

**PHYSICAL AND CHEMICAL TRANSFORMATIONS DURING PULVERIZED
COAL COMBUSTION -- OPTICAL SYSTEMS FOR MEASUREMENTS**

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INTRODUCTION

One of the most difficult problems in developing diagnostic methods for coal combustion research is that of determining the composition of entrained coal, char, and mineral matter particles in the combustion zone. We have employed two laser-based techniques for the simultaneous measurement of the size, velocity, and elemental composition of particles in combustion flows. Laser spark spectroscopy [1,2], also called laser induced breakdown spectroscopy (LIBS) [3], is used to determine the elemental composition of coal particles. Sizing measurements are done using two-color laser light scattering [4].

Laser spark spectroscopy is a variation of conventional emission spectroscopy which uses a focused pulsed laser beam to generate an optical breakdown, commonly called a laser spark or a laser induced plasma. The origin and uses of this technique are well summarized [5]. Many of its properties are similar to those of conventional arc or spark plasmas as discussed in standard texts on spectrochemistry [6]. As with conventional techniques, the laser spark allows simultaneous multi-element detection. An important advantage is the ability to obtain information in hostile environments, in situ, where electrodes cannot be introduced.

Two principal applications for this technique are proposed. The first is the simultaneous measurement of size, velocity, and composition of single particles and is primarily an analytical research tool for coal combustion studies. The second is the measurement of bulk properties before, during, and after combustion by coaddition of hundreds or thousands of individual spectra. This can be envisioned as an on-line monitor in an operating combustor. Our experiments have elucidated the advantages and difficulties which will be encountered in these applications.

INSTRUMENTATION

The apparatus was arranged so that sizing and spectroscopic information could be obtained simultaneously. A general apparatus diagram for all experiments is shown in a top view in Figure 1. Measurement of particle size and velocity using a two-color colinear beam has been more fully described elsewhere [4].

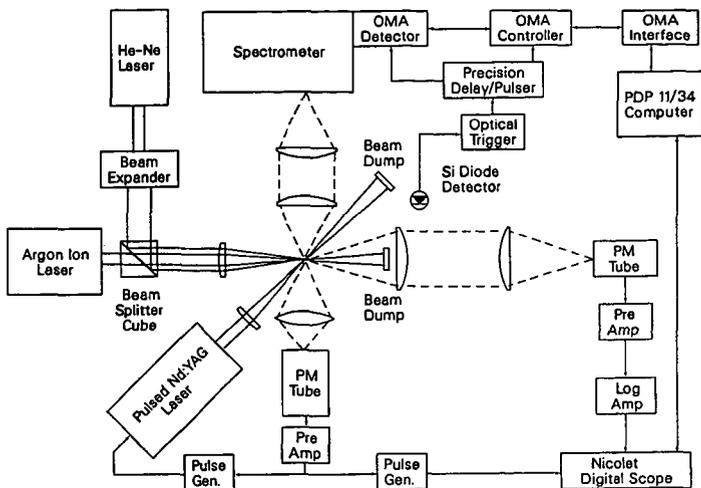


Figure 1. Top view of laser sizing and spark spectroscopy system.

Light Scattering Instrumentation

The two-color scattering technique permits an accurate estimate of particle size and velocity. Beams from He-Ne and Ar-ion lasers were combined using a beam splitter cube. Scattered light from particles passing vertically through the common focal volume was viewed with two photomultiplier tubes: one in the near-forward direction, and the other at 90 degrees to the laser beam axis. Particle scattering signals were used to fire a pulsed Nd:YAG laser, creating a high temperature laser spark from the particle.

This technique can be very satisfactorily calibrated to measure particle size by using regularly shaped particles and orifices. Particle velocity was calculated from a knowledge of the Ar-ion laser beam waist diameter and the transit time of a particle determined from the $1/e$ points in the measured near-forward scattered light intensity.

Laser Spark Instrumentation

Spectra were generated from the plasma formed by the focused Nd:YAG laser beam (Quanta Ray DCR-2, Q-switched, oscillator only). Laser energy was a nominal 110 mJ per pulse at 5320 Å. Important parameters for the acquisition of spectra were timing, optical alignment, and temporal resolution. The irradiance at the focus of the Nd:YAG laser beam was adjusted to ensure breakdown would occur only in the presence of a particle in the focal volume. This eliminated spurious data from a triggered breakdown of the entrainment gases.

The operation of the Nd:YAG laser Q-switch introduced a 250 μ s delay between the arrival of the trigger pulse and firing of the laser. Because the particles under investigation were moving, the optimum focal volume for the Nd:YAG

laser beam was displaced from that of the sizing laser beams. The mean particle velocity could be maintained at a fairly constant value ($\pm 10\%$) in the range of 1 - 5 m/s. We found that with proper experimental alignment of the three beams, about 90% of the particles which triggered the Nd:YAG laser actually formed a plasma due to laser induced breakdown.

Light from a laser spark was imaged on a silicon diode detector to generate a trigger pulse which initiated collection of the spectrum (Figure 1). The laser spark was imaged on the entrance slit of the spectrometer (Spex Model 1870) with a nominal 20 μm slit width and a gated, intensified diode array (PAR Model 1420). The emission spectrum was then digitized and stored on hard disc for subsequent analysis.

Previous investigators [2,7] have shown that time resolution is essential for analytical uses of laser plasmas. For times less than 1 μs following laser induced breakdown the emission spectrum was dominated by continua and lines due to ionized species. Time delays of at least 2 μs were necessary to discriminate against the continuum and to restrict the observed species to neutral and singly ionized atoms. Molecular spectra were observed but were due to recombination of atoms in the plasma, not from molecules originally in the sample. Integration times depended primarily on the intensity of lines observed in a given spectral region, and ranged from 1 to 10 μs for this study.

Particle entrainment system and reactor

Samples investigated were of two forms, liquid droplets or solids of various composition. Liquid droplets of pure substances or solutions were produced using a vibrating orifice generator and were dropped through the optical focal region under ambient conditions. They were used primarily to calibrate the scattering signal.

The entrainment of solid particles into a stream of purified dry nitrogen was done with a particle feeder. The fluidized solid particles were introduced along the vertical centerline of a circular premixed burner through a central tube. This was aligned below the intersection of the three laser beams as shown in Figure 1. The combustion region of the burner was 50 mm in diameter and was surrounded by a co-flow region for flow regulation and to prevent mixing with the laboratory atmosphere.

A flat flame above the burner surface produced a hot, vertically flowing column of gases into which the particulates were entrained. By varying the amounts of the fuel, oxidizer and diluent gases, one could control the combustion temperature and residual oxygen partial pressure in the hot environment. Methane and oxygen were used in this study, with nitrogen added as a diluent. Gas flows were controlled with mass flowmeters. Temperatures 50 mm above the burner surface measured with a Pt-Rh thermocouple in the absence of particles were on the order of 1500° C.

CALIBRATION

Calibration of the sizing apparatus

Calibration of the particle sizing apparatus was done by the measurement of near-forward scattering intensities of uniform liquid droplets and precision

pinholes. Once the calibration scale was established, the daily measurement of scattering intensity from a single reference pinhole was used to establish a current working curve. This is more fully described elsewhere [4].

Calibration of and factors affecting the spectroscopic signal

To be useful, the observed emission intensities had to be related to relative and absolute elemental compositions. There were several variables with which to deal: (1) incident laser power, (2) particle size, (3) particle composition and associated matrix effects, (4) location of the particle in the laser focal volume, (5) amount of the particle material removed and ionized, (6) plasma temperature and possible self-absorption, (7) image location on the spectrometer entrance slit, and (8) the lack of "standard reference materials" for coals on a particle-by-particle basis.

It was first necessary to establish the level of reproducibility of the emission signal for well-characterized, monodispersed, homogenous samples. The use of pure solid particles was not found to be particularly valuable for this purpose. Analytical lines for most metallic species found in coal were strongly self-absorbed in laser spark emissions from target particles consisting of the pure oxides or simple salts.

Calibration experiments were undertaken using homogenous solid particles composed of an ion exchange resin, Amberlite, loaded with calcium at 10 wt %. A typical spark emission spectrum is shown in Figure 2. A small magnesium impurity was present in the ion-exchange material, and additional lines due to Mg I and Mg II were also observed in this spectrum.

These multiple line spectra (and others discussed below) were fit by a non-linear least squares computer program using Lorentzian line shapes and reference intensities from the NBS collections [8,9]. The calculated reference intensities for each species were multiplied by a coefficient to fit the experimental data. Because the reference intensities were determined for standard concentrations [8,9], the ratio of the coefficients for different elements should be closely related to the relative elemental concentrations.

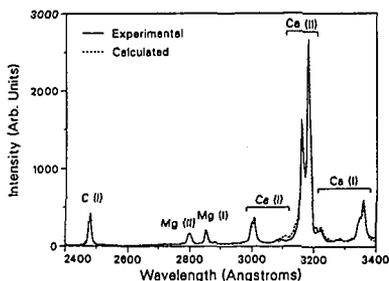


Figure 2. Laser spark spectrum of a single ion-exchange resin particle.

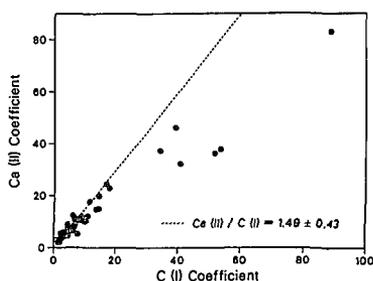


Figure 3. Least-squares fitting coefficients for Ca II and C I in 80 spark spectra.

/About 80 particles were analyzed for the various C, Ca, and Mg transitions. Ratios of metal/carbon coefficients were calculated in order to assess the reproducibility of emission intensities on a shot-to-shot basis. The intensities for Ca II and C I (Figure 3) are clearly correlated and show an initial linear relationship. Points corresponding to higher counts show a gradual saturation. Within the linear regime the scatter may be due to particle heterogeneity and shot-to-shot variations of the excitation within the plasma. The latter can be caused by variations in the coupling of the energy into the plasma, or the size or morphology of the particle. Even so, the existence of a linear regime is evidence of significant shot-to-shot reproducibility.

Previous studies [10] have shown that matrix effects exist for different atomic species included in a solid material using laser spark spectroscopy. This is typical of conventional emission spectroscopy techniques also. For a given matrix composition of a bulk phase the most volatile atomic species were preferentially removed in the high temperature plasma, and the observed elemental composition of the ionized material was found to differ from the bulk composition accordingly. We might also expect such effects in our study.

Measurements on solid particles will always have to contend with incomplete vaporization. Calculations based on the heat of vaporization of carbon indicated that the coupling of 1% of the available incident laser energy into a solid particle would completely vaporize particles no larger than 10 μm in diameter. For incomplete vaporization, particle heterogeneity could be a serious problem. However, it appears impractical to use a laser with sufficient energy to vaporize large particles.

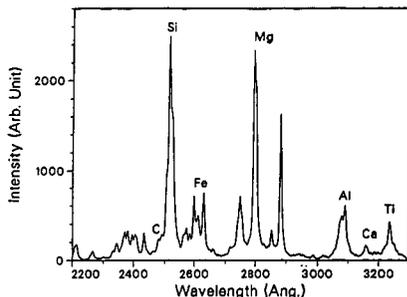
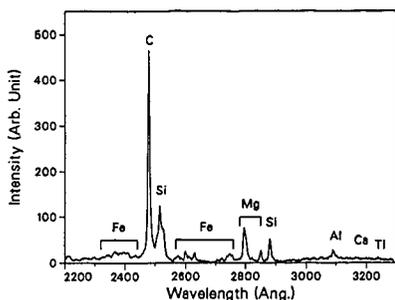
Coupling of the laser energy into the target particle is complicated by the complexities of hitting a moving particle with a pulsed laser beam at a stationary focal point. Careful control of particle feeding conditions and laminar flow of the gases above the reactor surface helped to minimize variations in particle velocity. Light scattering data indicated an axial velocity distribution of $\pm 10\%$ about a mean velocity of 2 m/s for pulverized coal particles. For a Q-switch delay of 250 μs , this would yield an axial variation of $\pm 50 \mu\text{m}$ in particle position. This is quite large compared to the calculated beam waist of 100 μm for our Nd:YAG laser, and is probably the dominant experimental variable for the coupling of incident laser light with the plasma.

RESULTS

Pulverized coal particles were entrained in the reactor system and spark emission spectra were collected with and without sizing data for single particles under different conditions. Three bituminous coals were studied: an Illinois #6, a Pittsburgh #8, and a Kentucky #11 coal. All had high temperature ash contents of 13 to 14% with varying amounts of inorganic constituents. Particles were size classified and the 63-75 μm diameter fraction for the first two coals, and the 30-50 μm diameter fraction for the third coal, were used here.

Qualitative Results

Extensive spectra were taken from 1900 to 7700 \AA to assign emission lines and determine sensitivity to trace components. Representative spectra of single particles for the same coal sample are shown in Figures 4a and 4b. Two of the



Figures 4a - 4b. Representative laser spark spectra of single coal particles.

most useful aspects of laser spark spectroscopy in the study of coal combustion are seen: the sensitivity to inorganic constituents in the organic material, and the capability for simultaneous multi-element detection.

The following elements were identified in these survey spectra at room temperature: C, H, O, N, Li, Na, K, Mg, Ca, Sr, Ba, Al, Si, Ti, Mn and Fe. Major species were silicon, aluminum, calcium, magnesium, iron, sodium, potassium and titanium. The rest were trace constituents. All the identifications were made from spectra of individual particles.

We also searched for sulfur and phosphorous lines. The array-spectrometer system was not sensitive at the sulfur resonance lines (1800-1900 Å), and phosphorous was simply not seen. Other trace metallic elements at lower concentrations, such as chromium and vanadium (with average bulk concentrations of 3-30 ppm), were not detected with our current instrumentation. Sensitivity to these elements may be improved by coaddition of many single particle shots. An ultimate detection limit for most metallic species in single coal particles is likely to be below 100 ppm. Molecular species originally in the coal are dissociated by the plasma and not observed. Recombination of hot atoms gave rise to strong CN bands, however, which obscured the regions from 3750-3900 Å and 4150-4220 Å. No other excited molecular or radical spectra were observed.

Experiments were also performed at combustion temperatures. While the residence time was quite short, the coal particles had ignited and were undergoing vigorous devolatilization at this point. Data of high quality, similar to Figures 4a and 4b, were collected in situ without significant degradation in the signal/noise ratio for ambient conditions.

Semi-quantitative results

The absolute mass sensitivity of the technique may be illustrated by considering the spectrum in Figure 5. Sizing data indicated that this particle was of 29.5 μm diameter. Based on a density of 1.5 g/cc for coal, this yielded a total particle mass of 20 ng. We assumed a plasma temperature of 1 eV (11,600 K) and calculated relative intensities for transitions of C and Fe. With an average carbon content of 83% (dry basis), the observed relative intensities

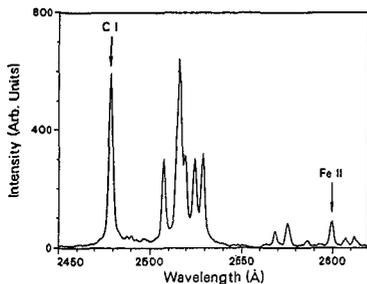


Figure 5. Laser spark spectrum of a single, 20 ng coal particle showing detection of 700 fg of iron.

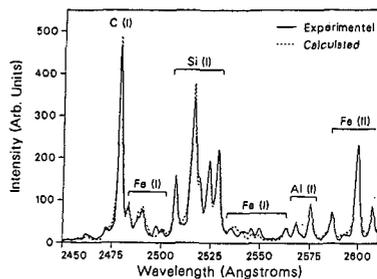


Figure 6. Comparison of experimental and calculated spectra for a single coal particle.

corresponded to detected quantities of 0.7 pg of iron. The actual absolute amount of material in the plasma was probably less due to incomplete vaporization of the particle during the excitation process.

Since coal is a very heterogeneous material, one expects a large variation in emission intensity for the observed constituents on a particle-by-particle basis. A convenient and systematic way of studying these variations is to examine the relative intensity for two elements for a large number of particles. If this is done over a narrow spectral bandwidth, then the optical system response will be reasonably constant and the observed intensity ratios can be semi-quantitatively related to reference intensities [8,9] for a given average plasma temperature.

For particles at ambient temperature and those examined after short residence times at combustion temperatures, we observed the spectral region from 2400 to 2650 Å and chose the ubiquitous C I transition at 2478 Å as the reference line. This region also contained several transitions due to Si I, Al I, Fe I and Fe II. Even though carbon is a major species, the C I line at 2478 Å is not likely to saturate since the lower level of the transition is at 2.68 eV.

In our first attempt at quantitative analysis, we obtained spectra from eighty particles of Kentucky #11 coal entrained at room temperature in nitrogen. Synthetic spectra were computed rapidly and produced a good fit to each individual spectrum as illustrated in Figure 6. Deviations between calculated and observed intensities for several Fe I and II transitions were probably due to a difference in plasma temperatures for our experiment and the reference intensity data. The least-squares analysis yielded fitting coefficients which we related to the relative concentration of the element.

Matrix effects also will alter these relative elemental line intensities with respect to the reference data [8,9]. While these variations may be most directly accounted for by calibration with suitable homogeneous reference particles, difficulties in making such standards may necessitate their evaluation

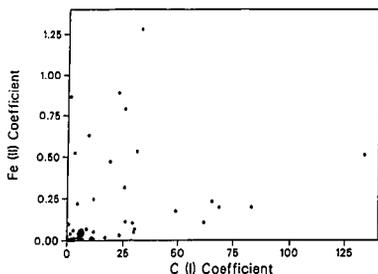


Figure 7. Relative amounts of Fe and C for 80 single coal particles.

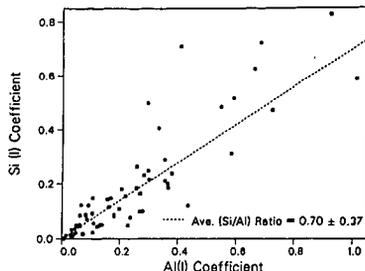


Figure 8. Relative amounts of Si and Al for 80 single coal particles.

through a detailed statistical comparison of bulk chemical analyses with a large number of laser spark spectra.

A plot of C I and Fe II fitting coefficients obtained from these spectra is shown in Figure 7 and illustrates the heterogeneity of the coal particles. Particles rich in iron show a random distribution of points with high Fe II coefficients, and are attributed to inclusions of iron-bearing minerals (predominantly pyrite). On the other hand, a second population of points is seen near the x-axis with low values of Fe II coefficients. These appear to be highly correlated with carbon content, and may be due to iron distributed homogeneously throughout the organic matrix. Scanning electron microscopy results on a sample of this coal substantiated that these two distinct iron populations exist [11].

A second example of relative elemental composition is shown in Figure 8 for silicon and aluminum from the same set of 80 spectra. These two elements appear to be correlated and present in comparable amounts. Some of the considerable scatter in the data is due to variations in plasma temperature; however, a much larger effect is that the various clay minerals containing aluminum and silicon may differ significantly in relative elemental composition. Further, another source of silicon in the coal is quartz, which would be completely uncorrelated with the silicon and aluminum present in clays.

In contrast to these two examples, sodium is often quite evenly distributed in bituminous coals, and this is illustrated in Figure 9 for 50 particles of the Kentucky #11 sample. This plot is of experimental intensities for the doublet at 5890 and 5896 Å, and these values have not been normalized against other transitions. The data illustrate the very uniform distribution of sodium in this coal despite differences in plasma conditions mentioned above.

DISCUSSION

Our results demonstrate the potential for laser spark spectroscopy as an *in situ* analytical technique for particulate composition in ambient and high

temperature environments. An obvious next step is the quantitation of emission intensities. This can take two directions: correlation with available bulk analyses through coaddition of many single particle analyses, and development of appropriate standard materials.

In the present study, the sizing capability was often not employed because sized particles were used. In general, however, simultaneous sizing and spectral analysis will allow an approximate mass analysis on each particle. The addition of hundreds to thousands of these could begin to emulate the bulk analysis. The study of coals with significantly differing composition could verify the sensitivity of the technique, and the likely result would be a semi-quantitative in situ analysis capability.

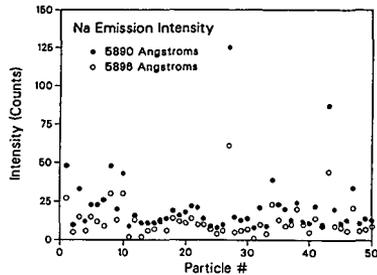


Figure 9. Distribution of sodium in spark spectra of 50 coal particles.

Experiments with uniform ion exchange resin particles have demonstrated that reproducible results can be obtained with well characterized particles. The difficulty in acquiring adequate calibration standards for quantitative analysis lies not only in their preparation, but also in the certification of their homogeneity on a particle-by-particle basis. A possible approach might be the doping of porous char particles with a given elemental species. The issue of emission intensity dependence on the amount of particle vaporized during excitation may be studied using reference particles with varying levels of incident laser energy.

Another important aspect of particle inhomogeneity is the evolving character of surface composition during combustion, since significant quantities of mineral species may coalesce on the particle surface. Incomplete vaporization of the solid during excitation would yield intensities not representative of the entire particle, and calculated compositions would be biased as a result.

The increase in mineral composition relative to the organic matrix during the combustion process would be expected to show an increasing amount of self-absorption and, finally, line reversal for the strongest transitions. This potential problem may be mitigated in the analysis of post-combustion material since ash particles are smaller than the initial pulverized fuel particles, and might be quantitatively vaporized by the incident pulsed laser beam.

CONCLUSIONS

The experiments described above have demonstrated that qualitative analysis can be performed on single particles, in situ, in hostile environments. The practical level of signal reproducibility has been measured, and the first indication of semi-quantitative results has been established. Problem areas have been identified. Some can be overcome while others will limit the applicability of the technique.

The studies will continue with emphasis on establishing the semi-quantitative capability of the combined techniques for well characterized coals, and for new homogeneous standard materials. The experiment will be integrated with a laboratory bench-scale combustor, and the capability to discern changes in coal composition during burning will be investigated by spectral analysis as a function of coal type, combustion residence time, and gas phase chemistry.

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