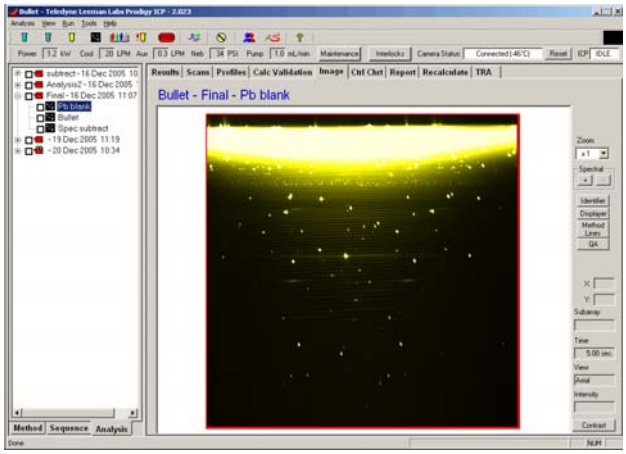

Figure 5. Spectrum of high purity lead "blank"

Figure 6. Elemental Fingerprint of Unknown Lead Sample

Once the analyst has the resulting elemental fingerprint (spectrum) for each sample, there are multiple options for the next course of action. For example, one may choose to perform a qualitative analysis of the fingerprint spectrum or to do a fully quantitative analysis on a select number of elemental constituents. Prodigy's software provides both of these capabilities.

A qualitative analysis can be performed by selecting the "QA" button within the software as shown in Figure 7.

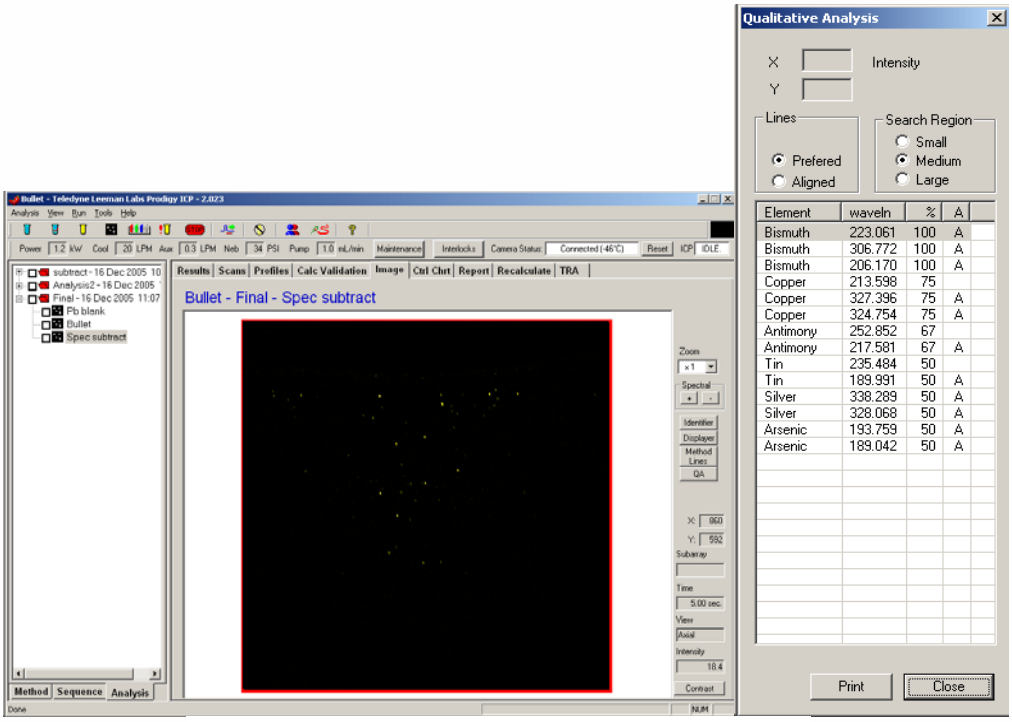

Figure 7. Display of Prodigy's "QA" function for a bullet lead spectrum.

Once the QA button is pressed, the software performs a statistical calculation based on the presence of the emission lines contained in the spectrum and then displays a table of the elements found in the sample. Qualitative analysis can also be performed on spectra without first performing a spectral subtraction. This is demonstrated in Figure 8 for a solution containing a mixture of 21 elements.

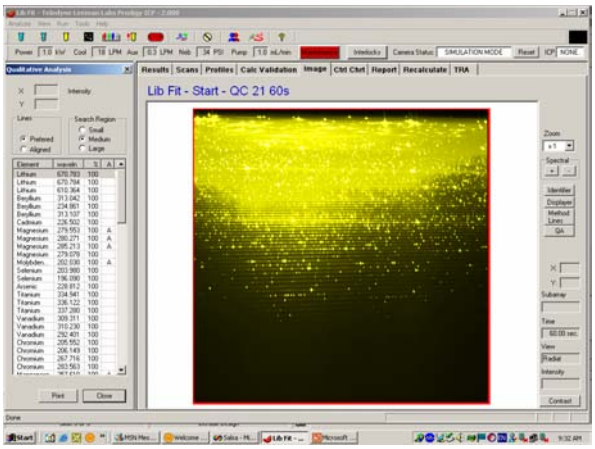

Figure 8. Demonstration of Prodigy's QA functionality for a solution containing 21 elements.

For researchers who need to perform fully quantitative analysis following acquisition of the elemental fingerprint, the conventional approach of calibration followed by analysis is performed. Results from 3 sample materials examined in this work are shown in Table 2.

C2415	(all values are reported in % of the element of interest)						
Line	**Run 1**	**Run 2**	**Run 3**	**Mean**	**SD**	**RSD%**	**Cert.**
Ag 328.068	0.003	0.003	0.003	**0.003**	0.00004	1.4%	**0.002**
Bi 223.061	0.050	0.049	0.040	**0.046**	0.00561	12.1%	**0.054**
Sb 206.833	2.972	2.924	2.874	**2.923**	0.04898	1.7%	**2.950**
As 193.759	0.201	0.203	0.203	**0.202**	0.00155	0.8%	**0.200**
Cu 324.754	0.088	0.088	0.092	**0.089**	0.00270	3.0%	**0.095**
Sn 189.991	0.332	0.330	0.329	**0.330**	0.00146	0.4%	**0.330**

C2416							
Line	**Run 1**	**Run 2**	**Run 3**	**Mean**	**SD**	**%RSD**	**Cert.**
Ag 328.068	0.004	0.004	0.004	**0.0040**	0.00006	1.5%	**0.0044**
Bi 223.061	0.094	0.093	0.093	**0.093**	0.00044	0.5%	**0.100**
Sb 206.833	0.791	0.781	0.779	**0.784**	0.00697	0.9%	**0.790**
As 193.759	0.050	0.049	0.050	**0.050**	0.00051	1.0%	**0.056**
Cu 324.754	0.058	0.058	0.058	**0.058**	0.00048	0.8%	**0.065**
Sn 189.991	0.094	0.094	0.093	**0.094**	0.00043	0.5%	**0.090**

B23								J. Forens. Sci. (47)	
Line	Run 1	Run 2	Run 3	Run 4	Run 5	Mean	%RSD	Koons, et al 2002	SD
Ag 328.068	0.0046	0.0045	0.0043	0.0042	0.0041	**0.0043**	4.5%	**0.0045**	0.00008
Bi 223.061	0.0118	0.0115	0.0112	0.0113	0.0109	**0.0114**	3.0%	**0.0109**	0.00013
Sb 206.833	1.0718	1.0204	0.9955	0.9597	0.9433	**0.9981**	5.1%	**0.9590**	0.015
As 193.759	0.0190	0.0160	0.0138	0.0143	0.0137	**0.0154**	14.6%	**0.0159**	0.0002
Cu 324.754	0.0110	0.0107	0.0098	0.0095	0.0099	**0.0102**	6.3%	**0.0111**	0.0002
Sn 189.991	0.2458	0.2369	0.2331	0.2305	0.2286	**0.2350**	2.9%	**0.2190**	0.003

Table 2. Quantitative analysis of 3 lead based materials. All values are reported in percentage of the element of interest. The values for bullet lead B23 is referenced to an analysis performed by Dr. Koons in the Journal of Forensic Science (47) 2002.

Other Applications for Elemental Fingerprinting

Other applications where elemental fingerprinting has become important include identification of the country of origin of crops and detection of drug tampering. Crops such as citrus, coffee and nuts take on an elemental fingerprint representative of the soil in which they were grown. Because soil composition differs markedly around the world, it tends to be a relatively easy task to identify the country of origin of crops.

A recent area of significantly heightened concern is with counterfeit drugs and/or drug tampering. This has become important for reasons including: homeland security, health and human safety and patent infringement to name just a few. A counterfeit drug is one that is manufactured by an unlicensed, uncontrolled facility that in effect is “steeling” the brand name of an over the counter or prescription drug maker. These counterfeit facilities often sell their drugs over the internet and are likely to be selling drugs of questionable safety and efficiency. Elemental fingerprinting has been a very powerful tool in determining the origin of drugs.

This technical bulletin has attempted to demonstrate the versatility and analytical potential of the Prodigy for applications which can benefit from Elemental Fingerprinting capability.

To discuss how Teledyne Leeman Labs can help you solve your elemental analysis challenges, contact us at 1-800-634-9942 or visit us at www.LeemanLabs.com.