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Laser-Induced Breakdown Spectroscopy of Trace Metals

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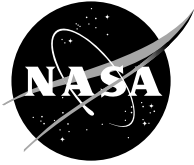
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Summary

An alternative approach for laser-induced breakdown spectroscopy (LIBS) determination of trace metal determination in liquids is demonstrated. The limits of detection (LOD) for the technique ranged from 10 ppb to 10 ppm for 15 metals (Mg, Al, Si, Ca, Ti, Cr, Fe, Co, Ni, Cu, Zn, As, Cd, Hg, Pb) tested.

Introduction

The detection and quantification of light elements and heavy metals within liquid samples and those produced by acid dissolution of solids are pertinent to industrial processing, environmental monitoring and waste treatment (refs. 1 to 5). To-date, laser-induced breakdown spectroscopy (LIBS) has been tested with limited success. Dissolved gases, particulate material and nucleation-induced bubbles produced by prior laser pulses can lead to misfocusing of the laser beam and can also serve as breakdown sites prior to the laser beam focus (refs. 1 to 3, 6, and 7). Additionally, the high local density within the liquid leads to rapid quenching which prohibits temporally selective detection, high collision rates which broaden spectral transitions and confines the plasma emission spatially rendering spatially selective detection problematic. Given these inherent difficulties, in situ LIBS analysis of liquids has not been widely successful with detection limits in the range of 1 to 100 ppm for light metals (refs. 1, 3 to 6, and 8 to 11). As a result, even fewer studies have investigated detection of heavy metals (refs. 1 to 3 and 6) with Hg being reported undetectable at 1000 ppm (ref. 3).

In contrast, solid surface analysis via LIBS exploits the strengths of the technique without the problems inherent to liquid analysis. Solid surfaces provide a uniform, well-defined sample surface. Additionally, the ambient background gas and pressure can be tailored to govern the plasma spatial and temporal evolution thereby optimizing detection conditions (refs. 12 to 16). Finally, surface analysis of a reproducible uniform material avoids the inherent difficulties associated with varying sample matrices, particle grain size effects, analyte dispersion uniformity and varying moisture content (refs. 17 and 18). In the work presented here, trace elemental identification within solutions is transformed into a solid surface analysis. Measurements for 15 metals (Mg, Al, Si, Ca, Ti, Cr, Fe, Co, Ni, Cu, Zn, As, Cd, Hg, Pb) are presented.

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Experimental Approach

Our approach consisted of evaporation of the analyte solution upon an amorphous graphite substrate followed by LIBS analysis of the substrate surface. Using calibrated pipets, aliquots of environmental standard solutions (commercially available solutions of the metal as a nitrate or chloride salt in roughly 2 percent HNO₃ or HCl, respectively) or diluted solutions prepared from these certified standards were deposited upon the carbon disks and then evaporated to dryness.

A pulsed Nd:YAG laser provided light at 1064 nm for the LIBS analysis with the same single laser pulse serving to both atomize and electronically excite the elements. Using a 300 mm focal length fused silica lens, the beam focus was placed approximately 1 cm behind the sample surface. The beam diameter on the graphite planchet was determined to be roughly 750 μm , resulting in a laser fluence of roughly 35 J/cm² and an intensity of 4.4 GW/cm² for a nominal 8 nsec pulse width.

LIBS emission from the expanding plasma plume was directed into a 1-meter fused silica optical fiber using a collimating beam probe. A 1/4 meter spectrograph fitted with a cooled intensified array camera generated the spectra for subsequent analysis. For low resolution survey spectra, a 147 groove/mm grating blazed at 300 nm was used while a 1200 groove/mm grating blazed at 300 nm provided sufficient spectral resolution for detailed analysis of the atomic and ionic emission.

Results from previous LIBS investigations exploring the effects of focussing. Laser excitation wavelength and laser repetition rate were used to select the conditions used here. Extensive testing of LIBS detection in different buffer gases and pressures confirmed results of prior LIBS investigations (refs. 12 to 16) and led to the choice of 75 Torr Ar.

Results

Substrate Characterization

Figure 1 shows low resolution LIBS spectra from an undoped carbon disk. With the exception of the carbon atomic emission lines at 193.3 and 247.8 corresponding to C atom transitions from the ¹P₀ level to the ¹D and ¹S levels, respectively, the ultraviolet region is free of substrate spectral emissions.

Analyte Spectral Transition Selection and Identification

Table I lists the spectral transitions associated with LIBS in this study for all 15 metals tested under higher resolution. In some cases, such as for Hg, multiple spectral regions were investigated. At higher resolution. The spectral transitions chosen for analysis possess a strong oscillator strength, a moderately low excited-state energy level, and a minimal of overlap with spectral emissions from other elements. Figure 2 illustrates some representative spectra for selected elements.

Linearity and Limits of Detection

To assess the analytical capability of our technique, we explored the linearity with analyte concentration and determined limits of detection. Analytical working curves were developed over a range of concentrations for As, Cd, Hg, Pb, and Cr. Figure 3 shows the results for As, Cr, and Pb. Identical results were obtained using either the peak or spectrally-integrated intensities of elemental emissions.

Given limited success with developing analytical working curves, an empirical approach was undertaken to determine limits of detection (LOD). In our approach, the LOD was assigned to the concentration that resulted in recognizable elemental emission ($S/N > 3$) in greater than 75 percent of the spectra of a series of single laser pulse LIBS spectra. Table 1 also lists the detection limits of the elements determined in this manner.

Although the limit of detection is revealing, it does not convey the minute aliquots that could be analyzed by the technique in screening for trace elements. The laser pulse, with a spot size of 0.075 cm, samples 0.13 percent of the analyte in the 1.0 ml liquid volume initially deposited. This calculation assumes that the deposited liquid uniformly covers an area 3.5 cm² and that the evaporation resulted in uniform deposition over the carbon planchet. The liquid was not deposited to the edge of the planchet to avoid loss of material by runoff. For an initial liquid concentration of 0.1 ppm, this corresponds to 130 pg of trace metal sampled. For iron, this corresponds to approximately 2 picomoles of material. This calculated amount is competitive with those routinely reported using laser-induced fluorescence and graphite furnace atomic absorption spectroscopy. Another unique feature of the technique is the small volumes required. Taking the volume of the liquid cylinder with base equal to the laser spot size and height equal to the initially deposited liquid height, a single laser pulse samples a volume of 1.3 microliters. This calculated value is competitive with those routinely reported using laser-induced fluorescence and graphite furnace atomic absorption spectroscopy. Clearly, LIBS applied using our approach has potential for trace-element detection.

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TABLE I.—LIMITS OF DETECTION FOR THIS STUDY AND COMPARISON WITH OTHER RESULTS.

Element	This study		Other work
	LOD, ppm	Spectral transitions, ^{a,b} nm	LOD, ppm
Mg	0.01	279.55, 280.27	^a 3, ^b 9, ^c 100, ^d 1.9
Al	0.01	394.4, 396.15	^a 3, ^c 20, ^d 5.2
Si	0.01	288.16, 251-253	
Ca	0.01	393.37, 396.85	^c 8, ^e 0.3, ^h 0.13, ^d 25, ^e 0.8, ^f 0.4
Ti	0.1	323.4, 334-339	
Cr	0.1	266-268, 274-279, 283-288	^d 0.1
Fe	0.01	238-241, 260-263 273-276	^g 7.5
Co	>0.1	238-242, 340-348, 349-353	
Ni	0.01	221-223, 229-231	ⁱ 36.4
Cu	0.01	324.75, 327.4	
Zn	1.0	330.26, 330.29, 334.5, 334.56	
As	5	274.5, 278.02, 286.04	
Cd	1.0	214.44	^h 500
	0.1	226.5, 228.5	
Hg	10	253.65	^h undetectable at 1000 ppm
Pb	2	261.37, 261.42, 280.2, 283.31	^h 12.5
	10	405.78, 406.21	

^aMultiple wavelengths correspond to transitions of similar intensity in the LIBS spectra which proved equally useful in determining detection limits.

^bWhere wavelength ranges are listed, multiple transitions are present and were not fully resolved with our spectral resolution.

^cNg et al., ref. 6 (liquid aerosol).

^dArca et al., ref. 4 (liquid surface).

^eCremers et al., ref. 1 (solution).

^fArchontaki et al., ref. 9 (droplet).

^gYu et al., ref. 8 (liquid surface).

^hKnopp et al., ref. 3 (solution).

ⁱBerman et al., ref. 5 (liquid surface).

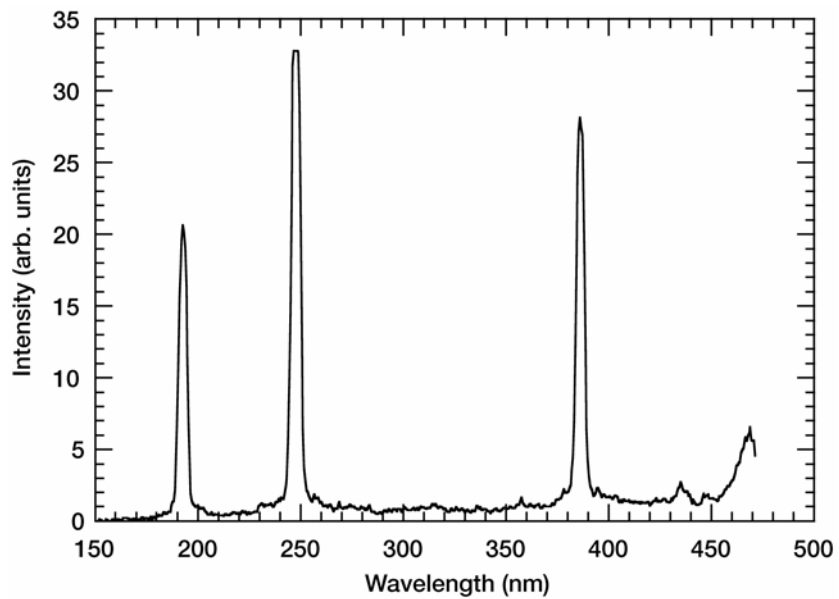


Figure 1.—LBIS spectrum for an undoped carbon disk in 740 Torr Helium from 150-470 nm. The excitation laser fluence to generate in the spectra was 225 J/cm². The emission was detected at a time delay of 5 μ s and integrated over a 0.1 μ s gate.

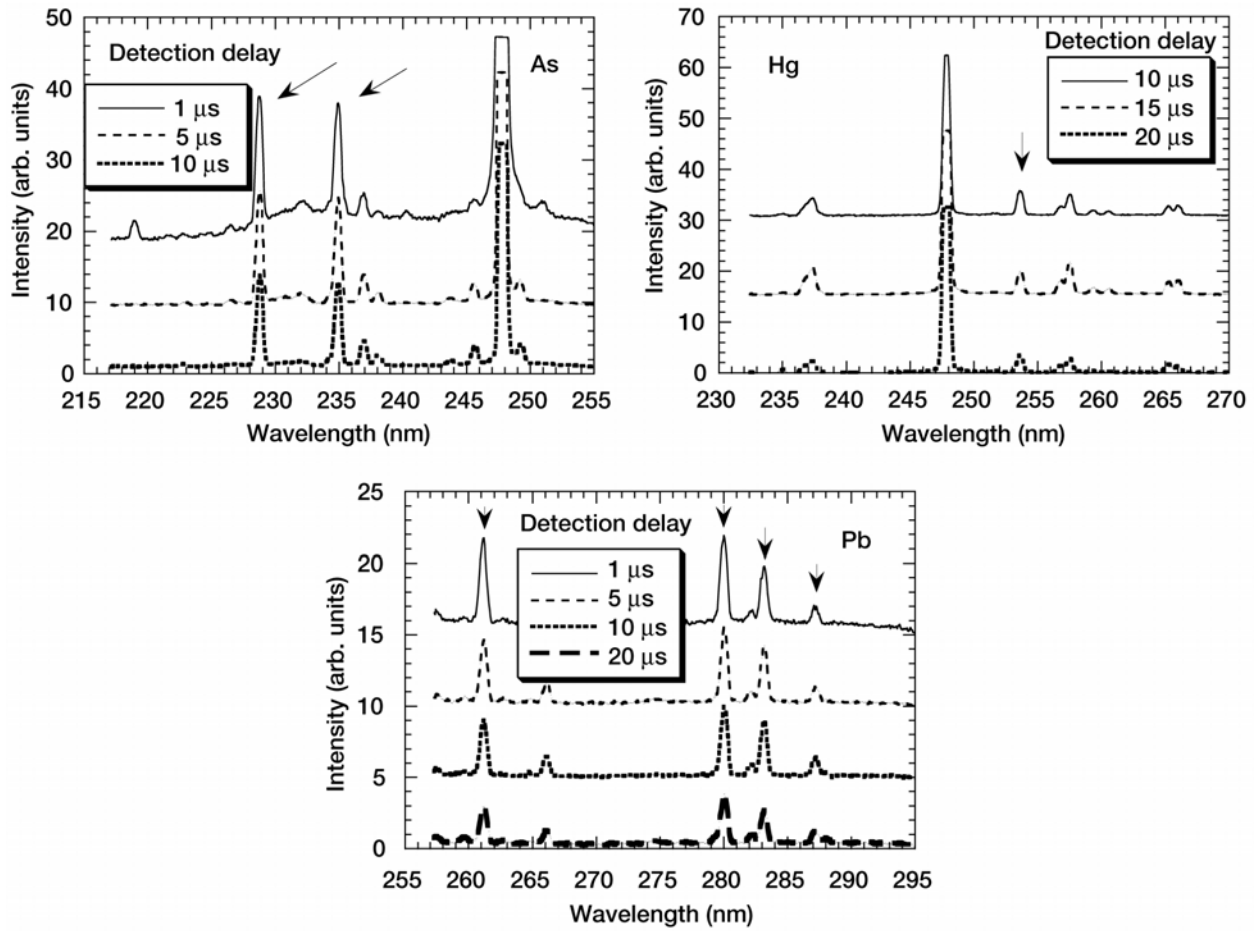


Figure 2.—High resolution LIBS spectra for As, Hg and Pb using a 1 μs gate with various delay times to monitor the emission. Arrows in the spectra indicate emission from the element of interest. The concentration of each metal in the deposited solution was 1000 ppm. For each spectrum, the signal was integrated over a 1 μs gate.

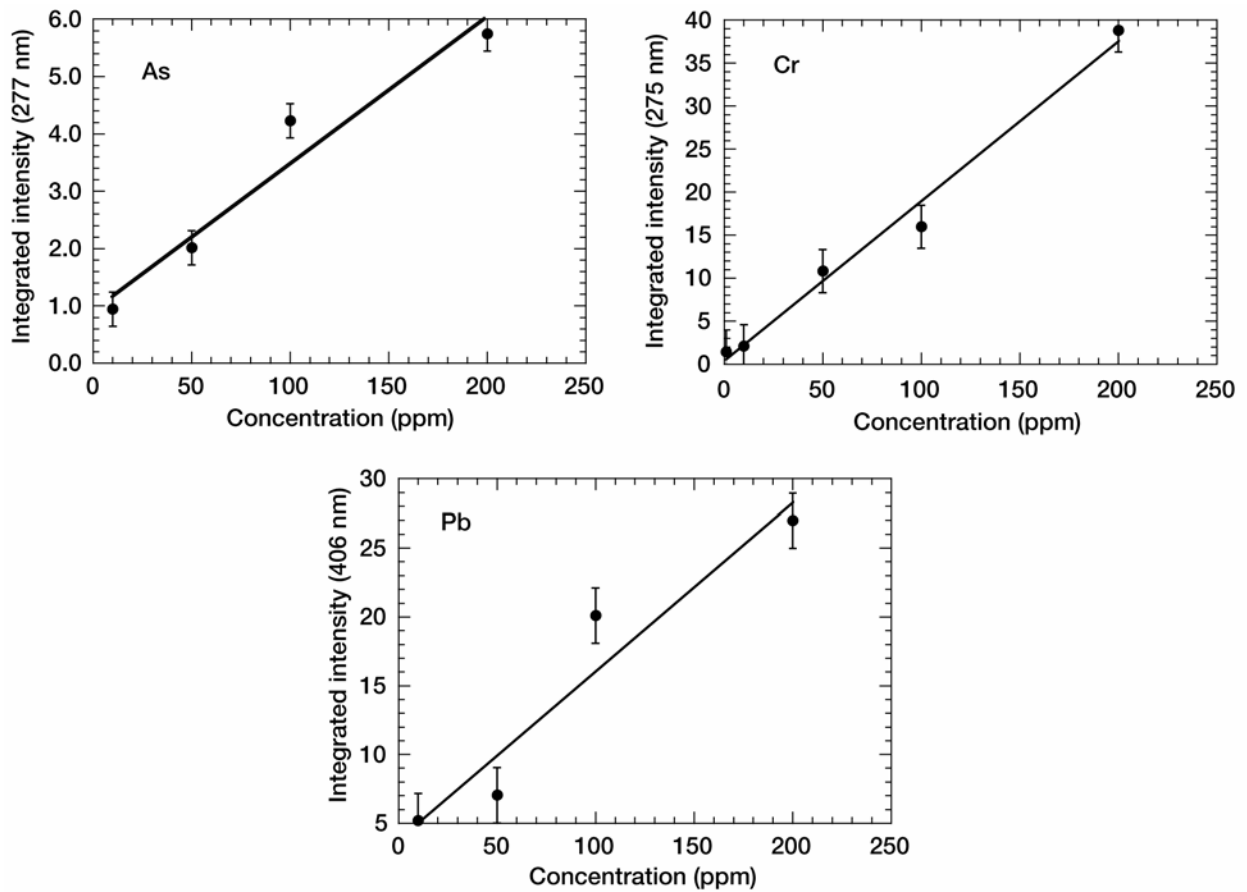


Figure 3.—Analytical working curves based on the integrated elemental emission from LIBS spectral transitions as a function of concentration for the elements As, Cr, and Pb.

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