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LASER INDUCED BREAKDOWN SPECTROSCOPY FOR ELEMENTAL PROCESS MONITORING OF SLURRY STREAMS

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LASER INDUCED BREAKDOWN SPECTROSCOPY
FOR ELEMENTAL PROCESS MONITORING OF SLURRY STREAMS

FINAL REPORT

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PERSPECTIVE

Patrick Zhang, Research Director - Beneficiation & Mining

On-line analysis and process automation are powerful tools for achieving optimal industry efficiency. The rewards of an effective on-stream analysis technique coupled with a modern process control scheme include improved recovery of P_2O_5 , reduced chemical consumption and improved concentrate grade. As the quality of phosphate reserves declines, improvement in plant efficiency is even more critical. Unfortunately, process control in phosphate beneficiation plants is still primitive. This is due to the following difficulties in analyzing the plant slurry: (1) multi-element analysis (P_2O_5 , CaO, SiO_2 , and MgO) is required for meaningful process control, (2) the slurry is a heterogeneous system with about 20-30% solids and (3) the major elements to be analyzed, phosphorus and calcium, are low in atomic number, thus preventing the use of the x-ray fluorescence technique which is widely adopted in other mineral industries.

Since its inception, FIPR has sponsored four projects for evaluating on-line analytical systems: a nuclear magnetic resonance (NMR) technique, an optical sensor, a neutron activation probe, and an X-ray diffraction system. Except for some limited applications of the NMR analyzer, none of the techniques has proven to be a satisfactory solution. Some analyzers have problems with their sample feeding systems, while the others do not give accurate analyses.

Laser Induced Breakdown Spectroscopy, LIBS, is a relatively new technology born shortly after the invention of the laser. In LIBS, a very energetic laser spark (plasma) is formed by focusing a laser to produce an irradiance in the range from 1-10 MW/cm². Breakdown occurs because the electric field at the focus exceeds the dielectric strength of the surrounding environment. LIBS has been studied in a wide variety of materials including many gases, solids and liquids. To date, this technique has been successful mainly in low level trace element analysis of liquid samples. The University of Florida is one of the pioneers in attempting to apply this technology on high-solids slurry for high-level analysis.

The major advantage of the LIBS is the potential for a rapid, in situ, multi-element analysis. This approach does not require a sample feeding/preparation system, because the plasma may be located either on the surface of, or be submerged in, the slurry.

Unfortunately, this project did not achieve the goal originally envisioned by the researchers due to the amount of water in the slurry and the large sizes of the particles analyzed. The project was, however, salvaged by shifting its focus on developing an off-line system. The bench-top system has proved to be a fast and reliable tool for quality control of the pebble fraction, which is done currently by visual observation.

ABSTRACT

The goal of this research program was to develop the method of laser-induced breakdown spectroscopy (LIBS) for applications in the phosphate industry. This would include rapid elemental analysis for P, Mg, Si and Fe in materials at various stages of phosphate mining and processing, using off-line, at-line and on-line measurement approaches. Several experimental systems were developed and evaluated. A research instrument with a high resolution spectrometer and gated, intensified CCD detector was used for initial fundamental studies. Several more compact instruments were then developed and optimized for measurements on powdered phosphate mineral samples. A final version of the compact instrument was field-evaluated. We conclude that, with careful preparation of standards, the method may prove useful for rapid laboratory measurements where accuracy and precision of $\approx 200\%$ is acceptable. At-line quantitative analysis may be possible with some automated sampling and sample treatment (grinding and drying). Online quantitative chemical analysis in phosphate slurries does not appear to be practical at this time using LIBS.

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EXECUTIVE SUMMARY

The goal of this research was to develop and evaluate laser induced breakdown spectroscopy (LIBS) for the rapid chemical analysis of minerals of importance to the processing of phosphate rock. In LIBS, a pulsed, high intensity laser is focused on a sample producing a bright plasma breakdown which vaporizes the sample and excites the vapor in a microplasma. The emission from this plasma includes spectral lines which can be used for qualitative and quantitative chemical analysis. The technique has been known since the invention of the pulsed laser in 1961 and has been evaluated for a wide range of applications with varying degrees of success. Precise quantitative analysis is difficult because the interaction of the pulsed laser with the sample is complicated and sensitive to the influence of many variables. During the last decade, improvement in detection approaches, especially the use of gated, intensified charge coupled devices (CCD), and the availability of highly reliable pulsed lasers has led to improved performance for LIBS, although, for many types of real world samples, useful quantitative analysis continues to be an elusive goal.

We began these studies with the construction of a research laser induced breakdown spectrometer which included a pulsed Nd:YAG laser source at 1064 nm with a maximum output pulse energy of 300 mJ. This was focused upon a sample stage which was computer controlled in three axes. A flexible optical system permitted measurements of the plasma emission at various angles using a 0.5 m focal length spectrometer fitted with an intensified, gated charge coupled device array detector. This system was capable of recording spectra with a time resolution of a few nanoseconds in a 10 nm spectral window anywhere in the ultraviolet to infrared spectral region.

The spectroscopic behavior of phosphate ores was studied, leading to the identification of sensitive spectral lines in appropriate spectral windows for the elements of interest. Optimization studies were made on the temporal and spatial development of the laser induced plasma on phosphate ores. Calibration curves were obtained for synthetic phosphate ore samples in order to determine the linear range of response for each element of interest. Sample presentation proved to be one of the more difficult problems and many approaches were evaluated, including pressed pellets with various levels of moisture and binding agents, loose sample in sampling boats, and, finally finely powdered samples simply pressed to double-sided adhesive tape. The latter technique proved to be the most effective both in terms of sampling precision and ease of application.

After the initial studies, a prototype field instrument was designed, using a compact laser and non-gated CCD spectrometer. Reliable spectra were obtained with a compact, non-gated CCD spectrometer using a pulsed Nd:YAG laser of 10-30 mJ pulse energy (at 1064 nm). After further optimization studies, a customized software was developed to collect spectra, make background corrections, calculate calibration curves and display concentrations of unknowns. The best precision obtainable was about 10% for averaging of 10-20 laser probings on one sample. With careful choice of standards of

similar composition as the unknowns, quantitative accuracy was limited to the order of 20%. This might be improved upon in the future with more sophisticated data processing and exclusion of the occasional erratic spectrum due to spurious laser-material interaction.

INTRODUCTION

This proposal dealt with the development of a practical Laser-Induced Breakdown Spectroscopy (LIBS) system capable of detecting elemental species in aqueous slurry process streams of importance to the phosphate processing industry. Real time on-line detection in slurry process streams is a problem of continuing interest for many environmental monitoring and process control applications. While a variety of useful sensors have been developed for monitoring flowing streams, they often tend to be unreliable in all but relatively clean samples. These include, for example, electrochemical probes and fiber optic based optical sensors which rely upon a chemical response in a permeable membrane. In some cases, complex and expensive methods such as x-ray fluorescence, x-ray diffraction, nuclear magnetic resonance and neutron activation have been applied for on-line process monitoring. For example, all of these have been evaluated or are being evaluated for the on-line determination of phosphorus and silica in mineral slurries during the processing of phosphate ores. Despite a wide variety of pressing needs, reliable elemental on-line monitors are not yet available and most trace elemental detection continues to be carried out using off-line techniques. Recent technological developments in the lasers used for LIBS and in multichannel spectroscopic detection systems have revived interest in the possibility of a practical LIBS on-line monitoring system. The LIBS technique has several distinct advantages over other analytical methods. It requires no sample preparation and can be carried out *in situ*, rapidly and in real time. Good detection limits and wide dynamic range have been demonstrated in a variety of sample matrices. LIBS is inherently a multi-element technique and capable of providing simultaneous multi-element determinations. Difficulties with LIBS include the very high continuum background which necessitates time resolution in the detection and generally inferior precision due to the very strong nonlinear nature of the laser/material interaction. In many matrices, calibration can be difficult. All of these difficulties play a role in the application of LIBS to phosphate mineral analysis. The goal of this project is to apply new technologies to develop LIBS as a practical, reliable technique for on-line monitoring in aqueous slurry process streams. Such a monitoring system, when applied to various points in the processing of phosphate minerals, would result in greater operator control of the separation and purification processes and increase the overall efficiency of phosphate recovery from the natural ore.

Laser-induced breakdown in gases was discovered in 1963 (Maker 1964), shortly after the invention of the pulsed laser, and has been reviewed by several authors (Moenke-Blankenburg 1989, Radziemski 1989). In LIBS, a very energetic laser spark (plasma) is formed by focusing a laser to produce an irradiance in the range from 1-10 MW/cm² (Raizer 1977). Breakdown occurs because the electric field at the focus exceeds the dielectric strength of the surrounding environment. Laser-induced breakdown has been studied in a wide variety of materials including many gases, solids and liquids. At atmospheric pressure, cascade ionization occurs when a few seed electrons absorb energy from the laser beam by inverse Bremsstrahlung. The plasma becomes opaque, absorbs more energy, and grows towards the focusing lens during the

laser pulse. The result is a luminous plasma with an initial temperature of 104 to 105 K and an electron number density of 10^{15} to 10^{19} cm^{-3} (Zapka 1981). By comparison, the DC arc has a temperature of 5000-7000 K and an electron number density of 10^{15} cm^{-3} and the argon inductively coupled plasma (ICP) has a temperature of 6000-10000 K and an electron number density of 10^{13} - 10^{15} cm^{-3} . Local thermodynamic equilibrium does not exist during the early stages in the development of the LIB plasma. In the first studies of LIBS, lasers with 1-2 J pulses of 10-30 ns were used. However, more recent studies have used 20-50 mJ pulses of 5-20 ns duration to produce peak powers of a few megawatts with commercially available lasers operating at 10-20 Hz. While many different types of lasers can be used, the Nd:YAG operating at the fundamental wavelength of 1064 nm has several advantages, most importantly, a high degree of reliability and high efficiency.

The spectral emission from a LIB plasma is time-dependent. Directly following the laser pulse, there exists a high energy-density short-lived plasma with emission which is characterized by an abundance of ionic lines on top of a broad recombination background due to the high temperatures (10^4 - 10^5 K). The broad, complex spectra is not very informative, and so it is best to delay and gate the detection to observe a portion of the emission occurring a short time after the decay of the majority of the background. This cooler, recombined plasma is most often used for spectrochemical measurements.

Work up to 1989 concerning the analytical applications of LIBS has been well reviewed in a monograph on the subject (Radziemski and Cremers 1989). More recent work has been summarized in several reviews (Rusak and others 1997, 1998). LIBS has been applied for the analysis of gases (Casini and others 1991, Smith and others 2000), fluids (Cremers and others 1984), and aerosols (Radziemski and others 1993, Smith and others 2000), molten metals (Aragon and others 1993), polymeric materials (Anderson and others, Anzano and others 2000), and solids. In the 5 year period from 1987-1992, there were at least 1000 publications on laser-induced plasmas, many having to do with physical studies involving the interaction of magnetic and electric fields with laser-induced plasmas, the influence of laser wavelength and pulse duration, the use of laser plasmas in mass spectrometry, the effect of particles and aerosols on plasma production, time resolved plasma imaging, temperature and number density measurements, ionization and plasma formation processes, UV-Visible continuum generation and x-ray generation. The restriction to a laboratory environment limits the main advantages of the LIBS method, namely its speed and simplicity. The goal of this proposal is to develop a practical field instrument for the real time detection of many trace elemental species in flowing process streams containing high solids loading. In order to achieve a reasonable reproducibility of results, many experimental factors must be controlled. For example, the exact location of the breakdown point relative to the sample and to the collection optics will critically influence the magnitude of the observed emission signal.

The spectral intensities of LIBS depend upon both the ablation and plasma characteristics (Majidi and Joseph 1992). Therefore, the major difficulty for a field instrument is the potentially poor reproducibility. Certainly, a direct application of LIBS to on-line elemental determinations in slurries without specially designed methods would be expected to give little useful information. This is a result of the inherent instability of laser produced plasmas, largely due to the profound sensitivity of the plasma to the matrix. In contrast, the major advantage of the LIBS approach is the potential for a rapid, *in situ*, analysis.

There are only two examples of the analysis of ore minerals by LIBS in the literature, two papers concerning Australian iron ores (Grant and others 1990, 1991). In the first paper these workers determined the suitable detection parameters for Fe, Si, Mg, Ca, and Ti in an iron ore sample. This was accomplished by measuring the temporal development and decay of the individual emission lines. They found that in order to achieve the best signal-to-noise ratio, a gate delay of 2-3 μs with a detection width of 1 μs was optimum. In the second publication, they reported on the quantitative results obtained for Si (390.55 nm), Mg (518.36 nm), Ca (431.86 nm), Ti (498.17 nm) and Al (396.15 nm) in a series of iron ore samples. They acquired data according to the optimum detection parameters described in their first publication. In all cases, an iron line at 389.56 nm was used as an internal standard. Because their detection system was only single-channel, each element (including the internal standard) was detected sequentially in time. This led to their somewhat poorer precision (3-26% RSD). Linear calibration curves were obtained for CaO and MgO over the concentration range of 0.01-10.8% and 0.005-1.47%, respectively. However, the calibration curves for SiO₂, Al₂O₃ and TiO₂ were found to be curved due to self-absorption. A second order fit was used in these cases.

METHODOLOGY

Figure 1 shows a schematic of our initial research LIBS instrument. It was designed to be as versatile as possible to allow for a variety of fundamental and optimization studies. The Nd:YAG laser (Laser Photonics, 300 mJ maximum pulse energy at 1064 nm) was directed to the sample stage through a focusing lens and a pierced mirror at 45°. The plasma emission was then collected at 180° via the mirror and focused on the entrance slit of a 0.5 m focal length spectrograph (Model SP-500, Acton Research) fitted with an intensified CCD detector (Model ICCD-576S, Princeton Instruments). A 2400 grooves/mm grating provided a reciprocal linear dispersion of 0.9 nm/mm at 425 nm. An entrance slit width of 20 μm was typically used. The focused laser spot diameter at the sample was 1 mm. This produced a typical irradiance of about 10^9 W/cm^2 . The sample stage was motorized for computer-controlled three-axis positioning.

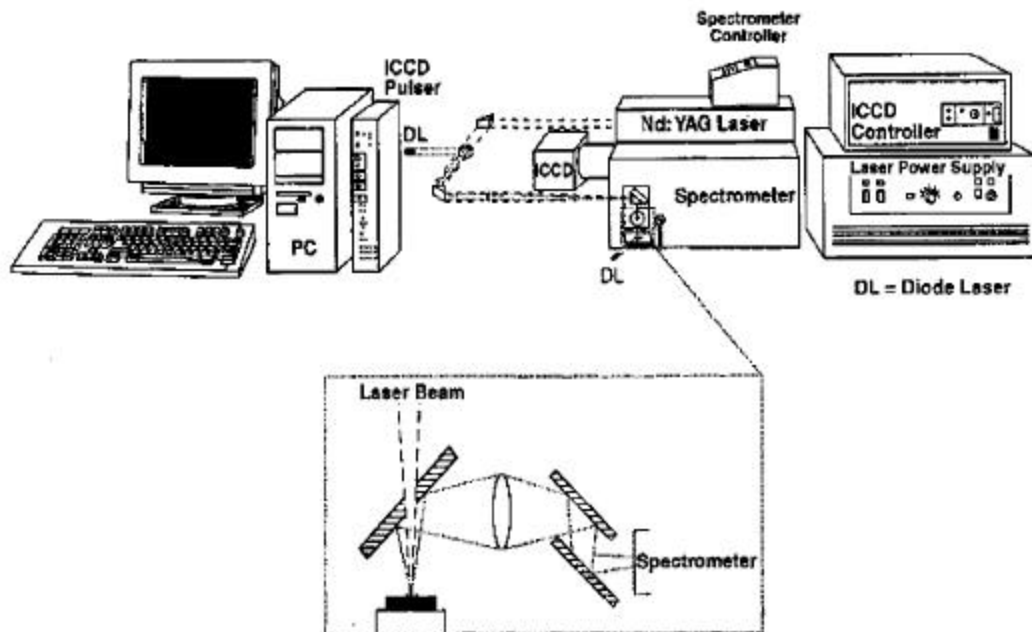


Figure 1. Schematic of the First Laser-Induced Plasma Spectrometer.

INITIAL OPTIMIZATION STUDIES WITH PHOSPHATE ROCK

For the initial optimization studies, the laser pulse energy was fixed at 180 m J, based on our preliminary studies which indicated that this pulse energy provided the optimum signal-to-noise ratio. Phosphate rock samples were obtained from NIST and CF Industries (Wauchula, FL). In all cases, the samples were used as received, which was as a fine powder with a typical particle size of ~ 100 μm . For most of these studies, they were mixed with 10% (by weight) cellulose binder, and pressed into pellets at about 5000 psi. Standard samples of phosphate minerals were prepared by dilution of NIST Florida phosphate rock standard (SRM 120) with calcium oxide (Alfa AESAR, Cat# 10684).

Calcium oxide was used as the diluent because it was the constituent of highest concentration in this reference material, therefore resulting in the least modification of the matrix (i.e. matrix matched standards). For these samples, the final concentration ratios were: (Binder/FL phosphate rock/calcium oxide) 10/90/0, 10/72/18, 10/59/31, 10/45/45, 10/22/68. These studies were aimed at optimizing several instrumental parameters and evaluating the initial analytical performance for a series of analyzed phosphate mineral samples which were provided by CF Industries.

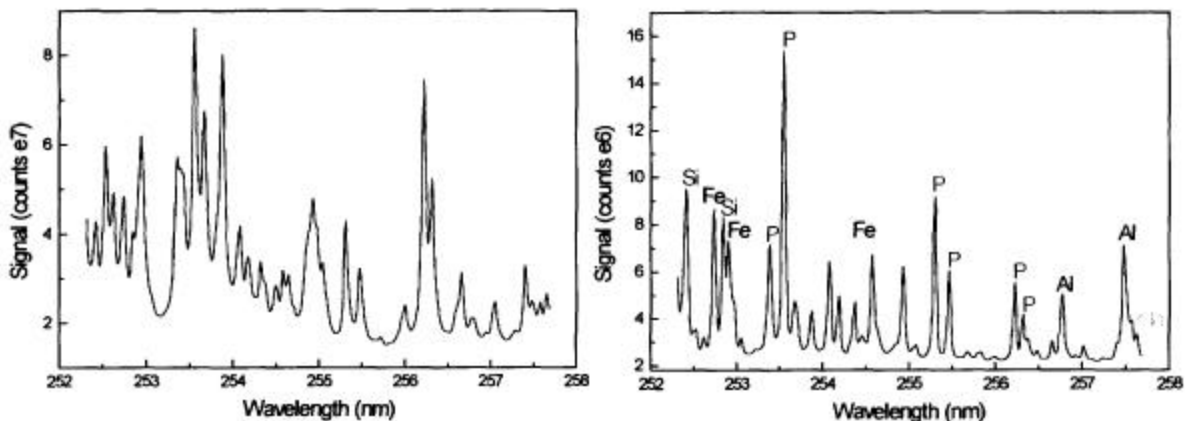


Figure 2. Influence of Measurement Delay Time on Phosphate Rock Spectra.

A study was made of the spectrum of Florida phosphate rock as a function of measurement delay time after the initiation of the laser spark. During the first 20 μs , the plasma changes radically from a complete continuum with no spectral features to a well-defined equilibrated system with well defined spectral features. Figure 2 shows two spectra from this study, comparing, on the left a spectrum of phosphate rock taken during the first μs of the plasma life, and on the right a spectrum taken after a delay of 4 μs . The signal-to-background ratio and spectral resolution in the delayed spectrum are clearly improved. The optimum delay time was found to be somewhat matrix dependent but a delay of 4 μs appeared to be appropriate for all of the mineral samples which were studied.

We also studied the influence of lens-to-sample distance and focal length upon the signal intensity using both right angle (side) optical detection and detection from the top using a mirror at 45° , pierced with a hole through which the laser beam could pass. Side collection proved to be much more sensitive to sample placement, as shown in the plot on the left in Figure 3. Collection of the signal from the top (shown in the right plot in Figure 3) proved to be almost immune to the position of the sample, at least over a sample displacement of 2 cm, especially when a longer focal length lens was used.

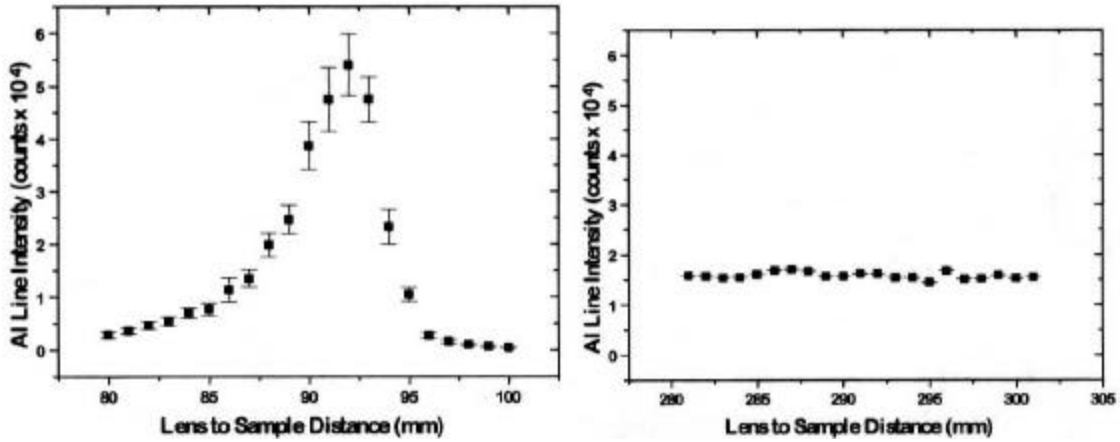


Figure 3. Influence of Laser Lens-to-Sample Distance on Spectral Line Intensity.

As part of a comprehensive study of precision in LIBS (Castle 1998) we also examined the repeatability of measurements taken over a week. For this study, Mo at a concentration near 2500 ppm in a pressed particulate sample was used. Four standards and two unknowns were measured at intervals of 24 hours. The results, displayed in Figure 4, gave a long-term precision of 11% and 13% for the two samples.

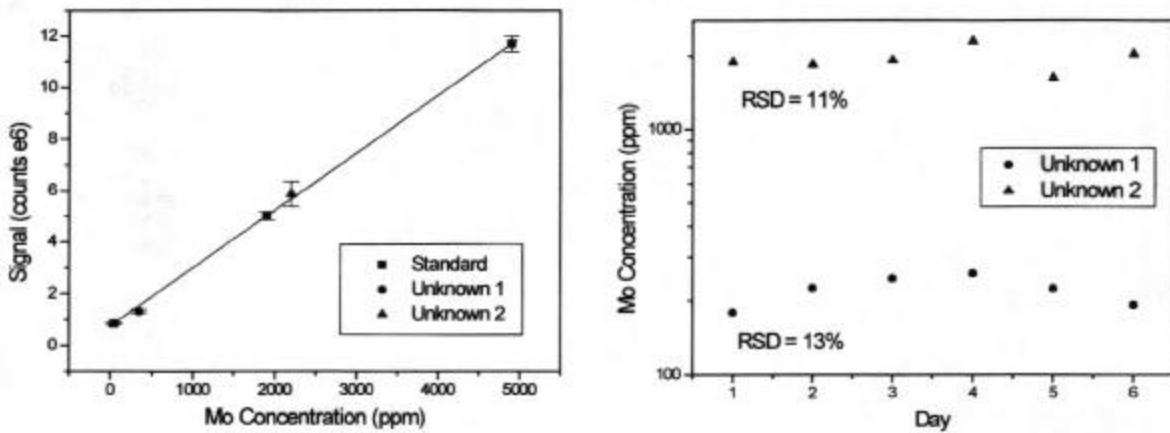


Figure 4. Long-Term Precision.

RESULTS

INITIAL ANALYTICAL RESULTS FOR PHOSPHATE MINERALS

For the analysis of the phosphate rock samples, a 2 μs gate delay and 15 μs gate width were used. Each measurement consisted of 50 laser shots and was repeated in triplicate on each sample. The natural samples supplied by CF Industries were received as loose powders which had already been milled to a fine powder, $\approx 100 \mu\text{m}$ particle size. These powdered samples were mixed with 10% cellulose binder and pressed into pellets for subsequent analysis. Each sample was measured 3 times with 50 laser shot tracks for each measurement. All samples were translated at $200 \mu\text{m s}^{-1}$ during the measurement. After analysis of the NIST Florida phosphate rock over the spectral range from 200 to 600 nm, the spectral window shown in Figure 5 was selected. Within this window, the emission lines of Si, Fe, P, Al, and Mn could be simultaneously monitored. All five of the prepared standards and four unknowns obtained from CF Industries were analyzed in this window. Calibration curves were prepared using the 254.60 nm line for iron, 255.49 nm line for phosphorus, 256.80 nm line for aluminum, and 252.41 nm line for silicon, and are shown in Figure 6. Good signal-to-noise was obtained for all concentration levels encountered which is reflected in the good precision and near unity correlation coefficients for the linear regression fits. These calibration curves were used to determine

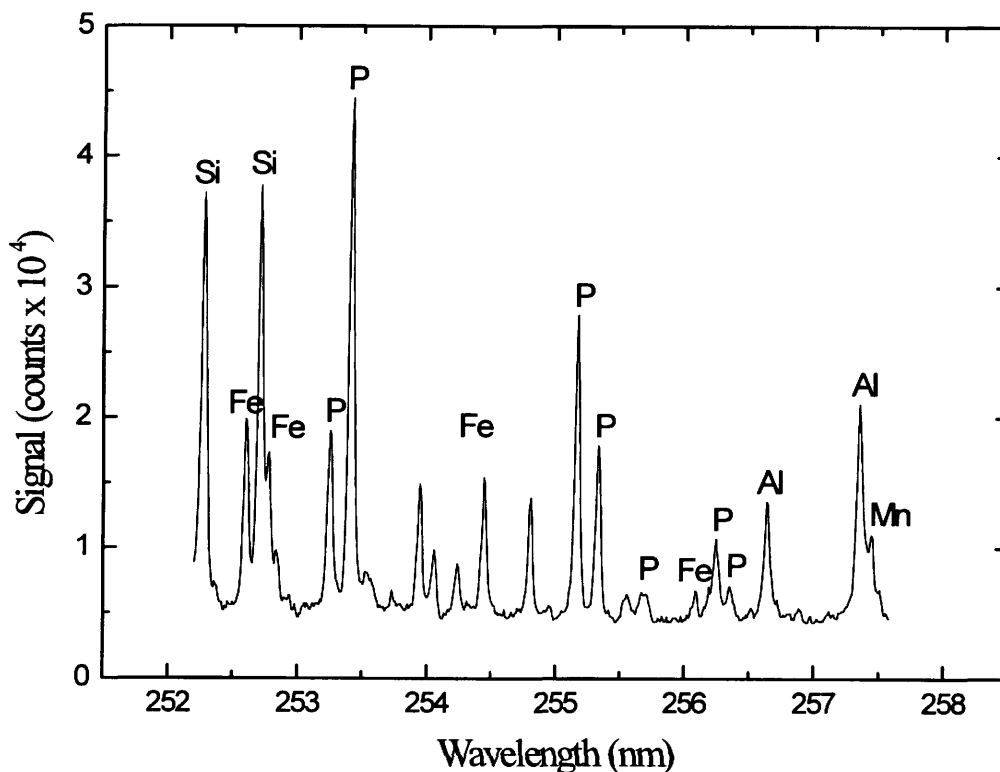


Figure 5. Spectral Window for Phosphate Mineral Analysis.

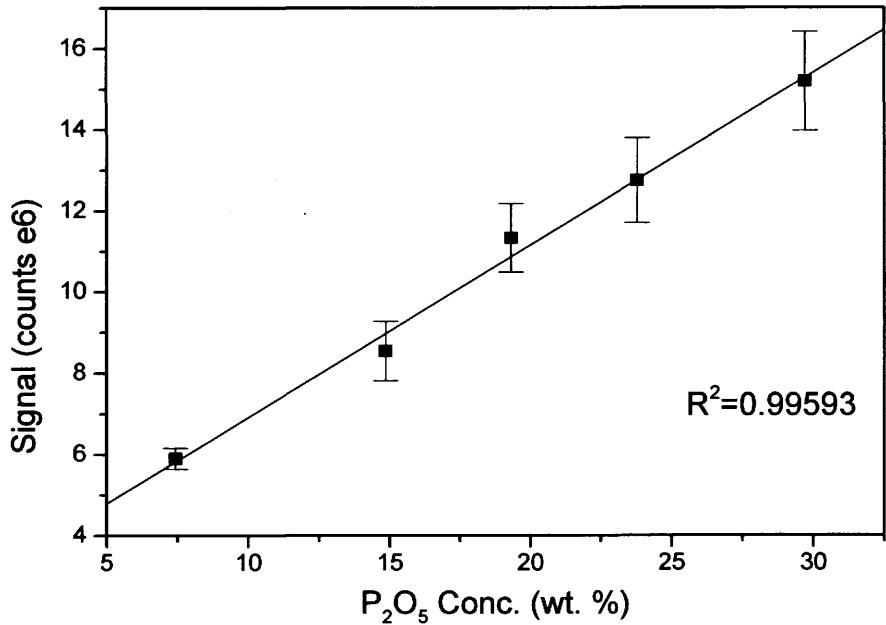


Figure 6. Calibration Plots for Various Species in Phosphate Ore.

the concentrations of the four elements in the CF Industries unknown samples. Table 1 shows the results of the analysis of the four samples, identified as #5, #17, A, and B. The tabulated "Act." is the concentration value (w/w %) reported by CF Industries (obtained from dissolution followed by laboratory ICP emission spectroscopy measurements). In general, there is good agreement between these results and those obtained from the LIBS measurements. In the case of the Si (SiO₂) measurements, we compare our results to the "Insolubles" determined by CF Industries. It is to be expected that some fraction of the insoluble component of these samples would be composed of material other than SiO₂.

Table 1. Quantitative Results from the Analysis of the CF Industries Phosphate Rock Samples.

Sample	Concentration (w/w %)							
	P ₂ O ₅		Fe ₂ O ₃		Al ₂ O ₃		SiO ₂	
	CF	LIBS	CF	LIBS	CF	LIBS	CF	LIBS
#5	25.2	31.1 ± 1.9	1.5	1.18 ± 0.09	3.2	1.95 ± 0.07	22.5	9.51 ± 0.64
#17	16.2	16.8 ± 1.4	2.4	1.10 ± 0.07	3.2	1.65 ± 0.07	27.6	8.24 ± 0.63
A	29.2	36.2 ± 6.7	1.2	1.38 ± 0.18	1.4	1.40 ± 0.14	12.1	8.28 ± 1.38
B	29.4	35.0 ± 5.5	0.85	1.05 ± 0.13	1.7	1.41 ± 0.17	12.6	7.95 ± 1.01

STUDIES OF PRECISION

We studied the effect of particle size on the precision of the LIB spectra, using natural phosphate ores. A sample of ore was obtained from CF Industries in two particle sizes, the original material which was composed of sizes ranging from about 1 cm to 300 μm , and a ground sample of the same material with a more uniform finer particle size of $\approx 200 \mu\text{m}$. The original coarse material was studied by simply placing it in a petri dish on the sample stage of the instrument. The finer material was studied as a loose powder and pressed into pellets. For each sample, 400 individual laser induced plasma were produced as the samples were translated perpendicular to the laser beam and the individual spectra were captured. Figure 7 shows typical raw data for the emission intensity of P, Si, Al and Fe lines from the coarse phosphate ore. The precision on a shot-to-shot basis ranges from 43.9% to 60.3%. This is not surprising, considering the nature of the sample and the fact

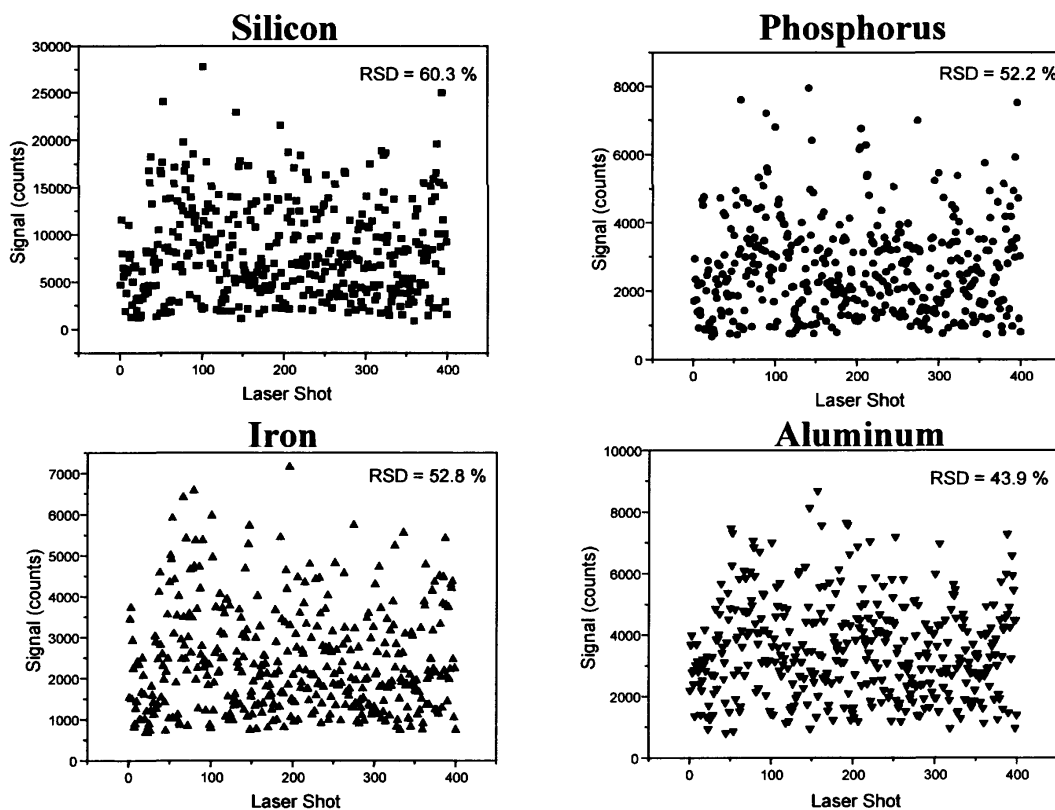


Figure 7. Raw Spectral Line Intensity Data for 400 Laser Shots on Coarse Phosphate Ore.

that each laser pulse generally strikes an entirely different particle of widely varying composition. If the data are averaged as four sets of 100 shots, the precision improves markedly. Table 2 compares the precision obtained for the coarse sample and for the finer sample, both as a loose powder and as a compacted pellet. Interestingly, the precision is

best for the coarse material and worst for the loose, fine powder. This is because the loose material tends to form a cloud of particulate material above the sample which obstructs the next laser pulse and causes more erratic breakdown in subsequent plasma.

Table 2. Precision Results for Coarse and Fine Phosphate Ore.

	<u>Silicon</u>	<u>Phosphorus</u>	<u>Iron</u>	<u>Aluminum</u>
Loose Coarse Material				
Average Signal	8175.3	2659.6	2389.52	3490.97
Shot-to-Shot RSD	60.3	52.2	52.8	43.9
Measurement RSD	2.7	1.6	3.6	3.3
Loose Fine Powder				
Average Signal	4854.8	2388.0	1674.9	2246.4
Shot-to-Shot RSD	71.9	66.5	53.6	49.9
Measurement RSD	13.0	10.5	8.4	9.9
Pressed Fine Powder				
Average Signal	15907.1	8171.4	5543.2	4904.8
Shot-to-Shot RSD	44.1	42.6	43.6	35.6
Measurement RSD	10.3	12.2	11.2	8.4

This also accounts for the fact that the average signal intensity is lower for the loose, fine powder than for the coarse material. The highest signal intensities were observed for the compacted, fine powder samples but the precision for these was about the same as for the loose, fine powder. These results are encouraging in respect to the potential for on-line measurements because they indicate that it is possible to obtain good signal-to-noise with satisfactory precision using a relatively small number of laser shots, even on very coarse samples.

DEVELOPMENT OF THE COMPACT LIBS INSTRUMENT

Because of the complexity and cost of the research LIBS instrument which was constructed for the initial studies, we investigated the possibility of designing a compact, portable, less expensive version of this instrument. We found that reliable results could be obtained with lower laser pulse energy if the same irradiance was maintained by tighter focusing of the laser beam. We therefore substituted a 50 mJ per pulse Nd:YAG laser manufactured by Big Sky Laser. This unit costs less (\$10 K compared to \$19 K for the Laser Photonics laser) and is much more compact, portable and rugged. We also evaluated a customized compact CCD spectrometer (Model SD2000, Ocean Optics, Inc.). The incorporation of these two compact components in the instrument design resulted in an instrument which was more functional for a plant laboratory or field environment. After two field evaluations and laboratory optimization, numerous modifications were made which resulted in the final prototype instrument shown schematically in Figure 8. We eliminated the pierced mirror and instead collected the plasma emission using a fiber optic probe mounted at one side of the sample stage, 40° from the axis of the laser beam. The Ocean Optics spectrometer was equipped with a 3600 groove/mm grating and 25 μm entrance slit with a spectral window of 220-310 nm. Previous studies had identified numerous spectral lines in this region for the elements of interest, P, Si, Mg and Fe. A single axis motorized stage was used which automatically translated the sample during the measurement. Although this spectrometer could not be gated to discriminate against the early continuum background emission, it was found that the S/N and precision were adequate and that with careful alignment of the fiber optic probe, the signal contribution due to continuum emission could be effectively minimized.

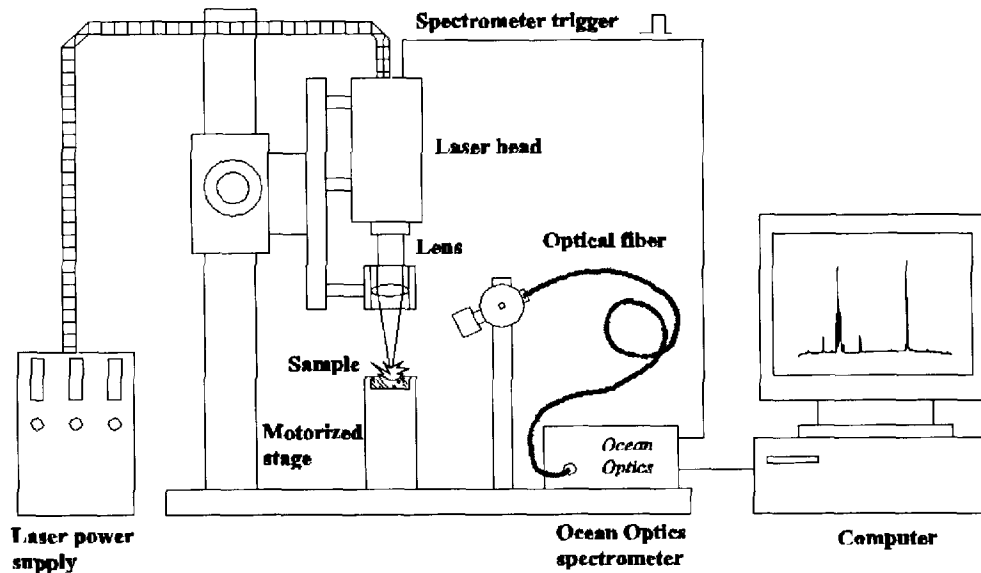


Figure 8. Schematic of the Compact LIBS Instrument.

Two sample presentation techniques were evaluated. The original approach, using pressed pellets, was not only time consuming, but also appeared to limit the precision due to the sensitivity of the laser interaction to the morphology of the pressed sample surface. Signal intensities would vary 20-40% just due to variations in the amount of pressure used to produce the pellet in the pellet press. The quality of the pellet surface was also very sensitive to the moisture content of the sample and the degree of mixing with the binder. We compared the pellet technique with simple distribution of the powdered sample on a double-sided adhesive tape (Scotch 3M) mounted on a microscope slide. Figure 9 shows typical calibration plots obtained for Si using both methods. The tape method proved to be just as reliable and a great deal faster and was adapted for all further studies.

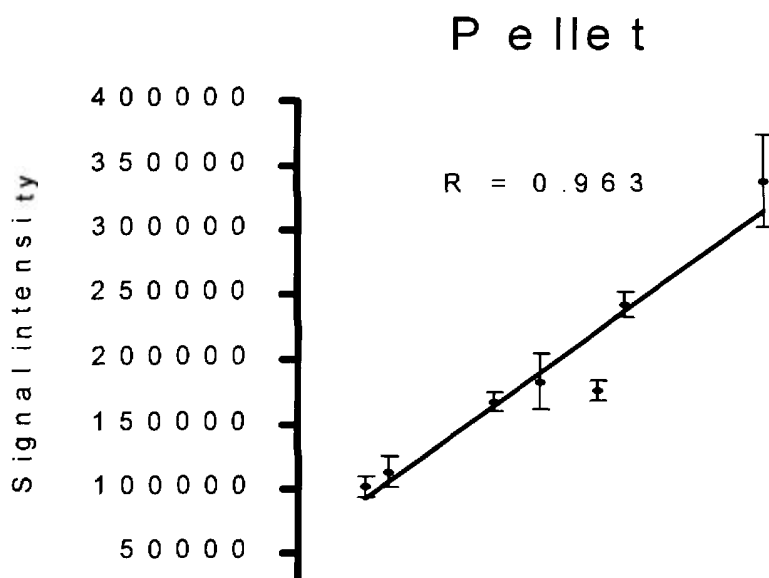


Figure 9. Comparison of Pellet and Tape Sample Presentations for Si Calibration Function.

DETERMINATION OF RANGE OF LINEARITY OF CALIBRATION PLOTS FOR ANALYSIS OF Fe₂O₃, SiO₂, P₂O₅ AND MgO IN SYNTHETIC CALCIUM CARBONATE SAMPLES

Most of the concentrations of species of interest in phosphate ores range from 0.1 to 40%. One has to use care in selecting the analytical lines for such high concentrations and the range of linear response may not extend over all concentrations of interest. In order to characterize the range of linear response for pure samples (not diluted in binder and pressed into pellets), a study was made by constructing calibration curves with synthetic standards made from Fe₂O₃, SiO₂, P₂O₅ and MgO prepared in a calcium carbonate matrix.

Samples were prepared by blending pure Fe_2O_3 , SiO_2 , P_2O_5 and MgO in CaCO_3 . The samples were prepared by weight and homogenized in a shaker mill for 20 min. Sample presentation was on the double-sided adhesive tape, on microscope slides. The tape was buried in sample, pressed gently with a clean microscope slide, held vertical and tapped on the bench to remove excess material. This procedure left a smooth, thin layer of sample on the surface of the tape.

Calibration plots were generated using the portable LIBS instrument shown in Figure 8 and a customized software which automatically determines the background in the vicinity of selected spectral lines (a total of eleven lines for the four elements under study), averages the data from several laser shots (10 in the present experiment), plots the

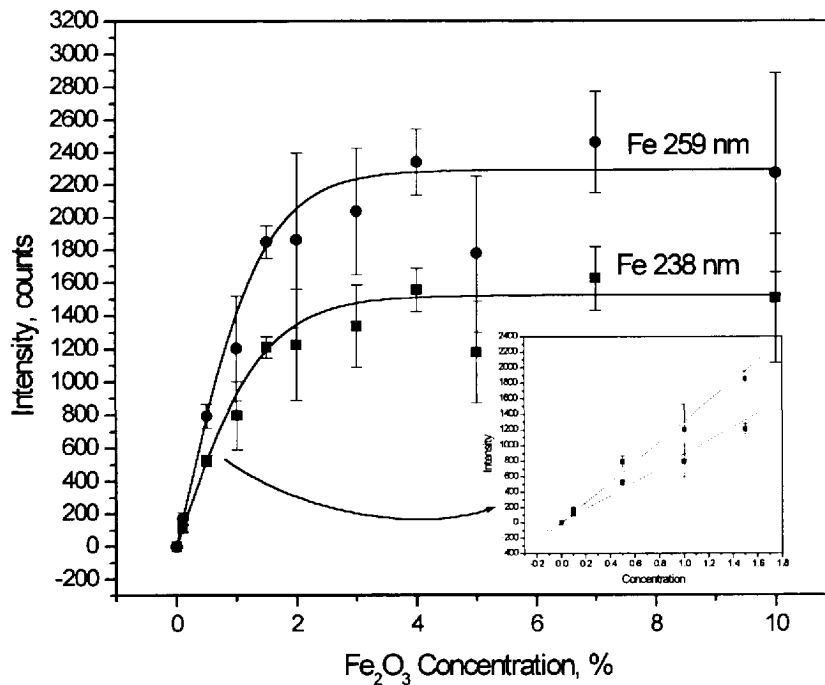


Figure 10. Calibration Curves for Synthetic Fe_2O_3 Standards.

results and fits a function to the data. Three Si lines were evaluated, at 288.158, 250.690 and 251.6 nm (the last being an unresolved triplet). All exhibited a linear response up to an SiO_2 concentration of approximately 13%. Four Mg lines were studied, two atomic lines at 285.213 nm and 293.654 nm and two ionic lines at 292.875 nm and 277.8 nm (an unresolved triplet). The two atom lines exhibited linear response up to about 0.8% MgO while the two ionic lines were linear up to about 1.8-2% MgO . Two phosphorus lines were evaluated at 253.401 nm and 255.328 nm. These have similar transition probabilities and exhibited similar linear response, up to a P_2O_5 concentration of 5-6%. Two strong ionic lines were studied for iron, 259.940 nm and 238.204 nm, both exhibiting linear response for Fe_2O_3 to about 2%.

Figures 10-13 show the calibration functions for Fe_2O_3 , SiO_2 , P_2O_5 and MgO , respectively. These results indicate that, with careful choice of analytical line, the upper concentration limits for these four compounds are 2%, 13%, 6% and 2%, respectively.

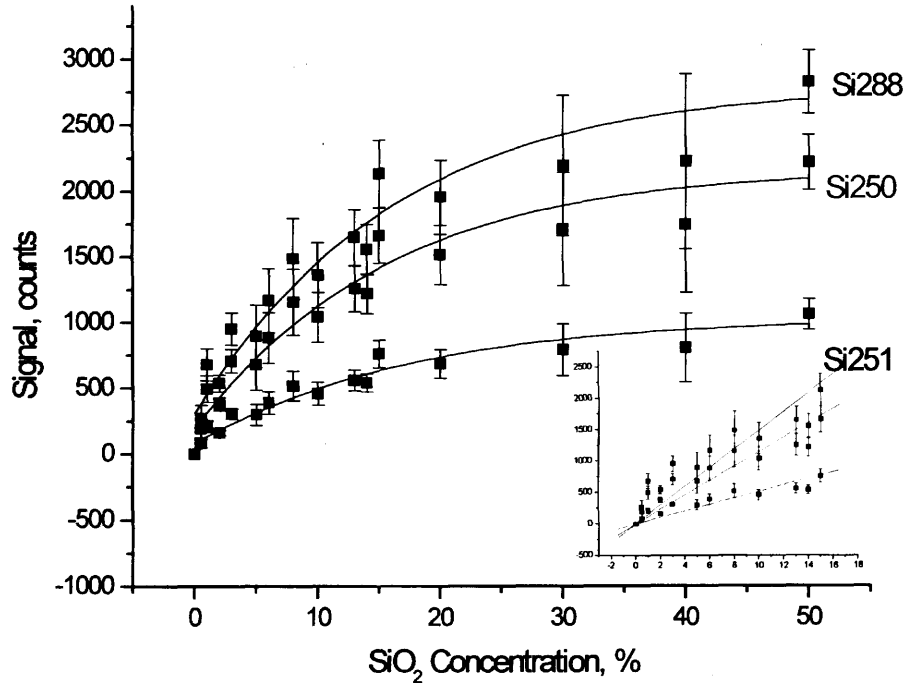


Figure 11. Calibration Curves for Synthetic SiO_2 Standards.

These are reasonable for the concentrations of interest in many ore samples which were studied, except for P_2O_5 which may fall in the range of 20-30%. Some samples also may contain up to 30% SiO_2 , which also is well above the range of linear response for this compound. We have noted that, when constructing calibration functions with natural phosphate ore samples, the ranges of linearity tend to be somewhat greater than those obtained with these synthetic samples. These results therefore indicate the minimum ranges of linear response which can be expected when using these spectral lines.

Within the linear range of response, the relative precision of these measurements is typically about 15-20%. We evaluated possible sources of uncertainty in the spectral line intensities and found that the precision is mostly limited by the erratic nature of the laser-material interaction. Figure 14 shows the intensity fluctuations in the laser intensity for three series of 50 laser shots. As is typical for this type of Nd:YAG laser, the uncertainty is about 1%.

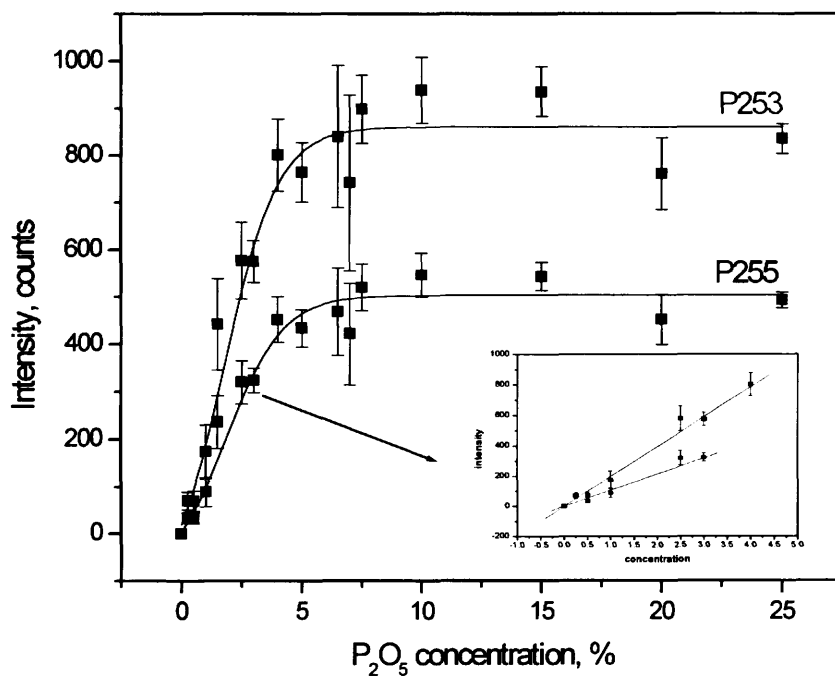


Figure 12. Calibration Function for Synthetic P_2O_5 Standards.

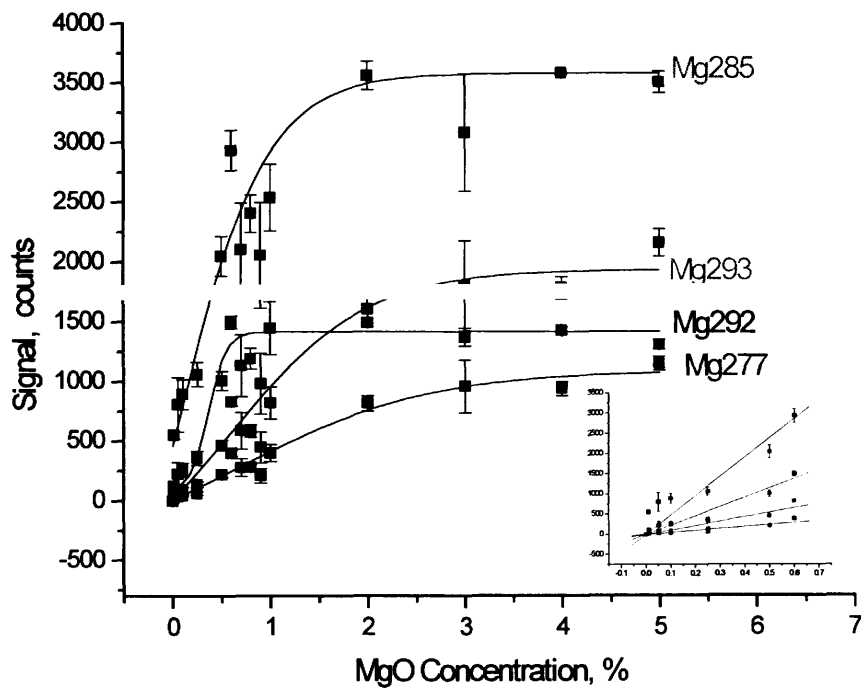


Figure 13. Calibration Curves for Synthetic MgO Standards.

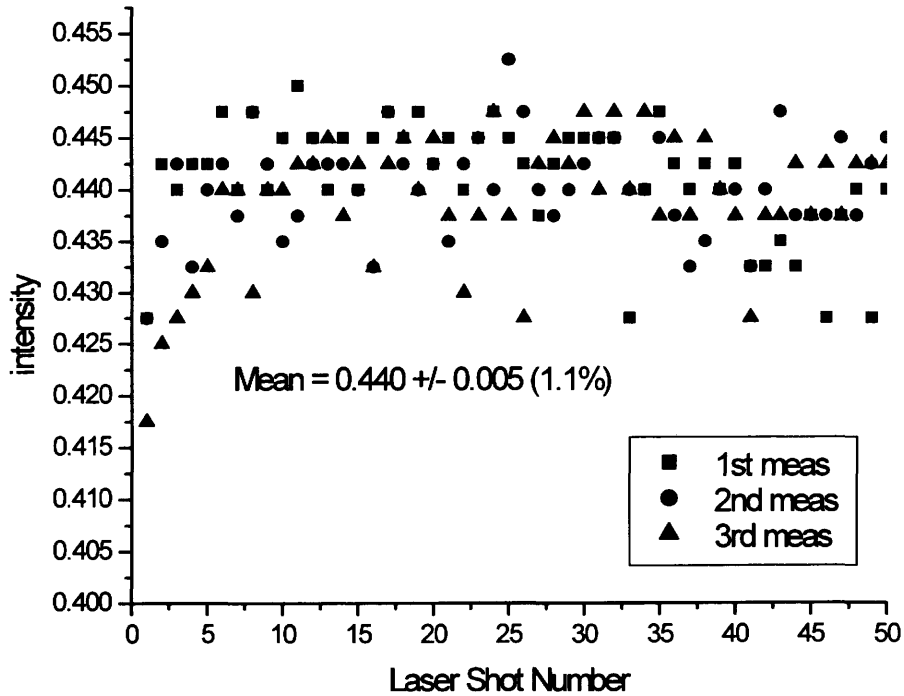


Figure 14. Intensity Fluctuations in the Nd:YAG Laser Output.

FIELD EVALUATIONS

A prototype instrument was delivered to CF Industries, Hardee Phosphate Complex, Wauchula, FL, for evaluation in August, 1999. This instrument had manual sample translation and used the earliest, most primitive version of the operating software. A set of ten standards was developed, consisting of several certified materials and a series of powdered composite samples which had been analyzed by the CF Laboratory. Initial studies were limited to the determination of P, Fe and Mg. The selected standards and their compositions are listed in Table 3.

Table 3. Initial Set of Ten Phosphate Ore Standards.

Std. #	Std. Identity	Concentrations		
		P ₂ O ₅	Fe ₂ O ₃	MgO
1	UF #2	29.22	1.45	0.5
2	NIST 120c	33.34	1.02	0.32
3	NIST 21	33.36	1.09	0.33
4	NIST 22	33.06	1.1	0.35
5	7/18	28.71	1.76	0.62
6	7/19	28.13	1.55	0.57
7	7/20	28.34	1.47	0.63
8	6/6	28.65	1.76	0.75
9	6/7	28.95	1.76	0.76
10	6/8	28.96	1.7	0.61

The standards and samples were deposited on double-sided adhesive tape, as described above, and attached to microscope slides for analysis. Four iron lines at 238, 259, 263 and 275 nm, and one Mg line, at 285 nm were chosen for construction of the calibration plots and analysis of unknowns. Measurements were made using 10 laser probings per sample, averaging the resulting 10 spectra and using the automated background correction and peak intensity determination procedure built into a customized operating software. Table 4 summarizes the results for three unknown samples, compared against CF Laboratory analysis. Accuracies ranged from -15 to +4%.

Table 4. LIBS Results for CF Industries Samples.

	Sample 4/15/98		Sample 4/17/98		Sample 10/29/98	
	% MgO	% Fe ₂ O ₃	% MgO	% Fe ₂ O ₃	% MgO	% Fe ₂ O ₃
Average	0.78	1.34	0.78	1.77	0.42	1.40
CF value	0.835	1.58	0.75	1.71	0.43	1.53
Error, %	-6.6	-15	+4	+3.5	-2.3	-8.5

Note: Field Test August 20, 1999; 10 standards, 10 laser shots per sample.

A subsequent evaluation was made at the University of Florida using our duplicate prototype LIBS instrument. In this study, a set of 12 new samples were obtained from CF Industries as finely ground powders and previously analyzed by their laboratories. Table 5 lists the 12 samples and their compositions. The seven identified as "PC" (originating from and analyzed in the CF Plant City facility) were added to the previous 10 as standards (yielding a total of 17 standard samples) and the other five (#8-

12, ground pebble taken from other locations) were treated as unknowns. The same four lines were used for the determination of iron and two Mg lines were added, 279 nm and 280 nm. Measurements were repeated several times over a period of several days under slightly different conditions. Figure 15 shows the four resulting calibration plots for the four Fe lines and Figure 16 shows the calibration plots for the three Mg lines, using all 17 new standards.

Separate calibration plots generated using only the five ground pebble samples (#8-12) yielded calibration slopes about 20% lower than those shown in Figures 15 and 16, indicating a significant matrix effect. We conclude that the most critical factors influencing the accuracy of this technique are:

1. The use of a sufficient number of standards (15-20) of similar matrix composition to that of the unknowns;
2. Restriction of the concentration ranges to within the linear portion of the calibration function; and,
3. Optimization of the measurement itself, including use of sufficient laser probings (10-30 shots per sample) and exclusion of spectra which exhibit erratic behavior (about 1 spectrum in 10).

Further improvements in the software, especially with respect to the exclusion of the occasional erratic spectrum, are continuing and the present version of the instrument is presently installed at CF Industries with a duplicate in use at the University of Florida. The sample translation is now automated and various improvements in the software have made the acquisition of spectra and the calculation of calibration curves and results for unknowns more user friendly. Table 6 shows the results of the most recent evaluation of strict unknowns, using the established set of 17 standards.

Table 5. CF Industries Samples Used for Standards and Unknowns.

Sample #	Sample ID	P ₂ O ₅	BPL	Fe ₂ O ₃	Al ₂ O ₃	MgO	SiO ₂
1	PC 4/18	29.80	65.43	1.45	0.83	0.69	8.14
2	PC 5/17	31.1	69.29	0.97	0.95	0.42	9.02
3	PC 5/18	30.47	66.90	0.96	1.01	0.39	10.65
4	PC 6/22	28.54	62.36	1.17	0.88	0.62	12.43
5	PC 7/3	28.98	63.24	1.66	0.94	1.02	9.33
6	PC 10/27	29.35	64.45	1.41	0.94	0.87	7.7
7	PC 4/19	26.97	59.23	0.94	1.03	0.98	14.54
8	5460	19.95	43.58	2.33	1.59	2.18	26.92
9	5465	27.63	60.38	1.56	0.85	1.48	9.39
10	5476	27.39	59.84	1.87	1.12	1.77	10.57
11	5807	23.62	51.60	1.74	0.91	2.21	16.22
12	5818	18.27	39.92	2.26	1.76	2.62	21.42

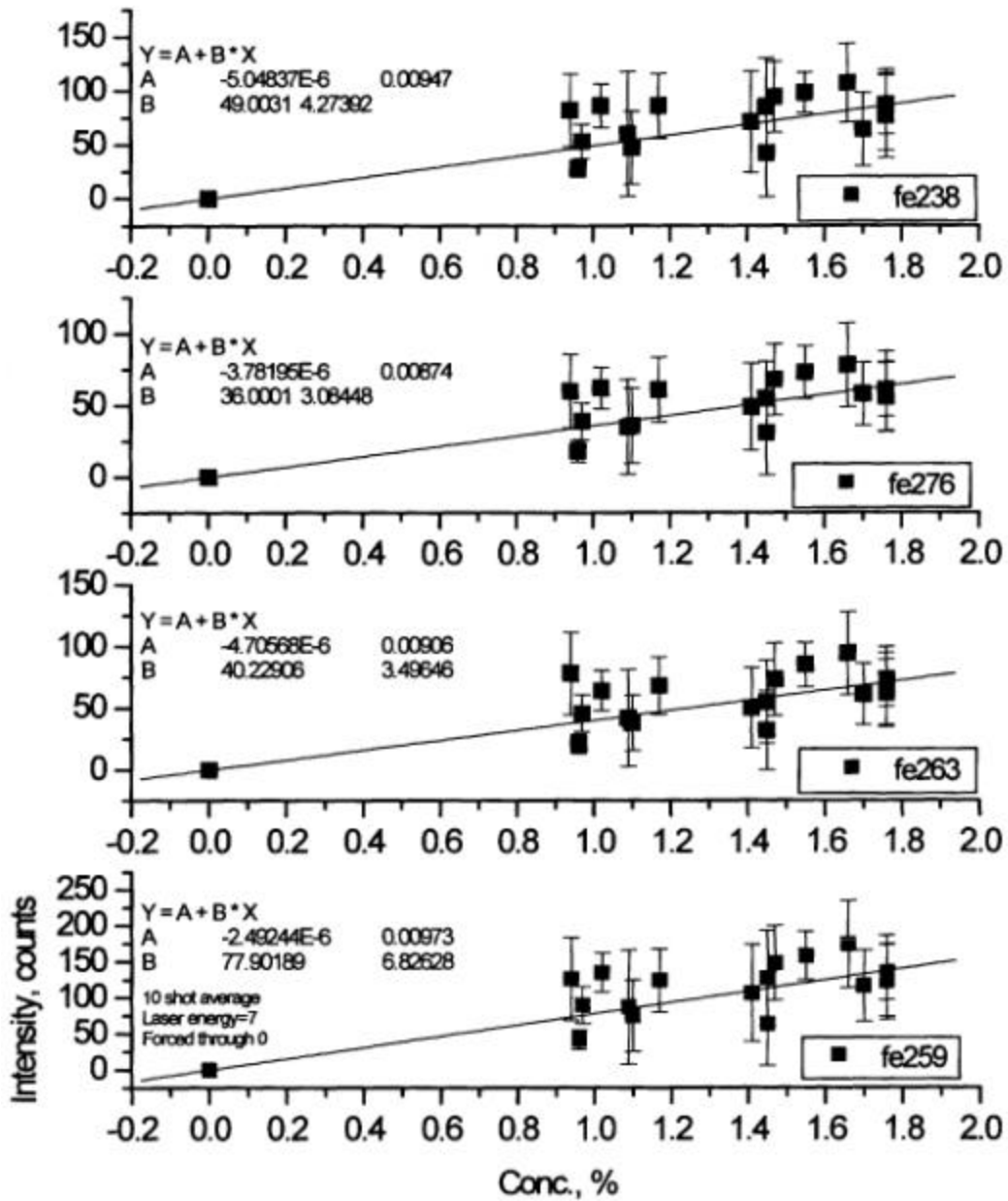


Figure 15. Calibration Plots for Four Fe Lines Using 17 Standards (CF Plant City Rock Samples).

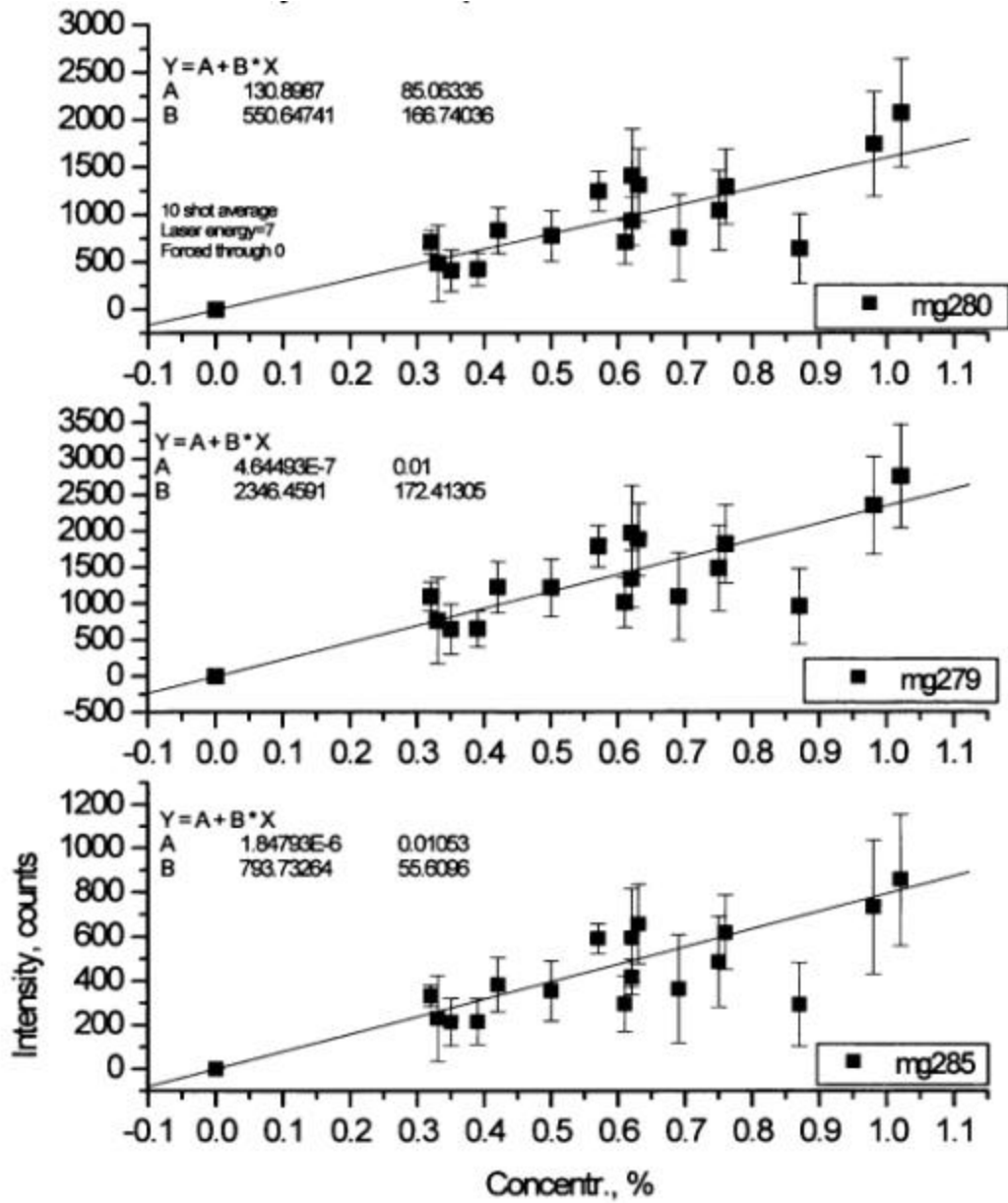


Figure 16. Calibration Plots for Three Mg Lines Using 17 Standards (CF Plant City Rock Samples).

Table 6. PortoLIBS Results Overview, CF Industries, May 3, 2000.

Unknown	CF Result % P ₂ O ₅	LIBS Result	CF Result % Fe ₂ O ₃	LIBS Result	CF Result % MgO	LIBS Result	CF Result % SiO ₂	LIBS Result
8057	28.68	24.34	1.67	1.70	1.12	1.89	8.89	15.50
8070	29.86	24.95	1.64	1.89	0.51	0.89	11.88	10.52
8075	20.32	22.60	3.34	2.97	0.70	1.25	31.96	15.90
8087	30.69	30.02	1.48	1.62	0.56	1.19	10.88	14.65
8196	19.44	19.40	3.07	3.83	1.31	2.01	34.25	25.76
Check 22	33.06	25.10	1.10	0.68	0.35	0.51	3.19	5.78

These results were obtained with the latest set of 17 standards and the new software with the calibration functions forced through zero. All samples were prepared by distributing the powdered samples on double sided tape mounted on a microscope slide, as described above. For this study all measured spectra were included in the data (e.g., none were excluded due to unusual laser-material interactions). The average accuracy ranges from 11% for P205 to 72% for MgO, with individual accuracies ranging from -50% to +112%. For ten of the 24 individual analyses, the accuracy was within 20% of the CF Laboratory value. Although we can expect some improvement in the future with better real-time statistical evaluation in the software, in general, one must conclude that even with careful selection of standards, the present technique is only capable of concentration estimates with ± 20 -30% accuracy.

CONCLUSIONS AND RECOMMENDATIONS

Laser-induced breakdown spectroscopy is capable of detecting all of the elements of interest in phosphate ores. Numerous spectral lines were found to be suitable and all could be detected within a rather narrow spectral window extending from about 220-310 nm. We found that the optimum sample presentation was simple coating of double sided adhesive tape mounted on a microscope slide. Samples must be dry and ground to a reasonably uniform particle size of ca. 100 mesh. Reliable spectra can be obtained with a compact, non-gated CCD spectrometer using a pulsed Nd:YAG laser of 10-30 mJ pulse energy (at 1064 nm). The best precision obtainable is about 10% for averaging of 10-20 laser probings on one sample. With careful choice of standards of similar composition as the unknowns, quantitative accuracy is limited to the order of 20%. This might be improved upon in the future with more sophisticated data processing and exclusion of the occasional erratic spectrum due to spurious laser-material interaction. A report on this project has been submitted for publication (Gornushkin and others 2000). Appendix A contains the operating manual for the present LIBS instrument and describes the operational procedures, sample preparation and software in more detail.

REFERENCES

- Anderson DR, McLeod CW, Smith TA. 1994. Rapid survey analysis of polymeric materials by laser induced plasma emission spectrometry. *Journal of Analytical Atomic Spectroscopy* 9: 67-72.
- Anzano JM, Gornushkin IB, Smith BW, Winefordner JD 2000. Laser induced plasma spectroscopy for plastic identification. *Polymer Engineering and Science*, in press.
- Aragon C, Aguilera JA, Campo J. 1993. Determination of carbon content in molten steel using laser induced breakdown spectroscopy. *Applied Spectroscopy* 47: 606-608.
- Casini M, Harith MA, Palleschi V, Salvetti V, Singh DP, Vaselli M. 1991. Time resolved LIBS experiment for quantitative determination of pollutant concentrations in air. *Lasers and Particle Beams* 9: 633-639.
- Castle BC, Visser K, Smith BW, Winefordner JD. 1997. Spatial and temporal dependence of lead emission in laser induced breakdown spectroscopy. *Applied Spectroscopy* 51: 1017-1024.
- Castle BC, Visser K, Smith BW, Winefordner JD. 1997. Level populations in a laser-induced plasma on a lead target. *Spectrochimica Acta B*, 52:1995-2009.
- Castle BC, Talabardon K, Smith BW, Winefordner JD. 1998. Variables influencing the precision of laser-induced breakdown spectroscopy measurements. *Applied Spectroscopy* 52: 649-657.
- Cremers DA, Radziemski L J, Loree TR. 1984. Spectrochemical analysis of liquids using the laser spark. *Applied Spectroscopy* 38: 721-729.
- Gornushkin I, Smith BW, Galbacs G, Winefordner JD. 2000. Quantitative analysis of phosphate ores using laser induced breakdown spectroscopy. *Fresenius' Journal of Analytical Chemistry*, submitted.
- Grant KJ, Paul GL, O'Neill JA. 1990. Time resolved laser induced breakdown spectroscopy of iron ore. *Applied Spectroscopy* 44: 1711-1714.
- Grant KJ, Paul GL, O'Neill JA. 1991. Quantitative elemental analysis of iron ore by laser induced breakdown spectroscopy. *Applied Spectroscopy* 45: 701-705.
- Majidi V, Joseph MR. 1992. Spectroscopic applications of laser induced plasmas. *Critical Reviews in Analytical Chemistry* 23: 143-162.

Maker PD, Terhune RW, Savage CM. 1964. In: Grivet P, Bloembergen N, editors. Quant. Elec. Proc. 3rd International Conf., Paris 1963. Vol. 2. Columbia University Press, p 1559-1576.

Moenke-Blankenburg L. 1989. Laser microanalysis. New York: John Wiley.

Radziemski LJ, Cremers DA. 1989. Spectrochemical analysis using plasma excitation. In: Radziemski LJ, Cremers DA, editors. Laser-induced plasmas and applications. New York: Marcel Dekker.

Radziemski LJ, Loree TR, Cremers DA, Hoffman NM. 1993. Time resolved laser induced breakdown spectrometry of aerosols. Analytical Chemistry 35: 1246-1252.

Raizer YP. 1977. Laser-induced discharge phenomena. New York: Consultants Bureau.

Rusak DA, Castle BC, Smith BW, Winefordner JD. 1997. Fundamentals and applications of laser-induced breakdown spectroscopy. Critical Reviews in Analytical Chemistry 27(4): 257-290.

Rusak DA, Castle BC, Smith BW, Winefordner JD. 1998. Recent trends and the future of laser-induced plasma spectroscopy. Trends in Analytical Chemistry 17: 453-461.

Smith BW, Hahn DW, Gibb E, Gornushkin I, Winefordner JD. 2000. Laser induced plasma spectroscopy for the characterization of aerosols and particulates. KONA, in press.

Zapka W, Tam AC. 1981. Probing heat diffusion after pulsed laser induced breakdown in metal vapors. Journal of the Optical Society of America 71(12): 1585.

APPENDIX

PortoLIBS

**A COMPACT LASER-INDUCED BREAKDOWN SPECTROMETER FOR
RAPID ANALYSIS OF PHOSPHATE ORES**

OPERATING MANUAL

VERSION 1.3

MAY 2000

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Laser Safety

The Nd:YAG laser used on the instrument emits about 20 mJ of light at a wavelength of 1064 nm, invisible to the eye. This laser is a Class 4 laser and therefore, its output beam is, by definition, a safety and fire hazard. Precautions must be taken to prevent accidental exposure to both direct and reflected beams. The pulse duration is quite short, about 5 ns, and therefore the peak power is several million watts. This is sufficient to seriously damage the eye. It is therefore extremely important that care be taken to avoid any reflection of the laser beam away from the sample area. A few important safety rules:

1. Always keep the green laser shield in place.
2. Always wear the YAG laser safety glasses while working with the instrument.
3. Limit access to the laboratory by unaware visitors during measurements.
4. Always turn the laser off while changing the sample.
5. Do not wear reflective jewelry below the wrists while using the laser.
6. When not in use, remove the security key from the laser to prevent unauthorized use.
7. In any emergency, the laser can be stopped rapidly by pushing the large red shut down button on the front of the power supply
8. Do not attempt to adjust, move or modify any of the connections between the laser head and the laser power supply.

Sample Preparation

The preparation of samples, or standards, for analysis simply involves attaching some powdered sample to a double sided tape mounted on a microscope slide.

- Prepare a microscope slide by attaching a 1 inch length of 3M double sided tape (3M #110 ½ Mounting Tape) to one end of the slide. Label with felt pen.
- Remove the protective strip from the top of the tape and deposit enough powdered sample to completely cover the tape.
- Gently press the sample against the tape with a spatula or a clean microscope slide to insure uniform adhesion.
- Tap the microscope slide on the lip of a waste beaker to remove all the excess sample. The surface of the tape should be coated with a thin layer of sample. Tap firmly enough to remove any large clumps of material.

Sample Measurement

1. With the laser OFF place the sample slide onto the sample stage in the milled slot, flush with the lip at the end. When the laser fires, it should strike the tape somewhere near the center of the tape near one end. You can move the sample around as necessary to expose a region of fresh material to the laser.
2. To take a measurement, press the RUN button on the laser power supply (laser settings: 6.0 energy, 1 Hz repetition rate, Q-switch on) and simultaneously switch on the stage motor drive (small motor control switch on the front of the instrument). After about 3 laser shots, use the mouse or the keyboard to begin data acquisition. The software will record the set number of laser shots and display the resulting spectra. At the conclusion, press the RUN button on the laser again to turn the laser off. Watch the sample stage motion. A limit switch will stop the motor at either extreme of direction. If this happens during a measurement, quickly reverse the motor direction with the motor control switch.
3. Continue taking measurements for all the standards followed by the unknowns. The display will indicate the number of the sequential data acquisition in the upper right corner of the screen. On any individual run, you have the option to repeat the measurement if for any reason you suspect the result (for example if the motor reached the limit switch during the run and stopped and you didn't notice).
4. Always be sure the laser is OFF during the insertion and removal of samples.

The prepared samples can be used at least several times. You can see on the sample surface where the laser has removed material. Try to find a uniform location on the tape surface where fresh sample remains. After 3 or 4 measurements a sample can be revived by gently rubbing the tape surface with a clean finger to redistribute the material on the tape. With care, a standard sample can probably be used for 6-10 measurements.

General Operational Procedure

- Power the computer if it is not already on.
- Power the laser with the key switch. Set power to 6.0, Q-Switch "on", Rate 1.0. Normally, these setting will come up automatically as the default values. After a few moments of warm up, the "run" button can be used to activate the laser output.
- Open the software (see notes below)
 - Short Form Software Startup:
 1. Double Click the portoLIBS icon
 2. Confirm the following settings:
 - Trigger external
 - Range 230-310 nm
 - Options: Analysis
 - Use Library: NO
 - # Acq.: 10 is typical
 - # Stds.: 17 is the current set
 - # Unks: as desired
 3. Go
 4. Go will prompt you to enter or verify concentrations of standards. Choose
 - Use Existing Standards? YES
 - Select File (currently "CF Calibration" for the set of 17)
 - View this file and close it
 5. Insert the first standard, start the laser and click "start" or go to take the first set of data.
- Measure sequentially the standards (typically about 10, presently we have defined a total of 17), followed by the unknowns. Observe the quality of the spectra as you go along, repeating as required, deleting outliers as required, etc. Deletions can also be made anytime after the conclusion of the measurements, working with the saved files.
- At the end of the run, press Calculate to view the calibration plots. Press New to view the next plots. Scroll through the calibration plots and examine them for linearity and good fits. Outliers can be removed and the plots forced through zero, if desired. Forcing through zero appears to be a good idea. Once you have viewed all of the calibration plots, you will notice that all of the analytical results are available in a small table in the lower right corner of the screen.
- If you wish to preserve the data, go to file menu and save the spectra. This is a good idea in general. The spectra can be deleted later, once the results are secure.

- Once the calculations are finished, go to Save Results and choose a directory in which to save the results. Save the results.
- The tabulated results can then be displayed as a text file. It will include the calculated concentrations for each unknown for each elemental line used. When several lines were used, the results can be manually averaged, watching for outliers which might be discarded.

Data Acquisition and Data Processing Routines

The PortoLIBS mini-spectrometer is designed for fast analysis of powdered samples. A tightly focused laser beam induces a breakdown on any solid sample. The breakdown results in a bright, high temperature plasma. The plasma consists of atoms and ions of the sample and the surrounding air. The atoms and ions are optically excited in the plasma and their relaxation yields featured emission spectra which are characteristic of the sample constituents. The emission is captured with an optical fiber and transported to the diffraction grating mini-spectrometer. A linear photodiode array serves as a light detector. Data are digitized and represented as two-dimensional arrays. One dimension is an ordering number of a single photodiode (which corresponds to a particular wavelength) and the second dimension is the intensity of light on this photodiode pixel. Data are further processed with a computer using a customized software.

A) General Software Description

A program for statistical data analysis is written in Visual Basic 6.0. The software offers the following options to an operator: (i) choice of appropriate operational parameters for the spectrometer (trigger type, spectrometer channel, display option, etc.); (ii) choice of parameters for analysis (number of repetitions, number of standards, number of unknowns); (iii) choice of elements and lines to be detected; (iv) display of current spectra; (v) linear regression calibration plot; and (vi) calculation of concentrations. The regression plot and calculated concentrations are instantly displayed on a monitor. The output data are saved and stored in a computer.

B) Operational Instructions

In *Windows*: double click on the PortoLIBS icon.

The *Main Menu Window* will be displayed with the following options.

1. Spectrometer Controls

Trigger

Auto- spectrometer starts from the internal trigger. Check this option if you want to check that the spectrometer and the software are functional or if you work with spectral libraries.

Ext- spectrometer starts from the external trigger (laser). This is the normal operational mode for a real-time data acquisition. Should be checked if you work with samples.

Range, nm

230-310- working spectral range. It should always be checked.

200-800- auxiliary spectral range. Low resolution window. You can use it if you want to see a visible part of the plasma spectrum. Never use this window for analysis.

2. Acquisition Controls

Options

Display- check this option if you just want to see how spectra look like. Spectra will be displayed on the monitor but no analytical parameters, like concentrations, spectral line positions or intensities, will be associated with these spectra.

Analysis- check this option if you work either with real samples or with library spectra. Standard concentrations and certain (chosen *a priori*) spectral lines are associated with the spectra. The *Analysis* option results in construction of calibration plots and determination of concentrations.

Use Library

Yes- check this box if you work with spectra stored in the computer

No- check this option if you work with samples.

3. Analysis Controls

El/Line button. Upon pressing this button, *Element/Line Menu Window* is displayed.

This Menu allows you to chose elements and their corresponding spectral lines from the offered list of Elements/Lines. Shown checked are the last used

elements/lines; they will be used as a default if you choose to **Cancel** this Menu. You can un-check some of the elements/lines and check new ones. After pressing the **OK** button they will be moved to the right text box and will be used as a new default set. You can now verify old or introduce new concentrations for your standards. Follow the prompts after pressing the **Enter Conc** button. Do not use Internal Standard option-it is not functional yet.

In the *Element/Line Menu Window* you have two other options. The menu button **Add** allows you to introduce a new Element/Line combination to the list of available elements/lines from the *Add Element/Line Menu*. After you introduced the combination, an Excel table with pixel values will show up. You have to introduce pixel values into the empty column of this table corresponding to the new spectral line. If you don't know those values yet, introduce some fake numbers; you can correct them later. Save the Table to
c:\PortoLIBS\Pixels\Pix.xls.

The menu button **Remove** opens the *Remove Selection Menu* from which you can discard undesirable element/line combinations. Pixel values for remaining element/line combinations will be adjusted automatically.

The **Conc** button displays either an existing or new Excel Table into which you introduce concentrations for standards. You can also edit this table externally using Microsoft Office Excel. The **Conc** button is equivalent to the **Enter Conc** button described above. Save the Table to *c:\PortoLIBS\Concentrations* under a desired name.

The **Pixels** button displays pixel positions for each analytical line from the list of available elements. Peak line intensities (raw *Peak*) and two values for background-to the left and to the right from the line -(*Left bkg and Right bkg*) are used for calculations. You can introduce new elements/pixels columns from outside the PortoLIBS software using Microsoft Excel but the better option is to use the **El/Line-Add** option as described above. You should not check pixel values every time prior to the analysis unless you introduce a new element/line combination.

#Acqs- number of spectra from the same sample to be averaged. We normally use 10. The minimum number is 2, the maximum is 50. This number is invalid if you work with spectral libraries: in this case a number of repetitive spectra is determined automatically.

#Std- introduce number of standards to be used for calibration (up to 50).

#Unks- introduce number of unknowns for analysis (up to 50).

4. Spectra Graph Controls

Go button starts taking data either from the spectrometer or from the library.

Before starting, specify which option you want to use: display or analysis and spectrometer or library in the *Acquisition Controls* window.

Repeat button allows you to repeat the last measurement if for whatever reason (strange looking spectrum, unusually high or low intensity, etc.) you do not like it.

Chk Line button allows you to check positions and intensities of spectral lines from different elements. Double clicking on an element name (Fe, Si, Al, etc.) will superimpose a marker on the most intense lines of elements on your current spectrum.

Recall Sp button. You can take a close look at every spectrum which you detected with the spectrometer. Pressing this button displays all acquired spectra names. If you want, you can delete any spectrum you don't like. The results will be automatically recalculated. This can be done between consecutive measurements or afterwards, when the calibration plot has already been built.

5. Regression Graph Controls

Calculate button starts calculations. As a result, a linear calibration plot for one element/line combination is displayed along with values for concentrations in the unknowns which are determined using this line.

Next button shows data for a next element/line combination.

Prev button returns data for the previous combination.

Force 0 option adds a (0,0) standard and forces the calibration plot through the origin.

6. Common Controls

Toss Std button allows you to remove any standard and recalculate the data. This may be useful when you have one or more obvious outlier on the calibration plot.

Initial Cfg button restores the initial data as they were before any transformation. This is a simple *Undo* option.

Clean All button makes the software ready for a new data acquisition cycle without quitting the program. However, it is safer to exit the program and to start it again before measuring every new set of standards.

Exit button terminates the program and returns you to *Windows*.

7. Calibration text window

Displays parameters of a calibration plot. A and B are the coefficients of a least square linear fit function; chi2 is the chi-square fitting parameter being minimized, and Q is the goodness of fit (the closer to unity the better).

8. Analysis text window

Displays the results of calculation of concentrations in tinknowns using the different element/line combinations.

9. Menus

File

-Save Results saves X-Y values for calibration plot and concentrations in unknowns into the chosen Directory/File. By default, the Directory/File path is set to *c:\PortoLIBS\Results*. The data are saved in an ASCII code. If you forgot to save your results, there is a backup file *Results.txt* in the same directory.

-Save Calibration saves only X-Y values for the calibration plot. A calibration file may be useful when one wants to mn only unknown samples without repeating the whole calibration procedure. At present, this option is not available. The default path is *c:\PortoLIBS\Calibration Plots*.

-Save Spectra allows you to save all spectra taken in a current run. The spectra are arranged into files which are named in correspondence with a standards/unknowns set. You just have to assign some specific identification name to this set of spectra which later will permit you to distinguish it from other sets. These spectra compile the spectral library which later can be used and processed with a computer. The default path is *c:\PortoLIBS\RecallSpectra*.

To use the spectra as a library, it is convenient to move them to *c:\PortoLIBS\VBRecallSpectra*.

-Print sends the current page to a printer.

Spectrometer

-Channels. This allows you to change coefficients for spectrometer wavelength calibration. These coefficients are specific for each Ocean Optics spectrometer. Do not change the coefficients unless you replace your model of Ocean Optics spectrometer with another model.

View

-Scale. Three options (*Auto*, *Manual*, and *Full*) are available which allow you to scale the spectra graph. Do not try to scale the calibration graph with these options--they are not applicable there.

-Grid. Displays X and Y grid lines in the spectra graph window.

-Back Color, Fore Color, Graph Color, Mask Color, Grid Color - change colors of corresponding objects.

Spectra

-Recall. Does the same as the **Recall Sp** button described above.

-Show Lines. Does the same as the **Chk Line** button.

-Show Pixels. Shows pixel positions on the spectra graph where peak and background intensities are taken for calculations.

Analysis

-Set Element/Line. Does the same as the **El/Line** button (see above).

-Set Concentrations. Duplicates the **Conc** button in the main window.

-Set Pixels. Duplicates the **Pixels** button.

-Remove Standard. Calls for the same procedure as the **Remove** button in the El/Line submenu.

-Add Standard. Not functional.

-Use Old Calibration Plot. Not functional.

10. Troubleshooting

1. Avoid pressing buttons in a random fashion: the software is not fully protected against unpredictable operator's actions. Know exactly what you are doing at each step.
2. If an error is generated, the software will terminate automatically; you just have to restart it.
3. In all other cases, please contact us:

Ben Smith: bwsmith@ufl.edu 352-392-8180

Igor Gornushkin: igorg@ufl.edu 352-392-0792.

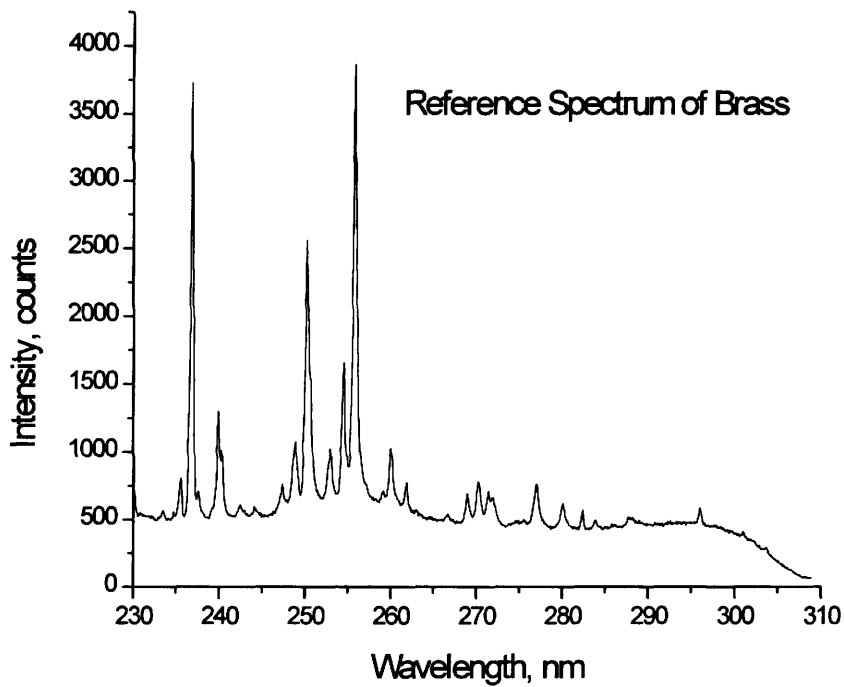
Final Standard Set

May 4, 2000

Std#	Sample Origin	%P ₂ O ₅	%Fe ₂ O ₃	%MgO	%SiO ₂
1	PC 04/18/98	29.80	1.45	0.69	8.14
2	PC 05/17/98	31.10	0.97	0.42	9.02
3	PC 05/18/98	30.47	0.96	0.39	10.65
4	PC 06/22/98	28.54	1.17	0.62	12.43
5	PC 07/03/98	28.98	1.66	1.02	9.33
6	PC 10/27/98	29.35	1.41	0.87	7.70
7	PC 04/19/98	26.97	0.94	0.98	14.54
8	5460	19.95	2.33	2.18	26.92
9	5465	27.63	1.56	1.48	9.39
10	5476	27.39	1.87	1.77	10.57
11	5807	23.62	1.74	2.21	16.22
12	8174 +3 pebble	12.55	1.70	1.76	53.80
13	5799 +3 pebble	18.43	1.02	4.98	18.26
14	8062 pebble	18.71	1.01	1.08	38.28
15	8145 pebble	26.86	2.14	0.94	16.32
16	8081 pebble	29.74	1.77	0.61	8.20
17	8237 pebble	31.24	1.34	0.34	8.71

Performance Check Spectrum

Using the brass "microscope slide" a spectrum similar to this should be obtained.



PortoLIBS Recent Results Overview

May 3, 2000

Unknown	CF Result P₂O₅	4/19 Run (19 standards)	5/2 Run (19 standards)	5/3 Run (19 standards)	Final Std Set (17 standards)
8057		26.25	25.34	24.62	24.34
8070		31.51	29.1	25.19	24.95
8075		24.31	23.8	22.46	22.60
8087		33.22	32.2	30.4	30.02
8196		23.43	22.2	19.5	19.40
Check 22		29.48	29.45	25.5	25.10
	CF Result Fe₂O₃				
8057		1.60	1.50	1.69	1.70
8070		1.88	1.74	2.00	1.89
8075		4.00	3.43	2.96	2.97
8087		2.08	2.05	1.61	1.62
8196		3.76	3.57	3.80	3.83
Check 22		0.97	1.10	0.68	0.68
	CF Result MgO				
8057		1.89	1.80	1.81	1.89
8070		0.66	-----	0.88	0.89
8075		1.35	1.51	1.22	1.25
8087		0.85	0.65	1.17	1.19
8196		2.01	3.00	1.98	2.01
Check 22		-----	-----	0.51	0.51

	CF Result SiO₂	4/19 Run (19 standards)	5/2 Run (19 standards)	5/3 Run (19 standards)	Final Std Set (17 standards)
8057		13.77	9.23	15.54	15.50
8070		11.01	-----	10.55	10.52
8075		24.26	24.97	15.93	15.90
8087		15.69	14.01	14.68	14.65
8196		36.92	44.95	25.81	25.76
Check 22		-----	-----	5.79	5.78