WSRC-MS-2000-00401

ERDA Paper: Quantitative Measurement of Chromium, Manganese, Rhenium, and Magnesium in Liquid by Laser-Induced Breakdown Spectroscopy

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A document prepared for ACS FALL MEETING 2000 at Washington, DC, USA from 8/20/2000 - 8/24/2000.

DOE Contract No. **DE-AC09-96SR18500**

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Quantitative Measurement of Chromium, Manganese, Rhenium, and Magnesium in Liquid by Laser-induced Breakdown Spectroscopy

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Grant No. Task order GA0046

Final Report

Submitted to

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May 29, 2000

WSRC-MS-2000-00401

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I. INTRODUCTION

British Nuclear Fuels Limited (BNFL), Inc. provides low activity and high level waste processing service at the Department of Energy (DOE) Hanford site. High level wastes will be processed as a pretreatment step prior to vitrification. The wastes are run through an ion exchange column to remove Tc from Hanford supernate tank waste. The effluent from the removal column goes to one type of radioactive glass and the stripped technetium goes to another higher activity glass. An on-line Tc monitor is required to monitor the column effluent to assure that technetium is sent to the correct process streams. The required technique has to be able to measure Tc below the 100-μg/L level. It should achieve at least 10% confidence interval at 1000 μg/L.

Laser induced breakdown spectroscopy (LIBS) is a laser-based, non-intrusive, and sensitive optical diagnostic technique for measuring the concentration of various atomic and molecular species in test media.[1,2] It uses a high power laser beam to produce a laser-induced plasma at the test point. The plasma atomizes and electronically excites the various atomic species present in the test volume in a single step. The intensities of the atomic emission lines observed in the LIBS spectrum are used to infer the concentration of the atomic species. LIBS has been successfully demonstrated its real-time monitoring capability in various field tests.[3-8] It uses gated detection to discriminate the strong plasma continuum background emission. It can provide a real-time measurement of several of the most critical metals. The major thrust of this work is to evaluate the analytical figures of merit of LIBS system for Tc measurement. The results of this study will be used to determine the feasibility of using LIBS as a Tc monitor at the DOE Hanford site.

In this work, current DIAL's LIBS system was optimized for detection of Cr, Mg, Mn and Re in liquid. Cr, Mg, and Mn have similar properties to technetium. Mg is chosen because some Mg lines are in the same spectral region as the most sensitive Tc lines. So we can evaluate the system sensitivity near the Tc emission lines. Various optical geometries which produce the laser spark in and at the liquid sample were tested to determine the best geometry for liquid measurement. The optimized experimental condition were determined and used to determine the limit of detection (LOD) of these four test elements. The results of the study is summarized below.

II. EXPERIMENTAL

The detail experimental setup of the DIAL LIBS system is described in reference 3 and is shown in Figure 1. The output (1064 nm) of a Nd:YAG laser was frequency doubled to 532 nm using a doubling crystal. A dichroic mirror was used to separate the frequency doubled output from its fundamental frequency. An ultraviolet (UV) grade quartz lens was used to focus the laser beam. The same lens was used to collect light from the laser-induced spark. Two UV-grade quartz lenses of focal lengths 100 mm and 50 mm were used to couple the LIBS signal to an optical fiber bundle. The other end of the fiber bundle was coupled to an optical spectrograph, whose entrance slit was replaced by the rectangular exit end of the optical fiber. An intensified charge coupled device (ICCD) detector attached to the exit slit of the spectrograph was used to detect the light from the laser spark. The detector was operated in a gated mode to record LIBS signal. To maximize the signal, the gate delay time and gate width were adjusted for each

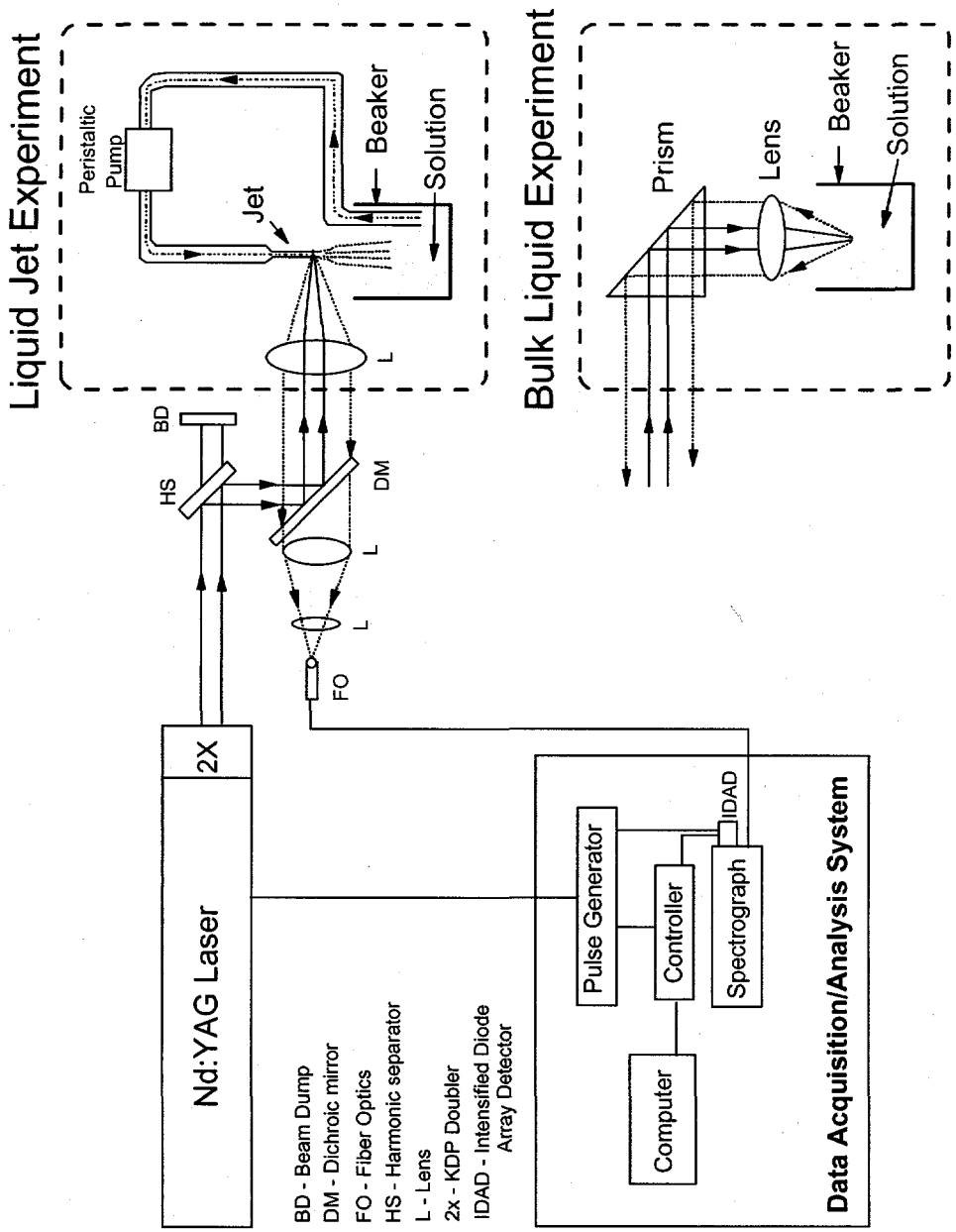

Figure 1. Experimental setups for liquid LIBS measurements.

element to achieve the best signal-to-noise ratio data. The spectrograph is equipped with two grating 2400 l/mm and 3600 l/mm, respectively. LIBS data were recorded with both grating to determine which grating give the best detection limit in a specified spectral region. Data acquisition and analysis were performed using a personal computer.

To determine the best experimental setup for solution measurement, the performance of two experimental setups (see Figure 1) were evaluated. The solution used in the study was prepared by diluting the ICP standard from AccuTrace in distilled water. In the first experiment, the sample solution was kept in a small beaker and laser beam was focused on the liquid surface to provide the measurement from the bulk sample. The scatter light by the splashed liquid droplet was properly blocked. The LIBS signal from the bulk liquid is collected in the backward direction. In the second experiment, a liquid jet system was assembled, to provide a stable solution jet. The liquid sample in a bottle was pumped by a peristaltic pump (Cole-Parmer Instrument Co.) through a tubing of 5-mm internal diameter (ID) to a custom-made nozzle. It produced a steady jet of 1.5-mm diameter. The laser beam was focused from the direction perpendicular to the liquid jet and LIBS signals were collected in backward direction.

III. RESULTS

The survey spectra of Cr, Mg, Mn, and Re were recorded to determine the most sensitive lines for this study. Table I lists the most sensitive lines of these elements found. The experimental parameters which can affect LIBS detection limit most are gate delay time, laser energy, and lens-to-surface distance. These parameters are carefully studied for both bulk liquid and liquid jet and the results are summarized below.

Element	Atomic lines
Mn	403.076 nm, 403.307 nm, 403.449 nm
Mg	279.553 nm*, 280.27 nm*, 285.2 nm
Cr	425.44nm, 427.48 nm, 428.972 nm
Re	346.046nm, 346.473 nm

* Ion lines

Gate delay time

To optimize LIBS signal, LIBS data were recorded at different laser energies and detection windows. Since the continuum background and atomic emission decay with different rates, it is possible to obtain an optimum detection window for each element. Figure 2 shows the variation of atomic line signal and background signal with time. The continuum background are dominated in the first several microseconds and decay much faster than the analyte signal at later time. By adjusting the gate delay time, LIBS data with best signal-to-background ratio can be recorded. Figure 3 shows LIBS spectra of Mg recorded at different delay times in bulk liquid and liquid jet. It is clear that a shorter delay time is required for the bulk liquid measurement than the liquid jet measurement for reasonable S/N ratio.

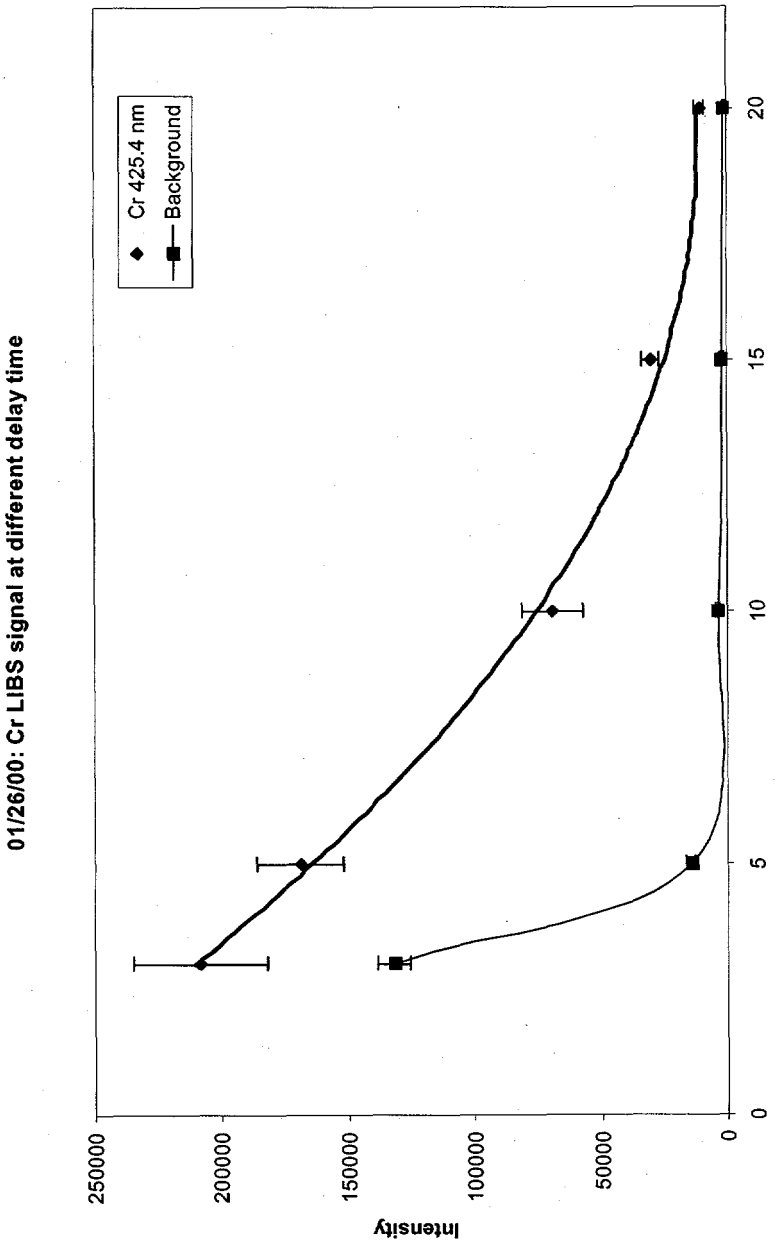

Figure 2. The variation of the atomic line signal and background signal with time.

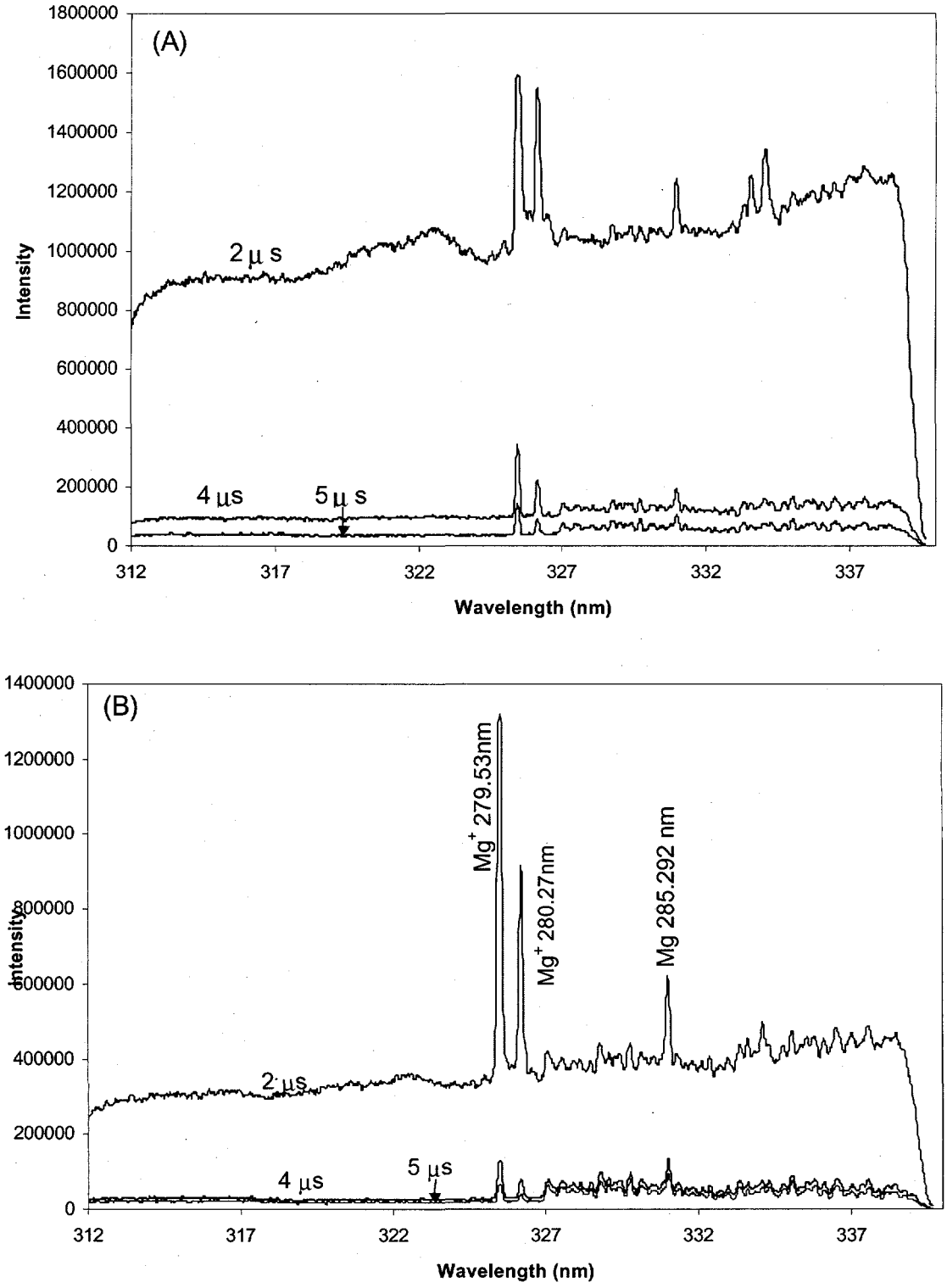

Figure 3. LIBS spectra of Mg recorded at different delay times in (A) bulk liquid and (B) liquid jet.

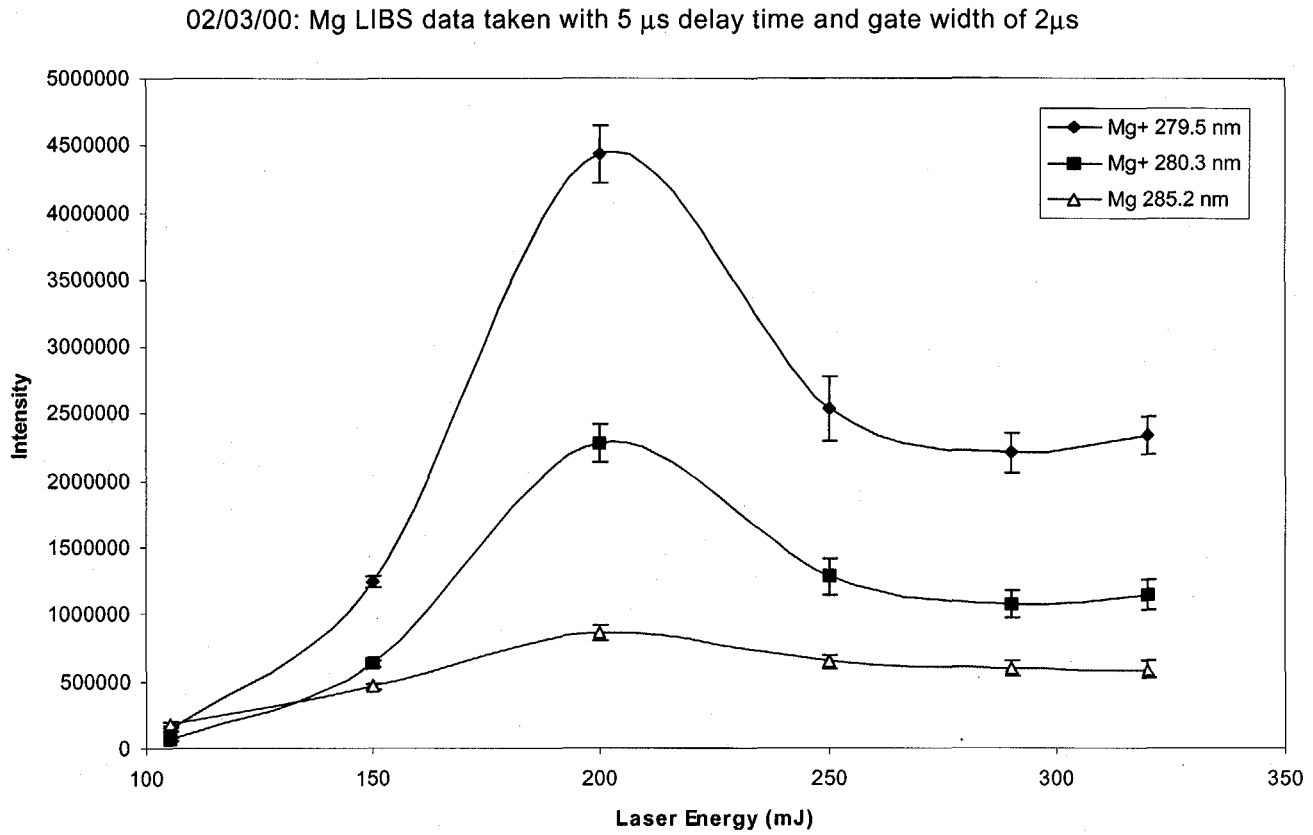

Figure 4. LIBS signal of Mg lines recorded at different laser energies.

Laser energy

LIBS spectra were recorded at different laser energies. Figure 4 shows LIBS signal of Mg lines recorded at different laser energies. The LIBS signal is increased with laser energy till the plasma density become too high which causes more laser energy to be absorbed by the plasma. Therefore less laser energy reaches the sample surface. Thus the intensity of continuum emission is increased and the signal intensity is decreased at high laser energy. The optimized laser energy for jet and bulk liquid measurement is between 150-250 mJ.

Lens-to-surface distance (LTSD)

LTSD is a critical parameter for the LIBS measurement of solid and liquid sample. A change of the LTSD of a few millimeters can affect the absolute analyte intensity. We found by defocusing the laser beam on the bulk liquid surface, the signal become more reproducible. However, the splash of the liquid due to laser shockwave will disturb the liquid surface and cause the poor precision. The LTSD is more critical in the liquid jet measurement due to its smaller surface. Figure 5 shows LIBS signal at different LTSD with a 20-cm focal length lens. When the LTSD away from the focal length just 1-mm, the LIBS signal dropped ~ 25 %. To improve LIBS's precision with a liquid jet system, a longer focal length lens is preferred.

Detection limit

In both experiments, LIBS signals were optimized for different atomic and ionic lines by adjusting gate delay time and gate width of the detector and also laser energy. LIBS signal of the various elements were recorded at different sample concentrations to obtain the calibration curves at optimized experimental condition. Figure 6 shows LIBS calibrations for Mn obtained from liquid jet measurement with delay time of 5 μs and gate of 10 μs at the laser energy of 200 mJ. The detection limit for Cr, Mg, Mn and Re were calculated based on the calibration data using

$C_L = 3ó / S$

where ó is standard deviation of the background signal and S is the slope of the calibration curve.

The LOD for Mn, Mg, Cr and Re in jet measurement were found to be better or comparable than that of the bulk liquid measurement. Table 2 list the LODs obtained from a liquid jet. The jet system is also preferable than bulk measurement because of the flexibility in changing the solution and easier to obtain optimized LIBS signal without the complication of liquid splashing and maintaining the surface to lens distance.

Table 2. Limit of Detection obtained from a Liquid Jet system

Element	Wavelength (nm)	LOD (μg/L)
Cr	425.4	400
Mg	279.55	100
Mn	403.076	700
Re	346.046	10000

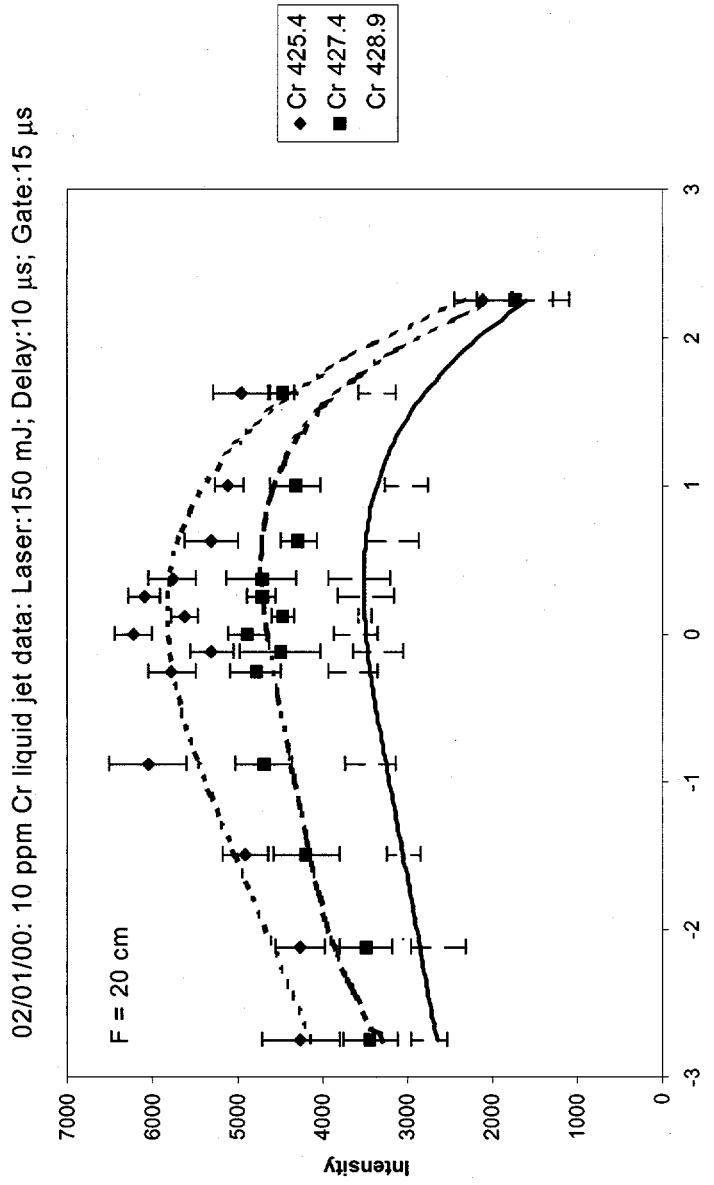

Figure 5. LIBS signal at different LTSD with a 30-cm focal length lens.

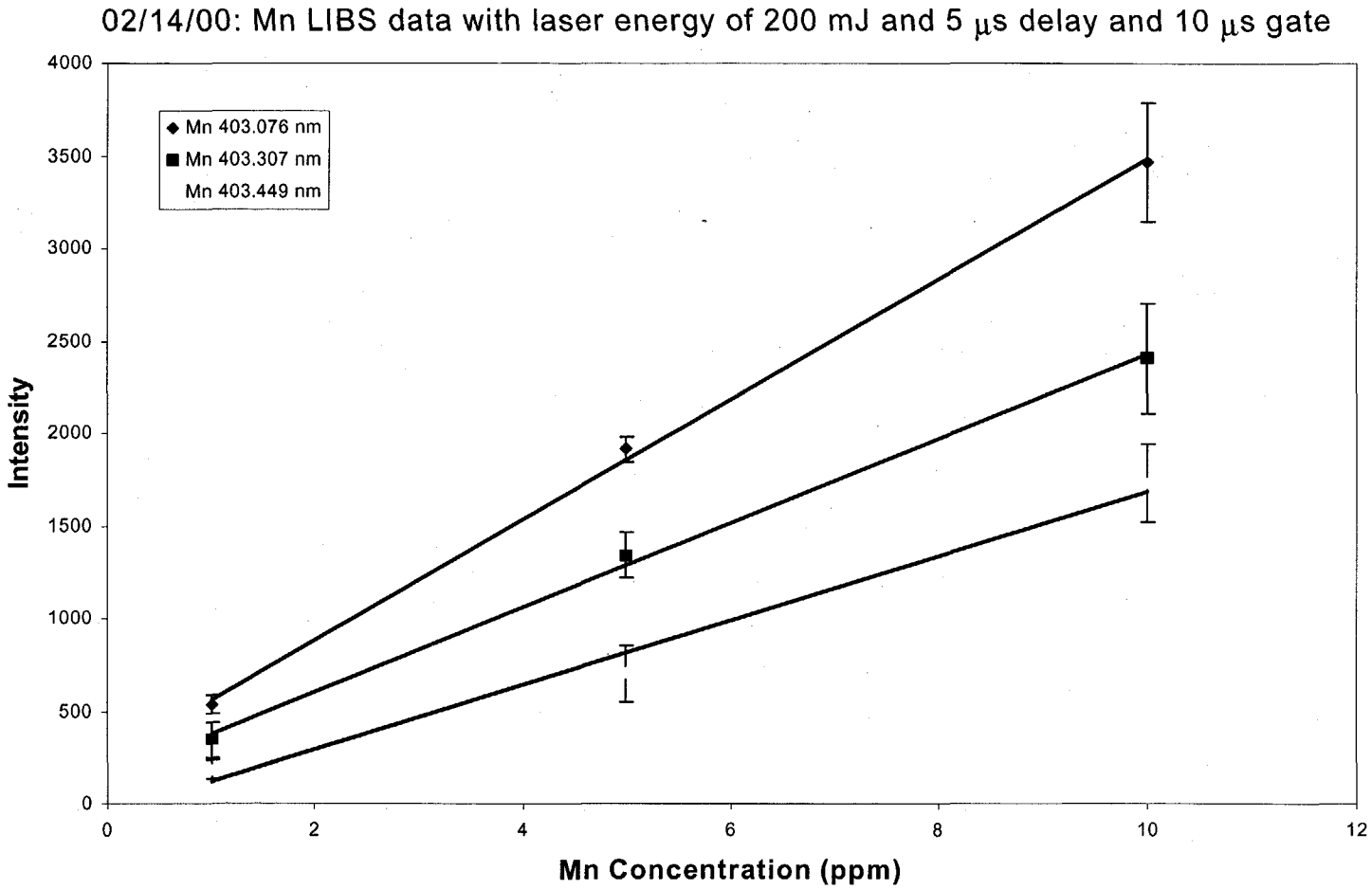

Figure 6. LIBS calibrations for Mn obtained from liquid jet measurement with delay time of 5 μs and gate of 10 μs at the laser energy of 200 mJ.

IV. CONCLUSIONS

A technique is needed to measure Tc during the waste process at DOE Hanford site. LIBS has the potential to be an on-line monitor to monitor Tc in the effluent from the Tc removal column to track the technetium removal process. In this work, we evaluate the analytical figure of merit of LIBS system for the element that has similar properties to Tc. Two experimental setups, bulk liquid and liquid jet, were tested to find the best sampling method for liquid application. We found that liquid jet method is easier to optimize and perform calibration than the bulk liquid method. It is perfect for on line measurement since the fresh sample liquid can continuously supplied. It also will not have the interference from bubbles formed by the preceding spark as in bulk liquid method. The experimental parameters which can affect LIBS' LOD were studied. The calibration data of the test elements were taken at the best experimental parameter for that element. We found that the LOD for all the test elements are better or comparable than that of the bulk liquid measurement.

The emission lines of technetium had reported by Meggars.[9] The most sensitive lines of Tc were found to be 254.324, 261. 0, and 264.702 nm. Current DIAL detection system has reasonable sensitivity in these spectral regions. According to Savannah River Technology Center, the LOD of Tc should be one-order better than LOD of Re. Therefore the estimated LOD for Tc in water is ~1 mg/L. This LOD is still not low enough for Tc monitor. More experiments for improving the sensitivity of the system are needed. A double excitation method that uses two consecutive laser pulses to excite the sample has been shown one to two order signal enhancement in solid and liquid measurement. It might be able to improve LIBS' LOD to achieve the requirement for Tc monitor.

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