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LASER-INDUCED BREAKDOWN SPECTROSCOPY: A NEW TECHNIQUE
FOR NONDESTRUCTIVE ANALYSIS OF SOLUTIONS

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Abstract

Laser-induced breakdown spectroscopy has been applied to the continuous determination of uranium in solutions. The technique is rapid, non-invasive, and unaffected by radioactivity. Powerful laser pulses are focused through an optical access onto the solution surface to produce a hot spark plasma. In experiments on static solutions, uranium concentrations between 0.1 and 300 g/L were determined, using a pulsed Nd:YAG laser and a time-gated photodiode array. A concentration of 4.2 g/L was measured with 1.0% precision in 3 minutes. Substances that absorb at the laser wavelength, suspended materials, and variations in the acidity of the solution have little or no effect on the results. Experiments are in progress on flowing streams contained in a test loop that simulates plant operating conditions.

1. Introduction

Continuous measurement of uranium concentrations in liquid streams is necessary in nuclear fuel cycle processing plants for criticality safety, process control, and nuclear materials accountancy. The solutions may contain high concentrations of fission products or neutron emitters that interfere with nondestructive gamma-ray, neutron, or x-ray techniques. A technique that is rapid, non-invasive, and unaffected by radioactivity and that requires neither sample handling nor preparation is desirable. Laser-induced breakdown spectroscopy (LIBS) appears to have all of these properties. We have investigated the application of LIBS to the measurement of uranium concentrations in solution.

In the LIBS technique, powerful laser pulses are focused through an optical access onto the solution surface to produce a hot spark that vaporizes a small volume of the solution and generates a high-temperature plasma consisting of electrons and electronically excited atoms. The plasma light is spectrally and temporally resolved and measured, using techniques of atomic emission spectroscopy. In a processing plant, the optical access could be a flow cell with an optically transparent window that is inserted into the pipe or a by-pass loop containing the flowing solution.

We have completed our experiments on static solutions and are now experimenting with flowing streams contained in a test loop. Thus, our work is incomplete, but enough results have been obtained to show the feasibility and potential of the LIBS technique and to justify the presentation of this progress report.

2. Experimental Equipment and Methods

A schematic of the experimental arrangement that we have used for work on static solutions is shown in Fig. 1. Pulses from a Nd:YAG laser (usually operated at 250 mJ average pulse energy, 9 pulses/second) created the spark plasmas. Uranium solutions (0.035-300 g/L) in 4 $\underline{M}$ nitric acid were contained in sealed cylindrical glass vials. The laser pulses were focused on the surface of the solution, along a path perpendicular to the liquid surface, using a 50-mm focusing lens. The plasma light, viewed through the side of the vial along a direction parallel to the liquid surface, was focused on the entrance slit of a 0.5 m grating spectrometer.
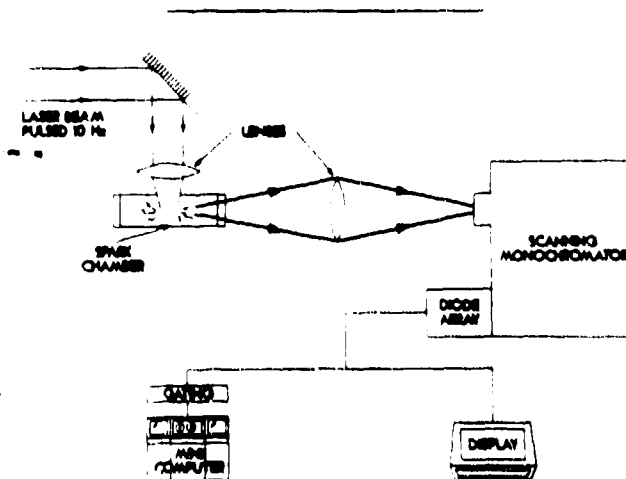

Fig. 1.
Schematic of the Experimental Arrangement for LIBS.

The spectrally resolved light was detected using a diode array rapid scanning spectrometer system. The detector, which consists of a microchannel plate image intensifier and linear photodiode array (1024 diodes in 25.4 mm), has maximum sensitivity at 480 nm. The detected signal was time resolved by applying a gate pulse to the image intensifier positioned in front of the photodiode array. The time after spark initiation at which uranium detection began and the width of the detection window were controlled by precisely timing the gate pulse relative to the laser pulse. Time resolution of the plasma signal was used to minimize detection of the strong continuum radiation at early times after spark formation.

Measurements of the uranium signal were made by averaging the spectra from a large number of laser sparks. The net uranium signal was computed as the number of counts above the background level in a spectral region defined by an emission line (peak area). In some cases, the net signal was ratioed to a background signal, computed as the number of counts in an interference-free region 0.1-0.2 nm wide near the uranium line.

3. Results

The goals of our experiments on static solutions were to optimize the experimental parameters, to select strong uranium lines free of interference, and to determine the detection limit and concentration range that could be measured. In previous work with the LIBS technique[1] on solutions containing alkali and alkaline earth elements, the spark was formed in the bulk liquid. This avoided the problem of spark perturbation due to surface agitation and splashing that occurs if the spark is formed on the surface of the liquid. However, the temperature of the spark is much lower in bulk excitation than in surface excitation. For uranium solutions, we found it necessary to use surface excitation, because spark formation in the bulk of the solution gave no detectable uranium signal, even at a concentration of 300 g/L. With surface excitation, a detection limit of 0.1 g/L was obtained. Other advantages of surface excitation are that the plasma light will not be absorbed by other materials in the solution and that suspended particles will not perturb spark formation nor scatter the plasma light to as great an extent. However, with surface excitation, the signal strength is sensitive to the distance between the focusing lens and the liquid surface. Also, in a flow cell, it is always necessary to have an air space above the solution for formation of the spark.

The factors considered in optimization of the experimental parameters were the strength of the uranium signal and its reproducibility. The parameters we investigated included laser pulse energy and repetition rate, focal length of the lens that focused the laser pulses on the solution surface, and the timing of data collection. The parameters we considered optimum are listed in Table I. Detailed results will be published elsewhere.

In searching for suitable uranium lines, we examined the spectral region from 350-700 nm, which contains many strong uranium lines. Although emission lines from both neutral atoms and singly ionized uranium were observed, the lines from singly ionized uranium were considerably stronger. The wavelengths and relative intensities of the strongest of these lines are given in Table II. Although the strongest uranium line listed in the table is at 367.0 nm, the strongest signal obtained with the diode array came from the 409.0-nm line, because of the greater sensitivity of the detector at that wavelength. Accordingly, we used the 409.0-nm line for most of our measurements. Figure 2 shows a small section of the spectrum surrounding this line. The uranium lines at 385.5, 386.0, and 386.6 nm could

not be used because of interference by cyanogen band emission. Cyanogen is formed from nitrogen (in air and solutions) and carbon atoms (in air as carbon dioxide) that combine in the cooling spark plasma.

TABLE I. Optimum Experimental Parameters

Laser

      Nd:YAG - Wavelength 1064 nm

      Surface excitation

      Pulse width 15 nsec

      Pulse energy - 250 mJ/pulse

      Repetition rate - 9 Hz

      Focusing lens - 50 mm focal length

Time Resolution

      Delay - 10 μsec

      Window - 200 μsec

TABLE II. Some Strong Uranium Lines Observed in a Laser Spark[a]

Wavelength (nm)	Relative Intensity
367.0	1.00
370.2	0.42
378.3	0.57
383.1	0.44
385.5[b]	--
386.0[b]	--
386.6[b]	--
389.0	0.42
393.2	0.91
406.3	0.31
409.0	0.92
411.6	0.31
417.2	0.46
424.2	0.50
424.4	0.44
434.2	0.34
436.2	0.26
447.2	0.23
451.5	0.11
454.4	0.30
462.7	0.10
464.7	0.06
468.9	0.08

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[a] Measurements were made on a 10 g/L solution. The spectral response of the detection system was calibrated using a tungsten filament radiance standard lamp.

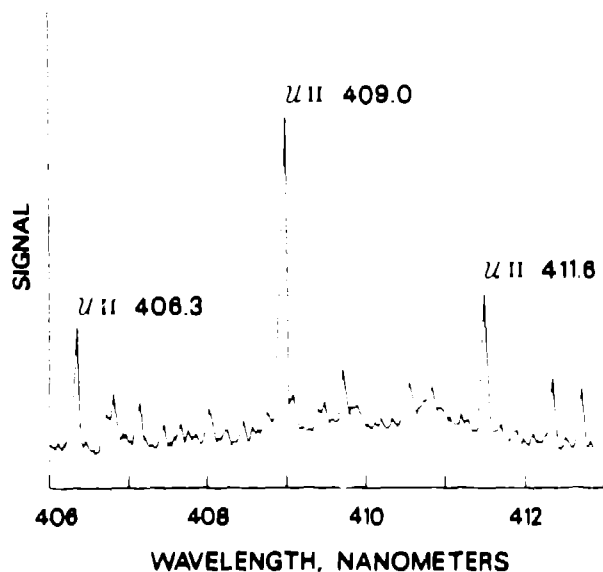[b] Cyanogen band emissions interfere with these lines.

U II 409.0

U II 406.3

U II 411.6

WAVELENGTH, NANOMETERS

Fig. 2.
Spectrum between 406 and 413 nm, obtained from a solution containing 10 g uranium/L in 4 $\underline{N}$ nitric acid. Prominent uranium lines are marked.

A calibration curve (Fig. 3) of the net intensity of the 409.0-nm signal vs uranium concentration is nearly linear over the range 0.1-300 g/L. The precision of the method was determined at a concentration of 4.2 g/L, from spectra obtained by averaging 50, 100, 200, 800, and 1600 sparks. Ten replicate measurements were made for each case. The results are presented in Table III. In each case, the highest precision is obtained when the uranium signal is ratioed to background. A precision of 1.0% RSD was obtained when 1600 sparks were averaged, corresponding to a measurement time of 3 minutes.
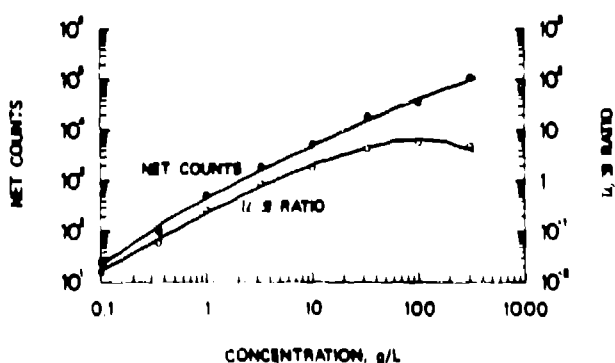

CONCENTRATION, g/L

Fig. 3
Calibration curve for uranium concentrations from 0.1-300 g/L. Dark circles represent the net uranium counts above background. Light circles represent the ratio of net uranium counts to number of background counts in an interference-free region 0.1-0.2 nm wide near the uranium line.

TABLE III. Precision of Uranium Determination as a Function of Number of Pulses Averaged[a]

Pulses Averaged	% RSD Net Signal	% RSD Ratio
50	13.3	7.9
100	12.2	8.6
200	7.2	5.0
800	4.5	2.7
1600	1.8	1.0

[a] Measurement made on solution containing 4.2 g uranium/L. Net signal refers to area under uranium 409.0 nm peak above background. Ratio is net uranium counts divided by counts in a background region 0.1-0.2 nm wide near the uranium line.

We investigated the effect of changes in acidity of the solution on the strength of the uranium signal by varying the nitric acid concentration from 1 to 6 M. No effect was found. Addition of copper nitrate, which absorbs at the laser wavelength, to the solution produced no reduction in the uranium signal until the absorbance of the solution exceeded 1.5. Similarly, the suspension of carbon black in the solution had no effect until the carbon black concentration exceeded 1 g/L. These results demonstrate that the LIBS surface excitation technique is little affected by other materials in the solution.

4. Conclusions and Future Work

The use of LIBS to analyze static uranium solutions at concentrations of interest for process stream analysis has been successfully demonstrated. We have constructed a test loop and flow cell and are presently conducting experiments on flowing streams. Factors that we are investigating include the effects of a simulated industrial environment on analytical performance, spectral interference due to other metallic substances (for example, zirconium, aluminum, stainless steel, and fission products) in the stream, and calibration methods suitable for in-situ analysis. Spectral interferences will no doubt be encountered, but uranium has so many emission lines that we are confident that some that are free of interference will be found. The LIBS technique will also be useful for determination of other elements besides uranium in process streams, and we plan to investigate its application to the determination of plutonium, americium, thorium, zirconium, and others in the future.

Reference

1. D. A. Cremers, L. J. Radziemski, and T. R. Loree, "Spectrochemical Analysis of Liquids Using the Laser Spark," Appl. Spectroscopy 38 (1984), pp. 721-729.