Analysis of Trace Evidence Using A Combined Raman/LIBS Microscope System

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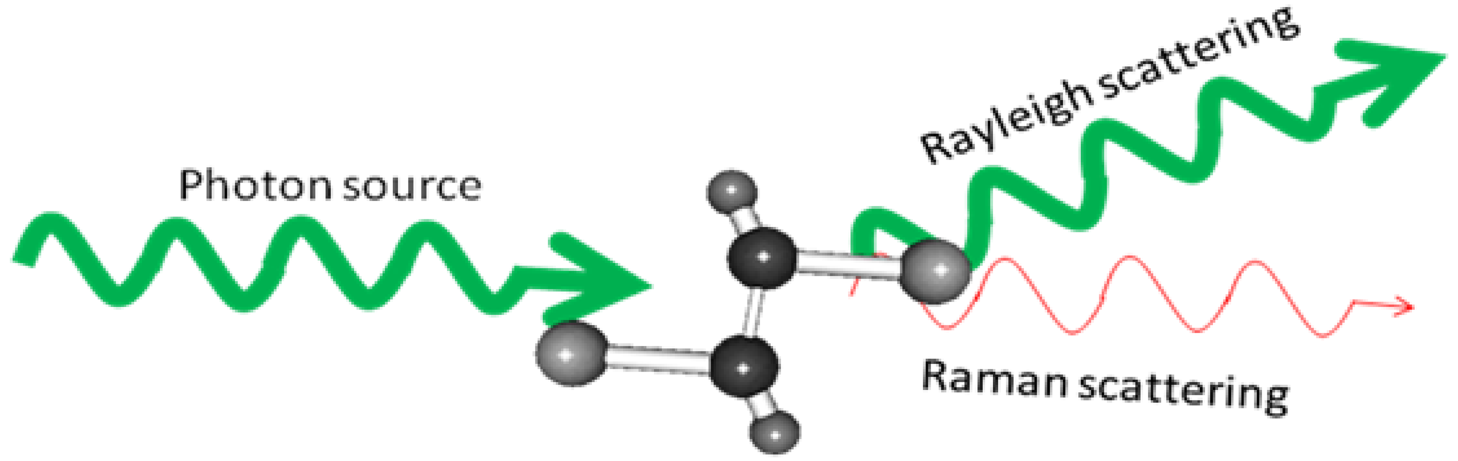
Abstract

The introduction of newer analytical methods of analysis is critical to the forward development and increased discrimination of trace evidence. Over the past decade, Raman spectroscopy and laser-induced breakdown spectroscopy (LIBS) have independently demonstrated the ability to provide significant benefits when examining microscopic evidence. As the continued development of databases and refined methodologies for these technologies moves forward, the ability to apply these techniques for more probative sample interrogation techniques is also being developed. The ability of combining Raman and LIBS in a searchable platform for manual or automated modalities offers a new window into areas of trace analysis that is typically overlooked due to time and technology restraints. Samples containing numerous organic and inorganic components have historically been separated and examined on a particle by particle basis, with the exception of gunshot residue (GSR) and soils, where inorganic portions of these samples have been subjected to automated scanning electron microscopy methods. The combination of a Raman/LIBS methodology may provide a mechanism for analyzing larger sample populations containing both organic and inorganic components in a single analysis, thus providing significant data in forensic trace evidence comparisons. In addition, the analysis of trace materials using a combined system provides multiple analytical testing methods on the exact samples of interest, limiting the potential for sample loss and sample preparation contamination. This presentation will examine the use of a combined Raman/LIBS system (rap-ID Particle Systems GmbH) for the analysis of single particles and large particle population samples to evaluate the benefits and limitations of such a technique in "real world" forensic applications.

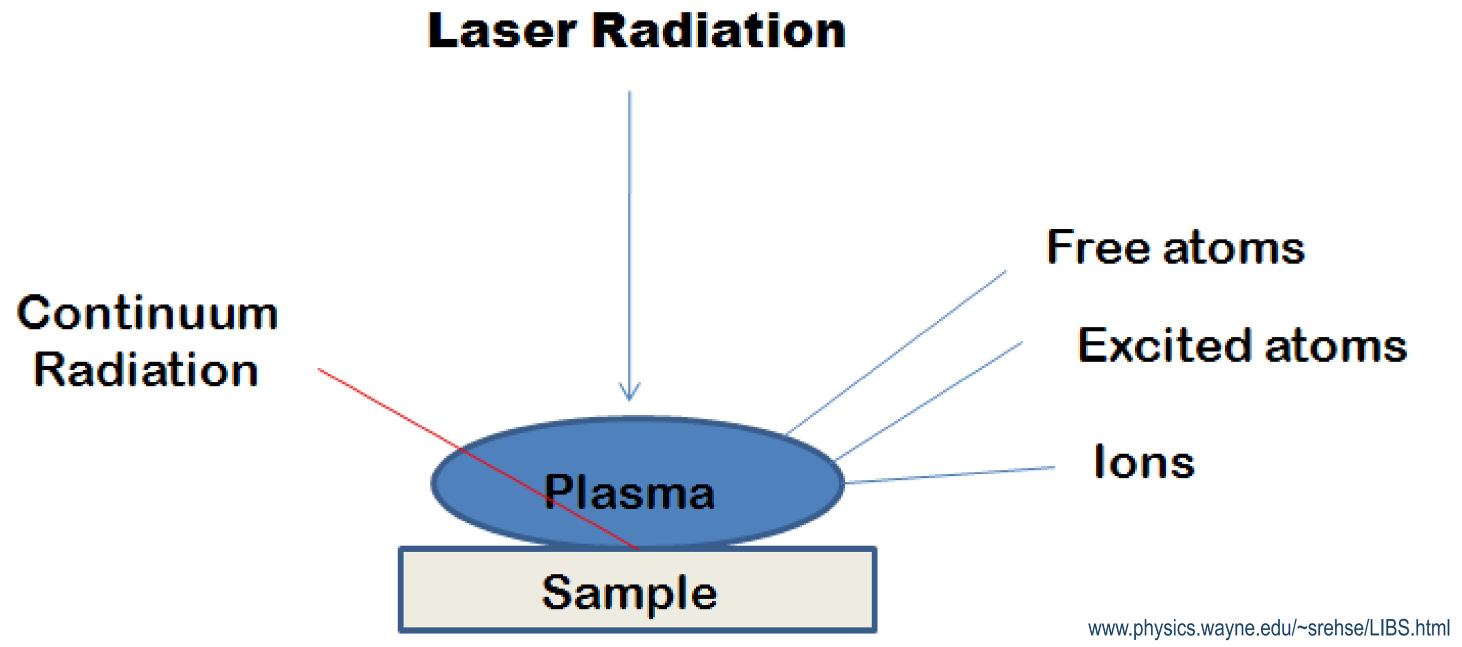
Raman Spectroscopy

Vibrational spectroscopy is the study of the interaction between electromagnetic radiation (light) and the molecular bonds of matter (solids, liquids and gases). Raman spectroscopy is a type of vibrational spectroscopy capable of obtaining information about the structure and properties of molecules based on their vibrational transitions.



Laser-Induced Breakdown Spectroscopy (LIBS)

LIBS is an atomic/molecular spectroscopic technique that uses pulses of intense laser light to vaporize a small amount of a target. The vaporization creates a high-temperature (10,000 K – 20,000 K) plasma plume in which the constituent elements or molecules of the target are excited and ionized. As the plasma cools, the atoms, ions and molecules lose energy via the spontaneous emission of optical wavelength photons. This light is collected, dispersed by a spectrometer and the resulting emission peaks are analyzed to accurately identify all the elements that were present in the target. This method can be used to identify constituent elements or to quantitatively analyze the target.



www.physics.wayne.edu/~srehse/LIBS.html

Objectives of Automated Analysis

Soil

Comparison of Soil Sample A and Soil Sample B to determine if particle population demonstrates consistent compositional analysis of particle size and chemistry based on the inorganic portion (LIBS) and organic portion (Raman).

GSR

Conduct automated analysis of a GSR sample to determine if presence of inorganic particulate consistent with GSR primer residue (Pb/Ba) in conjunction with particle size can be demonstrated. In addition, this study evaluated the ability of an incorporated Raman system to provide corroborative data on the organic portions typical of discharged firearms in the same sample.

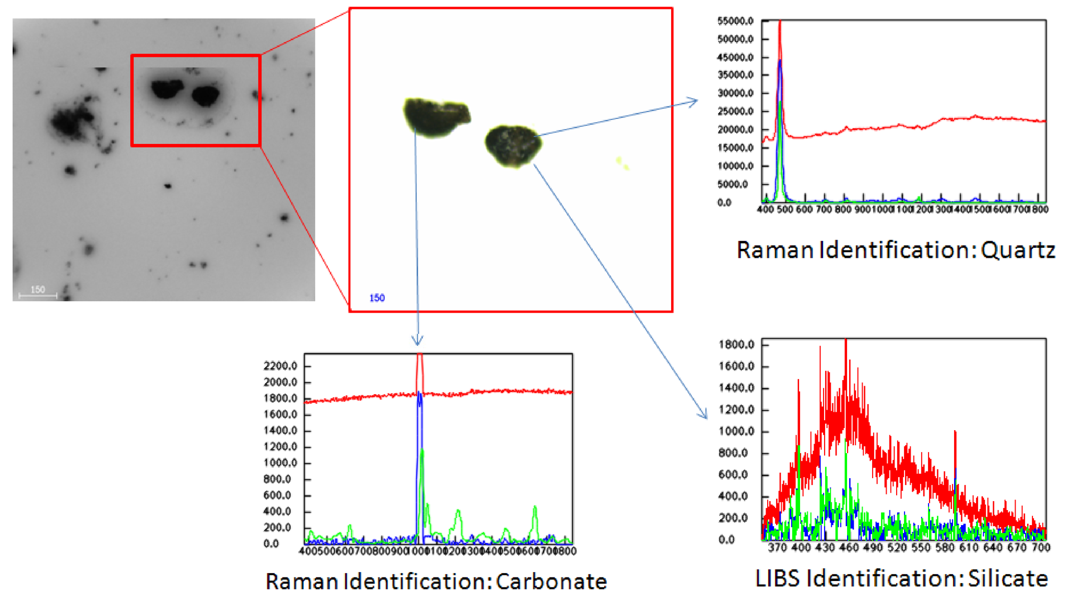
Instrument Parameters

Raman Spectroscopy

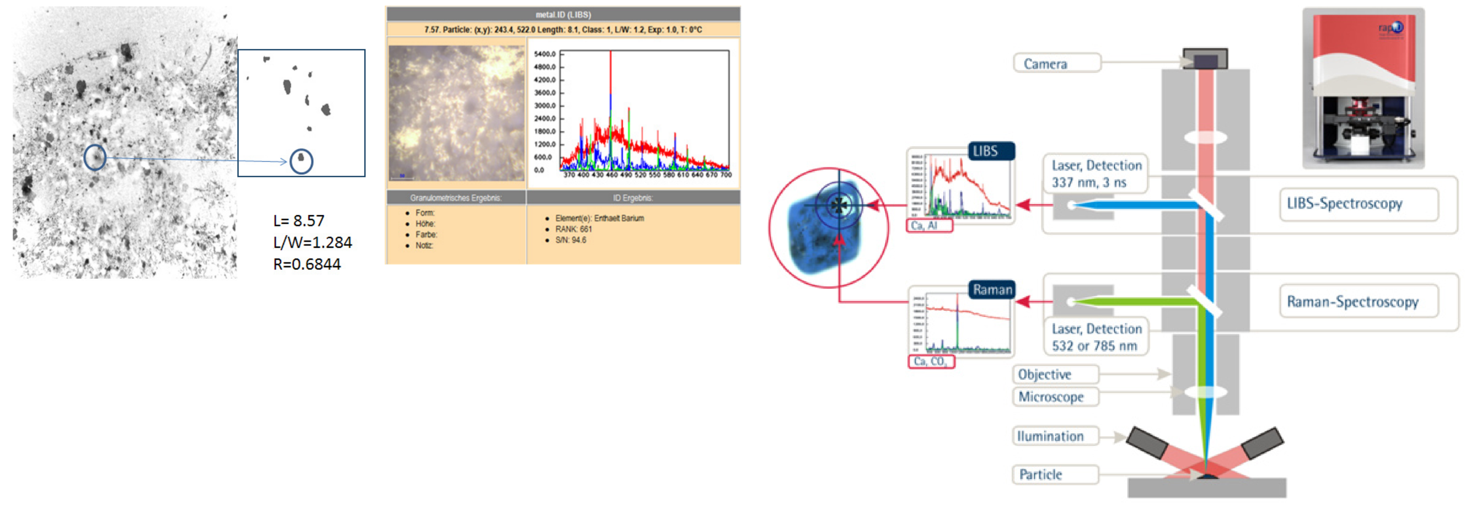
- Instrument: SPE raman.ID + metal.ID
- 532 nm Laser Excitation
- Automated Exposure 5-60 seconds
- Spectral Resolution: 8 cm^{-1}
- Spectral Range: 400-2000 cm^{-1}

LIBS

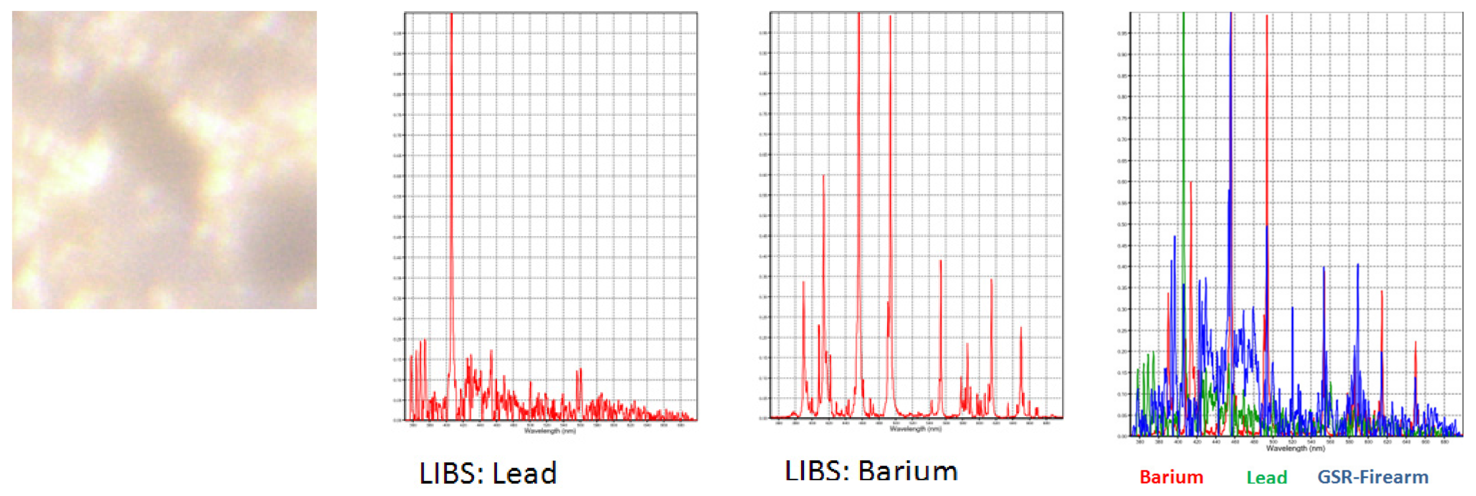
- Instrument: SPE raman.ID + metal.ID
- Laser: Pulse-LASER, 100 µJ, 3 ns
- Spectral Resolution: 1 nm
- Spectral Range: 350-800 nm
- LIBS: Laser-induced breakdown spectroscopy: identification of particles larger than 5 µm with a measurement time of 1 sec/particle



Combined Raman/LIBS of Soil Particles



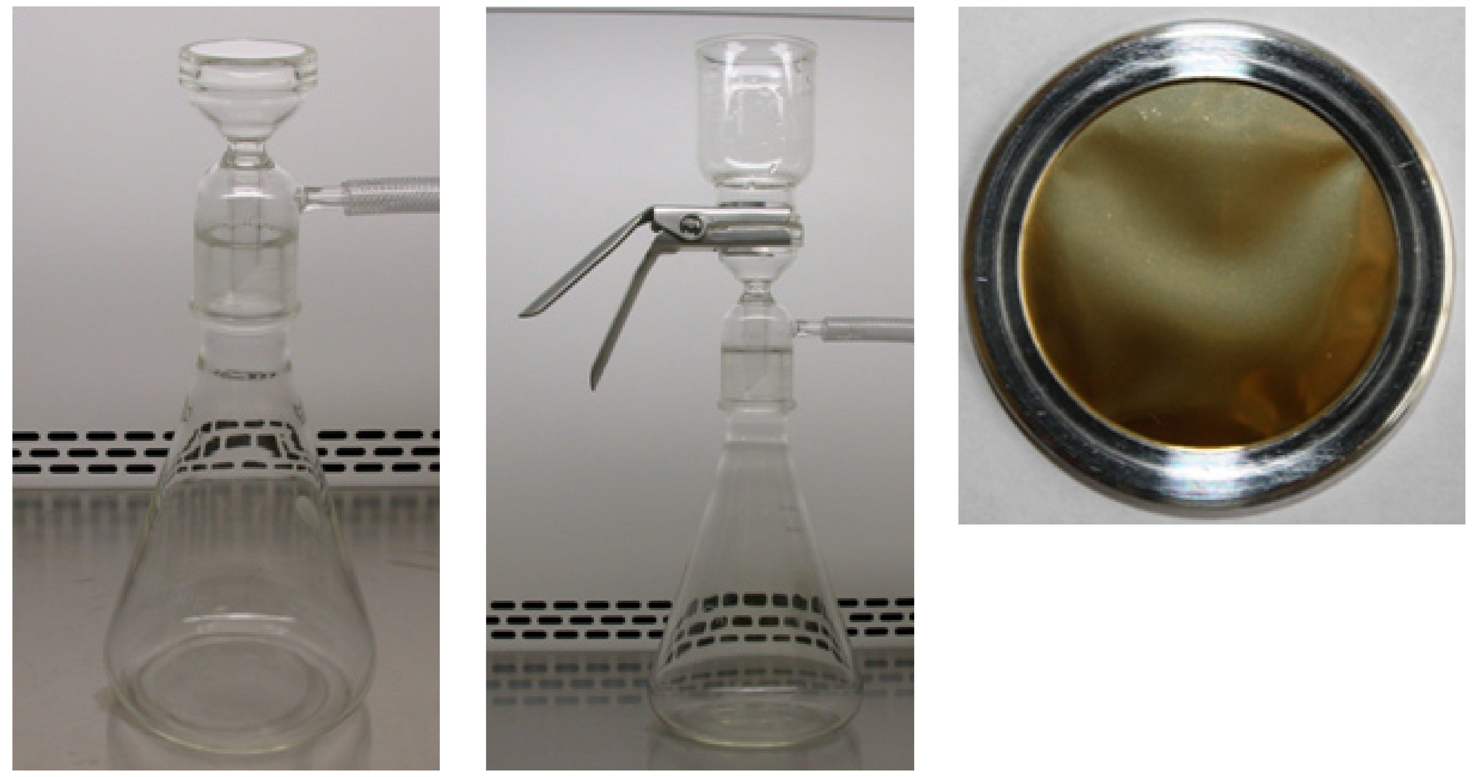
Left and Middle: Automated Database Search of GSR Particle. Right: Combined Raman/LIBS Microscope System Schematic of the Combined Raman/LIBS Microscope System



LIBS Characterization of a GSR Particle

Sample Preparation

Samples prepared for automated analysis were collected on synthetic swab material, removed and placed in individual vials. The vials were filled with methanol to cover the swab material and sonicated for two minutes. Samples were prepared for analysis through filtration onto 0.8 micron polycarbonate filters (gold coated) using a microfiltration apparatus.



Filter apparatus without funnel (left) and with funnel (middle). Gold coated polycarbonate filter used for sample preparation (right).

Automated LIBS of Soil Samples

Sample A

Size Distribution (non-cumulative) of Found and Measured Particles							
	Number	Size Distribution [µm]					
-	-	>=2.00	>=5.00	>=10.0	>=25.0	>=50.0	>=100.0
Analyzed	**1000**	**0**	**0**	**187**	**689**	**124**	**0**
GlassB-1	20	0	0	3	8	9	0
Glass fiolax	12	0	0	1	6	5	0
Glass A	34	0	0	6	22	6	0
Organic	221	0	0	47	151	23	0
Silicate	377	0	0	89	256	32	0
Org. Mat.	10	0	0	1	7	2	0
Na	2	0	0	0	1	1	0
Fe	5	0	0	0	4	1	0
Cu + Zn	1	0	0	0	1	0	0
Fe + Cr (5%)	22	0	0	0	15	7	0
Fe + Cr (15%)	64	0	0	2	48	14	0
Cr	1	0	0	0	1	0	0
Chalk	212	0	0	35	159	18	0
Background	10	0	0	2	5	3	0
Al (Zn)	9	0	0	1	5	3	0
All Particles	**6013**	**1326**	**1735**	**1953**	**689**	**254**	**56**

Sample B

Size Distribution (non-cumulative) of Found and Measured Particles							
	Number	Size Distribution [µm]					
-	-	>=2.00	>=5.00	>=10.0	>=25.0	>=50.0	>=100.00
Analyzed	**997**	**0**	**0**	**0**	**722**	**275**	**0**
GlassB-1	3	0	0	0	2	1	0
Glass fiolax	11	0	0	0	9	2	0
Glass A	8	0	0	0	6	2	0
Silicate	269	0	0	0	207	62	0
Fe	2	0	0	0	1	1	0
Fe + Cr (5%)	1	0	0	0	0	1	0
Chalk	699	0	0	0	493	206	0
Barium	2	0	0	0	2	0	0
Al (Zn)	1	0	0	0	1	0	0
All Particles	**12073**	**2318**	**2953**	**3788**	**1529**	**979**	**506**

Automated LIBS of GSR Samples

Size Class µm	All	5-15	15-25	25-50	50-100
All Particles	354	266	58	27	3
Fibres	1	0	0	1	0
GSR (Pb, Ba)	77	77	0	0	0
Organic	18	18	0	0	0
Background	18	18	0	0	0
Na	2	2	0	0	0
Ca	34	34	0	0	0
Ba	1	1	0	0	0
Cr	1	1	0	0	0

LIBS of Automated Analysis of GSR Sample from Back of Hand

Größenklasse [µm]	Alle	5-15	15-25	25-50	50-100
All Particles	1217	876	261	69	11
Fibres	0	0	0	0	0
GSR (Pb, Ba)	108	108	0	0	0
Steel	4	4	0	0	0
Background	21	21	0	0	0
Na	4	4	0	0	0
Organic	9	9	0	0	0
Ba	53	53	0	0	0
Al	1	1	0	0	0

LIBS of Automated Analysis of GSR Sample from Firearm Surface

Results

Differences in the number of particles and distribution of similar particles containing the same chemical composition were noted in the soil sample. However, a soil sample is not homogenous in nature between samples. Further research into the statistical significance of large particle populations is necessary to attribute likelihood of a common source.

LIBS analysis identified particles with elemental composition of potential GSR particles (Pb/Ba) in both hand (77 particles) and firearm (108 particles) surfaces, and corresponding size and shape values for particles. A large population of burned carbon particles (60 particles) and unidentified organic material (224 particles) were identified by Raman spectroscopy. Continued spectral evaluation is being conducted to determine if the organic components identified can be correlated with burned or unburned organic primer gunshot residue powder or burned/unburned primer residue.

Discussion

- Automated analysis of soil and GSR demonstrated the ability to characterize large populations of particulate in a short amount of time.
- Development of mineral-specific databases are imperative to "real world" applications.
- Sample preparation is critical in recovery of particulate.
- Sampling substrates need to be evaluated to optimize collection and reduce background artifacts.
- Validated research must focus on the statistical significance of large populations of particles. What percentage of particles from Q and K must be present to make associations statistically significant?
- The ability of the combined Raman and LIBS application for GSR holds untapped potential. A methodology that can identify organic and inorganic components of GSR in a single analysis can potentially provide complementary information supporting further evidence of being in the environment of a discharged firearm, reducing the potential false positive of an inorganic analysis alone due to environmental sources.
- Antimony was not detectable due to the LIBS instrument configuration evaluated in this study.