Elemental "Fingerprinting" for Quality Control and Forensic Applications

One of the promises of array detector inductively coupled plasma (ICP) systems has been the ability to measure all elements in an unknown sample. Sometimes referred to as *elemental fingerprinting*, this capability can be extremely powerful for quality control (QC) and forensic applications. To take advantage of this capability, the ICP system employed must provide full wavelength coverage as well as the spectral data handling tools needed to do the "fingerprinting." This article will demonstrate some of the elemental fingerprinting capabilities of ICP.

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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 laboratory needs to determine whether bullet lead fragments from different crime scenes can be linked to a single perpetrator. This is an analytical challenge that is ideal for elemental fingerprinting. This article will show how ICP's wavelength coverage and spectral data-handling capabilities make it possible to fingerprint bullet lead.

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 laser's ability to directly vaporize a small quantity of the sample in question (5–1000 mg) 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 (Fremont, California) was interfaced to the Teledyne Leeman Labs Prodigy ICP system (Hudson, New Hampshire). Figure 1 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.

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

Results and Discussion

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 the ICP system's software. 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 2 and 3. The resulting elemental fingerprint is shown in Figure 4.

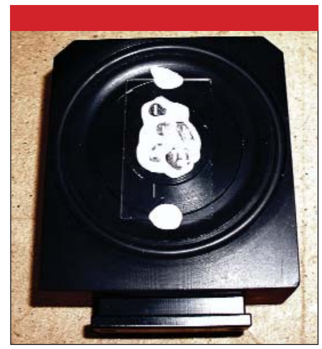

Figure 1: Lead fragments mounted in a laser cell.

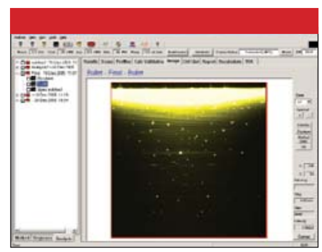

Figure 2: Spectrum of unknown lead fragment 1.

Table I: Instrument operating conditions

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	
Aperture	610 μm × 610 μm square Defocused V-knob 1.2 marks (~800 m)
Power	4.4 J/cm^2 (60% power – in focus) ~3.3 J/cm^2 final
Frequency	10 Hz
Scan speed	150 m/sec
Line length	2000 m with multiple passes

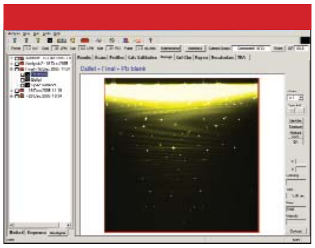

Figure 3: Spectrum of high purity lead blank.

Figure 4: Elemental fingerprint of unknown lead sample.

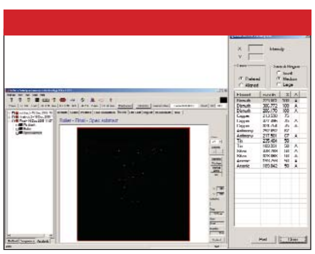

Figure 5: Display of the software's "QA" function for a bullet lead spectrum.

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 might choose to perform a qualitative analysis of the fingerprint spectrum or to do a fully quantitative analysis on a select number of elemental constituents.

A qualitative analysis can be performed within the software, as shown in Figure 5.

For a semi-quantitative analysis, the software performs a statistical calculation based upon the presence of the emission lines contained in the spectrum and then displays a table of the elements found in the sample. Qualitative analysis also can be performed on spectra without first performing a spectral subtraction. This is demonstrated in Figure 6 for a solution containing a mixture of 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 three sample materials examined in this work are shown in Table II.

Other Applications for Elemental Fingerprinting

Other applications in which 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 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 "stealing" 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.

Table II: Quantitative analysis of three lead-based materials.*

C2415									
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	**0.004**	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									
Line	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Run 5**	**Mean**	**%RSD**	**Ref. 1**	**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

* All values are reported in percentage of the element of interest. The values for bullet lead B23 were taken from reference 1.

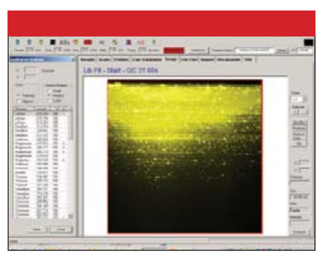

Figure 6: Results from a qualitative analysis of a solution containing 21 elements.

References

(1) R.D. Koons and D.M. Grant, *J. Forensic Sci.* **47**(5), 950–958 (2002).

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