

**checkbox:** Oral Presentation

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**Title:** Elemental Characterization Using Laser-Induced Breakdown Spectroscopy (LIBS) for Forensic applications

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**Abstract Text:** The ability of LIBS (Laser-Induced Breakdown Spectroscopy) to provide rapid multielemental microanalysis of bulk samples (solid, liquid, gas, aerosol) in the parts-per-million (ppm) range with little or no sample preparation has been widely demonstrated. LIBS induces the vaporization of a small volume of sample material with sufficient energy for optical excitation of the elemental species in the resultant sample plume. The vaporized species then undergo de-excitation and optical emission on a microsecond time scale, and time-dependent ultraviolet-visible spectroscopy fingerprints the elements associated with the spectral peaks. LIBS is typically a surface analytical technique, with each laser pulse vaporizing microgram or submicrogram sample masses. However, the rapidity of sampling (typically 10 Hz laser repetition rate) and ability to scan a sample surface, ablate a hole into a solid sample with repeated laser pulses, for depth profiling or focus the laser spark below the surface of a liquid sample permits more versatile analyses and provides sufficient statistics for bulk sampling. The greatest advantage of LIBS is its capability for remote chemical analysis of samples with minimal handling and little or no sample preparation, which minimizes generation of waste to the microgram per pulse of ablated material. The instrumentation and operation of a LIBS system is simpler than some of the more sensitive techniques, and analysis times on the order of minutes, make it more amenable for real-time analysis of chemical processes.

Advantages • Real-time detection. Identification of metals and non-metals in seconds. • Robust instrumentation, with no moving parts in the instrument. • Multielemental analysis. We can detect a number of ions at the same time. • Minimal sample preparation and negligible waste generation. • Continuous monitoring capability. Depth profiling and mapping can be accomplished.

Theory and Practice of LIBS The first step in LIBS is occurrence of breakdown followed by plasma formation. Breakdown can occur when a laser beam of sufficient energy is focused onto a small volume ( $\sim 14 \times 10^{-9}$  cm<sup>3</sup>), creating a power density inside the volume exceeding tens of gigawatts per square centimeter. During the transitory bombardment of the high-energy laser pulse (typically a few nanoseconds), a small amount of material (in the range of micrograms to nanograms) can be readily excited and vaporized under the intense energy-matter interaction. This plasma appears as intense light followed by a loud sound as a loud spark as it expands outward at a supersonic speed in all directions. During the first several hundred nanoseconds of plasma formation an intense broadband continuum of light is released as a result of the bremsstrahlung process. The plasma has a characteristic lifetime depending upon the transitory nature of electron densities and ionic species

present in the plasma. Spectral emissions from ionized, neutral, and molecular species occur sequentially after plasma is formed. The spectral peaks observed between 0.5 to 2 microseconds after plasma formation are mostly due to ionized species present in the plasma. Between 2 and 10 microseconds, the main contributions of emission lines are from the de-excitation of neutral atoms. The emission peaks that occur after 10 microseconds are due to both the de-excitation of neutral atoms and simple excited molecules resulting from radiative recombination. Interference in the spectral measurement of an element can thus be eliminated by carefully selecting the time at which the measurement is taken relative to the time of plasma formation. The optimal time is unique for each element, providing a second characteristic for identification in addition to the spectra. As a minimally destructive method of elemental analysis, LIBS provides many benefits for use in a variety of trace evidence analyses. Uses discussed in this presentation include rapid identification of counterfeit currency and identification of bone fragments. This technology is field portable and has the potential to be used real-time during criminal investigations.