

Evaluation of Laser-induced Breakdown Spectroscopy As Technetium Monitor

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ABSTRACT

The analytical figure of merit of a laser-induced breakdown (LIBS) system was evaluated for technetium measurements in liquid. LIBS data of elements that have similar properties to Tc such as Cr, Mn, and Re were studied. Various optical geometries which produce the laser spark in and at the liquid sample were tested. The calibration curve for Mn, Cr, and Re were obtained at the optimized experimental conditions with bulk liquid and liquid jet. We found that measurements using a liquid jet provide better detection limits than the bulk liquid measurements. The detection limits of Mg, Cr, Mn, and Re in a liquid jet measurement are found to be 0.1, 0.4, 0.7, and 10 ppm, respectively.

1. INTRODUCTION

Technetium is a product of the nuclear power cycle. The most stable Tc isotope is ^{99}Tc . It has a half-life of 2.1×10^5 years and decays via beta-emission. Due to the long half-life and the relatively high yield from uranium decay, DOE desires to separate technetium from non-radioactive and short life components of the tank waste. They plan to isolate it with other long life radionuclides in a geologically stable waste form for long term safe storage. An on-line monitor for technetium is needed for this waste processing. On-line monitoring during the waste processing will ensure Tc is properly removed from the processed effluent. The on-line Tc monitor has to be able to measure Tc below the 100- $\mu\text{g/L}$ level. The technique should achieve at least a 10% confidence interval at 1000 $\mu\text{g/L}$.

Laser-induced breakdown spectroscopy (LIBS) is an optical diagnostic technique which can provide on-line process analysis of the concentration of various atomic and molecular species in test media.¹⁻⁴ 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. Time-gated detection is generally used in LIBS to discriminate the strong plasma continuum background emission. LIBS has successfully demonstrated its real-time, multi-metal monitoring capability in various field tests.⁵⁻⁸ It provides a real-time measurements of many critical metals. Recently, some works were reported on LIBS applications to measure the elements present in the liquid samples.⁹⁻¹⁴

In this work, we evaluate the analytical figure of merit of LIBS system for the Tc measurement by studying LIBS data of elements that have the properties similar to Tc. Mn, Cr, and Re all have five d-type valence electrons as does Tc, and they have an ionization potential close to Tc. Therefore, they were chosen as the test elements in this study. The emission lines of technetium from arc and spark emission spectra were reported by Meggars.⁹ The most sensitive lines of Tc were found to be 254.324, 261.0 and 264.702 nm in inductively coupled plasma optical emission spectroscopy (ICPOES) measurements.¹⁵ Since Mg has the emission lines close to the most sensitive Tc lines, it was also selected as a test element to use the Mg measurement to evaluate the system sensitivity near the spectral region of the Tc emission lines.

LIBS does not have good sensitivity in liquid measurements due to its relatively shorter plasma lifetime.¹ Our approach first optimized our LIBS system for liquid measurements of the test elements; and then tested various optical geometries to produce a spark in and at the liquid sample. Finally, we used the best experimental setup found to determine the limit of detection of those test elements. The results of the various studies are discussed.

2. EXPERIMENTAL

The experimental arrangement of the LIBS system is described in Reference 5 and is shown in Figure 1. A frequency-doubled Nd:YAG laser (Continuum Surelite III) was used in all the measurements. The laser has a repetition rate of 10 Hz and pulse width of 8 ns. An ultraviolet (UV) grade quartz lens of 300 mm focal length was used to focus the laser beam to a spot size of approximately 0.03 mm. The same lens was used to collect light from the laser-induced spark. Two UV-grade quartz lenses of focal length 100 mm and 50 mm were used to couple the LIBS signal to an optical fiber bundle. The fiber bundle is formed by 80 single fibers of 0.01mm core diameter. The rectangular exit end of the optical fiber was coupled to an optical spectrograph (Model HR460, Instruments SA Inc, Edison, NJ) and used as an entrance slit. The spectrograph

was equipped with 1800 and 3600 l/mm diffraction gratings of dimensions 75 mm × 75 mm. A 1024 × 256-element intensified charge coupled device (ICCD) (Princeton Instruments Corp., Princeton, NJ) with a pixel width of 0.022 mm was attached to the exit of the spectrograph and used to detect the light from the laser spark. The detector was operated in gated mode using a high voltage pulse generator (PG-10, Princeton Instruments Corp., Princeton, NJ) and was synchronized to the laser output. Data acquisition and analysis were performed using a personal computer. To maximize the signal, the gate delay time and gate width were adjusted for each element to achieve the best signal-to-noise ratio data. LIBS data were recorded with both 1800 l/mm and 3600 l/mm gratings to determine the grating that gave the best detection limit for the test elements.

To determine the best experimental setup for solution measurement, the performance of two experimental setups (see Figure 1) were evaluated. The solutions used in the study were prepared by diluting the ICP standards from AccuTrace in distilled water. In the first experiment, the sample solution was kept in a small beaker, and the 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 was 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 inner diameter to a home-made nozzle. The flow rate of the liquid was 65 ml/min. 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.

3. RESULTS

The most sensitive lines for Cr, Mg, Mn, and Re were determined from the survey spectra recorded at various spectral regions and experimental conditions and are listed in Table 1. The selected lines were used to study the effects of the experimental parameters and to determine the limit of detection (LOD) of the test elements.

Table 1. Most sensitive atomic lines in the liquid measurements.

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

3.1 Effects of Experimental Parameters

The experimental parameters which can affect detection limits most are gate delay time, laser energy, and lens-to-surface distance. These parameters were carefully studied for measurements in both bulk liquid and liquid jet, and the results were summarized below.

3.1.1 Gate delay time

The laser spark lifetime was found to be about two times shorter in liquid than in air.¹ Water has high ionization potential (12.6 eV) and relatively high electronegativity (~ 0.9 eV).¹⁶ Hence, it contributes less charged particles in laser-induced plasma. This results in much weaker laser-induced plasmas in water than in air. Since the continuum background and atomic emission decay at different rates, it is possible to obtain an optimum LIBS signal with a properly selected detection window. Figure 2 shows the variation of atomic line signal and background signal with time. It is clearly shown that the continuum background is dominated in the first several microseconds and decays much faster than the analyte signal at a later time. The data shown were recorded from a liquid jet. The bulk liquid data also shows a similar trend. By adjusting the gate delay time, LIBS data with the best signal-to-background ratio can be recorded. Figure 3 shows the variation of signal to background ratio 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 a reasonable S/N ratio. In most of the work, a gate pulse delay of 2 - 10 μsec and width of 10 - 15 μsec was used to maximize the signal.

3.1.2 Laser energy

In LIBS, a high pulse energy laser beam was used to form a plasma to prepare and excite the sample. The laser energy can affect the property of the induced plasma and the analytical figure of merit of the LIBS measurement. The LIBS signal was proportional to the laser energy while the laser plasma was in the optical thin region. The LIBS spectra of all the test elements were recorded at different laser energies. Figure 4 shows the LIBS signal of Mg lines recorded from a liquid jet at different laser energies. The LIBS signal was increased with laser energy till the plasma density became too high, which caused more laser energy to be absorbed by the plasma. Therefore, less laser energy reached the sample surface. Thus, the intensity of the continuum emission increased, and the signal intensity decreased at high laser energy. The optimized laser pulse energy for jet and bulk liquid measurements found in this work was between 150 - 250 mJ.

3.1.3 Lens-to-surface distance (LTSD)

The laser-induced plasma has a very small plume size. A change of the LTSD of a few millimeters can affect the absolute analyte intensity. Therefore, keeping the LTSD a constant during the measurement is very important for system accuracy and precision. 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 the laser shockwave disturbed the liquid surface and caused poor data precision. The LTSD is more critical in the liquid jet measurement due to its smaller surface. Figure 5 shows the LIBS signal at different LTSD with a 20-cm and a 30-cm focal length lens. A shorter focal length lens can produce a small beam waist, and, therefore, stronger breakdown. But it also has a smaller depth of focus. Therefore, it is more sensitive to the change of LTSD. When the LTSD was moved away from the focal length just 1mm with a 20-cm focal length lens, the LIBS signal dropped $\sim 25\%$. To improve LIBS's precision with a liquid jet system, a longer focal length lens is preferred.

3.2 Comparison of the bulk liquid and liquid jet measurements

Since LTSD can affect LIBS signal, it is very important to maintain LTSD during the

calibration and measurement. In the bulk measurement, to maintain LTSD means to keep the same water levels in the sample container in all the measurements. It is very difficult to achieve LTSD within 1-mm accuracy. In the liquid jet measurement, calibration is done by changing the solution bottles (source). The LTSD can be maintained easily as long as the jet is stable. Therefore, it is easier to perform calibration and measurement in the jet measurement than in the bulk measurement. Furthermore, if the sample in the jet system is continuously flowing, it won't suffer from the interference from bubbles formed by the previous spark as in the case of the bulk liquid measurement. Therefore, the liquid jet measurement also provides better precision. The signal-to-background ratio of the Mg line at 279.55 nm at the delay time between 2 μ s to 5 μ s for liquid jet and bulk liquid has a percent relative standard deviation (% RSD) of 4.9% and 7.8 %, respectively. We have compared LODs of Mn, Mg, Cr and Re from bulk liquid and liquid jet measurement and found that the LODs from the jet measurement were better or comparable with that of the bulk liquid measurement.

3.3 Detection limit

In both experiments, LIBS signals were optimized for different atomic and ionic lines by adjusting the gate delay time and gate width of the detector and also the laser energy. The LIBS signals of the various elements were recorded at different sample concentrations to obtain the calibration curves at optimized experimental conditions. Figure 6 shows LIBS calibrations for Re obtained from liquid jet measurements with delay time of 8 μ s and gate of 15 μ s at two different laser energies.

The detection limits for Cr, Mg, Mn and Re were calculated based on the calibration data using

$$C_L = 3\sigma / S$$

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

The LODs for Mn, Mg, Cr and Re in jet measurement were found to be better than or comparable to that of the bulk liquid measurement. Table 2 lists the LODs obtained from a liquid jet. The jet system is also preferable over the bulk measurement because of the flexibility in changing the solution and ease in obtaining optimized LIBS signals without the complication of liquid splashing and maintaining the surface-to-lens distance. To compare the sensitivity of our system with others, a comparison of the LODs obtained in this work with previous works was made. The LODs of Mg 279.55 nm can be found from the literature and is also determined in this work. Hence, it is used in this comparison. The results are shown in Table 3. It is clear that we have achieved much better LOD using the liquid jet than the previous works.

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

Element	Wavelength (nm)	LOD (μ g/ml)
Cr	425.4	0.4
Mg	279.55	0.1
Mn	403.076	0.7

Re	346.046	10
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Table 3. The limit of detection of Mg in water using the ionic line at 279.55 nm.

	LOD ($\mu\text{g/ml}$)	Sampling Method
Cremer et al. ¹⁷	100	Bulk Liquid
Archonatki and Crouch ¹⁸	1.9	Isolate Droplet
This Work	0.22	Bulk Liquid
	0.1	Liquid Jet

4. CONCLUSIONS

A technetium monitor for waste process facilities can provide in situ, real time measurement during waste processing to avoid the time and labor-intensive sampling process. LIBS has great potential in this application. We have explored the possibility of detecting Tc in liquid using Cr, Re and Mn as test elements. LIBS signals in bulk liquid decay faster than those from the liquid jet. Therefore, it is necessary to use a shorter delay time to obtain comparable signals. We found that the LODs for Mn and Cr in jet measurements are better than or comparable to those of the bulk liquid measurement. The jet system provided a more stable signal and samples were easier to switch than the bulk liquid method. It is easier to perform calibrations with the jet than with bulk sample.

Our current system has reasonable sensitivity in most sensitive Tc lines found in arc and spark emission spectra. According to SRTC, the LOD of Tc should be one order better than the LOD of Re in ICPOES measurements. Assuming the LOD in LIBS is proportional to that in ICPOES, the roughly estimated LIBS LOD for Tc in water is 1 mg/L. This LOD is still not low enough for the desired Tc monitor application. Since LIBS and ICP have different excitation conditions, the most sensitive Tc ion lines found in ICP measurements might not be the most sensitive lines for LIBS measurements. Reference 19 has shown that the neutral lines of Tc at 423, 426, and 429 nm (near the Cr and Mn lines in this work) are very sensitive with LIBS. We will need to collect the survey spectra of Tc to determine the most sensitive Tc lines for our application. We will continue improving the sensitivity of our current system for liquid application. The double excitation method, which uses a pair of laser pulses to excite the sample, has shown one to two orders of enhancement in solid and liquid measurements in the literature.^{20,21} We will evaluate this method for the improvement of LIBS' detection limits.

Acknowledges

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Figure Captions

Figure 1. Experimental setups for liquid LIBS measurements.

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

Figure 3. LIBS signal-to-background ratio at different delay times.

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

Figure 5. LIBS signal at different LTSD with a 30-cm focal length lens and a 20-cm focal length lens.

Figure 6. LIBS calibrations for Re obtained from liquid jet measurement with delay time of 8 μs and gate of 15 μs .

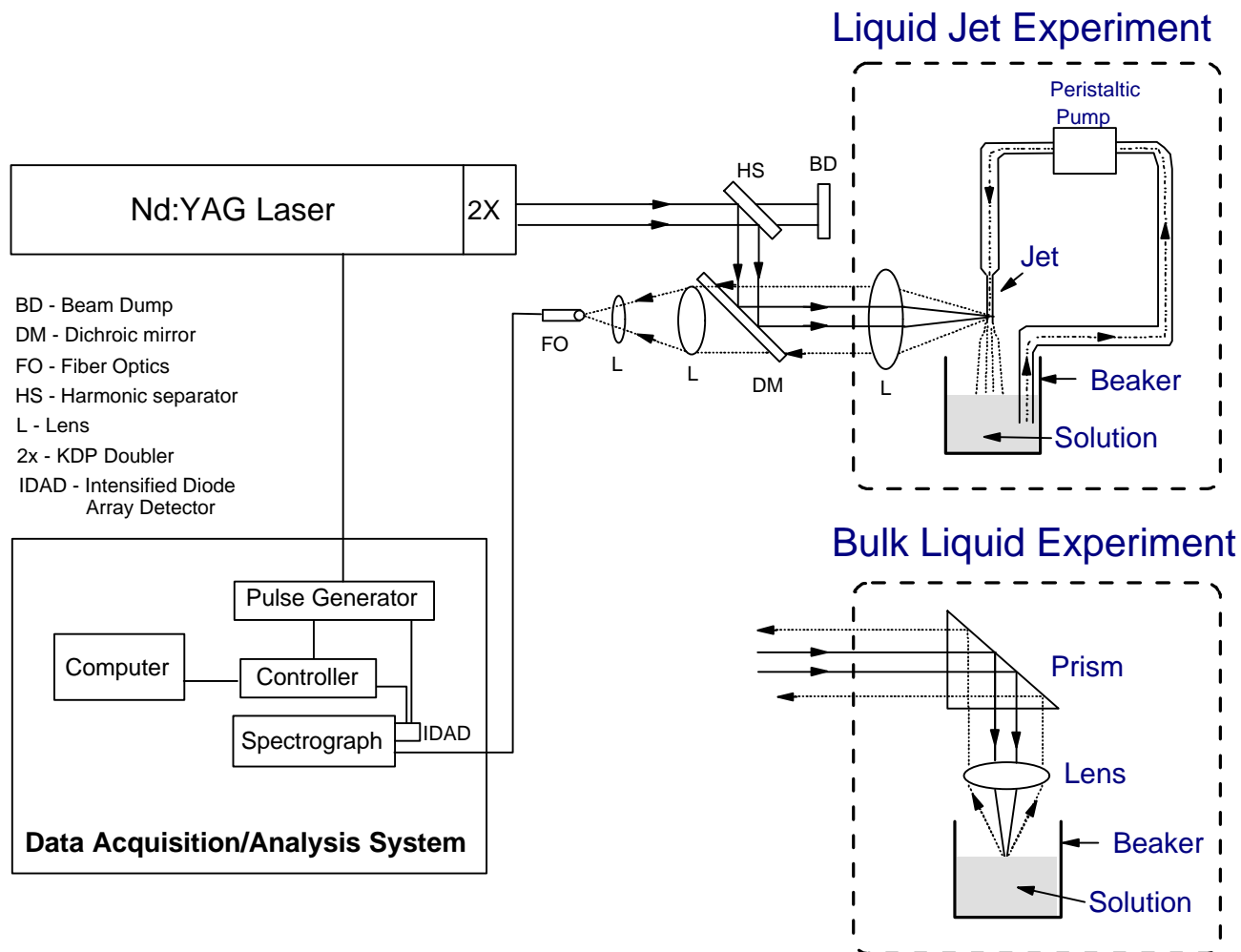


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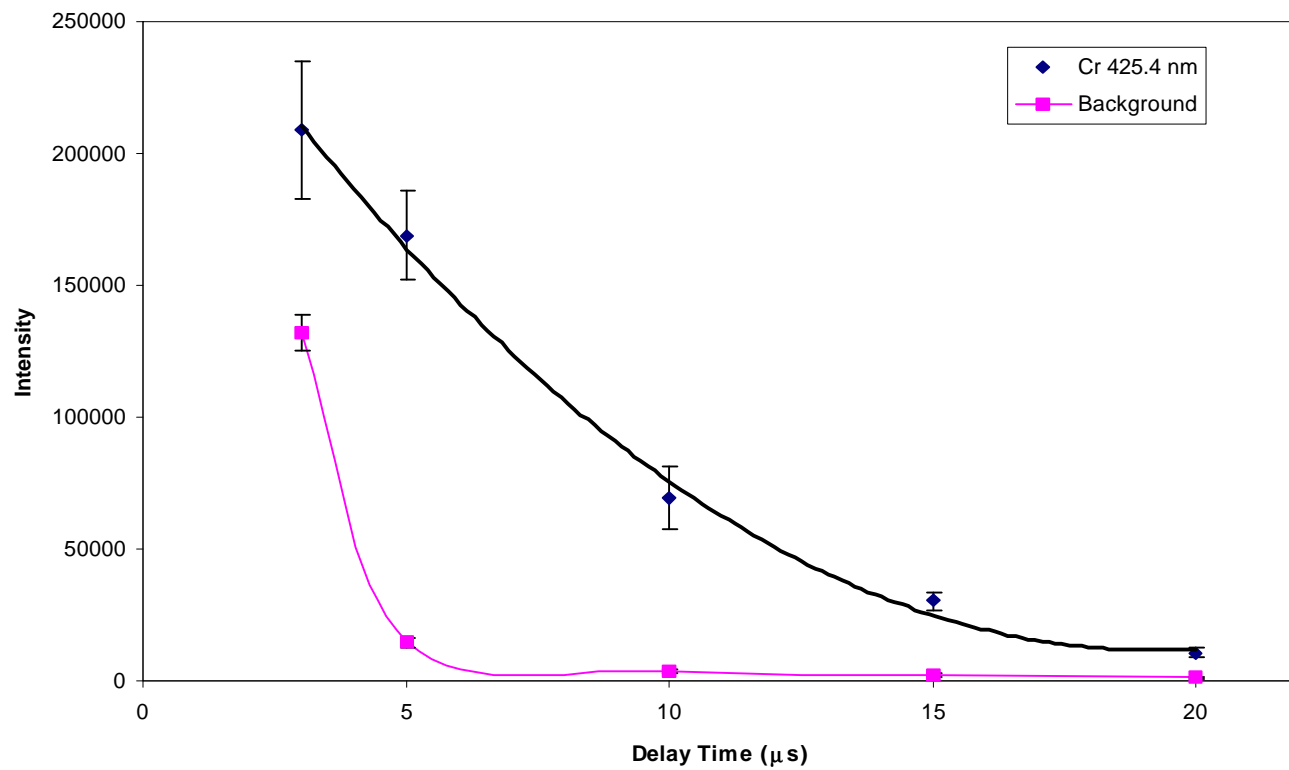


Figure 2. The variation of the atomic line signal and background signal with time.

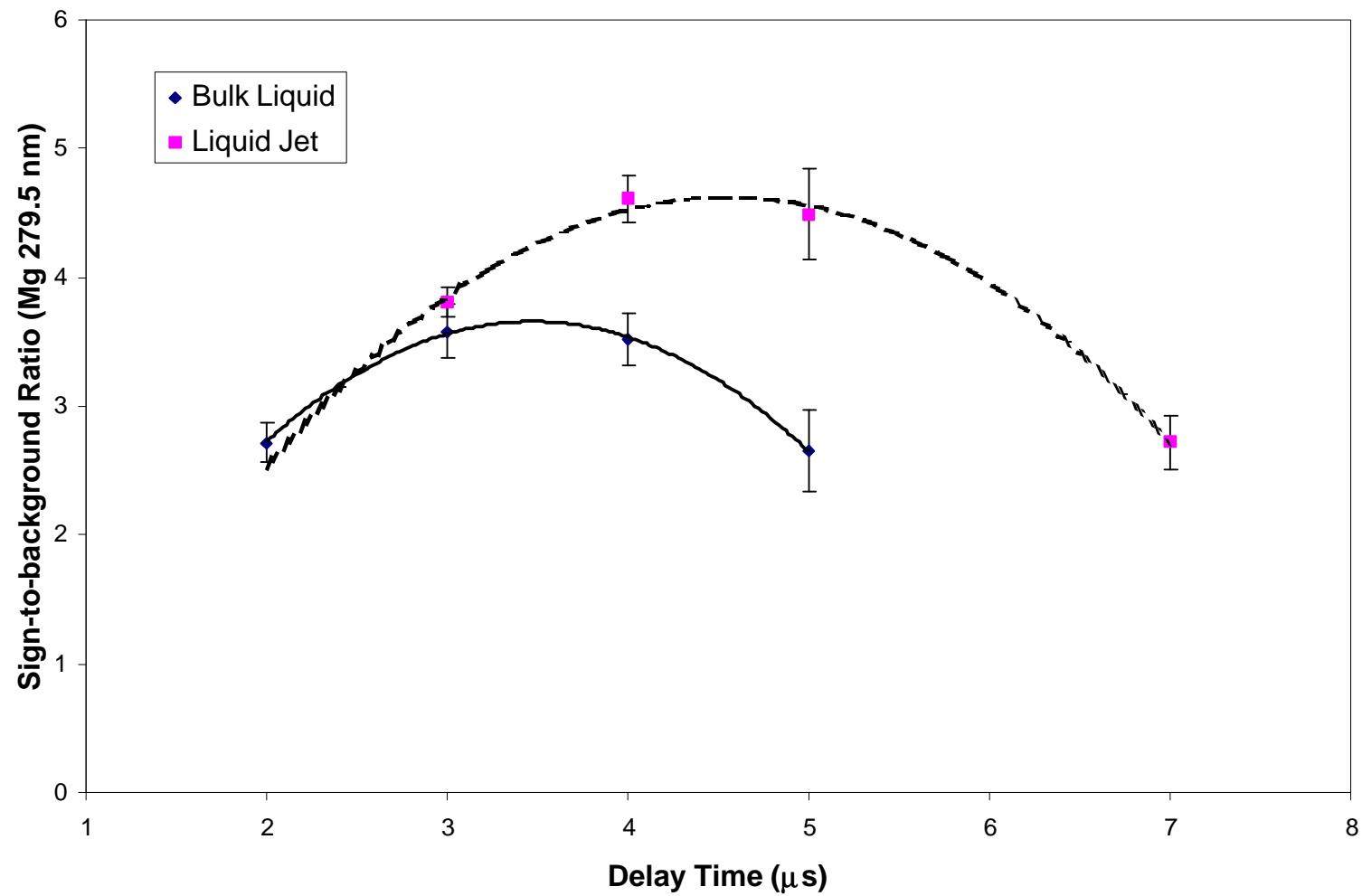


Figure 3. LIBS signal-to-background ratio at different delay times.

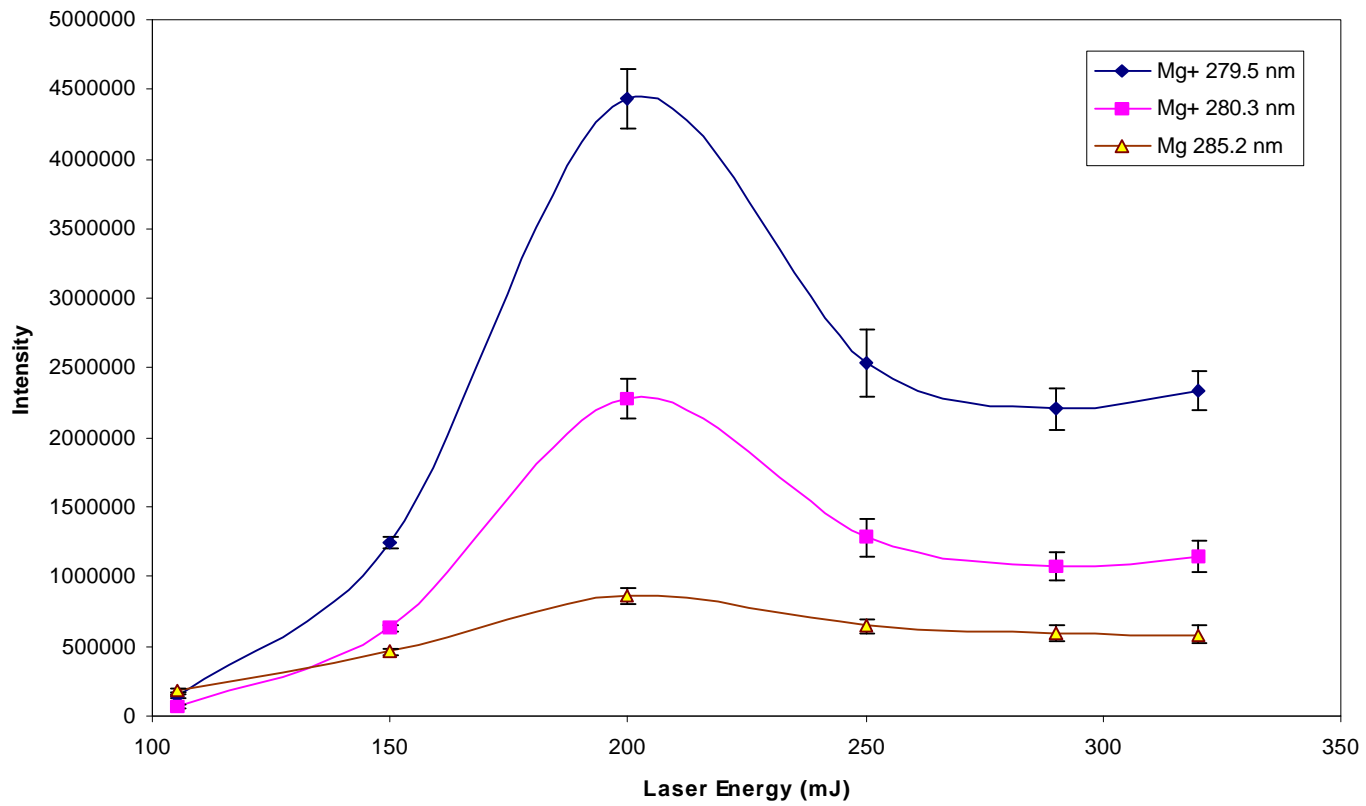


Figure 4. LIBS signal of Mg lines recorded from liquid jet at 5 μ s delay and 2 μ s gate and different laser energies.

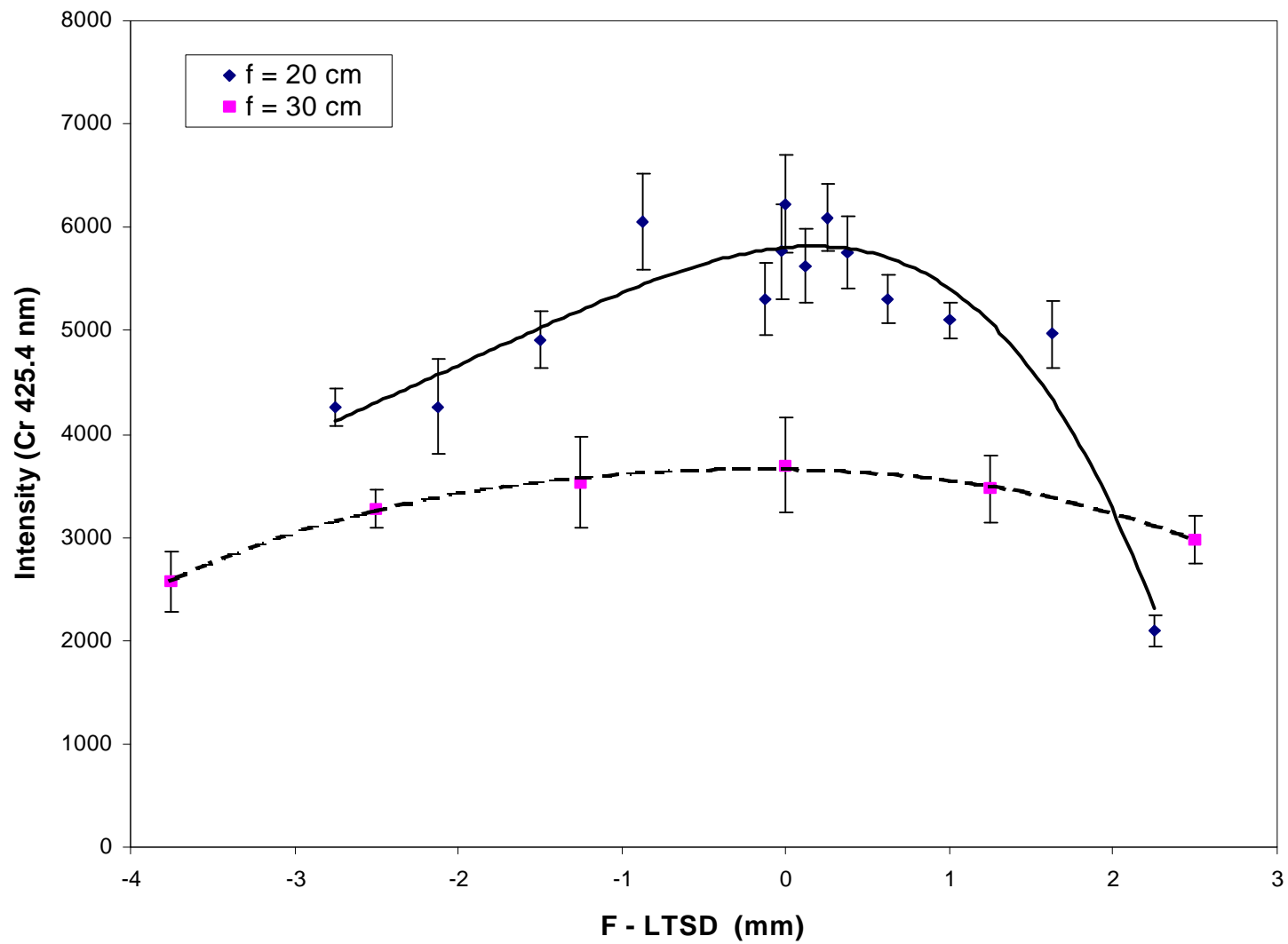


Figure 5. LIBS signal at different LTSD with a 30-cm focal length lens and a 20-cm focal length lens.

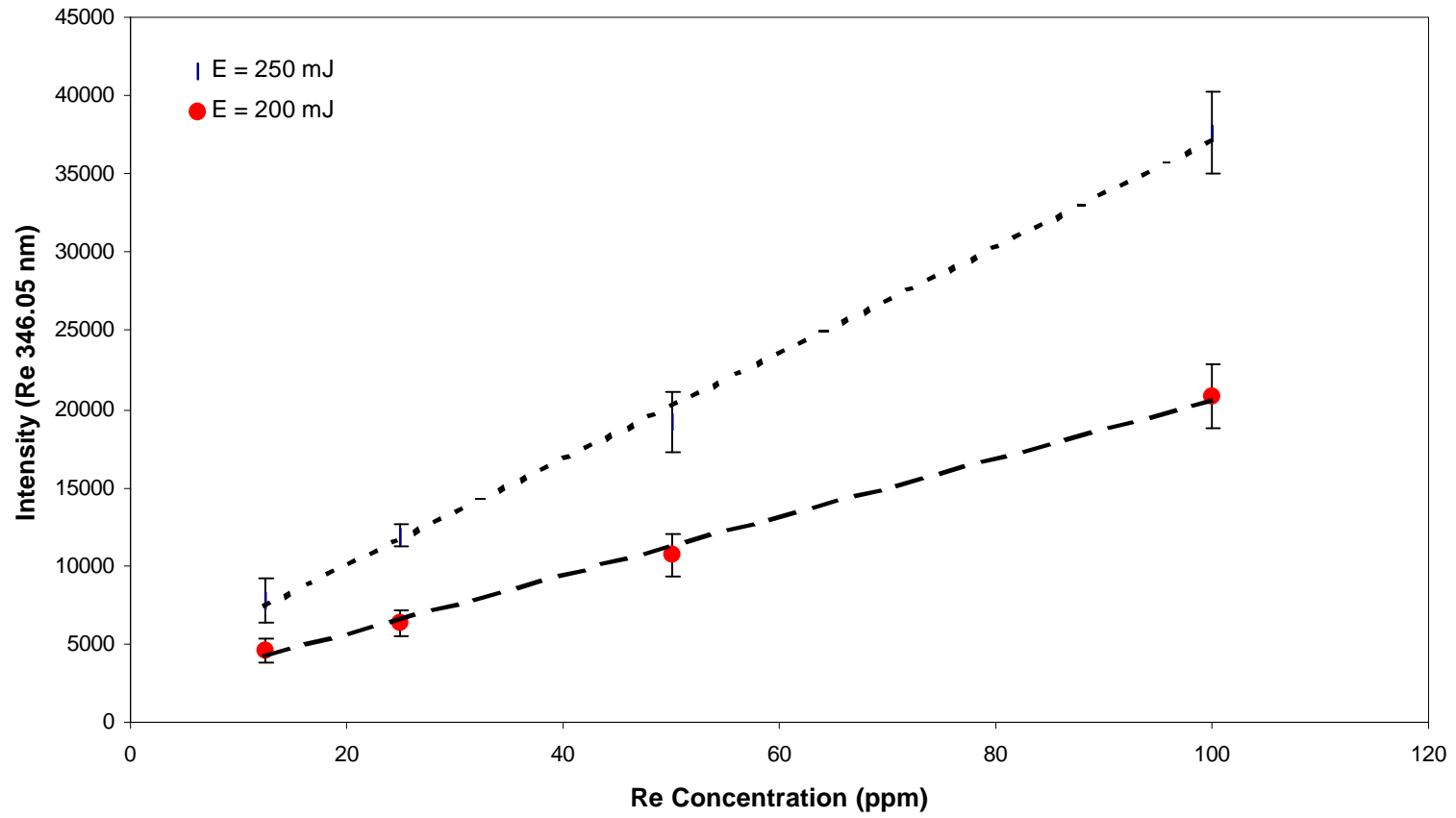


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