Development of a method for automated quantitative analysis of ores using LIBS ☆

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Abstract

This paper reports the development of a method for real-time automated quantitative analysis of mineral ores using a commercial laser-induced breakdown spectroscopy instrument, TRACER^{TM} 2100, fitted with a recently developed computer controlled auto-sampler. The auto-sampler permits the execution of methods for performing calibrations and analysis of multiple elements on multiple samples. Furthermore, the analysis is averaged over multiple locations on each sample, thus compensating for heterogeneous morphology. The results for phosphate ore are reported here, but similar methods are being developed for a range of ores and minerals. Methods were developed to automatically perform metallic element calibrations for supplied phosphate ore samples containing known concentrations of the following minerals: P_2O_5, CaO, MgO, SiO_2 and Al_2O_3. A spectral line for each desired element was selected with respect to the best combination of peak intensity and minimum interferences from other lines. This is a key step, because of the observed matrix dependence of the technique. The optimum combination of the time interval between the laser firing (plasma formation), signal detection, and the duration of the optical detection was then determined for each element, to optimize spectral line intensity and resolution. The instrument was capable of analyzing the required elements in the phosphate ore samples supplied with 2–4% relative standard deviations for most elements. Calibrations were achieved for P, Ca, Mg, Al and Si with linear regression coefficients of 0.985, 0.980, 0.993, 0.987 and 0.985, respectively. Preparation and analysis time for each sample was less than 5 min. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the key goals of the United States National Mining Association strategy is to develop technologies for superior exploration and resource characterization. Resource characterization can be improved by performing direct analysis of the ore during the extraction process in order to avoid low-grade dilution. Presently no field compatible instrument is available at the mine site to provide reliable analysis in real-time for grading the ore during the extraction process. This problem has been identified as an important concern by many open-pit mining organizations. Significant savings in processing costs and energy use can be achieved by developing an instrument for on-site element analysis enabling the operators to selectively extract the highest quality ore in real time. Laser induced breakdown spectroscopy (LIBS) is an important new analysis technology that permits fast, direct, inorganic analysis with minimal sample preparation [1,2].

Presently, most surface mining operations must rely on either laboratory-based analysis or expensive, massive, centrally located instruments, such as neutron activation analyzers, to monitor the extraction process. This requires samples to be collected, transported to the instrument, analyzed, recorded, and the data transmitted back to the pit location. This process is slow, subject to numerous errors, and does not support real time management of the extraction process. The US Department of Energy, in conjunction with the US National Mining Association, is sponsoring a project to develop methods for the real-time anal-

ysis and grading of ore at the mine site. The work reported in this paper focuses on developing the necessary analytical methods and demonstrating the feasibility of rapid analysis of phosphate ores at the mine site using a currently available commercial laser induced breakdown spectroscopy instrument, the TRACER™ 2100, fitted with a newly developed, automated and programmable multi-sample positioning stage.

2. Experiment

2.1. Samples

A series of known composition phosphate ore samples were supplied by the Simplot Smokey Canyon Mine to assess the viability of using the TRACER™ 2100 system to quantify the concentration of the following desired elements: P, Ca, Mg, Si, Al and C. Seven samples with the reported compositions, shown in Table 1, were supplied. In addition, a number of selected US Geological Survey (USGS) standard rock samples, with accurately known compositions, were used to supplement the mine-supplied samples to add accuracy and dynamic range to the calibrations.

2.2. Equipment and technique

The commercially available TRACER™ 2100 laser element analyzer, a LIBS instrument manufactured by APTI, was utilized for this experimental work. The instrument utilizes a pulsed Nd:YAG laser that ablates the sample, located in

Table 1
Supplied samples and reported concentrations (ND, not determined)

Sample	P_2O_5 %	Al_2O_3 %	MgO%	CaO%	SiO_2 %
SC 30-9	17.3	4.2	0.3	25.10	21.7
SC 38-4	19.85	2.66	1.74	ND	11.57
SC 12-9	21.12	1.93	0.43	30.20	3.92
SC 30-2	22.89	2.25	0.73	39.60	16.3
SC 17-5	24.49	2.69	0.25	34.20	16.5
SC 18-6	26.65	2.83	0.34	38.60	17.7
SC 17-1	29.67	0.90	0.85	44.50	5.14
SC 33-1	32.93	1.17	0.23	ND	6.21

Table 2
TRACER™ 2100 specifications

Laser	
Wavelength	1064 nm
Peak power	40 MW (5-ns pulse)
Max pulse rate	10 pulse/s
Pulse width	< 7 ns
Spectrometer	
Type	Czerny-Turner
Bandwidth	190−800 nm
Grating	2400 l/mm 1800 l/mm
Resolution	2 Å
Coverage	65 nm
Detector	
Intensified CCD	1024×128 pixels
Readout	1 MHz
Gate resolution	< 0.1 s
Quantum efficiency	Peak 16%, typical 14%
Spatial resolution	50 μm

an enclosed sample chamber, and produces a plasma fireball. A spectrograph collects the optical plasma illumination by means of fused-silica optics and steering mirrors [3]. The spectrum is then recorded on an intensified CCD detector, while instantaneous quantitative element analysis and display are accomplished through proprietary embedded software. The instrument is capable of displaying a full spectrum scan from UV to near IR (180−800 nm), or a specified spectral window of 30 nm. (Complete TRACER™ 2100 specifications are furnished in Table 2.)

Full-spectrum scans are best suited for qualitative analysis and element identification, whereas the small spectral segment examination is recommended for quantitative analysis based on a specific element spectral line. The technique is centered on identifying a spectral line, as well as gate delay (time in microseconds between plasma formation and emission detection) and width (time duration, in microseconds, for emission detection) parameters that provide a clear peak despite the presence of interfering spectra. The selected line must be associated only with the presence of the element in question, and therefore, its atomic concentration [4]. Other variable parameters that affect precision are laser power, repetition rate, number of shots, and number of spots sampled.

To provide for analysis of multiple sampling locations on any given specimen (to account for heterogeneities), as well as multiple sample testing, the instrument was fitted with a newly developed servo-controlled, sample positioning stage that accommodates 18 13-mm-diameter by 1−3-mm-thick pellets. The programmable stage automatically positions the beam on the desired locations of each sample, allows the required number of shots at each position, and then moves to the next sample. The TRACER™ 2100 instrument and the inside of the sample chamber showing the automated stage are shown in Fig. 1.

2.3. Instrument performance verification

Before initial experimentation began, the

Fig. 1. TRACER™ 2100 instrument and the inside of the sample chamber showing the automated multi-sample positioning stage.

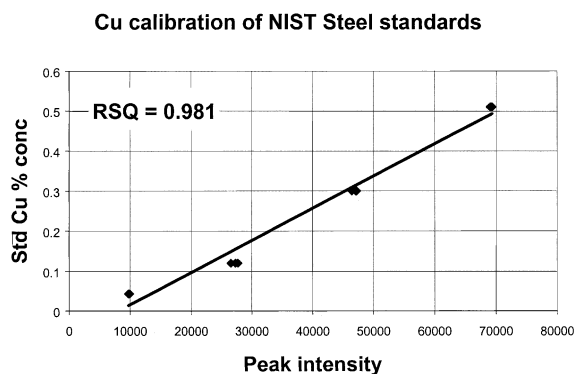**Cu calibration of NIST Steel standards**

Fig. 2. Cu calibration in NIST steel standards.

TRACER™ 2100 was put through a series of known tests to verify initial operating conditions of the machine and check for proper sample position and operating parameters.

The first test performed was the calibration of Cu in National Institute of Standards (NIST) steel samples, with a dynamic range of 0.0013−0.46 weight percent (weight percent concentration will be referred to as wt.% onwards). These samples are used to provide a homogenous medium to baseline the TRACER™ 2100. On a fully functioning machine the results of this test should yield a minimum linear regression coefficient (RSQ) value greater than 0.96 and minimum relative standard deviations (R.S.D.) of 3−4% for a 25-shot run. An RSQ of 0.981 for Cu was achieved, as shown in Fig. 2, using the NIST samples, and an R.S.D. of 2.1% was recorded. Both indexes were well within the acceptable precision/accuracy criteria.

2.4. Sample preparation

Samples were prepared in the form of homogeneous, hard-pressed, dried pellets. This minimal sample preparation, accomplished in a total time, less drying, of approximately 5 min from start to finish, aimed to (a) ensure sample uniformity and rigidity; (b) increase repeatability, precision and accuracy; and (c) eliminate interference from external factors such as humidity.

Due to the fact the samples were supplied in 200-g tubs, which had settled out, the samples

were first mixed to ensure no grain size separation had occurred. Two grams of sample were then hand-ground in an agate mortar until no resistance could be felt. The better ground the sample, the higher precision results. For example, it was found that sample R.S.D. values fell on average from 8% to 3% as a result of better grinding.

One gram of each sample was then pressed at 18 000 psi for 1 min. As an optional step, the sample was then dried in an oven for 15−20 min. On average, only a drop of 0.04 g was recorded on drying. Drying did slightly improve the R.S.D., but depending on the precision required, this step may not be necessary in most cases. The measurements were then taken immediately after the preparation process. However, it should be emphasized that no response variation has been recorded in relation to elapsed time duration between sample preparation and actual measurement.

3. Results

3.1. Element calibrations

The main elements of interest in the phosphate ore study were P, Ca, Mg, Si and Al. All elemental concentrations were supplied by the mine, but were of unknown origin and accuracy. Calibrations were performed at a shot rate of 1−2 per second, with 15 shots taken on three to five sample locations on each pressed pellet.

3.1.1. Phosphorus

After examining various P spectral lines, the two most intense lines, located at 253.56 and 255.32 nm, shown in Fig. 3, were chosen as most likely candidates for calibration. Initially, the parameter settings were set as previously used on other ore samples with respect to gate delay, width, and laser energy. These settings of a 4-μs delay and 1-μs width gave good initial calibrations for P at an RSQ of 0.96. However, they yielded a poor linear response at lower phosphate concentrations (below 15%). To overcome this phenomenon, the system parameters were syste-
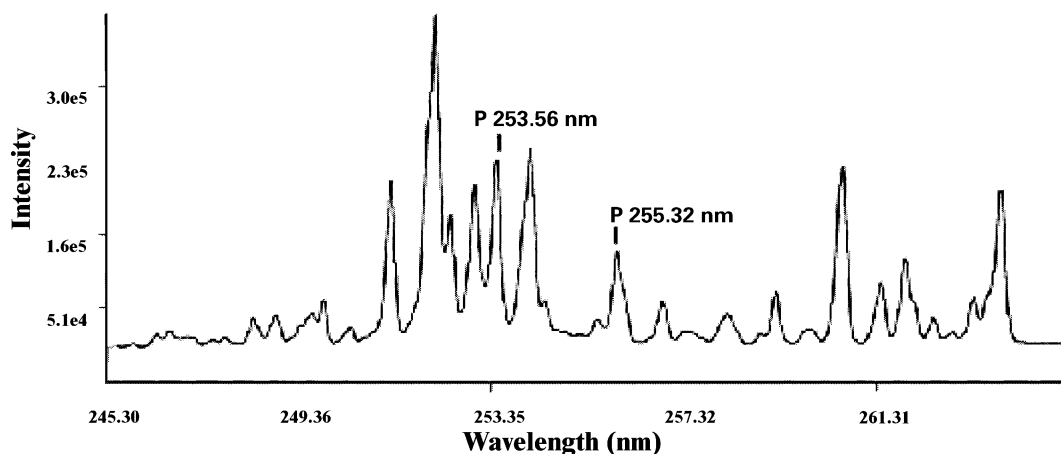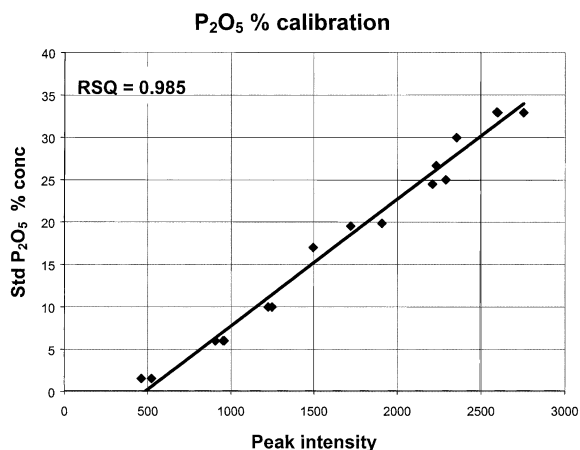
Fig. 3. P lines at 255.32 and 253.56 nm.

matically varied through increasing both the delay and width, while maintaining constant laser energy. A calibration was performed at each setting. From these results, the calibration resulting in the best RSQ and linear response was achieved using the P line at 255.32 nm (chosen over the P line at 253.56 nm due to interference from Ca), a delay of 8 μs, a width of 4 μs, and laser energy of 195 mJ. An RSQ of 0.985 was achieved as shown in Fig. 4. Using this calibration P can be accurately determined down to a 1% concentration.

3.1.2. Calcium

It was found that the 558.87-nm line, using a delay of 4 μs, width of 8 μs and a laser energy of 195 mJ gave the best calibration with an RSQ of 0.985, as shown in Fig. 5.

3.1.3. Aluminum

Large Ca peaks caused significant interference with the Al line using conventional settings. The best calibration, an RSQ of 0.987, was obtained using the 306.69-nm line at a 2-μs delay, 1-μs width and a 195-mJ laser energy, as shown in Fig. 6.

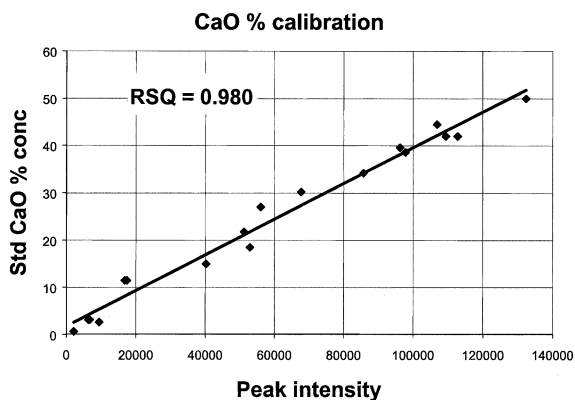Fig. 4. Calibration of P_2O_5 in phosphate ore and rock standards.

Fig. 5. Calibration of CaO in phosphate ore and rock standards.

Al$_2$O$_3$ % calibration

RSQ = 0.987

Fig. 6. Calibration of Al$_2$O$_3$ in phosphate ore and rock standards.
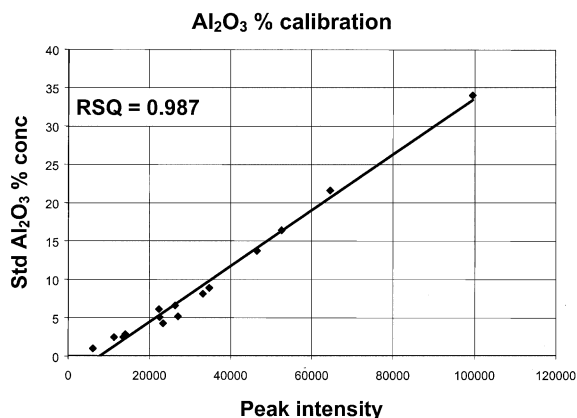
MgO % calibration

RSQ = 0.993

Fig. 7. Calibration of Mg in phosphate ore and rock standards.

3.1.4. Magnesium

Magnesium was found to give the best calibrations at long delay and width settings. A delay setting of 8 μs and a width setting of 4 μs were used. However, Mg gave better calibrations at a lower laser energy setting, approximately 115 mJ, due to the fact that the 285.21-nm line emission was very intense. An RSQ of 0.993 was achieved as shown in Fig. 7.

3.1.5. Silicon

The Si 288.16-nm line suffered from Ca interference and the best calibration, shown in Fig. 8, was obtained by using a delay setting of 4 μs, width setting of 2 μs, and a laser energy level of 195 mJ. A correction was applied to the Si concentrations based on the amount of Ca in the sample causing interferences with the Si peaks. This correction was applied to all samples with Ca concentrations greater than 11%, resulting in an RSQ of 0.985. The parameters used for the calibration of each element are summarized in Table 3.

3.2. Precision and accuracy

In order to assess the precision of the TRACER^{TM} 2100 analysis of phosphate ore samples, four pellets of one specific phosphate ore sample, were made and run against the previously established calibrations. An analysis of P, Mg and
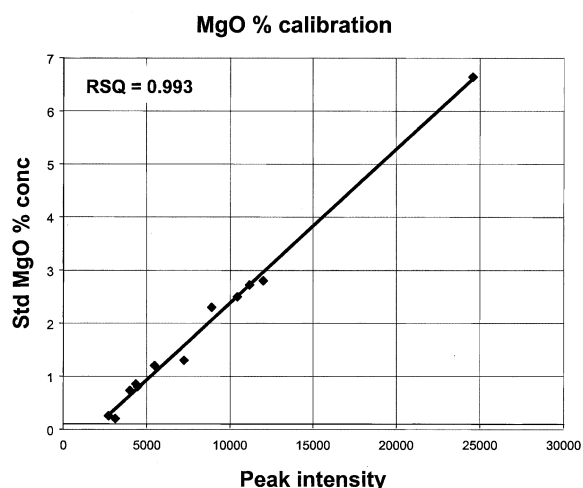
Si were run at 10 spots on each pellet using 15 shots per spot site. Two shots each with the highest and lowest values were removed from the calculation (done automatically in the software). For P, the average relative standard deviation was 3.79% with a maximum value of 7.9% and a minimum value of 2.5%. Complete shot data are presented in Table 4. Similar experiments were carried out for both Si and Mg. For each spot, the relative standard deviations averaged 2.9% and 3.6%, respectively. Precision for Ca and Al were also found to be in the same general range of 3–5%.

The accuracy of the TRACER^{TM} 2100 analysis was validated using a USGS rock standard, Ma-

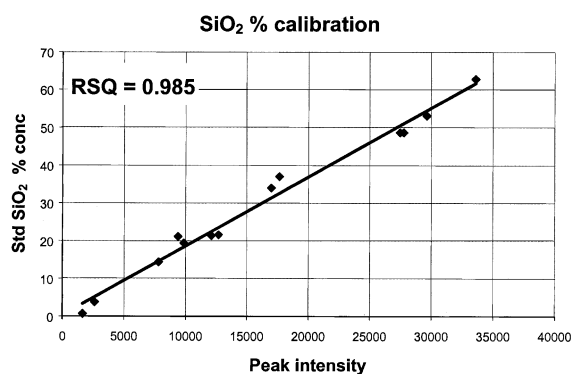**SiO$_2$ % calibration**

RSQ = 0.985

Fig. 8. Calibration of Si in phosphate ore and rock standards.

Table 3
Final TRACER™ settings for phosphate ore and rock standards

Element	Line (nm)	Delay (μS)	Width (μS)	Energy (mJ)	No. of shots	No. of spots
P	255.32	8	4	195	15	5
Ca	558.87	4	8	195	15	3
Mg	285.21	8	4	115	15	5
Si	288.16	4	2	195	15	3
Al	306.69	2	1	195	15	5

rine sediment (MAG-1) [5], that was included in the calibrations. The accuracies achieved were within 1.82% of certified value for Al (16.4 wt.%), 2.16% of certified value for Si (50.4 wt.%), and 6.25% of certified value for P (0.16 wt.%). This compares very well to accuracies provided by ICP, which were 1.2% for Al, and 0.9% for Si. A full comparison between the TRACER™ 2100 and ICP is provided in Table 5.

3.3. Ore grading demonstration at the mine site

As a final demonstration of the utility of the TRACER™ 2100 and its associated methods for on-site ore grading, the instrument and sample preparation equipment were transported to the Smokey Canyon Mine face in Idaho. The instrument incurred no damage as a result of being transported for 3 miles over a very rough, unpaved mine road. Despite the rough trip, no re-calibration was required. The TRACER™ 2100, powered from a gasoline motor generator, ran successfully for approximately 5 h.

Test samples previously pelletized and analyzed in the laboratory were re-analyzed in the field. These samples provided comparable results in the field to those obtained in the lab. Mine samples for field analysis were then 'scraped' from the four primary seams — the Upper Rich, Lower Rich, Buckshot, and Hanging Wall Shale, and analyzed using identical sample preparation procedures used in the laboratory (hand grinding,

Table 4
Relative standard deviation for P on each 15 shot sample site (average R.S.D. = 3.79%)

Run	R.S.D. (%)									
1.00	3.23	3.84	3.99	2.52	2.96	2.35	4.29	5.12	2.67	2.45
2.00	3.83	4.31	5.78	4.28	3.77	5.41	4.32	3.92	2.54	4.20
3.00	4.14	3.69	2.16	7.38	4.39	2.90	2.54	2.30	3.43	3.69
4.00	2.55	3.15	2.98	4.52	4.09	3.42	4.20	3.23	5.63	5.27

Table 5
Accuracy comparison between TRACER™ and ICP-AES techniques on MAG-1 NIST standards

Element	Certified values	TRACER		ICP-AES	
		Reported	% Accuracy	Reported	% Accuracy
Al	16.4 %	16.1 %	1.82	16.6 %	1.200
Si	50.4 %	51.5 %	2.18	50.9 %	0.900
P	0.16 %	0.15 %	6.25	0.16 %	0.100
Fe	6.8 %	6.8 %	0.1	7.2 %	5.800
Cr	97 ppm	95 ppm	2.06	100 ppm	3.090
Zr	135 ppm	130 ppm	3.7	125 ppm	7.400

pressing and minimal or no drying). Although the field analysis did not produce the same precision obtained in the laboratory, the ore samples were correctly graded as 'low-grade', 'high grade' or 'premium grade.'

4. Summary and conclusions

Methods were successfully developed for the rapid analysis and grading of phosphate ore using a LIBS instrument. The TRACER[TM] 2100, fitted with an auto sampler, is very capable of analyzing the elements requested in the phosphate samples supplied, with an acceptable level of precision and accuracy. In addition, the practicality of on-site analysis and grading of ore was successfully demonstrated through trials at the Smokey Canyon phosphate mine in Idaho.

Excellent calibrations for P, Al, Ca, Mg and Si, were achieved with correlation coefficients greater than 0.98. Initial levels of precision were satisfactorily achieved both within a sample and from sample-to-sample. However, precision increased with improved sample homogenization through more thorough grinding prior to pellet pressing and by sampling more spots on each pellet. Typical relative standard deviations, in the region of 2−4%, were repeatable on all provided samples. Although ore samples require grinding to homogenize the distribution of most elements, total preparation and analysis time was approximately 5 min per sample using the new automated sample stage. Acceptable TRACER[TM] 2100 settings

for analysis of each element were also identified and established. Using the developed methods, the instrument demonstrated a strong potential for future use in on-site, real-time ore grading.

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