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CONTINUOUS MEASUREMENT OF URANIUM CONCENTRATIONS WITH THE LASER SPARK

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ABSTRACT

Laser-induced breakdown spectroscopy has been applied to the continuous determination of uranium concentrations between 0.1 and 300 g/L in flowing solutions. The technique is rapid, non-invasive, and unaffected by radioactivity. A concentration of 10 g/L was measured with 0.8% precision in 3 min. 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. High concentrations of zirconium, cadmium, aluminum, or stainless steel in solution do not interfere.

INTRODUCTION

Continuous measurement of uranium concentrations in liquid streams is necessary for criticality safety, process control, and nuclear materials accounting. 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, unaffected by radioactivity, and that requires neither sample handling nor preparation is desirable. The laser spark, more formally known as 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 into a by-pass loop containing the flowing solution.

We have worked with both static and flowing solutions. Static solutions in sealed containers were used for the successfully completed proof-of-principle experiments. Additional experiments were performed on flowing streams contained in a test loop in order to simulate plant operating conditions as much as possible.

EXPERIMENTAL EQUIPMENT AND METHODS

We measured uranium concentrations from 0.1-300 g/L, generally in 4 M nitric acid. A schematic of the experimental arrangement is shown in Fig. 1. Pulses from a Nd:YAG laser (a minimum energy of 60 mJ/pulse is needed) created the spark plasmas. The uranium solutions 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. The plasma light, viewed through the side of the vial along a direction parallel or at 45° to the liquid surface, was focused on the entrance slit of a 0.5 m grating spectrometer.

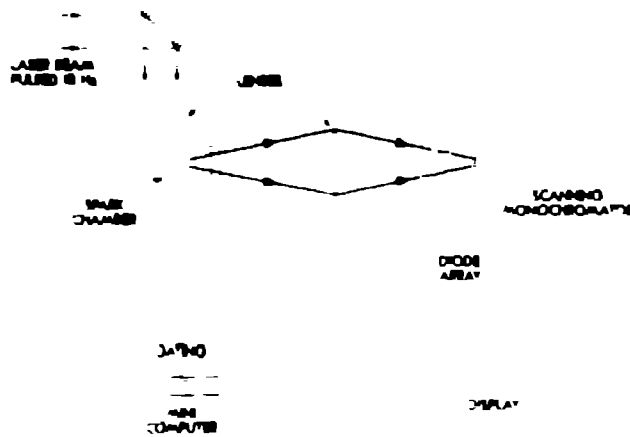


Fig. 1. Schematic of the Experimental Arrangement for LIBS.

The spectrally resolved light was detected with a photodiode 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), had 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.

Experiments on flowing solutions have been conducted with two flow loops. The larger loop can circulate 12 L of solution and the smaller loop 0.5 L. Both loops are constructed of stainless steel components. The optically transparent flow cell, sketched in Fig. 2, was designed so that the solution would be doubly contained.

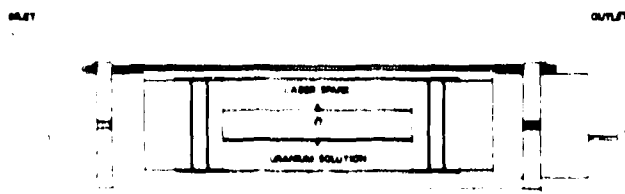


Fig. 2. Sketch of flow cell.

RESULTS

The goals of our initial experiments 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 technique¹ on solutions containing alkali and alkaline earth elements, the spark was formed in the bulk liquid. For uranium solutions, we found it necessary to form the spark at the liquid surface because spark formation in the bulk of the solution gave no detectable uranium signal. With surface excitation, a detection limit of 0.1 g U/L was obtained. Other advantages of

surface excitation are that the plasma light will not be absorbed by other substances in the solution and that suspended particles will not perturb spark formation nor scatter the plasma light to as great an extent. However, signal strength is sensitive to the distance between the focusing lens and the liquid surface, and there must always be 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 found to be optimum are listed in Table I.

TABLE I. Optimum Experimental Parameters

Laser

Nd:YAG - wavelength 1064 nm
 Surface excitation
 Pulse width 15 ns
 Pulse energy - 250 mJ/pulse
 Repetition rate - 9 Hz
 Focusing lens - 50 mm focal length

Time Resolution

Delay - 10 μ s
 Window - 200 μ s

In searching for suitable uranium lines, we examined the spectral region from 350-700 nm, which contains many strong uranium lines. We used the 409.013-nm line for most of our measurements. In the presence of zirconium, which interferes with the 409.0-nm line, the 411.610-nm line was used instead. Both of these lines are shown in Fig. 3. The many small peaks in the spectrum are all uranium emission lines, not noise.

A calibration curve of the net intensity of the 409.0-nm signal versus uranium concentration is nearly linear over the range 0.1-300 g/L. The precision of the method was determined at several concentrations from spectra obtained by averaging 50, 100, 400, 800, and 1600 sparks. Ten replicate measurements were made for each case. The results for a concentration of 10 g/L are given in Table II. In each case, the highest precision is obtained when the net uranium signal is ratioed to background. A precision of 0.8% RSD was obtained when 1600 sparks were averaged, corresponding to a measurement time of 3 min. If a precision of 5% is adequate, a measurement can be made in 10-15 s.

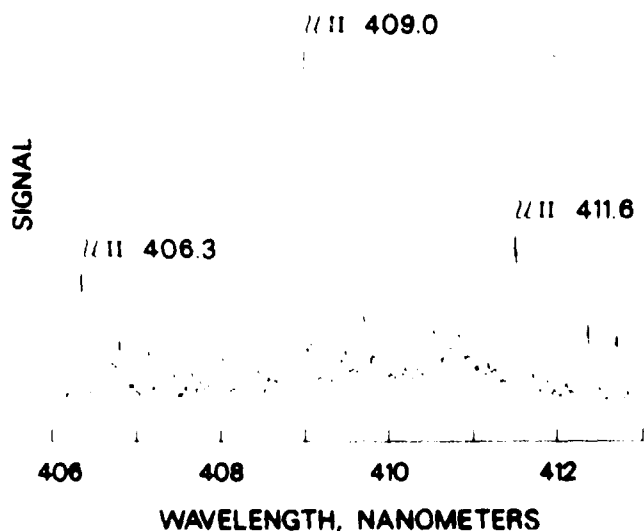


Fig. 3. Spectrum between 406 and 413 nm, obtained from a solution containing 10 g uranium/L in 4 M nitric acid. Prominent uranium lines are marked.

TABLE II. Precision of Uranium Determination as a Function of Number of Pulses Averaged*

Pulses Averaged	% RSD Net Signal	% RSD Ratio
50	7.7	5.6
100	6.3	2.9
400	3.1	2.6
800	1.9	1.9
1600	1.3	0.8

*Measurement made on solution containing 10 g uranium/L. Net signal refers to area under 409.0-nm peak above background. Ratio is net uranium counts divided by counts in a background region 0.2 nm wide near the uranium line.

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

Relatively high concentrations of zirconium, aluminum, stainless steel, or cadmium did not interfere with the determination of uranium, except for the previously mentioned spectral interference of zirconium with the 409.0-nm line. A uranium concentration of 1 g/L can be readily determined in the presence of 55 g Zr/L by use of the 411.6-nm line.

CONCLUSIONS AND FUTURE WORK

The use of LIBS to analyze uranium solutions at concentrations of interest for process stream analysis has been successfully demonstrated. Experiments on flowing streams are continuing to determine the effects of a simulated industrial environment on analytical performance, measure long-term laser stability and reliability, and devise calibration methods suitable for in-situ analysis.

In facilities that process enriched uranium, the laser spark could be used to monitor waste streams for criticality control. Input and intermediate process streams could be measured for process control and, in combination with flow rates, for in-process inventory estimation and materials accounting. Measurement of uranium isotopic compositions probably cannot be made because the high electrical field in the laser spark produces Stark broadening of the uranium emission lines. The technique should also be useful for determination of other elements besides uranium in process streams. We plan to investigate its applicability to the determination of plutonium, americium, thorium, zirconium, and others in the future.

REFERENCE

1. D. A. CREMERS, L. J. RADZIEMSKI, and T. R. LOPEE, "Spectrochemical Analysis of Liquids Using the Laser Spark," *Appl. Spectroscopy*, 38, 721 (1984).