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LIBS system with compact fiber spectrometer, head mounted spectra display and hand held eye-safe erbium glass laser gun

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Abstract

LIBS (Laser Induced Breakdown Spectroscopy) systems are capable of real-time chemical analysis with little or no sample preparation. A Q-switched laser is configured such that laser induced plasma is produced on targeted material. Chemical element line spectra are created, collected and analyzed by a fiber spectrometer. Line spectra emission data is instantly viewed on a head mounted display. "Eye-safe" Class I erbium glass lasers provide for in-situ LIBS applications without the need for eye-protection goggles. This is due to the fact that Megawatt peak power Q-switched lasers operating in the narrow spectral window between 1.5um and 1.6um are approximately 8000 times more "eye-safe" than other laser devices operating in the UV, visible and near infrared.

In this work we construct and demonstrate a LIBS system that includes a hand held eye-safe laser gun. The laser gun is fitted with a micro-integrating sphere in-situ target interface and is designed to facilitate chemical analysis in remote locations. The laser power supply, battery pack, computer controller and spectrophotometer components are packaged into a utility belt. A head mounted display is employed for "hands free" viewing of the emitted line spectra. The system demonstrates that instant qualitative and semi-quantitative chemical analyses may be performed in remote locations utilizing lightweight commercially available system components ergonomically fitted to the operator.

Key Words: Laser induced breakdown spectroscopy, Elemental analysis, Fiber spectrophotometer, Atomic emission line spectra, Eye-safe laser, Laser gun, Erbium glass laser, Wearable LIBS system

Introduction

The attraction of real-time in-situ chemical analysis in remote locations without sample preparation bodes well for the potential of wearable LIBS systems. Nearly all of the components required for construction of such a system are commercially available. Laser pulse optical delivery and pickoff systems for close coupled in-situ analysis techniques are an exception as they are not readily available. This is especially true for Class I Q-switched lasers that produce plasmas with pulses of less than two Megawatts peak power. A major effort in this investigation was spent in the design, integration and testing of two brassboard plasma delivery/optical pickoff systems and in-situ eye-safe LIBS gun. A previous in-situ laser gun used for detection of malignant skin tissue utilized similar optical delivery/detector designs [1]. Two in-situ laser delivery systems were used to perform qualitative analysis on various standards as well as four different rock samples of local origin. At the completion of the lab work, a brassboard LIBS gun system was integrated into a multi-pocketed flak vest. The vest pockets were filled with the LIBS system components including battery pack, computer, fiber spectrometers and a head mounted computer display. The wearable electronics and in-situ LIBS gun were subsequently employed for field use demonstrations.

Instrumentation

Two LIBS gun brassboard delivery/optical pickoff systems were constructed and evaluated. The first system incorporates a modified Kigre MK-830 High Efficiency Side Pumped (HESP) diode pumped solid state laser, an optical triplet lens system, integrating sphere and fiber pick-off. This breadboard assembly is designated the “IS” breadboard and is shown in figure 1.

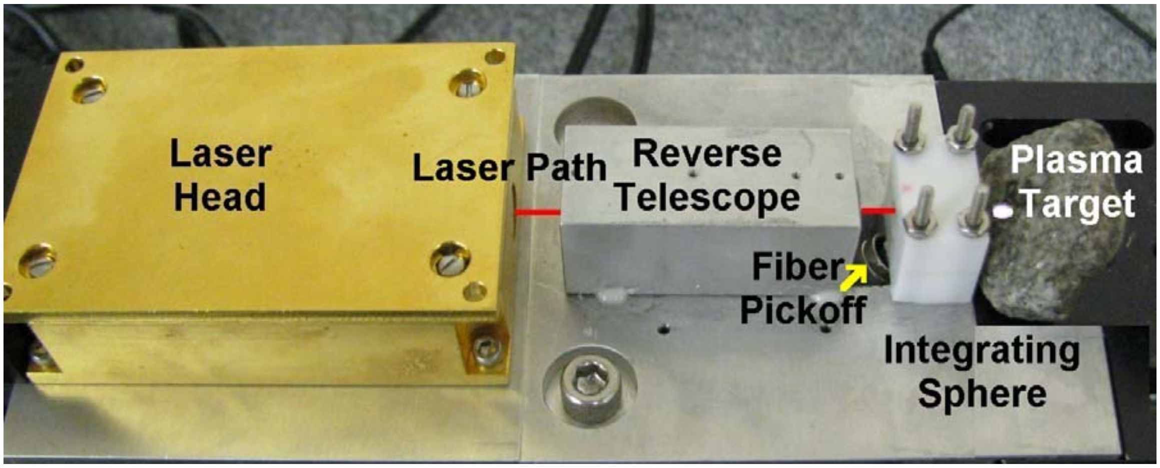
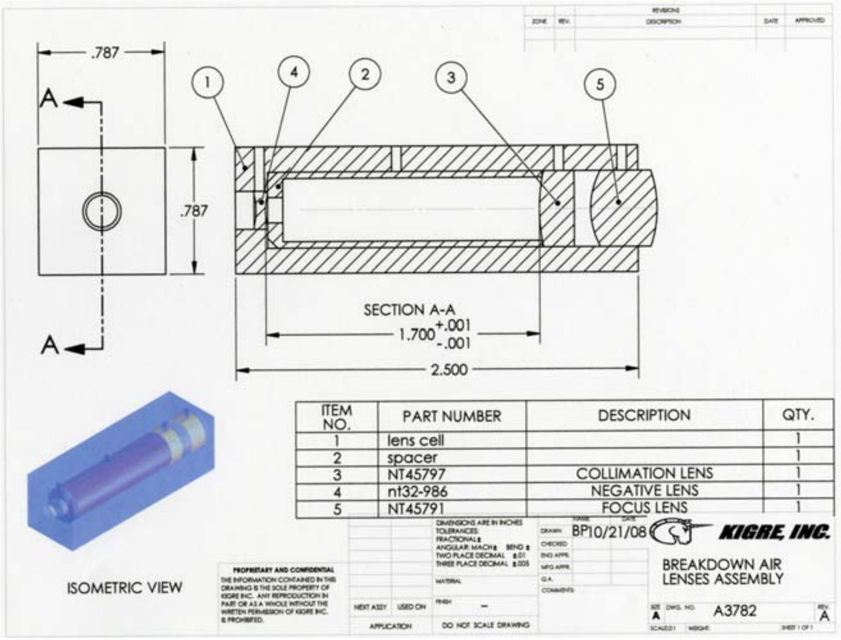


Fig. 1 - Eye-safe in-situ LIBS gun “IS” brassboard

The IS beam delivery system includes a MK-830 laser modified to produce 10mJ energy/pulse, 7ns pulse width for ~ 1.4 Megawatts peak power per pulse at 1535nm wavelength. A design schematic of the IS beam delivery and focusing optics (labeled “Reverse Telescope”) is shown in figure 2. The IS beam delivery system includes an 8x beam expander, collimator and 25mm focal length optics. A packaged version of this optical delivery system is commercially available from Elcan Optical Technologies [2]. The integrating sphere is manufactured from polytetrafluoroethylene (PTFE) Teflon® that exhibits high reflectivity (~ 99 %) from the UV through the visible spectrum. Two 5mm port holes were positioned at each end of the 12mm diameter sphere to allow transit of the focusing laser beam. The position of the integrating sphere is such that the focal point and plasma air breakdown become incident on any object placed against the integrating sphere exit port hole. The fiber spectrophotometer pickoff is mounted into the underside of the integrating sphere at an angle that points directly at the center of the exit portal. A 2mm diameter sapphire window is attached to the end of the fiber pickoff for protection and to facilitate cleaning. We considered placing a small objective lens on the end of the pickoff fiber to further enhance line spectral emission capture. However, this and many other system improvement ideas were not implemented as part of this investigation.



ITEM NO.	PART NUMBER	DESCRIPTION	QTY.
1	lens cell		1
2	spacer		1
3	NT45797	COLLIMATION LENS	1
4	nt32-986	NEGATIVE LENS	1
5	NT45791	FOCUS LENS	1

Fig. 2 - IS brassboard 8X 25mm focal length lens system

The second system, designated “45 degrees”, incorporates a modified Kigre MK-830 laser, a 3x optical doublet lens system, a 45° dichroic mirror, a 6mm focal length lens for plasma generation, a 12mm focal length lens for line spectra delivery into the fiber and a fiber pick-off. The 45° mirror exhibits high transmission for near infrared wavelengths and high reflectivity for UV and visible wavelengths. The 45° breadboard delivery system is shown in figure 3.

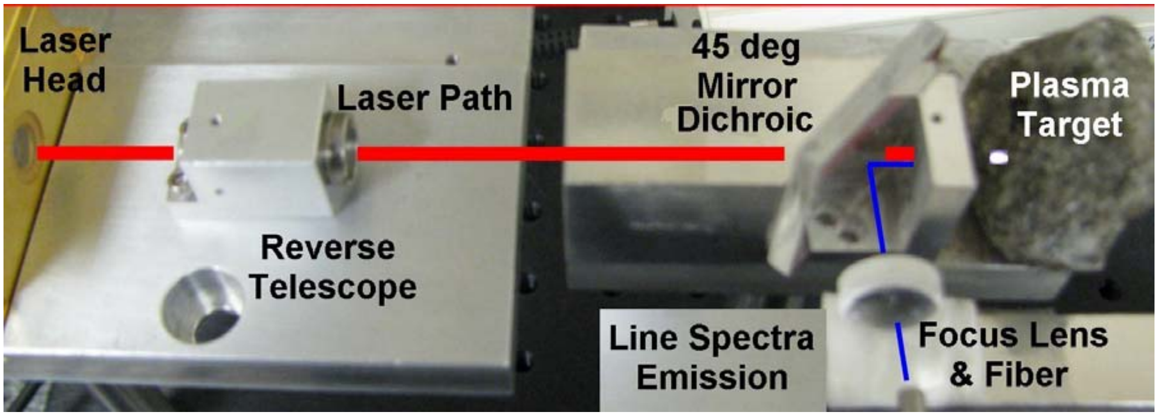


Fig. 3 - Eye-safe in-situ LIBS gun 45^o brassboard

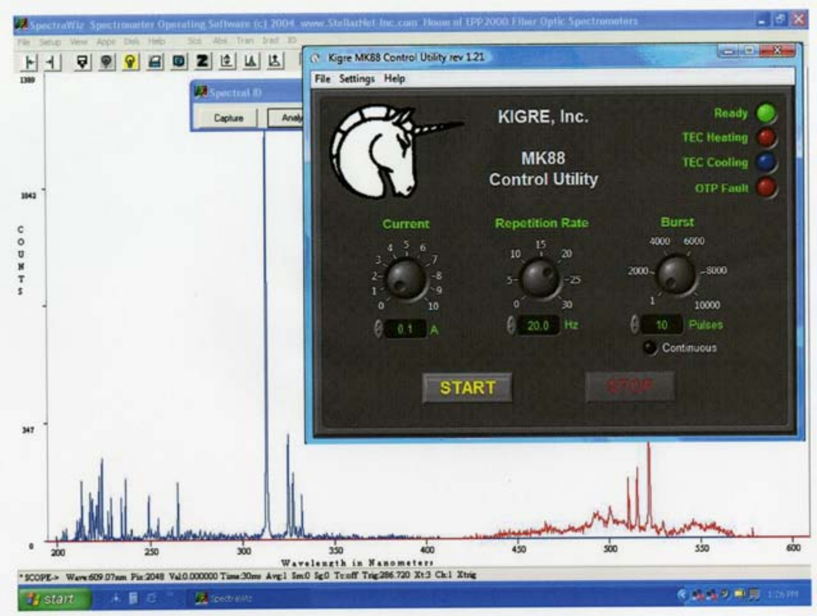
Our system employed a number of spectrometers including one Avantes AvaSpec-2048-USB2 (193 – 465nm), three Stellarnet EPP2000 units (200 - 800nm) and one Ocean Optics S2000 fiber spectrometer units as shown in figure 4 [3, 4, 5].

Fig. 4 – Spectrometers for breadboard wearable in-situ LIBS system testing

A small (~ 1 x 7 x 10") Acer Aspire One laptop computer served as both a laser and spectrometer controller utilizing Kigre laser and spectrometer USB interface software. A Polarmate Universal 16/19VDC 111W hour rechargeable lithium battery pack was enlisted as a portable source to power the laser, computer and spectrometers. The computer and battery pack are shown in figure 5.

Fig. 5 – Battery pack & laptop computer for wearable in-situ LIBS system

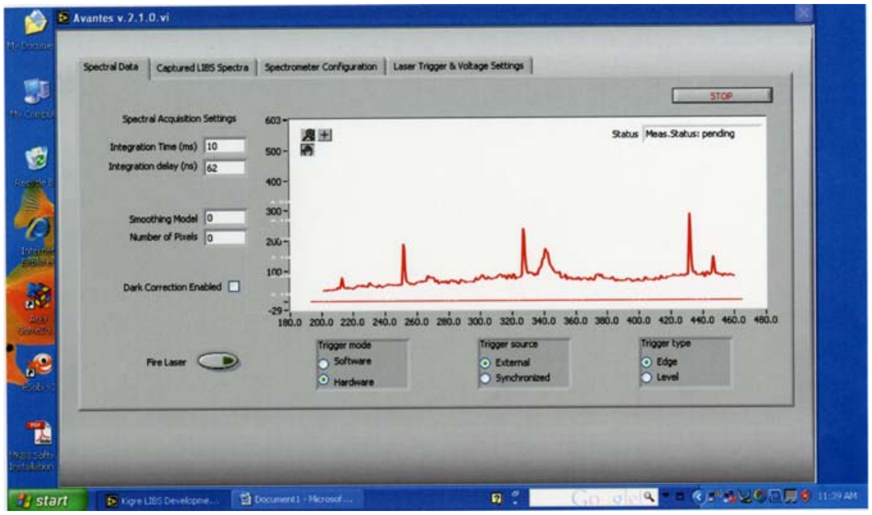
Stellarnet software was used in conjunction with Kigre laser driver software and the “IS” in-situ laser gun to produce the LIBS spectra presented in this paper. Three separate Stellarnet spectrophotometer units covering the spectrum from 200nm to 800nm were initially adapted. A screen shot display of the SpectraWiz® and Kigre laser driver software is shown in figure 6. Experiments were also performed with an Avantes spectrometer configured with customized software that combined Avantes AvaSoft® and Kigre laser driver software. The combined AvaSoft® spectra-Kigre laser software screen shot is shown in figure 7. A schematic of the breadboard components is shown in figure 8.



Current 0.1 A
Repetition Rate 20.0 Hz
Burst 10 Pulses

*SCOPE-> Wave:609.07nm Pix:2048 Val:0.000000 Time:30ms Avg:1 Sm:0 Sg:0 Tc:off Trig:286.720 Xt:3 Ch:1 Xtrig

Fig. 6 - Screen shot display of the SpectraWiz® and Kigre laser driver software



Spectral Acquisition Settings
Integration Time (ms) 10
Integration delay (ns) 62
Smoothing Model 0
Number of Pixels 0
Dark Correction Enabled ☐
Status Meas.Status: pending
Trigger mode ○ Software ● Hardware
Trigger source ● External ○ Synchronized
Trigger type ● Edge ○ Level

Fig. 7 - Screen shot display of combined AvaSoft® spectra-Kigre laser software

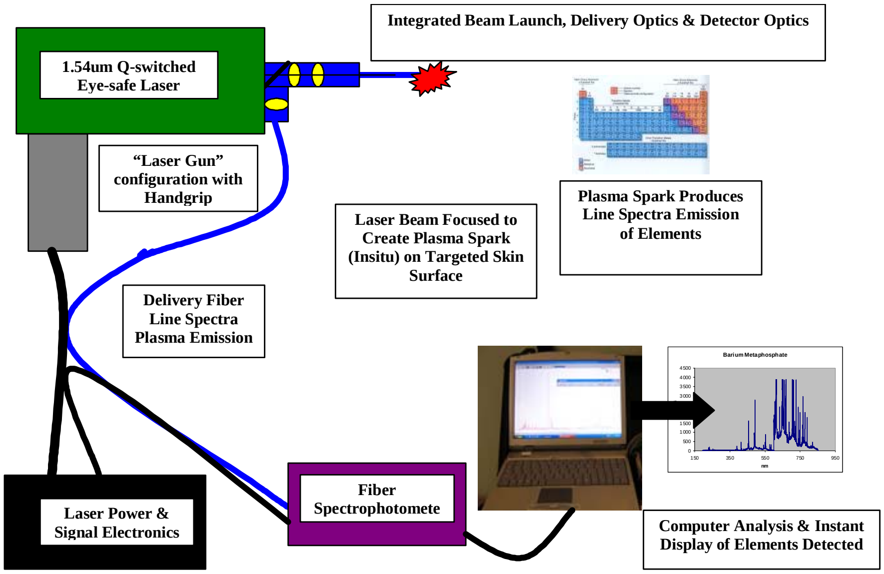


Fig. 8 – Breadboard schematic of hand held eye-safe in-situ LIBS system

The integrating sphere Kigre in-situ LIBS laser gun, a hand-held computer track mouse and an Intevac Universal I-PORT™ head mounted computer display were initially integrated as part of a lab breadboard test bed. The Kigre laser gun and USB hand-held finger mouse are shown in figure 9. The Intevac Universal I-PORT™ head mounted computer display eye-piece is shown in figure 10 [6].

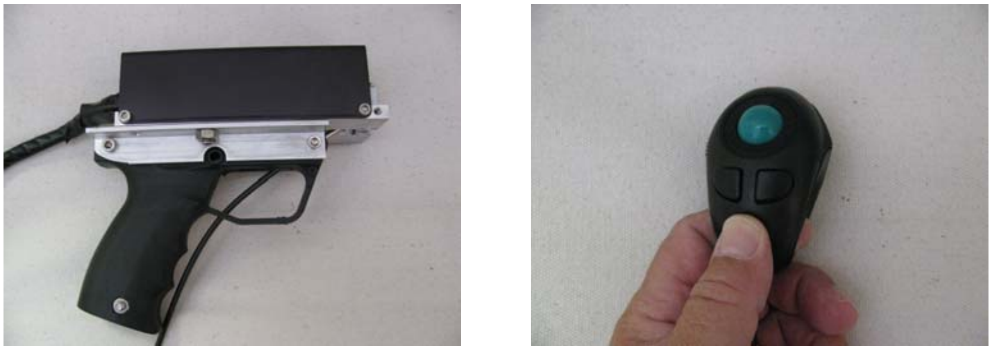


Fig. 9 – Kigre LIBS laser gun and USB hand-held finger track mouse

Fig.10 – Intevac Universal I-PORT™ head mounted computer display

Kigre manufactured OEM equipment includes the laser power supply, modified HESP eye-safe laser head and USB laser computer controller interface [7]. These components are shown in figure 11.

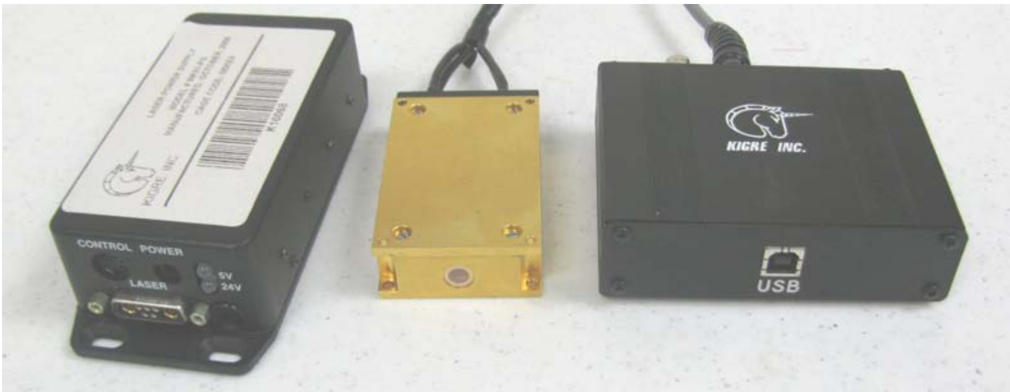


Fig. 11 - OEM laser power supply, HESP laser head and USB laser computer control interface

Wearable LIBS system components were initially assembled and tested together on a mannequin in the laboratory as shown in figure 12. The system components were then donned by a Kigre engineer for field operations as shown in figure 13.

Fig. 12 - Wearable LIBS system components assembled on mannequin

Fig. 13 - Wearable LIBS system components assembled on engineer

Experimentation

Stellarnet spectrometer units are configured with a standard two microsecond time gate. The delay in activation of the spectrometer helps to avoid the laser induced plasma's initial bremsstrahlung emission. Figure 14 shows the plasma emission timeline including blackbody continuum observed at the onset of the plasma. Some targeted materials benefit from longer spectrometer gate times which help circumvent excessive Matrix effects and allow better capture of the stronger less encumbered emission lines. Matrix effects are adverse host influences that often result in line masking and inconsistent line spectra intensity [8]. These affects may be attributed to material textures, chemical composition and other chemical host properties. In general, obtaining predictable and repeatable spectra becomes more difficult when lines of interest are partially or completely blocked due to matrix effects [9, 10].

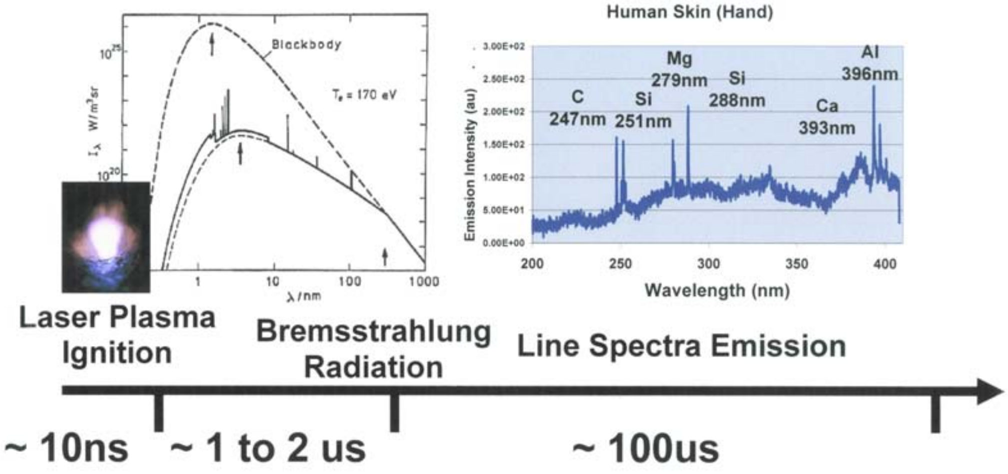


Fig. 14 - LIBS radiation emission timeline

In the absence of a significant gate time, spectrometers operating in air will invariably pick up noisy broad emission bands created immediately following the plasma ignition along with numerous broad nitrogen and oxygen lines. LIBS spectra shown in figures 15 and 16 demonstrate the difference in "air" spectra taken with and without a 2 microsecond delay time gate. The LIBS laser gun and integrating sphere pickoff system were used to collect the following spectra using a Stellarnet spectrometer unit with range from 400 to 600nm. Without the timed gate delay we observe additional background noise and increased nitrogen and oxygen line emission. When a 2 microsecond spectrometer gate delay is instituted, the background noise is reduced and the nitrogen and oxygen emission lines are greatly diminished or eliminated.

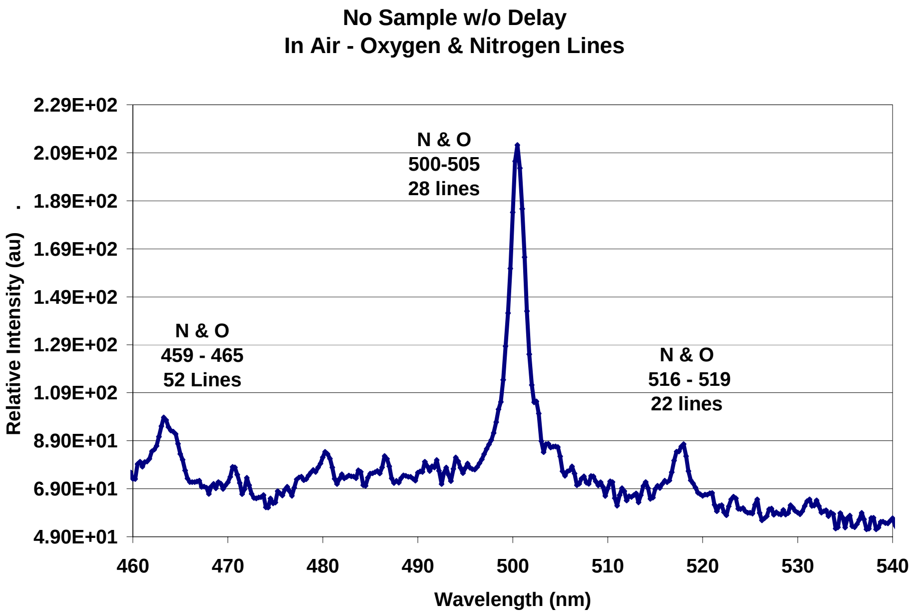


Fig. 15 - LIBS gun spectra of air w/o delay time gate

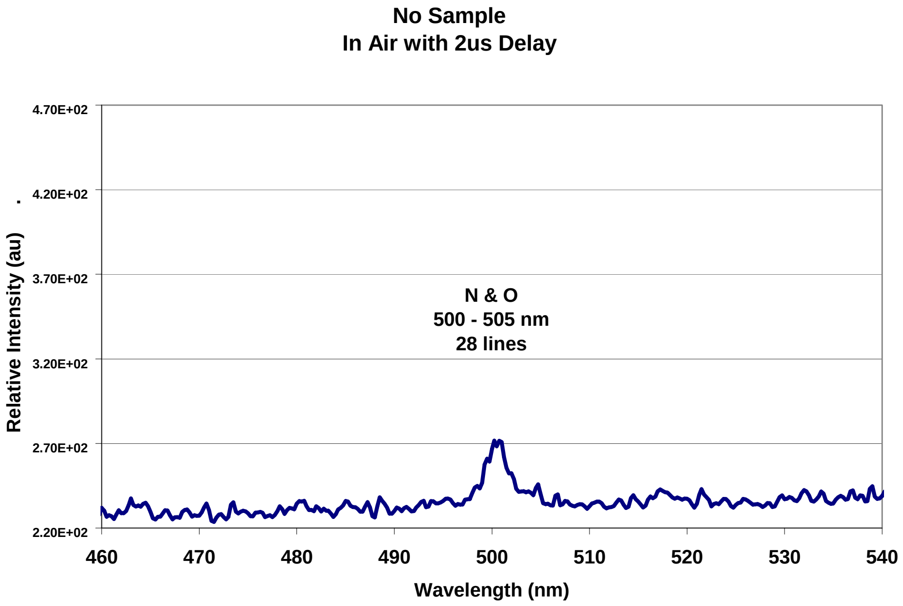


Fig. 16 - LIBS gun spectra of air with 2μs delay time gate

The LIBS laser gun and integrating sphere pickoff system were commissioned to collect "in-situ" the spectra shown in figures 17 through 24. These amorphous and crystalline material samples consist of known or familiar compositions. Line spectra for each "known standard" was gathered using two Stellarnet spectrometer units with spectral ranges of 200 to 400nm and 400 to

600nm. Due to the laser's relatively low peak power (~ 1.2MW), only the stronger emission lines were observed.

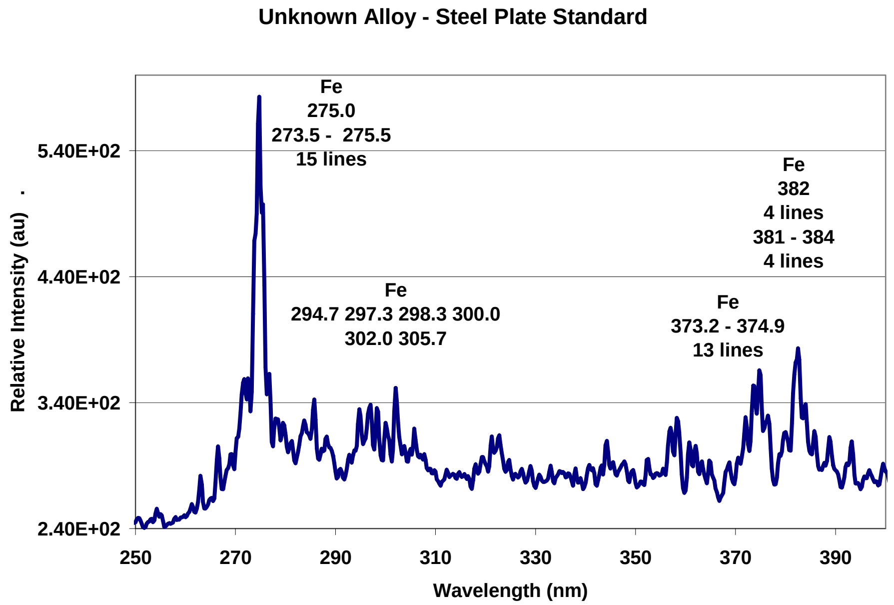


Fig. 17 – Iron Steel plate standard

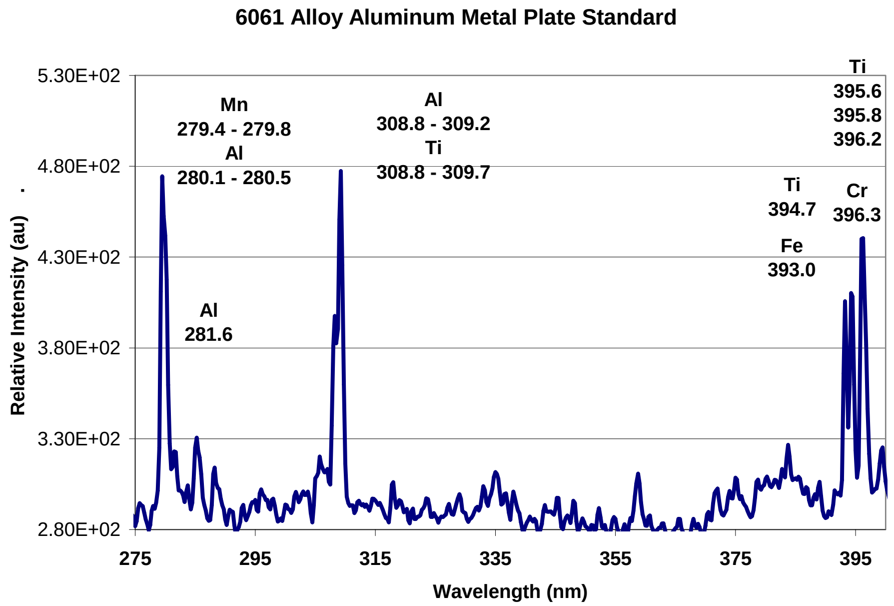


Fig. 18 – Aluminum plate standard

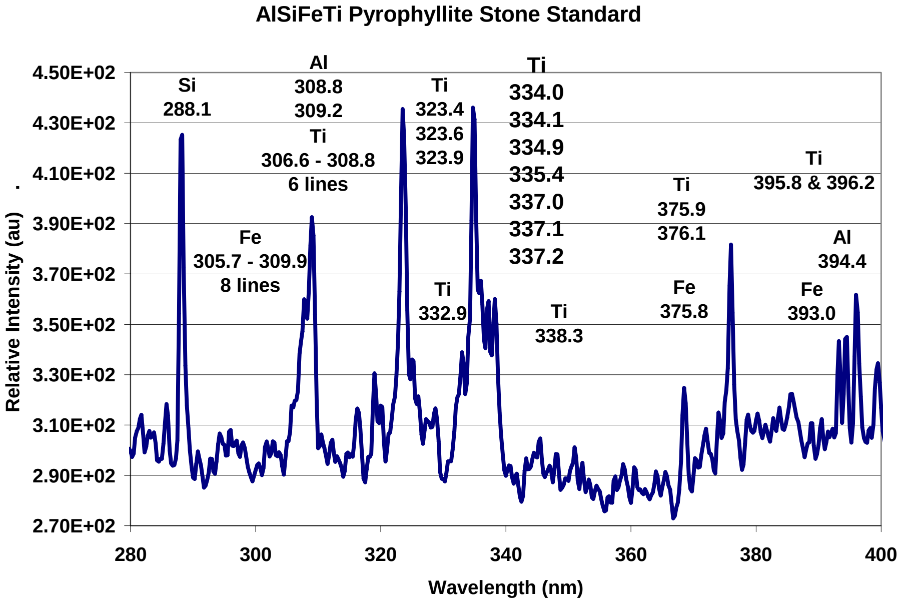


Fig. 19 – Pyrophyllite mineral standard

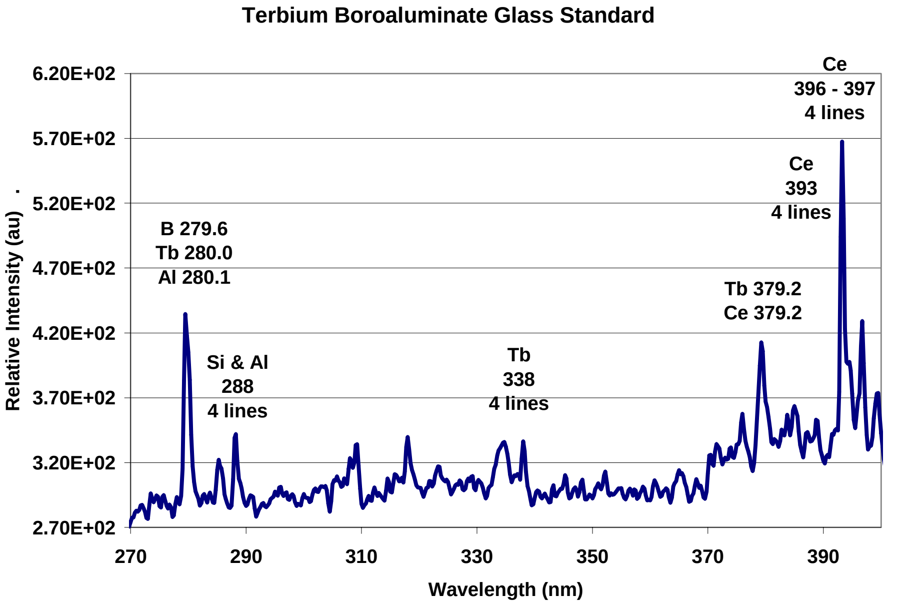


Fig. 20 – Terbium glass standard

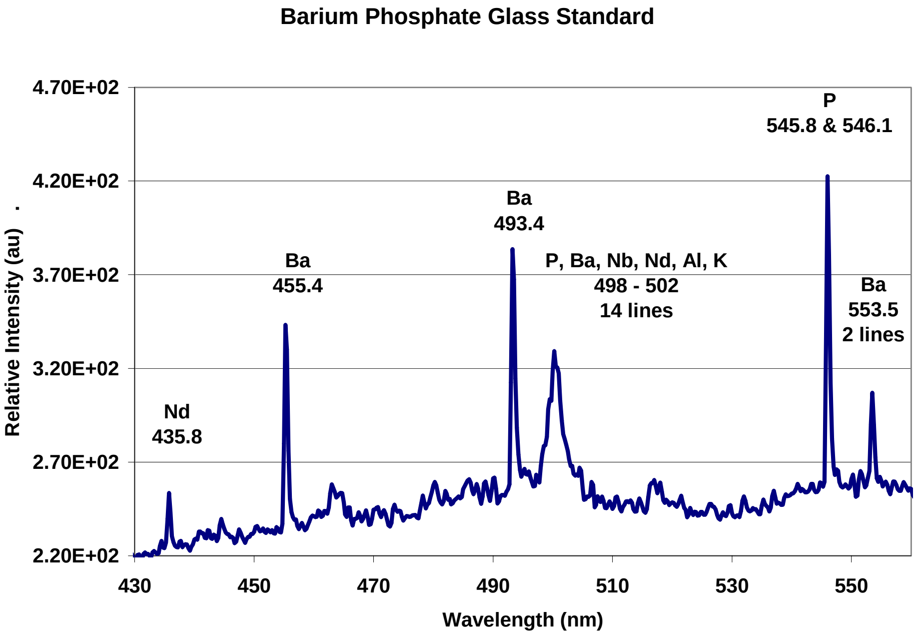


Fig. 21 – Barium phosphate glass standard

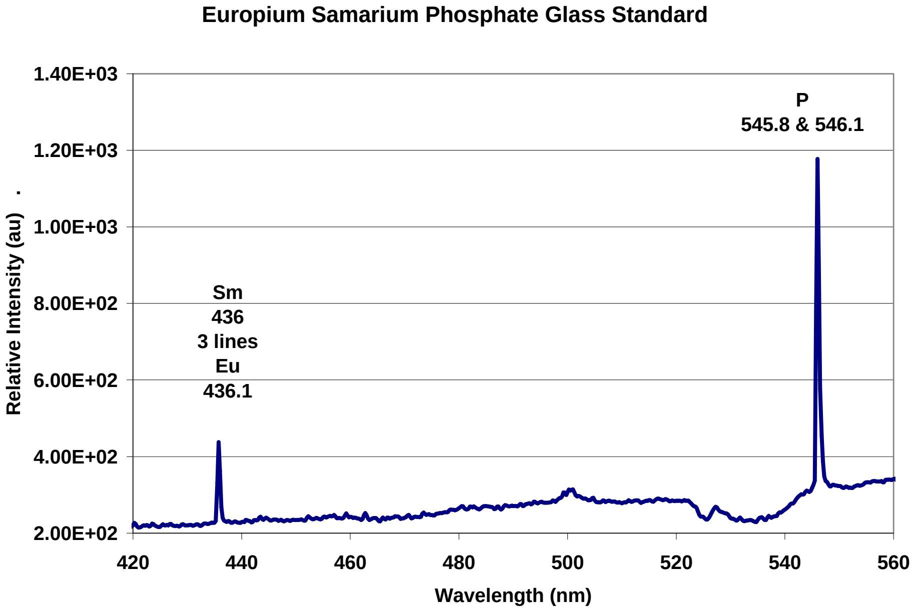


Fig. 22 – Europium phosphate glass standard

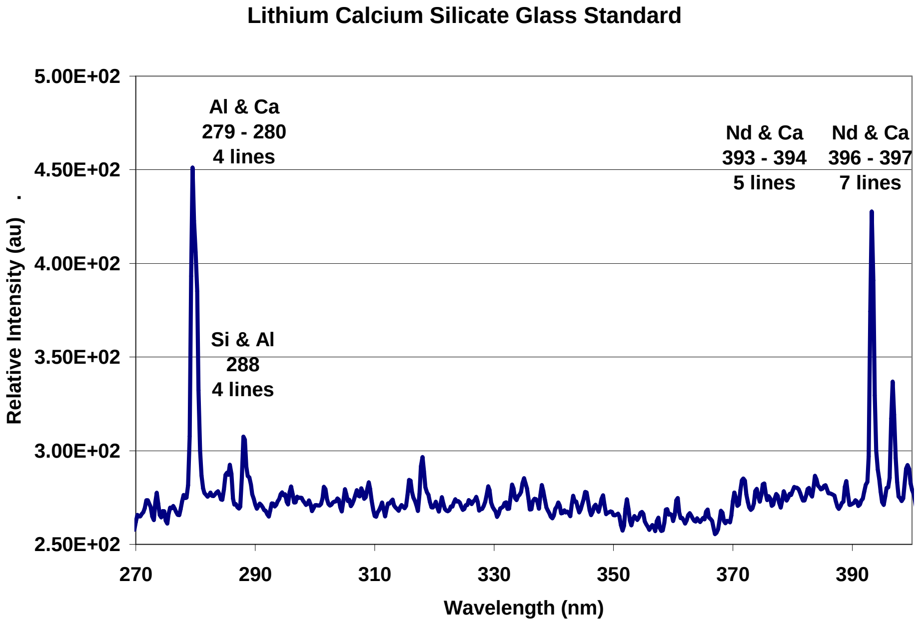


Fig. 23 – Lithium silicate glass standard

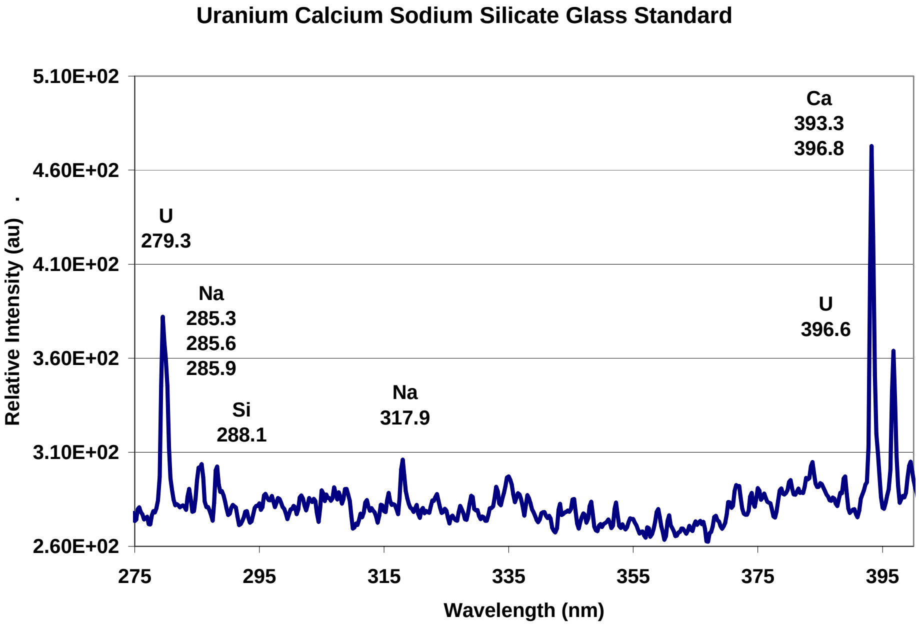


Fig. 24 – Uranium silicate glass standard

Four rocks of unknown composition were chosen at random for LIBS testing. Comparing "known standard" LIBS spectra, we were better able to identify many of the elements present in a number of rock samples with totally unknown compositions. These four rocks are shown in figure 25. Unknown rock spectra were captured with the LIBS laser gun/integrating sphere pickoff system and collected in-situ with the same protocol as the spectra of "know standard" materials. LIBS spectra for rocks #1 through #4 are shown in figures 26 through 29.

Fig. 25 – Rock samples with unknown compositions

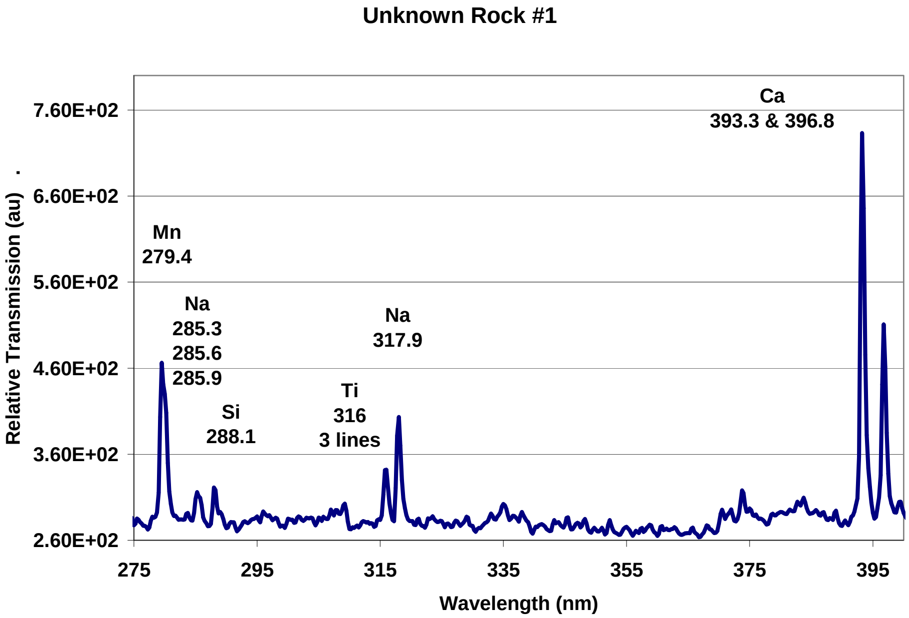


Fig. 26 – Unknown Rock #1

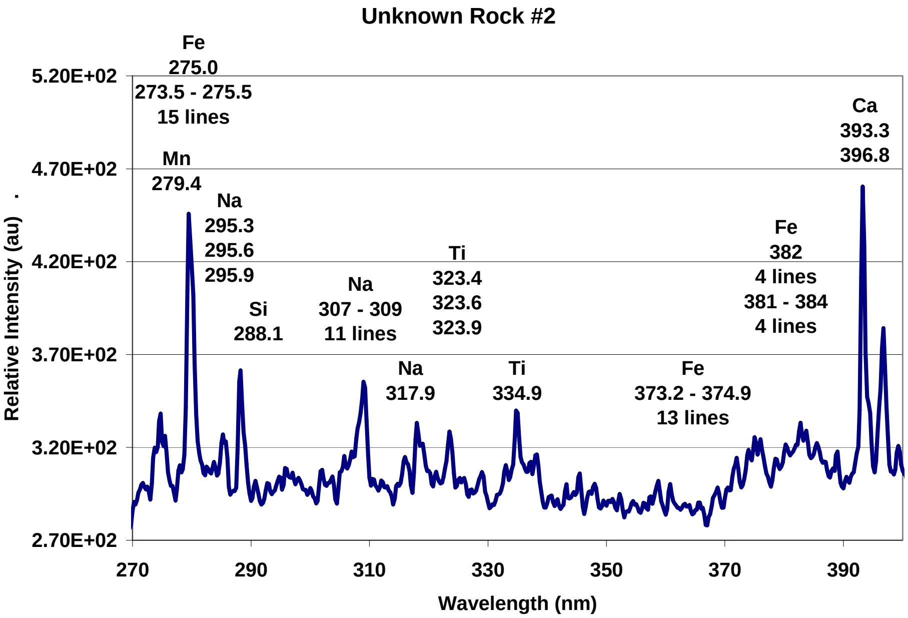


Fig. 27 – Unknown Rock #2

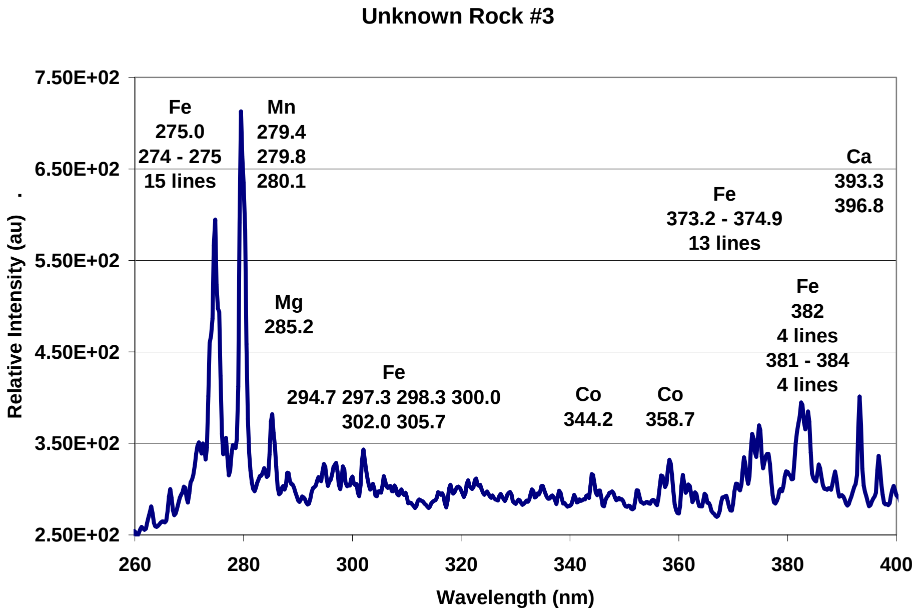


Fig. 28 – Unknown Rock #3

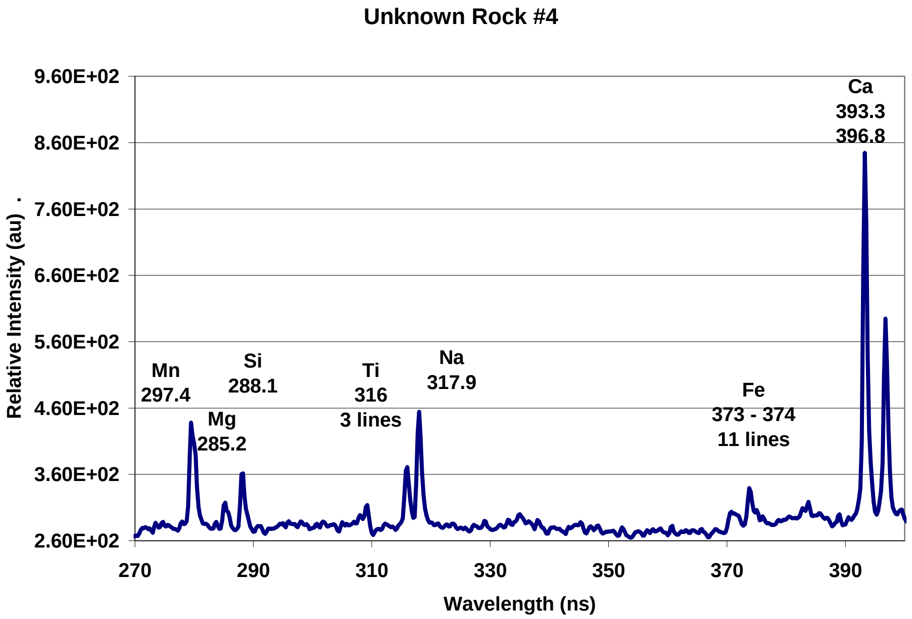


Fig. 29 – Unknown Rock #4

Analysis

We utilized the online U.S. National Institute of Standards "NIST Atomic Spectra Database Lines" to identify the chemical elements revealed in the LIBS spectra [11]. This online data base provides precision line wavelength and relative line strength information. Such information is especially useful when observing the spectra produced from lower peak power laser sources as typically, only the strongest lines are observed. All four of the rocks with unknown composition exhibited lines indicating significant concentrations of calcium and manganese. Rock #1 has little or no iron. Comparisons of relative peak height and multiple line emissions for a given element indicate that Rock #2 contains high concentrations of sodium, iron and titanium. Rock #3 appears to have significant iron, cobalt and manganese concentrations and little or no sodium. Rock #4 spectral lines indicate higher silica and calcium and low concentration levels of iron.

Conclusion

Compact, low cost, rugged laser/computer/fiber spectrophotometer components are readily integrated into a wearable eye-safe in-situ LIBS field chemical analysis system. Wearable LIBS systems may be assembled from commercially available components and are suitable for qualitative and semi-quantitative analysis field-testing of various materials. Wearable chemical analysis systems are conceivably attractive for use in numerous applications including mining, geology, anthropology, oil exploration, remote medical diagnostics and biological and chemical weapons detection [12,13,14,15,16,17,18,19,20,21]. Eye-safe in-situ LIBS provides the operator with enhanced real-time sensitivity, awareness and association with targeted materials in field environments. It allows for instantaneous evaluation of a material's color and texture with simultaneous exposure of the materials chemical composition without sample preparation.

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