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TITLE LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS): A NEW SPECTROCHEMICAL TECHNIQUE

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LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS): A NEW SPECTROCHEMICAL TECHNIQUE*

by

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ABSTRACT

We have used the breakdown spark from a focused laser beam to generate analytically useful emission spectra of minor constituents in air and other carrier gases. The medium was sampled directly. It was not necessary to reduce the sample to solution nor to introduce electrodes. The apparatus is particularly simple; a pulsed laser, spectrometer, and some method for time resolution. The latter is essential in laser-induced-breakdown spectroscopy (LIBS) because of the strong early continuum. High temperatures in the spark result in vaporization of small particles, dissociation of molecules, and excitation of atomic and ionic spectra, including species which are normally difficult to detect. In one application, we have monitored beryllium in air at concentrations below $1 \mu\text{g}/\text{m}^3$, which is below 1 ppb (w/w). In another we have monitored chlorine and fluorine atoms in real time. LIBS has the potential for real-time direct sampling of contaminants in situ.

INTRODUCTION

In atomic emission spectrochemistry, the light from an excited sample is spectrally analysed to yield qualitative and quantitative information about the elemental constituents. The more traditional emission techniques employ arc or spark excitation. Recently atomic flame fluorescence and the inductively coupled argon plasma (ICP) have become useful analytical tools. None of these techniques is particularly portable or usable outside of the analytical laboratory. We have created a field-deployable version of spark spectroscopy by using a pulsed laser to generate a free-standing spark by dielectric breakdown (1,2). We use the acronym LIBS for laser-induced breakdown spectroscopy; its time resolved version is sometimes called TRELBS. Except where noted, we discuss only the time-resolved version.

LIBS has been used to analyze airborne samples (both aerosols and particles) (3), to detect beryllium (3), chlorine, and fluorine (2,3), and to detect species in the product stream of a coal gasifier (4). For details we refer the reader to the references. Here we summarize the important features of the technique and some of the results.

EXPERIMENTAL

The basic apparatus for observing LIBS with time resolution can be quite simple. A version we have used extensively is shown in Fig. 1. A 5- to 20-cm focal length lens focused the beam to fluence levels which were sufficient to

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break down ambient air. Light from the plasma was collected and imaged on the slit of a scanning spectrometer. A variety of photomultiplier tubes with extended uv or ir response were used as detectors. The photomultiplier output was processed by a boxcar averager for time resolution and signal averaging. Observations with the photomultiplier and spectrometer gave the maximum sensitivity over the range 200 to 900 nm. By contrast, the diode array detection described below monitored a wide spectral range, useful for survey work not requiring maximum sensitivity.

In the time-gated diode-array version of LIBS, we coupled the output of the diodes to a multichannel analyzer. Figure 2 shows the schematic of this arrangement. Often the light impinging on the array went through a microchannel plate image-intensifier, which can have a gain of 25,000. This system was sensitive to wavelengths between 350 and 800 nm. Its utility is illustrated in Fig. 3, which contains the LIBS spectrum of oxygen at various times t_d after spark initiation. Figure 3 also illustrates the necessity for time resolution. At early times the continuum and ionic lines dominate, but at late times the spectrum becomes quieter and neutral lines which have analytical utility are prominent.

A simple, time integrated version of diode-array LIBS is shown schematically in Fig. 4. This apparatus was used to observe species in the effluent stream of an experimental coal gasifier at Brigham Young University. Species detected in this experiment are listed in Table I.

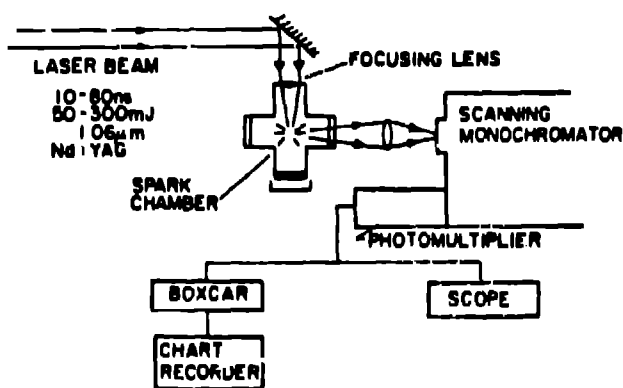


Fig. 1. Diagram of the photomultiplier tube and boxcar apparatus for time-resolved LIBS.

DIODE ARRAY TRELBS

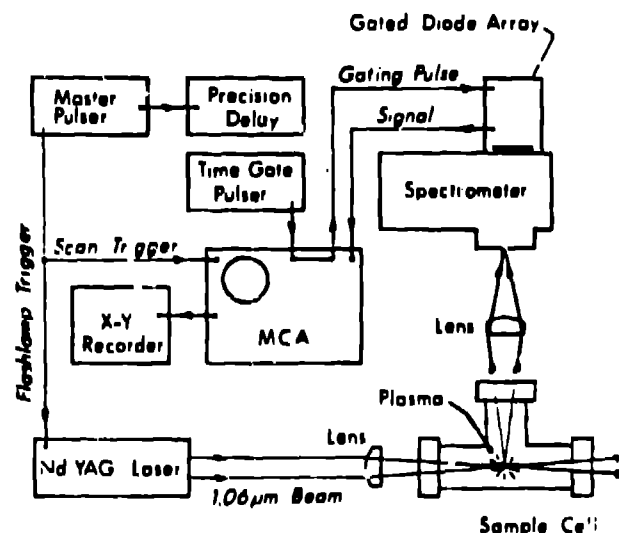


Fig. 2. Diagram of apparatus used in the time-gated diode-array version of LIBS.

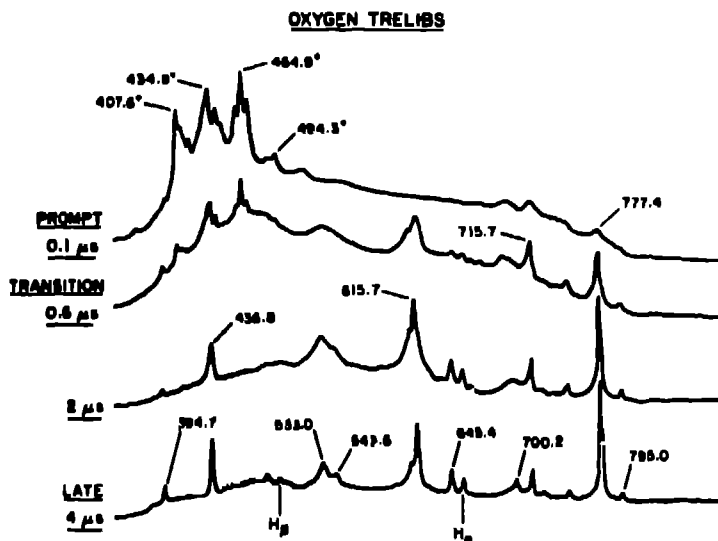


Fig. 3. Spectra of once ionized and neutral oxygen atoms at various times following plasma formation.

LIBS APPARATUS - BYU CONFIGURATION

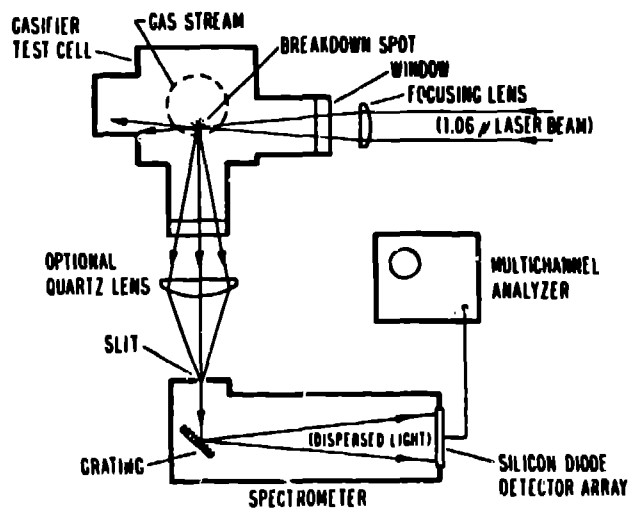


Fig. 4. Apparatus used to monitor atomic and molecular species contained in the effluent of an experimental coal gasifier.

RESULTS

LIBS was first applied to the real-time monitoring of airborne beryllium particles. These particles were generated in the laboratory by ablation from a solid beryllium block, or by a nebulizer/heat-pipe arrangement. The high temperature of the spark (20,000 K at $t_d = 0.5 \mu s$; 10,000 K at $t_d = 10 \mu s$) vaporized the particles and excited neutral and once ionized beryllium. The strongest beryllium feature was the Be II doublet at 313.1 nm. Figure 5 shows the results of monitoring that feature while beryllium particulate was admitted to the sampling cell. Concentrations in the spark chamber were between 1 and $10 \mu g/m^3$.

In a second application, LIBS was used to detect fluorine and chlorine in air. As sources of these atoms we used a variety of freons, SF_6 , and CCl_4 . The high spark temperature dissociated the molecules completely and excited the upper energy levels of Cl and F. Their concentration was then monitored by infrared transitions. Working curves relating signal to concentration for chlorine are shown in Fig. 6. The slopes of these curves were proportional to the number of chlorine or fluorine atoms in the source molecule. These slopes were normalized to see how well the LIBS technique could identify the number of atoms in the molecule. The results are contained in Table II, and are promising.

In addition to demonstrating real-time detection and atom counting we measured the limit of detection for many atoms. We calculated the limit of detection (C_L) from

$$C_L = \frac{2\sigma}{S}$$

TABLE I

BYU TEST DATA: DETECTED SPECIES
(Preliminary Results)

Atomic
Na ⁰
K ⁰
Ca ⁰
O ⁰ , O ⁺
O ⁰ , C ⁺ , C ²⁺
Ca ⁰ , Ca ⁺
Si ⁰
Mg ⁺
Molecular
CN
N ₂
CO
O ₂

TABLE II

COMPARISON OF RATIOS OF SENSITIVITY TO THE NUMBER OF
CHLORINE OR FLUORINE ATOMS IN A MOLECULE

Parent Molecule	Number of Cl Atoms	Relative Sensitivity
(CH ₃) ₂ CHCl	1	1.02
CCl ₂ F ₂	2	1.92
C ₂ Cl ₃ F ₃	3	2.81
CCl ₄	4	4.00 (reference)
Parent Molecule	Number of F Atoms	Relative Sensitivity
CCl ₂ F ₂	2	2.08
C ₂ Cl ₃ F ₃	3	3.06
SF ₆	6	6.00 (reference)

where C is the rms noise on either the background or the signal, and S is the slope of the working curve. Results are shown in Table III. The limits of detection are sufficiently low to allow several applications which we are considering.

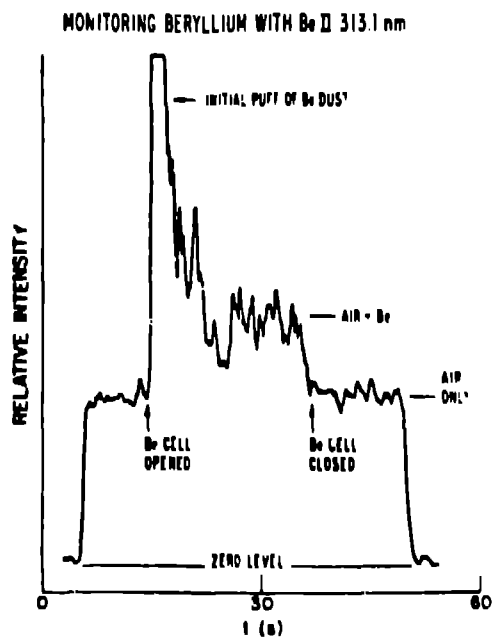


Fig. 5. Variation of Be II emission signal as beryllium particulate was admitted to the sample chamber.

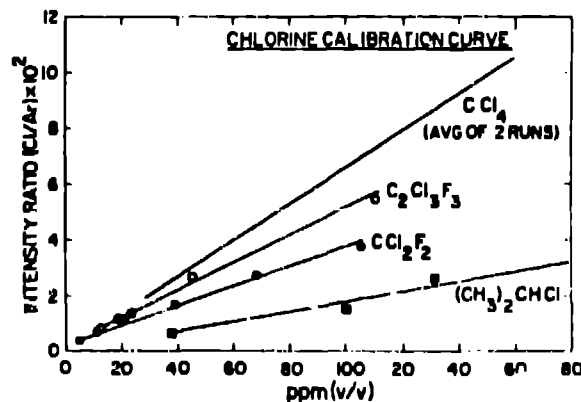


Fig. 6. Demonstration of the feasibility of atom counting with LIBS. The slopes of the working curves indicate the number of chlorine atoms in the parent molecule.

SUMMARY AND CONCLUSIONS

We have demonstrated that analytically useful atomic spectra can be generated by LIBS and analyzed in real time. The detection apparatus is relatively simple; even the current laboratory apparatus is movable. With the utilization of small lasers and electronic miniaturization, a very small portable unit is feasible. We are working on a prototype model of such a unit, one which would be capable of making in situ spectrochemical measurements in the field.

LIBS has a number of distinct features which are spectrochemically advantageous. These are summarized in Table IV. Table V contains a number of projected applications.

TABLE III

DETECTION LIMITS OF VARIOUS ELEMENTS IN AIR USING LIBS WITH TIME RESOLUTION

Element	Analytical Line	C_L ppm (w/w)	Delay Time (μ s)
Cl	837.5 nm	20	2
F	685.6 nm	40	2
P	253.3 nm	1.2	2
S	921.2 nm	200	2
Be	313.1 nm	0.0006 (0.8 μ g/m ³)	4
As	228.8 nm	0.5	2

TABLE IV

ADVANTAGES OF LIBS AND THE SPECTROCHEMICAL IMPLICATION

LIBS Advantages	Consequences
Atomic emission spectroscopy	* multielement capability
High temperature	* vaporizes particulates * excites species which are normally difficult to detect, such as chlorine and fluorine
Absence of electrodes	* no electrode wear * reduces interferences and eliminates plasma perturbation by electrodes
Direct sampling	* removes some analytic flicker noise * eliminates sample handling, offers real-time detection
Conventional sampling	* all the advantages of being electrodeless, but pulsed operation may be disadvantage.
Simple apparatus	* field operation

TABLE V

APPLICATIONS

- * Direct air sampling
- * Point detection
- * Monitoring of secure-room air
- * Monitoring of surfaces and clothing

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