# Final Scientific/Technical Report

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**Title**: Development of Real-time Coal Monitoring Instrument
**Topic/ Subtopic**: 56/c
**Grant award number**: DE-FG02-08ER84946

**B. Proprietary Data Legend**: None in this document.


## Introduction

Energy forecasts suggest that as the world's oil reserves deplete, the demand for oil will keep increasing exponentially over the next decade. Achieving energy independence and preparing for a better future, which is less reliant on foreign oil requires harnessing alternative energy resources. Non-oil fossil fuels and biofuels have proven to be the two feasible alternate energy sources. Significant efforts are under way to make these alternative fuels more efficient and at the same time reduce their harmful byproducts, such as the release of carbon dioxide ($CO_2$) and sulfur (S), especially from coal-based fuels.

Of the fossil fuels, coal is one of the most widely used, accounting for approximately 49 percent of domestic electricity production, and its demand is projected to grow more with the predicted oil crunch and the major push for energy independence. However, if coal is to be the next major resource of power, then it has to meet certain requirements, which are related to environmental safety standards.

Combustion of coal creates ash and releases some amount of sulfur that eventually forms harmful sulfuric acid. A 2 MW coal powered plant will generate >2% of sulfur per hour [1] along with other harmful elements. These chemicals contaminate the air and surrounding water systems, and pose a threat to human, animal and plant lives. Real-time monitoring of coal fossil fuel is important to ensure a control on the concentration of harmful chemicals, such as mercury (Hg), S, lead (Pb) and other constituents, that make up the ash material. At the same time, it is also required to obtain a quantitative estimate of its heat content because it is related to the power generation efficiency.

The "Clean Air Mercury Rule" establishes "standards of performance" limiting mercury emissions from new and existing coal-fired power plants, and creates a market-based cap-and-trade program that will reduce nationwide utility emissions of mercury in two distinct phases. The first phase cap is 26 tons per power plant by 2010, and emissions will be reduced by taking advantage of "co-benefit" reductions - that is, mercury reductions achieved by reducing sulfur dioxide ($SO_2$) and nitrogen oxides (NOx) emissions under the 'Clean Air Interstate Rule.' In the second phase, required by 2018, coal-fired power plants will be subject to a second cap, which will reduce emissions to 15 tons per power plant upon full implementation. For the coal mining and utility industry, fast and reliable coal quality assessments are becoming ever more important in identifying and quantifying trace element concentrations in the supplied coal to coal-fired power stations.

In Phase I, RMD evaluated and demonstrated the feasibility of a laser induced breakdown spectroscopy (LIBS) system for real-time monitoring of coal. This technology has the potential to be as precise as the current nuclear-based methods used at power plants. At the same time it is

portable, less expensive and does not involve harmful nuclear radiation. Using proper calibration procedures, the heat value of coal can be estimated based on the spectral information provided by the signal. Sampling strategies were developed and evaluated in combination with statistical analytical procedures to provide information on bulk samples.

## Degree to which Phase I has Demonstrated Technical Feasibility

Technical Objectives of Phase I

The goal of the Phase I effort was to evaluate and characterize the use of LIBS for monitoring coal quality, and demonstrate the feasibility of replacing existing neutron-gamma and X-ray fluorescence instrumentation with LIBS for coal quality monitoring. With this target in mind, the primary objective during the Phase I effort was to demonstrate quantitative LIBS measurements of carbon and all constituents of coal fuel from different blends of coal samples. An important aim of Phase I was to determine the feasibility of using LIBS to sample large volumes. This goal was achieved, and we gained much understanding of the strengths and limitations of LIBS, as well as identified the technical areas where research must be done to make LIBS practical for this application.

In particular, we found the following important points:

1. Linear relations between the spectral peak intensity/areas, and concentration of the analyte, can be obtained under controlled experimental conditions.
2. Matrix effects have to be precisely controlled and their effects studied and well understood before forming calibration relations. Therefore, careful calibration sample preparation is required.
3. Spectral lines need to be chosen carefully to avoid non-linear effects such as self-absorption and self-reversal.
4. Linear relation is obeyed within certain range of analyte concentration. Beyond, a certain concentration (approximately < 5%-10%) the linear relation is difficult to obtain and matrix effects play a big role.
5. Calibration is robust against interference from ash elements of coal. However, carbon burns in the presence of oxygen. This may affect the linear relation for both oxygen and carbon.
6. Calibration curves for ash materials can be obtained and so also for organic and inorganic oxygen and hydrogen. Carbon content then can be derived based on the knowledge of these constituents.
7. Sulfur is not easy to detect using LIBS under high temperature conditions of the plasma. New methods need to be employed to seek out sulfur content and its detection.
8. LIBS, provides complete analysis of coal i.e., it can detect total carbon (volatile, non-volatile) and also organic and inorganic oxygen.
9. Heat content can be calculated in a number of ways provided quantitative concentration analysis is ascertained using calibration procedures.

The ultimate objective is to complete the research and development on this technique and to assemble and test a portable prototype LIBS-based instrument for a specific application i.e., for monitoring various blends of coal at a power plant or mine site. This prototype will be brought to commercial coal using facilities, and tested and compared to existing techniques. In this way, we will gain an understanding of the practical issues in the workplace and get valuable feedback

from actual users. We have already made arrangements to test the system at commercial coal burning power plants.

The result will be a technology that will help the utility companies improve energy efficiency and at the same time keep a control on toxic discharges. Further objectives would be to continue to investigate other applications where the LIBS techniques can be used, and to develop and market a suitable LIBS instrument for those applications.

The technical objectives of Phase I were to demonstrate the feasibility of using LIBS for coal monitoring, evaluation of its heat content, and detect trace elements, in particular quantification of the amount of trace elements, carbon and possible detection of sulfur.

The particular tasks undertaken to achieve our objectives include the following:
1. Examine the feasibility of using LIBS for real-time measurement of concentration of coal constituents.
In this particular section, we will briefly discuss issues related to safety issues, optical and sampling considerations of the LIBS system and the nature of spectral information obtained based on our studies in Phase I.

2. Demonstrate that the detection of a few random samples is a statistically significant quantitation for bulk loads supplied to a customer.
Here, we describe the experiments we performed on geological samples and try to determine if statistical analysis can be used to distinguish between different categories of coal samples. No calibration is attempted.

3. Carry out testing using calibrated samples.
In this task, we study three sets of samples:
**(i)** Coal pellets sample made by us from nanopowders of C, Al and Si.
Our aim was to synthesize simplest form of coal and to see if the signals from its constituent elements follow a linear relation to their concentrations. We chose three elements viz., carbon, aluminum and silicon to demonstrate potentials and limits of LIBS technique for quantitative analysis. This sample was tested by Ocean Optics., (OO) covering a range of 200 nm-420 nm.
**(ii)** Pellets made from calibrated powders purchased from coal repositories in Argonne National Laboratories (ANL).
The signals from these samples were also recorded by Ocean Optics, Dunedin, FL (OO) system under same experimental conditions as sample 1. The aim was to see if linear relation could be obtained between intensities as a function of concentrations of constituents, which were apriori known from the analytical laboratories. It also would provide us a framework by comparing with studies of sample 1 the limitations of LIBS to matrix effects.
**(iii)** Pellets from calibrated powders purchased from Vanguard Systems (VS).
These samples were sent out to Applied Spectra Inc., Fremont, CA (AS) for measurement and were later analyzed at RMD. The aim was get an independent set of measurement from another LIBS system with different spectrometer and detector characteristics.

Now we describe these tasks in some details:

*1. Examine the feasibility of using LIBS for real-time measurement of the above parameters.*

Safety and LIBS system details

The goal of this task was to evaluate whether LIBS instruments are available to meet certain safety standards and also adequate to be used in-situ in real time.  We explored some existing LIBS systems e.g., from Ocean Optics (Florida), Laser Analysis Technologies, Ltd., (Australia) and Applied Spectra, Ltd., (California). Each of these systems is operated with the laser at several mJ and 1064 nm wavelength.  This wavelength is eye-safe, though at such high pulse energies, the safety concerns have to do more with the experimental design and associated safety procedures.  Placing proper enclosures to avoid spurious reflections, and use of safety glasses with appropriate attenuation coefficient for the laser, can make the system perfectly eye-safe.

We also found that Ocean Optics (OO) and the Laser Analysis Technologies (LAT) systems have been used outdoors at the sites and the latter system has been used to study coal samples. However, these systems have not yet been continuously operated and monitored for several weeks and, therefore, it is difficult to evaluate their relative performance.  One big advantage of both the OO and LAT system is that their power requirements are relatively low and are generally more rugged than the Applied Spectra (AS) system.  The AS system's detector is cooled and has an intensifier – which means the detector has to be properly shielded. However, the AS system is temperature stabilized and, therefore, can offer better quantitative results in comparison to OO and LAT systems, whose measurements can change from winter months to summer months. Another significant advantage of the Applied Spectra system is the increased sensitivity to low signals, which the other two systems do not offer. Signal levels for ICCD systems are in general an order of magnitude larger than for the CCD systems.

We evaluated both systems and found the sensitivity of the AS system to be superior and also more quantitative.  The readout time in the AS system is a factor of 10 slower than that of the OO system, but in general this delay is not a major constraint because the measurement and analysis time does not exceed a few minutes.

Optics

Optics is an important part of a field instrument especially when there are restrictions on easy access to the target sample or non-uniformity of sampling methods. We explored several optical designs but restricted our range to a maximum of 2m.  We evaluated two different measurement sets with one in which the excitation focusing lens was about two inches from the coal target versus a measurement in which the focusing lens was 2 meters away. The signal strength reduced proportional to the numerical aperture and the SNR also degraded. Increasing the energy two times did not help much.  In both cases a fiber was placed within a few cms from the target and was able to collect good signals.  Even though the signal reduced at longer distances, the SNR was still better than 10 for some strong peaks. The detection system was then changed to a confocal arrangement in which the signal was rerouted through a lens into a fiber, which was placed at the image plane of the target, as seen by the focusing lens. Placing the fiber in proximity to the target had higher throughput compared to the confocal arrangement due to reduced numerical aperture seen by the lens 2m away. At 2m we could not detect signal especially from carbon using the confocal arrangement with a 2 inch lens for collection optics. However, when the LTSD was changed to 2 inches for an F#1 lens, signals considerably improved. The signal for a fiber held close to the target was, however, highly unreliable because

of variable target to sample distance as the sample moved or the surface profile changed as it was scanned. The instrument from AS did the best in terms of signal to noise due to the use of a cooled detector. In conclusion, 2-5 meters of sample distance with proper reflective telescope
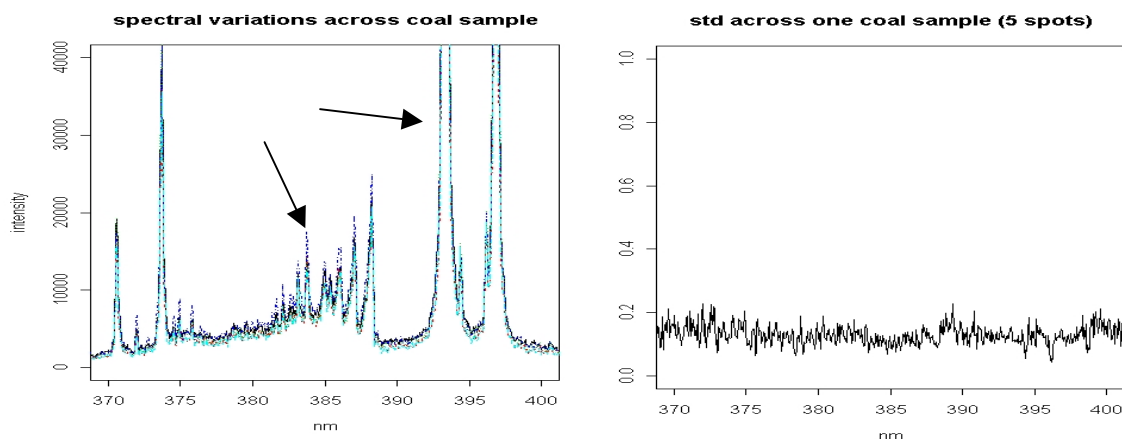


**Fig. 3: Left plot shows spectrum across a small range for the sake of clarity from five different locations of the same sample taken after scanning along the sample. The plot on the right is the standard deviation (std) of the signal. No correction has been made for the laser intensity.**

optics to accommodate high NA might work well for a confocal setting. When designing a system for site use, this aspect has to be considered.

Sampling issues

Next we explored how much sample size we need to probe in order to get reliable estimates of quantities such as concentration of trace elements from the coal sample. We made measurements on geological coal rock samples (non-calibrated) and looked at variation across the surface i.e., 100 random spots were analyzed across different sections, each separated by several cm, with about 20 shots per spatial location for depth profiling. We report the average quantities and their standard errors (see **Fig**. **3**, for an example of spectra from a bituminous sample). The signal does vary along different locations, and a scan with ~100 shots across a surface area separated by 1 cm or scanning a crushed sample and then averaging the resulting signal provides a reliable indication of the average coal quality. Surface impurities can confound studies, but the first few shots can be expended to clean the sample while also looking at crushed pieces to reveal the interiors.

One crucial aspect of sample preparation we observed is that when the powdered samples are studied, the signal varies significantly. Samples of size 10 mm$^3$ or those made from nanopowders and formed into pellets exhibited smaller variability in signal strength for multiple laser shots. Pellets made from 20-100 mesh powders were much less stable and would disintegrate under a laser induced shock wave.

Spectral Information

The relative concentration of various trace elements in coal range from 0.01%-5%. Most of the impurities are in the form of oxides such as $MgO$, $CaO$, and $Al_2O_3$. Aluminum oxide, Iron oxide and silicon dioxide are the major components of coal ash content. There are several other
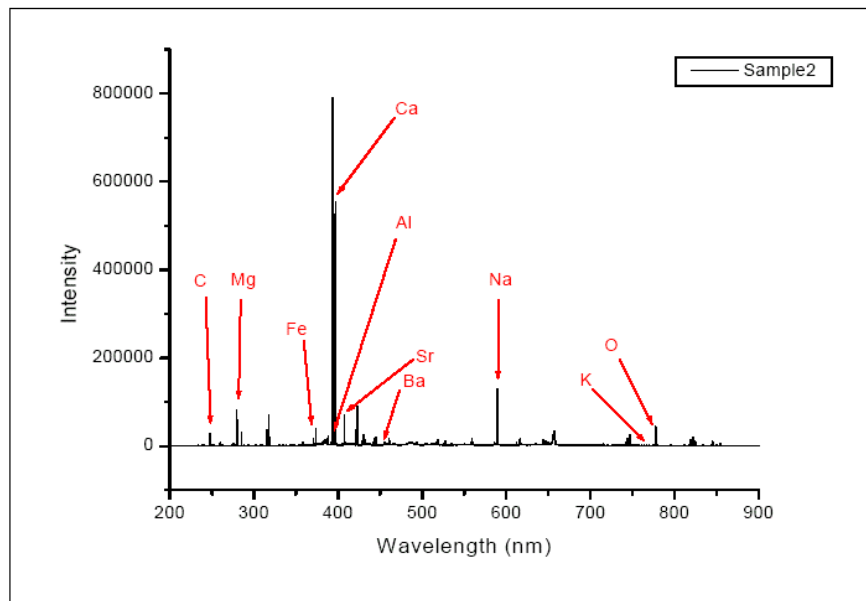
**Fig. 4: A typical spectrum from Bituminous coal is shown. The spectra was recorded by AS echelle spectrometer using Nd:YAG 1064 nm excitation.**
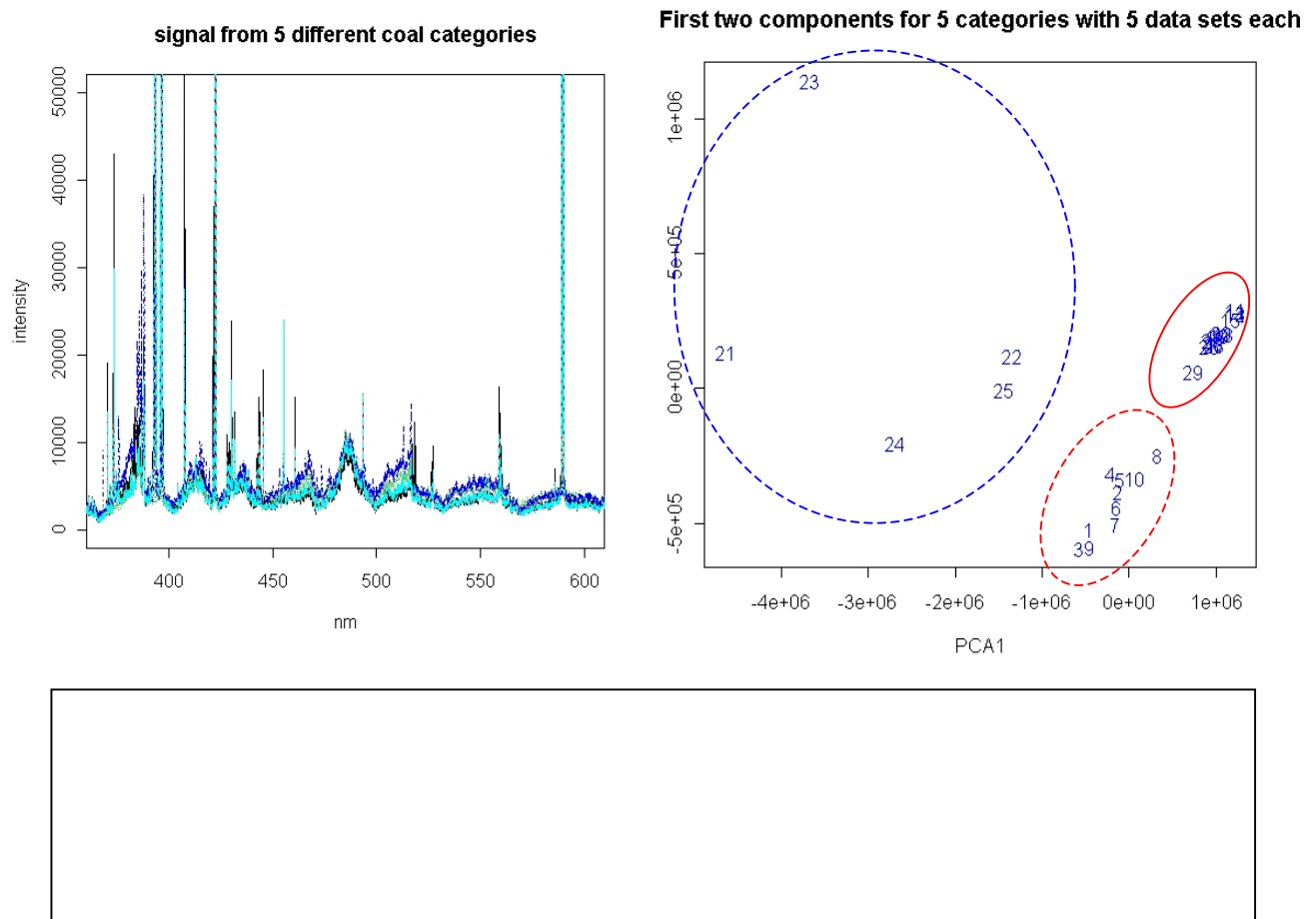
elements in coal as well, but they are in very small quantities. We were able to detect most of the important elements in single shot experiments. Some examples are Si, Al, Mn, Mg, Na, K and Ti. We were unable to detect sulfur from our samples, whose concentration was in the range 0.5%-2% in some of our calibrated samples. We are trying to extend the range of our LIBS system to probe sulfur bands deep in the NIR region (>900 nm). We show, as an example in **Fig**. **4,** some of the spectral features of trace elements identified from a geological coal sample. Besides trace quantities of minerals, we were also able to detect hydrogen and oxygen in the sample. To make sure that the detection was from sample and not ambient air, we performed some of the experiments under helium environment. Detecting hydrogen and oxygen is essential in order to provide heat content estimates. The real challenge would be to determine if oxygen can be determined by direct measurement in ambient air environment in real situations e.g., at power plant locations.

We later suggest alternative strategies to determine oxygen content from coal by adjusting for the air oxygen concentration using theoretical formulations. Some of these tasks could not be carried out in Phase I and would be the primary focus of work in future.

*2. Demonstrate that the detection of a few random samples is a statistically significant quantitation for bulk loads supplied to a customer.*

In this task we explored the variation of signal across sample. It is known that coal is a very heterogeneous sample due to the nature of its formative history. This is one reason why analytical techniques require the sample to be crushed to fine mesh powder, thoroughly mixing it before it is quantified. Our goal was to find out if we could perform random sampling on broken pieces of coal at several locations and at several depths of the sample, and statistically analyze their composition.

Geological coal samples, which were obtained from a vendor, had the following specifications: There were 6 samples in all, which varied from peat, lignite, bituminous, sub-bituminous, and anthracite to graphite. We removed the peat sample because at power plants most coal samples would fall in the bituminous to anthracite range.  We also introduced an unknown volcanic rock sample in order to evaluate whether the LIBS analysis can differentiate coal from a different species.  The volcanic rock looks identical to anthracite sample and is carbon black in color, and was not visually distinguishable from coal samples. The samples were analyzed both in air and under He as the background gas.  Some of the molecular bands such as CN swan bands disappear in He environment, except in samples, which have some inherent nitrogen present in the form of volatile matter. The geological samples were studied under similar conditions as the "calibrated samples" to be discussed in the next section.  But before quantitatively analyzing the composition, we sought to discriminate between the different categories of coal using principle component analysis (PCA).  PCA looks for features in the data which have the maximum variance amongst the observables (which in our case is the intensity of the spectral lines). PCA creates a linear combination of variables which best distinguishes different samples from a given set. **Fig. 5** demonstrates that we were able to distinguish a non-coal sample using PCA, and also were able to categorize low heat content coal from a relatively high heat content coal. We see that #21 through #25 encircled by a blue dashed line, are the data from which the volcanic rock are clearly demarcated.  Data sets #1 through #10, encircled by red dashes, are from lignite and sub-bituminous, while the rest are from bituminous, anthracite and graphite samples.  However, further categorization of the different coal sub-categories amongst the high or low heat content could not be distinguished.  One reason could be due to the fact that the number of data sets is significantly smaller (5 per sample), while the numbers of variables are high (which consists of intensity at 14000 wavelengths).  Selectively choosing a spectral region or selecting intensity ratios of relevant wavelengths, the categories can be made to separate out. What is seen in the adjacent plot of **Fig. 5**, is that the spectral features for different samples look almost identical with very little spectral variations.  However, PCA can sensitively select orthogonal linear basis and selectively separate out the different category. For a larger set of data, and with more categories tested on a new set of samples, we get better discrimination between all the categories (see **Fig**. **16**).

**signal from 5 different coal categories**

**First two components for 5 categories with 5 data sets each**

Correlation between Spectral Intensity and element concentration

**Table 1** shows intensity values of spectral peaks of a few chosen important trace elements. First, it is clear from a cursory glance that carbon content is increasing as a function of sample number. This is expected because the samples were numbered according to grade in the increasing order of heat content. One outlier is sample #6. This sample has unusually low carbon content. The reason is that in this blind study, a volcanic rock was inserted amongst the coal samples to determine how effectively the LIBS technique can isolate the sample. The PCA was seen to clearly demarcate this sample visually. From the table it is seen that it has unusually high content of Ca, implying it is a calcified rock sample. As for the rest of the samples, which are all from different coal categories, the intensity values do not show any obvious trend. But, when data variance is analyzed the resulting structure can be extracted by the PCA. However, one can see that Mg, Ca, and Na peak strengths are smaller for groups #4, #5 and #7 compared to #2 and #3. Because the spectral signatures are strongest for these lines, they provide a large bias to the PCA analysis. Another feature is that sample 3 has in general more ash content than other samples. Therefore, even if it has slightly higher carbon content as specified by C line intensity, the heat efficiency may be reduced due to increased ash content.

To evaluate heat content, we had to perform calibration experiments. Calibration experiments provide correlation of intensities or their ratios to concentrations of the elements. Then, based on calibration plots, one can determine the heat content for the sample. Below, we discuss some of these issues.

| | INTENSITIES | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C (247.85nm) | Mg (279.55nm) | Si (288.15nm) | H (656.28nm) | O (777.19nm) | Ca (393.36nm) | Al (396.15nm) | Na (588.99nm) | Sr (407.77nm) |
| Sample #2 | 8300 | 15400 | 500 | 8700 | 4800 | 139300 | 5700 | 43300 | 15000 |
| Sample #3 | 13000 | 12600 | 2800 | 15000 | 14400 | 301450 | 12700 | 46800 | 9800 |
| Sample #4 | 10300 | 6200 | 530 | 8800 | 6000 | 71600 | 9000 | 3600 | 13600 |
| Sample #5 | 24500 | 2300 | 3100 | 900 | 18600 | 90700 | 12500 | 5500 | 13800 |
| Sample #6 | 6800* | 222000 | 116700 | 22800 | 39400 | 1182100 | 115400 | 155900 | 21900 |
| Sample #7 | 30400 | 3,000 | 3400 | 12600 | 23600 | 81200 | 9400 | 4200 | 12500 |

Table1: Average Intensities for main spectral peaks (20 laser pulses, accumulated)

Notes:
- Gas applied to sample to reduce ionization of atmosphere.
- Data averaged over 5 different sample sites, 20 laser pulses accumulated at each site

3. Perform LIBS using calibrated samples.

The goal of this task was to establish calibration procedures. LIBS technique rely on spectral intensity or peak areas, which can vary from shot to shot and also will vary due to matrix effects. There are two ways to calibrate for these effects. One is to estimate the plasma characteristics using Boltzman-Saha equation for plasma dynamics. In this method, one has to take into account the absolute laser power used, calibrate for detector uniformity across the wavelength range and determine plasma temperature accurately. Instead, we chose a second method where relative peak intensities and areas were ratioed from a prepared known standard. The calibrated ratios were then compared to the observed ratios to get estimates of the elements.

LIBS cannot accurately estimate the quantity of an unknown if that element is present in the sample at very high concentration. This is essentially due to saturation effects mainly originating from non-linearities such as self-absorption induced by the dense plasma. Under this situation it becomes difficult to estimate the high carbon content which varies in coal samples from ~60% to 90%. One could instead determine the percentage of ash, hydrogen, and oxygen content, and, hence determine the remaining amount to be that of carbon and obtain the heat content.

Heat content calculations by themselves are not as important as calibrating accurately for determining [C], [H] and [O]. Once these have been calibrated out, there are several equations available and tested to determine the heat content. The equations in general provide reliable estimates of the heat content, though in most cases there is some reasonable bias, which has to be corrected for.

Hence, below we attempt to prove that reliable data can be obtained from LIBS by following careful calibration procedures.

Standards prepared to check for LIBS linearity

Calibration sample preparation is the first aspect of the procedure. We adopted two approaches. In the first approach we fabricated a set of samples, which emulated coal properties, while in the second approach we acquired pre-calibrated coal sample powders and pressed them into pellets for our study to develop calibration procedures.

For the first approach, we decided to simplify the coal system. After looking at several sets of coal calibration data we hypothesized that the most simplest coal sample can be emulated by choosing carbon, which ranges over 70%-90% of the total coal mass, and then choosing the largest constituents of the ash: silicon and aluminum oxides. We further simplified the process by choosing pure elements rather than their oxides. Next, we purchased fine powders of carbon, aluminum and silicon (grain size <0.1μm from Alfa Aesar). The powders were thoroughly mixed in the presence of ambient air and were sonicated to ensure a uniform dispersion of the constituents. We prepared the samples as follows by wt.%:

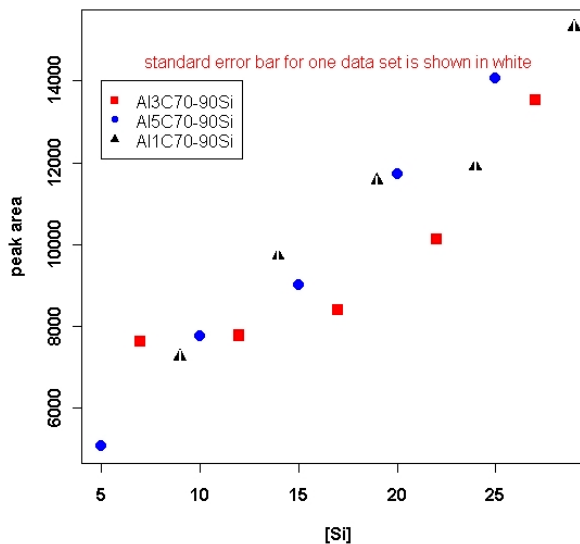**Al:** 1%, 3%, and 5%
**C:** 70%, 75%, 80%, 85%, and 90%
**Si:** (100-Al-C)

I.e., we prepared five concentrations of carbon and then made three sets (5 samples each) of each by mixing three different concentrations of aluminum. Si was then added to make the total quantity to be ~2 gm. The pellets were then pressed under a hydraulic pressure of 100,000 psi. We tabulate one of the sets of the three,

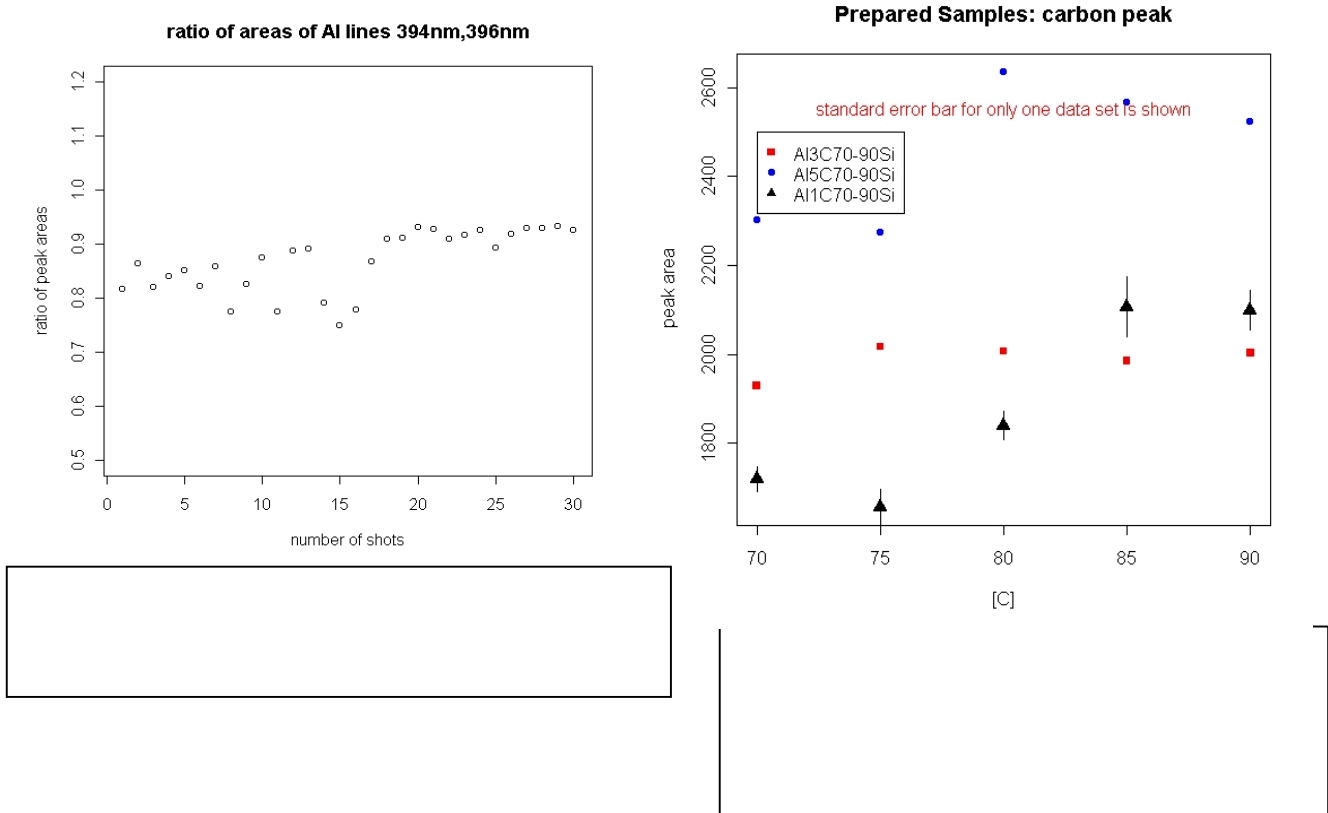**Prepared Samples: silicon/carbon ratio**



**Prepared Samples: silicon peak**



| C% | Si% | Al% |
|----|-----|-----|
| 70 | 25 | 5 |
| 75 | 20 | 5 |
| 80 | 15 | 5 |
| 85 | 10 | 5 |

| 90 | 5 | 5 |

The pellets were then subjected to LIBS study using the OO system and RMD Nd:YAG laser. All the pellets were studied under similar conditions i.e., laser energy 60 mJ and pulse delay ~2.5 μs. Confocal arrangement was used to study all the samples, and the distance between the lens and the target was kept fixed. The sample was scanned along a perpendicular direction to the beam and 10 averages for 10 different locations were obtained. We summarize some of our observations in **Fig. 6.** Our conclusions based on the analysis are as follows: 1. **Good linearity is observed for trace element - Si.** 2. **The ratio of Si to C peak also exhibits good linear relation, thus indicating that** 3. **Carbon signal peak does not show monotonic variations with concentration and** 4. **the correlation coefficients are not influenced by the presence of other trace elements.** Linearity is expected in particular for Si 288 nm peak, which is not a resonance line. The peak values of the Si spectrum do not change appreciably, signifying that if experimental conditions are properly maintained the data is repeatable. We also see that standard errors are small, thus implying that nanopowder synthesized pellets provide very stable spectra. (Intensity variations are averaged out in standard errors). **Fig. 7** shows the carbon peak signal versus its concentration and no obvious linear trend is observed. Also, C peak area is seen to vary by ~20% even though the standard error does not show it. This either implies sensitivity to alignment or sample inhomogeneities (nanoparticles quickly aggregate and do not easily disperse when mixed dry). Similar situations are seen for the ratios of Si (>25% variation for a fixed concentration ratio).

One could argue that though the concentration is changed across the calibrated samples, density of the carbon may have remained the same because hydraulic pressing may not generate a monotonically increasing density of carbon. One could also equally argue that LIBS is not quantitative for very high concentrations of the analyte due to non-linear processes such as re-absorption of the signal. Also, the data were taken under atmospheric conditions, where coal is likely to burn under high temperature conditions in the presence of oxygen. Secondary effects include formation of CN molecule, which shows its presence in the form of swan bands in the range 380-390 nm. The variation of linearity plots in the three sets suggests that the signal is very sensitive to experimental conditions i.e., ensuring LTSD is kept fixed and also ensuring that target to the probe distance is kept fixed.

To find out how the plasma conditions are affected as the sample is moved relative to the lens and fiber, we performed LIBS in aluminum and looked at the two neighboring Al lines i.e., 394 nm and 396 nm. The same number of shots was acquired i.e., 10 averages for 10 different



ratio of areas of Al lines 394nm,396nm



Prepared Samples: carbon peak

locations. **Fig. 8** shows the ratio of peak areas for line 1: line 2. We see signal variation of ~ ±3% suggesting changing plasma conditions (mostly temperature effects). This would imply that rather than optical alignment, matrix effects are the cause of the large spread in the y-axis values.

As we mentioned above, the main constituents of ash are oxides of silicon and aluminum, and the rest is mainly coal and volatile matter. To prepare calibrated coal samples is challenging because that would imply selecting known quantities of several organic compounds, which characterize coal. Coal formation is very complex and, therefore, we simplified the problem to three major elements to determine the robustness of our calibration procedures.
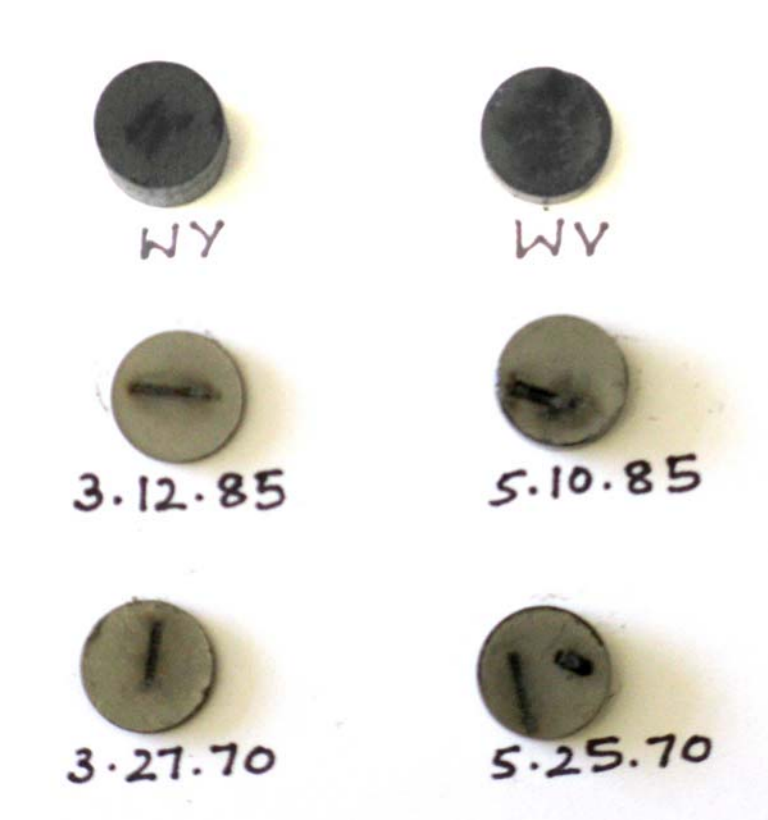
Calibrated coal samples

Even though one cannot simulate a real coal composition in a laboratory, one can purchase samples from coal repositories and have them analyzed in a laboratory using other methods. Then one can selectively pick samples with a suitable concentration range of the constituents and perform LIBS on those set of samples to develop a calibration procedure. Below we describe those methods.

**Table II: Vanguard Solutions samples: elemental composition**

| Name/element(wt%) | H | O | Al₂O₃ | C | SiO₂ | Ash |
|---|---|---|---|---|---|---|
| VS006 | 4.41 | 8.68 | 4.54 | 67.84 | 10.8 | 17.42 |
| VS016 | 4.84 | 6.31 | 4.62 | 69.55 | 9.2 | 16.69 |
| VS026 | 4.86 | 8.23 | 3.57 | 72.06 | 6.84 | 12.26 |
| VS036 | 4.13 | 3.22 | 1.49 | 85.13 | 2.67 | 5.67 |
| VS046 | 4.49 | 1.97 | 2.9 | 80.06 | 4.96 | 10.32 |
| VS056 | 4.81 | 3.22 | 1.49 | 85.13 | 7.62 | 12.88 |

Two sets of samples were purchased. Set 1 was from an analytical laboratory (Vanguard Solutions, Inc., Ashland, KY) (VS), and set 2 was from the Argonne premium coal sample program (ANL, Argonne, IL). Both sources provided us samples in the powder form and were fully characterized by ASTM methodology (see **Table II** for VS samples). Samples obtained were 20 mesh from ANL and 100 mesh from VS. They were sealed in an air-tight container. However, the pellets were made under ambient conditions. This could have resulted in some oxidation of the sample, which could not be ascertained.
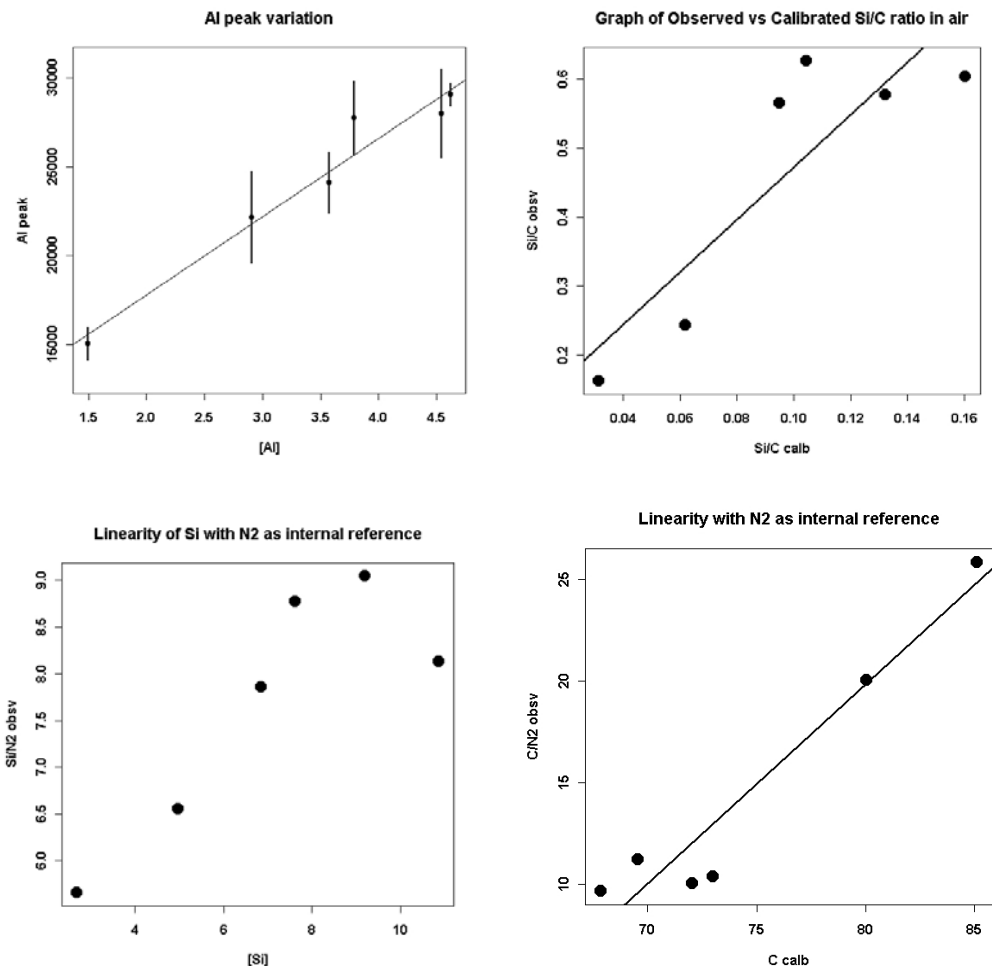
The powder was then formed into pellets and was subsequently analyzed by LIBS. The pellets from these samples were considerably porous in comparison to the ones made in the laboratory, possibly because the laboratory samples were prepared using nanopowders, while the purchased coal repository samples had fixed particle ranges of 20-100um. The difference can be seen on the surface after the laser ablation. The features are shown in **Fig. 9** for the samples ANL and our own. Each single laser pulse removes a large amount of material from VS samples, and the variation is significantly larger than from the nanopowder-based samples. This fact should be kept in mind when analyzing the data. (**Actually, all the ash elements have been calibrated in their oxide forms**
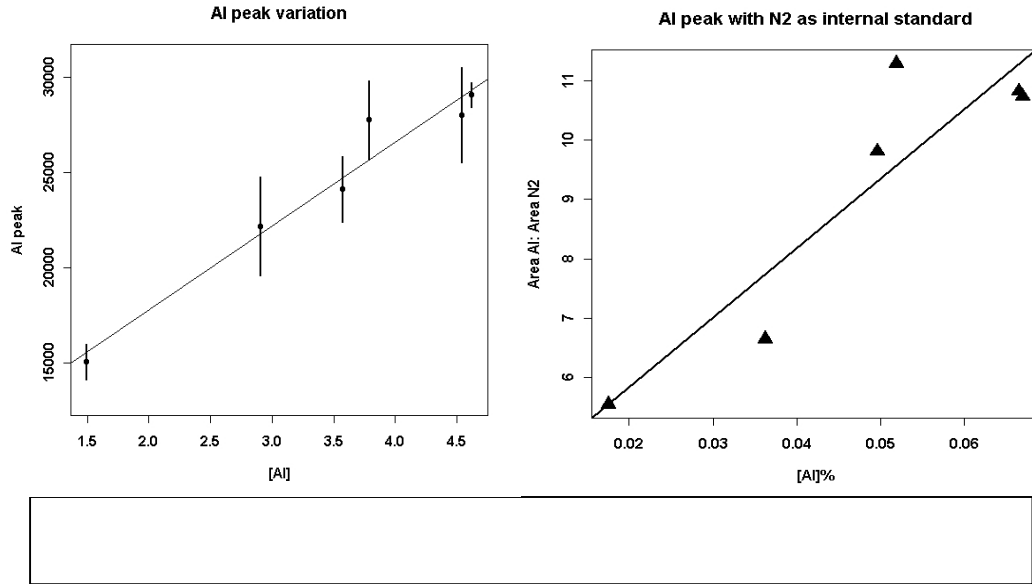
**i.e., SiO₂, Al₂O₃ etc. Henceforth, the oxides will only be referred to by their elemental symbol, and it is to be understood that the X-axis represents the oxides for all ash elements, in particular Si, Al, K, and Mg discussed here**).

First, we describe all the data that were taken under atmospheric conditions. We decided to test VS samples using the AS system, which had a longer wavelength range than our OO system, (which has a restricted wavelength range of 200-400 nm). The experimental conditions were different than for our system. Hence, VS data should not be compared to data from our nanopowder samples described previously. However, the ANL samples were tested under
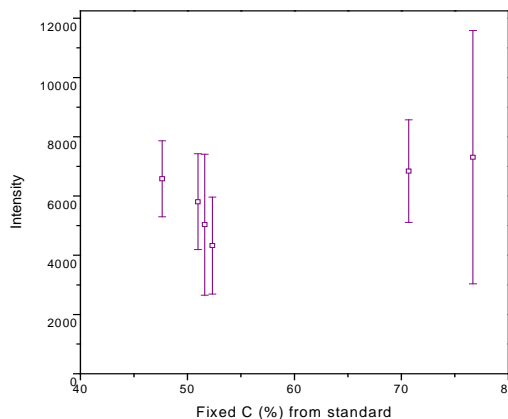


identical conditions as the nanopowder pellet samples in our setup and, hence, the two data can be compared – bearing in mind that pellet formation from large mesh size samples will have their own limitations. To summarize:

- Nanopowder based pellets and ANL samples studied by same apparatus and under similar conditions.
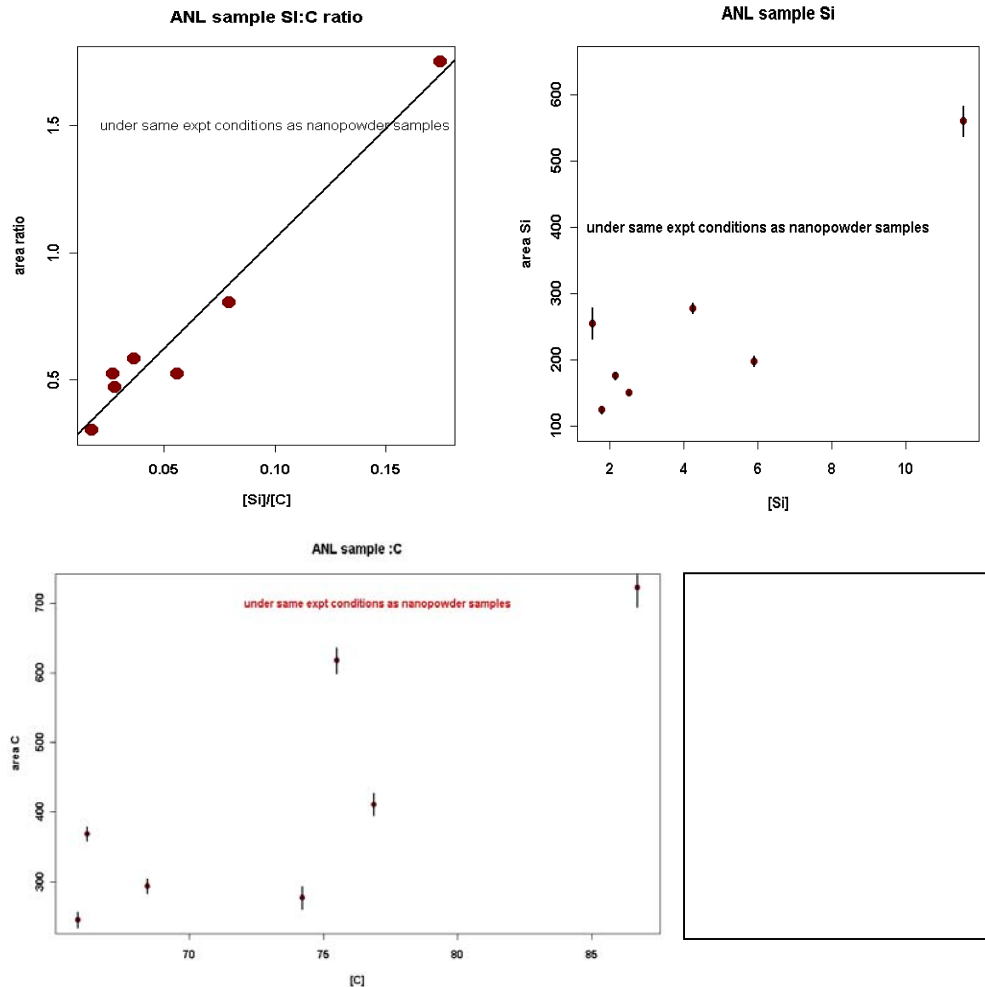- VS samples tested with a different laser and spectrometer system.



**Figures 10** and **11** summarize some important points for the VS set studied. In general, we plot both the ratios and the peaks for trace elements against their corresponding concentration ratios, or concentration, as the case maybe. Carbon being a major element with high concentration, we initially take it as an internal standard. What we notice is the following: **1. <u>An observable linear trend for trace elements is seen when either the peaks or the ratios with respect to major element - C is plotted</u>**. The linearity is better for peak strength than for the ratio indicating that the carbon signal has a larger variation than previously noticed in our samples. **2. <u>Linearity in C peak versus concentration is not apparent</u>**. When the C peak is plotted versus concentration of C we notice a weak monotonic trend (not shown) as the concentration goes up. But it is this trend which causes the Si/C ratio to be noisy. Therefore, we decided to use nitrogen present in the air as our internal standard, knowing that N2 is the major component of the air and its concentration remains steady at ~70%. **3. <u>When we take the ratios of either the trace elements or carbon with respect to N2 we see much better linear trend than was seen previously with C as the internal standard.</u>** This observation is important because now it tells us that under proper experimental conditions one may be able to
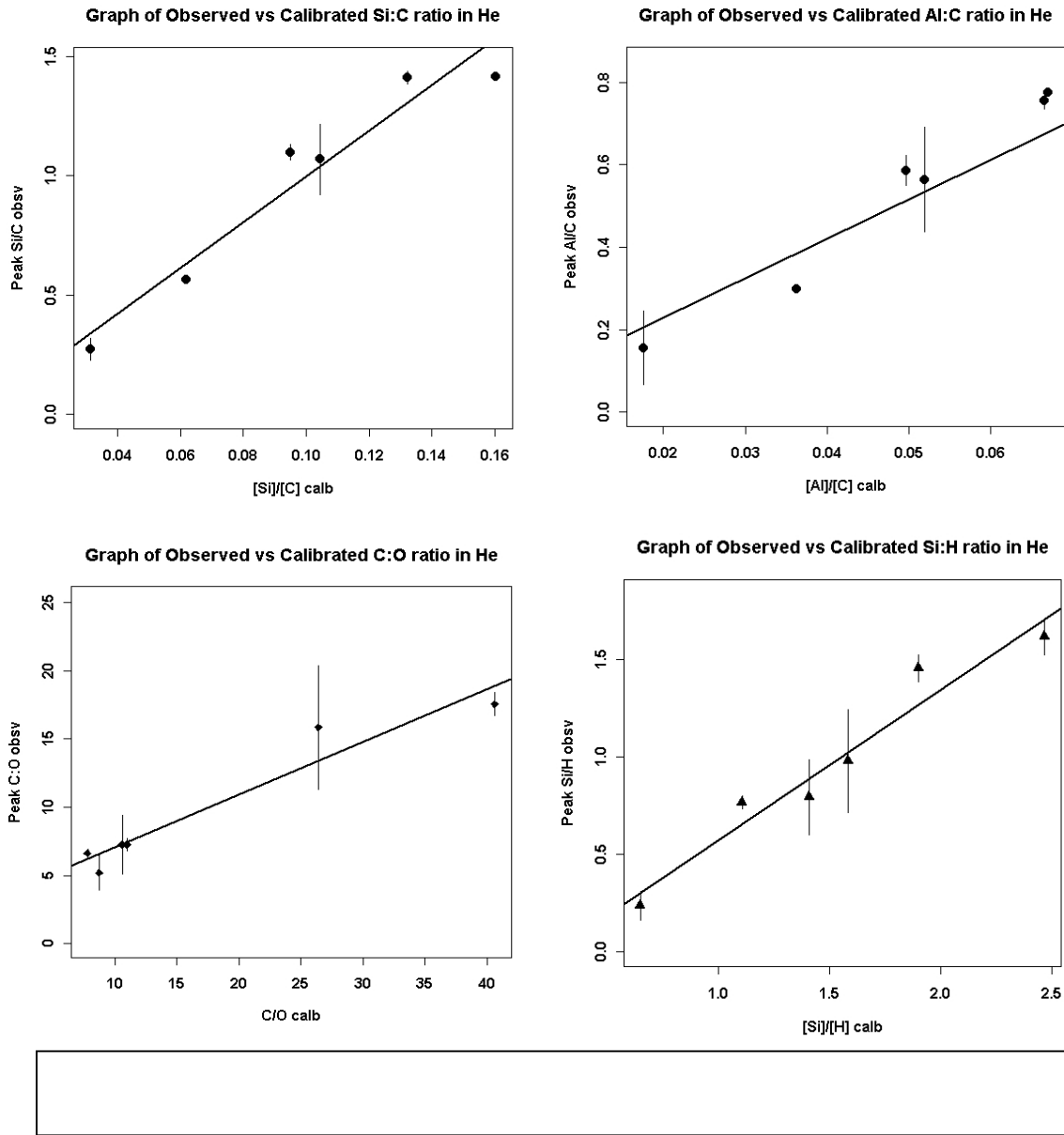
calibrate even for a major constituent of coal i.e., Carbon. This is strikingly seen in **Fig. 10** (bottom right plot) where C/N2 exhibits a strong linearity. Si/N2 ratio tends to show some non-linearity at higher concentrations of Si. In general nonlinear effects seem to appear in Si for concentration range >6%. This effect was not seen in nanopowder-prepared samples. Similar features are observed for Al line (309nm), (see **Fig. 11**) which was analyzed as described above. Al peak shows much better linearity since its concentration range is generally lower than Si. A linear trend is also seen for N2 as internal standard. The linear trend is weaker for the ratio than for the peak strength. Our general conclusion is that when the samples are probed under ambient conditions, there is a lot of variability in linearity, and good linearity is obtained only when experimental conditions are maintained uniformly across all the runs.

We believe that some variability observed is due to sample porosity. To show this, we made some measurements on powder on a double-sided tape and measured the C peak and also the C-Si ratios. **4. <u>The carbon signals show a monotonic trend for pellet samples, which are not seen for powdered samples</u>** (compare **Fig**. **12** and **Fig**. **14**).

Before we describe the studies under He for the VS samples, we would like to digress a bit and point out that ANL samples also showed good linearity, and that the carbon peak was linearized with N2 as internal standard. We show two representative plots as proof. First, the peak areas when compared to those of **Fig**. **6** and **8** are significantly lower. The pellet disintegrated after few shots. Second, the ratio of Si/C is a factor of ~2 off. An important difference between the two samples is that our samples are composed of mixtures of Al, Si and

C, while the ANL samples are actually oxide mixtures i.e., $Al_2O_3$, $SiO_2$ carbon and many other trace impurities. Moreover, carbon in the ANL pellet consists of both fixed and volatile hydrocarbon. This study is important to suggest careful calibration sample preparation. In our view, the best procedure would be to select calibrated samples, which have finer than 20 mesh. Alternatively, one could perform LIBS on large coal chunks, which are picked from a known group (i.e., study several samples across different groups based on heat value) and then send it to analytical laboratory for analysis. In this case the calibration would be more reliable. The only problem with this method is that one must selectively pick coal rocks, which fall into different blends or category.

**Graph of Observed vs Calibrated Si:C ratio in He**



**Graph of Observed vs Calibrated Al:C ratio in He**



**Graph of Observed vs Calibrated C:O ratio in He**



**Graph of Observed vs Calibrated Si:H ratio in He**



Next, we return to discussion of samples studied under Helium atmosphere. These are the VS samples studied by the AS system. For samples that were monitored in He gas, **Fig. 14** and **Fig. 15** summarizes the results. We will not elaborate on them but point out that **1.very good linearity is observed under these conditions**. One drawback of this procedure is that N2 is now no longer available as an internal standard. Therefore, a new way has to be found to obtain information about the carbon content. **2. The way to do this is to calibrate for ash, oxygen and hydrogen content. This would then enable us to fix a value for total carbon content.**

C peak, fitted to 410.5x[C%]-12500

However, we notice that under proper controlled conditions, we could achieve a monotonic relation for carbon peak as a function of its concentration. This is seen in **Fig. 14**. This linearity was obtained only when the coal powder was compressed to a ton of pressure. Our results with powder on a double-sided tape did not result in monotonic functionality. However, the linearity was not consistent and varied from experiment to experiment.

Non-linearity corrections procedure

One can correct for the temperature nonlinearity by taking ratios of a trace atomic element, which have spectral signatures in the first and the second ionization states. For example, Mg-I and Mg-II spectrum can be observed in most of the coal samples. Therefore, if one plots the ratio of the peaks of the two ionization states of an element (Mg) against normalized intensity ratio of element of interest e.g., Si/C (normalized to the respective concentration), then one can fit an algebraic function using the following set of equations [2]



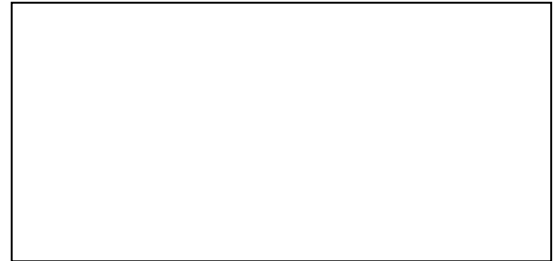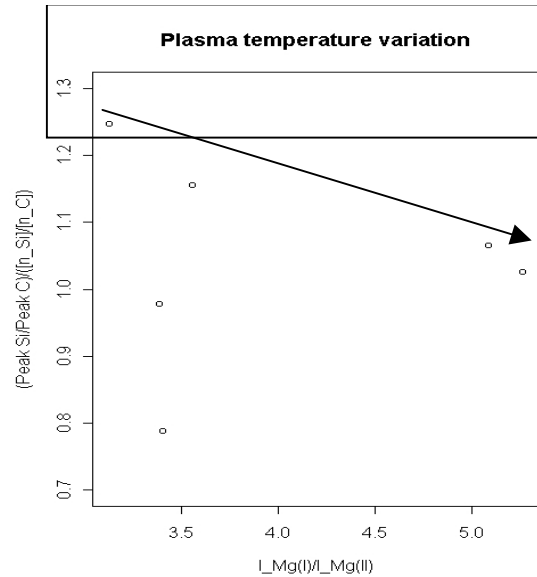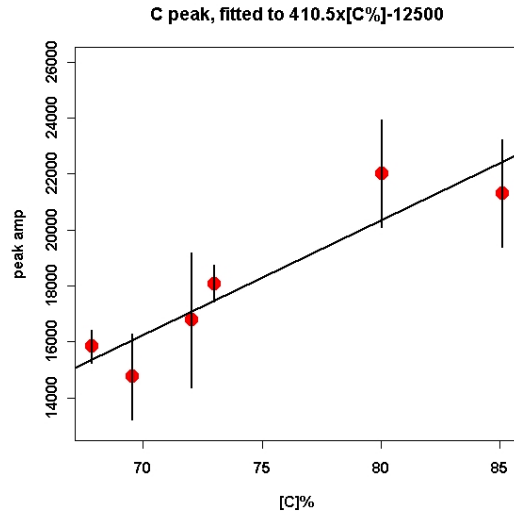$$\frac{I_i^1}{I_i^2} = \frac{g_i^1}{g_i^2} \exp\left[-\frac{(E_i^1 - E_i^2)}{kT}\right]$$

$$\alpha_i = K_i I_i^{\,b} [I_j^1 / I_j^2]^c$$

The first equation is the Boltzmann's distribution for the intensity ratios of Mg-I and Mg-II lines originating from the same ground state, while the second equation is the overall correction factor which has to be multiplied to observed ratios such as [Si]/[C]. Here, K and the exponent b are the correction factors for species i, and c is the plasma temperature correction factor for the emission pair from Mg.

When we plot the above function for the data set measured under He atmospheric conditions, we find a temperature trend indicated by the arrow (see **Fig. 16**), although the temperature change is not significant for 4 out of 6 sets of samples. However, for two cases the peak ratio variability is large (y-axis variation at x-value of ~3.5). This large variation in the data suggests other non-linearities could be present.

Heat-Content Calculations

There are several ways to calculate heat content. Ref [3] provides a good review of different empirical formulations used and we will also recourse to one of the formulas listed in the

reference. Heat content in general is expressed in terms of wt% of C, H, O, S and N. One could change the formulations by accounting for total ash content in which case O, N are not needed. If one could determine the concentration of these elements, then one could hypothesize a hydrocarbon of the form $C_xH_yO$ and using the combustion reaction compute the stoichiometric ratio. This ratio is shown to be empirically correlated to the heat content [4]. However, not all coal is homogeneous and it is not clear if this formulation is better than those proposed in ref [3] and widely used.

To get a feel for heat value calculations we re-analyzed the data set from the geological coal samples. We measured the intensity ratio of the respective carbon/N2 and hydrogen/C peaks and then based, on our calibration curve, evaluated how much would be the concentration of each C and H. We left out oxygen content and also no sulfur was seen in our experiment. We reasoned that for the amount of S and O present in the coal, their contribution would balance each other out to some degree and hence we ignored their contribution in the present calculations.

In our calculations we are assuming that the intensity and the experimental parameters did not change significantly. However, as mentioned earlier, there is a significant difference between the pellet samples from the coal powder and the coal itself. Pellet powder is loose and crumbles after few high-pulse laser shots. On the other hand, coal is a hard solid and its nature is significantly different than a pellet. Visually one can make out the difference in reflectivity from the geological samples and the coal samples. Therefore, the plasma characteristics are expected to be very different. This is also reflected in our calculations, which shows a large bias from the actual value obtained from other laboratory measurements.

Based on **Fig. 10**, we derive a linear relation between the carbon content and the peak intensity value for the emission line at 247.5 nm. This relation is given by the equation:

Y [C%] = (1/410.5) (X amplitude counts + 12500)

From **Table I**, we estimate the carbon content to be 50%, 62%, 55%, 90%, and 104% for samples #2, #3, #4, #5 and #7, respectively. Though the numbers exceed 100%, they are in the ball park to clearly distinguish between categories. We also get a value for the hydrogen (again not using the ratio formula) but using the peak strength as a function of its concentration. In our calibration set we found the hydrogen peak average was ~20000 counts for 4% [H]. On this basis, from Table I we estimate that [H] present in the sample is in the range of 1.7%, 3%, 1.8%, 0.2% and 2.5% for the geo-samples. The H to Si ratios does not follow the calibration curves.

Finally, we made use of the following formula by Dulong (not accounting for the sulfur and oxygen)

Q (Btu/lb)=145 * C%+620.28 * H%+40.5 * S%-77 * O%

to get Btu value as 8328.8, 10850.0, 9066.2, 13161.6, 16642.4.

The Btu values do not convey much by themselves as long as the respective concentrations of the elements in coal have been determined correctly. The values are in the ballpark with significant bias, but as we mentioned earlier, it could be due to sample preparation technique.

It is a five term formula proposed by Mason and Gandhi [3] and is as follows:
Q=198.11*C+620.31*H+80.93*S+44.956.58*Ash-5153.

It was shown that after correcting for bias, the standard deviation of the calculated value from measured value was 129Btu/lb and was the lowest in comparison to other formulas used.

Although, we showed that contribution per lb from sulfur and oxygen is small, for tons of quantity of coal, this error becomes very large. Therefore, we emphasize that accurate evaluation of concentration of all the constituents listed in the above formula is necessary. Once, we achieve that, the next step is to use the formula, calibrate for the bias and then measure standard deviation from across a large number of samples.

We again reiterate that the way to perform the calibration experiment would be to first get the LIBS data from uncrushed but broken coal samples to access several different spots, average over several shots and then send the samples for laboratory analysis. This ensures that the pellet effects do not play any role in providing huge uncertainties in absolute values.
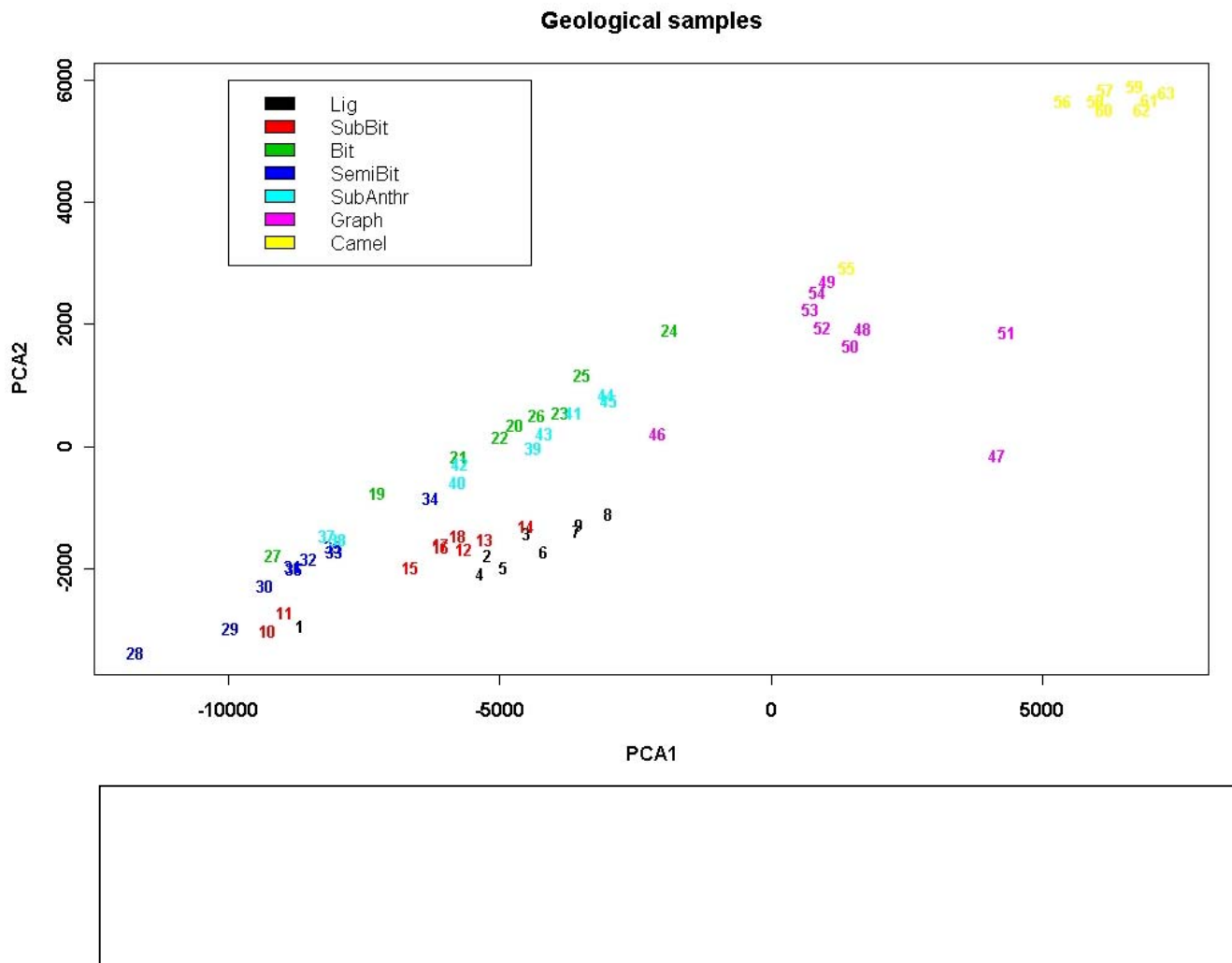
Sulfur

Lack of sulfur was a disappointment. None of the strong lines could be detected in the range we had access to. We do see two lines at 469, and 564 nm, which match the sulfur peaks, but because it lies amidst molecular bands of $C_2$ and seem to exhibit a non-symmetric structure typical of a dimer band, we are not able to precisely confirm its identity. (We also see a strong signal at 769nm but the signal is likely due to presence of K.) There is a strong sulfur line at 900nm reported by many researchers. We tested this range with a third spectrometer system and a cooled ungated CCD detector. Even under He conditions, it was not possible to detect sulfur in the restricted wavelength range we had access to. To determine how sulfur and oxygen would contribute to the heat content, typical concentration of sulfur in the VS sample is ~0.5% to 3% and oxygen ranges from 5 to 20%. For this variation, sulfur only accounts for 1% change, while oxygen accounts for 6%. About 80-85% is contributed by carbon and hydrogen accounts for the rest, which can be as high as 20%. Therefore, even if we miss detecting sulfur it would not affect the heat content calculations. However, for environmental safety reasons, detection of sulfur is required. We will renew our attempts to determine S concentration by probing plasma with a secondary laser system to look for $SO_2$ molecular spectrum.

4. Final system design.

Following our Phase I experiment, we established certain criteria for a final prototype design option. Several designs were considered for optics and spectrometer based on the data analyzed. Instead of describing the system design here, this particular task is detailed in the work plan.

As a final summary, we provide a discrimination plot based on PCA analysis on a second set of geological data with larger coal category and also larger data set (90 data for each sample – and 7 samples in all ranging from Lignite, Sub-Bituminous, Bituminous, Semi-Bituminous, Sub-Anthracite to Graphite and Camel Coal). Moreover, we reduced the number of variables (wavelengths) from 14000 to 2047. We performed the measurements after all calibration procedures were done and used the same experimental conditions as for the nanopowder pellets using the OO system. **Fig. 17** shows a nice discrimination amongst the categories thus proving that for a better controlled experiment and with larger data set, better discrimination can be obtained. Most importantly, PCA analysis enables us to seek out the different blends of coal available in a sample and correlate them to their respective heat content (based on linear calibrations). Despite reduction in the number of variables we were

able to distinguish the different coal categories. In future, we will use the full set of variables (200-900 nm) but selectively pick ratios of needed wavelength peaks and reanalyze the data. The loading vectors would be analyzed to see which peaks contribute most to the differences. In this particular case, as shown by loading vectors (not shown) peaks from ash elements

**Geological samples**



provide the maximum discrimination.


## Phase I conclusions:

- Procedure for calibration of coal samples was determined and accuracy conditions and concentration limits identified. Some samples are present at a concentration range of 0.1%. Even those elements – such as Na, K could be identified and linearity for trace elements demonstrated.
- High concentration elements have a limited range over which they exhibited linear behavior. In our case, it is carbon, silicon and oxygen. We suggested two ways to obtain a monotonic relation against their known concentration range and use a non-

linear empirical fitted model to account for their variation. The second option is to use nitrogen spectral features as internal standards.

- We also demonstrated that to a certain degree, principle components can be used to categorize samples into three basic categories – non-coal, low heat coal and high heat coal values. Some theoretical tools were identified to solve for signal non-linearities (other than looking for non-resonant spectral features).
- Calibration sample preparation conditions were elucidated. It was concluded that a reliable procedure would be to obtain coal rock samples, perform LIBS on several sets on which prior information is known, and then send them to be characterized by analytical laboratories. Also it is preferable to make calibrated samples from nanopowders and form into pellets under >50,000psi pressure.
- Heat content calculations were suggested. Further experiments are needed to refine the scope of these measurements.
- Experimental conditions for a real time instrument were explored and instruments identified. Requirements for optics and laser energy were determined.

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