

DETERMINATION OF ATOMIC SODIUM IN COAL COMBUSTION USING LASER-INDUCED FLUORESCENCE

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ABSTRACT

A laser-induced fluorescence spectrometer (LIFS) was assembled and sodium atom densities produced from the aspiration of solutions and direct introduction of a lignite into a flame were determined from fluorescence measurements. The average flame volume observed was 0.4 mm^3 . This small volume allowed the measurement of sodium concentrations as a function of vertical and horizontal flame position. Temperature profiles of the flames employed were also obtained and compared with the sodium atom densities. The sodium atom densities calculated from the fluorescence measurements (N_{fl}) are compared with the sodium atom densities calculated from thermodynamic considerations (N_{th}) and sodium concentrations derived from aspiration/introduction rates (N_{ia}).

INTRODUCTION

Many western low-rank coals contain significant quantities of alkali, primarily sodium, that is associated as salts of organic groups (1,2). Sodium content has been correlated with serious operational problems in combustion systems such as convective pass fouling (3,4). The flame-volatilized alkali can condense on surfaces of entrained fly ash particles forming low-melting-point layers which enhance adhesion of ash particles to heat transfer surfaces (5,6). Other studies relating flame composition and temperature to sodium volatilization have been published (7,8). These studies are all similar in that only the initial and final forms of sodium were analyzed. A few attempts have been made using mass spectrometry to directly measure amounts of alkali in coal-fed flames (8,9), with some difficulty. In order to accurately measure the density of volatilized sodium atoms in the flame region, an alternative approach is necessary.

Laser-induced fluorescence spectroscopy (LIFS) is well suited for probing various locations in flames to examine alkali release. This technique permits the quantitation of atomic species and has a small spatial resolution. The goal of this study was to determine if LIFS could be used to quantitate sodium atom densities in flames into which coal had been directly introduced, and to determine the effect of temperature and flame position on the sodium atom densities so measured.

EXPERIMENTAL

A laser-induced fluorescence spectrometer (LIFS) was used to measure the sodium atom densities produced from the aspiration of solutions and direct introduction of solids into a methane/argon/oxygen flame (2.9, 3.2, and 3.2 L/min, respectively). Argon (3.9 L/min) was used for the flame sheath. The excitation beam was generated by a flashlamp-pumped dye laser, focused and passed through a polarizing beam splitter. The horizontally polarized

beam was directed through the flame and the intensity of the vertically polarized rejected beam was monitored with a photomultiplier tube (PMT). The bandwidth of the laser beam was 2-3 Å, the maximum energy available was 1 J, and the pulse length was 500-1000 ns. The diameter of the laser beam in the sample region was 2.0 mm.

The fluorescence detector was mounted perpendicular to the excitation beam in the horizontal plane, and two convex lenses were used to collect the Na fluorescence and focus it on the monochromator entrance slit. A polarizing filter set to pass only horizontally polarized light was placed directly in front of the monochromator. A PMT was positioned at the monochromator exit slit. The monochromator settings used for the Beulah lignite studies produced a bandpass of 1.2 nm and measured a sample volume of 0.4 mm³. Various monochromator settings were used in the solution studies. Stanford Research Systems gated integrator/boxcar averagers were used to collect the signals from both PMTs. The first 300 ns of the fluorescence pulse was used to quantitate the sodium atom density. The boxcars were triggered by the laser flash via a photodiode.

The reported flame temperatures are those directly measured with a Pt/Pt-10%Rh thermocouple. The burner head was similar to that used by Daily and Chan (10). The radius of the burner head was 0.25 inch and the horizontal positions reported are those measured from the burner center with positive values indicating positions closest to the detector.

Solutions were aspirated into the flame via a Perkin Elmer nebulizer. The coal samples were introduced through a spouting bed coal feeder at a rate of 38.6 mg/min. The coal selected for the initial studies was a Beulah lignite. The proximate, ultimate, and ash analyses of this coal are shown in Table 1. A sized fraction between 200 and 325 mesh dried at 50 °C and 1 torr was used in this study.

The fluorescence intensity of the sodium solutions was defined as the difference between the intensity measured upon the aspiration of the analyte-containing solution less the intensity measured when plain deionized water was employed. The background signal for the coal studies was measured by tuning the laser and the monochromator to a wavelength 3 nm lower than the sodium doublet and introducing the coal sample. The fluorescence signal was taken as the difference between the intensity measured at the sodium doublet and the background measured at the lower wavelength.

The fluorescence data were obtained by taking ten points and averaging the results and calculating the standard deviation. The data among the original ten points not within a standard deviation were discarded leaving six to nine values to average for the reported data point.

The sodium atom densities were calculated in two different ways: from fluorescence intensities in the manner of Daily (11) to obtain N_H values, and from a thermodynamic model described by Benson (12) to generate N_H values. The total sodium concentrations in the flame were derived from sample aspiration/introduction rates following the procedure suggested by Winefordner and Vickers (13) to obtain N_{Ia} values.

RESULTS

The LIFS was assembled and tested by aspirating sodium-containing solutions into the burner. The fluorescence signal was found to be linear over three orders of magnitude of Na concentration ($N_{\text{Na}} = 7.6 \times 10^7$ atoms/mm³ to $N_{\text{Na}} = 7.6 \times 10^{10}$ atoms/mm³). The N_{H} values for these solutions varied from 1.0×10^7 atoms/mm³ to 1.0×10^{10} atoms/mm³ respectively. The fluorescence measurements were taken at the flame edge closest to the detector. Five different sodium salts (NaCl, Na₂CO₃, Na₂S₂O₃, NaCO₂C₆H₅ and NaOH) were analyzed in the solution studies. The fluorescence intensity was independent of the sodium source.

In order to correlate the fluorescence measurements to actual sodium atom densities in the flame, it was necessary to establish saturation of the fluorescence signal (11). Plots of fluorescence intensity vs. laser power were obtained for both the solution studies and the Beulah lignite profiles. The laser intensity necessary to achieve saturation in the solution studies was 1.5×10^6 W/cm² nm and 1.2×10^7 W/cm² nm for the coal studies.

A horizontal fluorescence profile produced by the introduction of Beulah lignite into the methane/argon/oxygen flame was obtained (Figure 1). These results show that significantly higher fluorescence is observed upon viewing the side of the flame closest to the detector. The maximum fluorescence was observed at 0.28 inch from the flame center, producing the corresponding maximum in calculated sodium atom density.

A vertical fluorescence profile taken at the flame center is shown in Figure 2. The fluorescence signal was highest directly above the burner head, and decreased to a constant value at positions between 0.115 to 1.115 inches above the burner. A vertical temperature profile taken at a position of 0.175 inch is shown in Figure 3. The temperature was greatest at a distance of 0.056 inch above the burner. The temperature decreased from 1710 °C to 1600 °C upon travelling from 0.056 to 1.525 inches.

A vertical fluorescence profile was taken at the horizontal position of 0.35 inch (Figure 4). This graph shows that the fluorescence initially increases with vertical position and then levels off at an intensity corresponding to 1.6×10^9 atoms/mm³. A vertical temperature profile was taken at the horizontal position of 0.35 inch (Figure 5). The temperature at this position increased rapidly with vertical position and leveled at a maximum near 1600 °C.

DISCUSSION

LIFS can measure changes in the density of sodium atoms generated by the introduction of solutions and solids into a flame. The linearity of the sodium concentration profile established this fact for solutions. The horizontal profile of Beulah lignite (Figure 1) establishes this fact for solids by showing increased fluorescence readings upon moving from outside to inside the flame zone.

The initial solution studies show that the LIFS can be used to quantitate sodium atom density in the flame, in addition to merely measuring differences in concentration. The

uniform increase in fluorescence signal with increased sample concentration demonstrates a range of concentration where quantitation is possible. The observation that the N_{ff} value is independent of the composition of the initial sodium salt indicates that equilibration of the sodium atoms with the other flame species is complete, and that this equilibrium is not significantly affected by the identity of the counter ion. It is significant that the N_{ff} values are only 14% of the N_{Ia} values, while the thermodynamic calculations (N_{ff}) predict that 83% of the sodium should be in the atomic form. The discrepancy between N_{Ia} and N_{ff} values is of a magnitude similar to that reported by Smith et al. (14). These workers attributed this discrepancy to the estimates which contribute to N_{Ia} , most significant in our case is the uncertainty in the degree of flame expansion. This explanation is realistic and therefore the difference between the percentages of sodium present in the atomic form calculated from the N_{ff}/N_{Ia} ratio (14%) and that from thermodynamics (83%) is most likely due to the inaccuracy of N_{Ia} .

The seemingly low N_{ff} values could also be due to decreased fluorescence intensity because of chemical reactions of the excited state sodium atoms (quenching). These types of reactions have been detailed by Muller et al. (15). In order to avoid this complication in our measurements only the initial 300 ns of the fluorescence was used for quantitation.

The calculation of the sodium atom densities depends on operation in the saturated state. Saturation was confirmed in both the solution and coal studies. The intensities needed for saturation are comparable to those reported by Smith et al. (14) for sodium solutions. Our observation that the saturation threshold is higher for solids than for solutions may be due to differences in the optical densities of the flames.

The horizontal profile of Beulah lignite (Figure 1) shows a maximum N_{ff} value at the flame edge closest to the detector. This asymmetry is a result of self absorption and/or the optical density of the coal entraining flame. A similar result was observed by Daily and Chan (10) when solutions of high sodium concentration were measured. This result points to the necessity of making measurements near the flame edge if accurate quantitation is desired.

The vertical fluorescence profile taken at the center of the flame (Figure 2) shows the fluorescence signal to be constant above 0.1 inch. Comparison of this result to the profile taken at the flame edge shows that the self absorption effect occurs up to flame positions of 1.115 inch. Comparison of Figure 2 with Figure 3 shows the fluorescence to be unaffected by small temperature changes. Comparison of Figure 4 to Figure 5 shows that the fluorescence apparently increases with flame temperature. The large variation in flame temperature at this latter horizontal position (0.35 inch) is because this is outside the burner radius and increasing vertical position moves the sample volume from outside to inside the expanded flame zone. Thus the fluorescence signal should increase as the observation point is moved into the active flame. (This latter fact leads to the conclusion that the data points taken at vertical positions of 0.015 inch are artifacts due to reflection of the laser off the burner head and do not represent actual sodium atom fluorescence.)

The vertical fluorescence profile taken at the flame edge (Figure 4) shows that N_{ff} reaches a maximum value of 2.1×10^9 atoms/mm³; this corresponds to 1.8% of the N_{Ia} value

(1.2×10^{11} atoms/mm³). The thermodynamic calculations predict 83% of the sodium to be released at equilibrium. The $N_{\text{H}}/N_{\text{Ia}}$ ratio for the coal (1.8%) is approximately 7.8 times smaller than that observed for solutions (14%). If we assume that equilibrium was reached in the solution studies, and that the N_{H} values are correct, then the N_{Ia} values are 5.9 times larger than the actual sodium densities. Incorporating this factor into N_{Ia} for coal produces the conclusion that the maximum amount of sodium present as atomic vapor in the flame containing Beulah lignite is 11%.

SUMMARY AND CONCLUSIONS

LIFS can be used to measure differences in sodium atom concentrations in both solution- and solid-containing flames. Quantitation of the sodium atom density is possible at the flame edge. The sodium atom densities produced from the introduction of Beulah lignite are not affected by small changes in temperature. The maximum percentage of sodium present as atomic vapor in the Beulah lignite flame was 11% of the total sodium in the coal.

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TABLE I.
Analysis of Beulah High-Sodium Lignite.

| Ultimate Analysis (wt% moisture-free) | | Ash Analysis (wt% ASTM) | |
|--|------|--------------------------------|------|
| C | 62.8 | SiO ₂ | 20.4 |
| H | 3.9 | Al ₂ O ₃ | 12.6 |
| N | 1.5 | Fe ₂ O ₃ | 10.8 |
| S | 1.7 | TiO ₂ | 1.2 |
| O | 16.8 | P ₂ O ₅ | 0.9 |
| ash | 13.3 | CaO | 18.9 |
| Proximate Analysis (wt% as received) | | MgO | 5.9 |
| H ₂ O | 34.9 | Na ₂ O | 6.3 |
| ash | 8.7 | K ₂ O | 0.0 |
| | | SO ₃ | 22.8 |

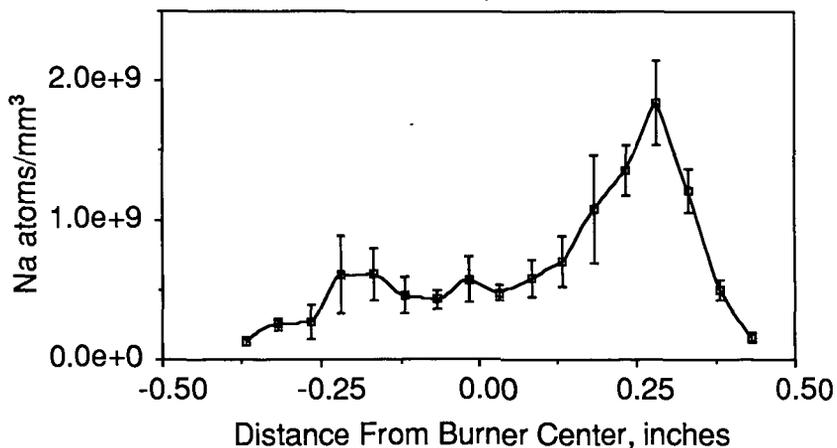


Figure 1. Horizontal fluorescence profile of Beulah lignite at a vertical position of 0.415 inch.

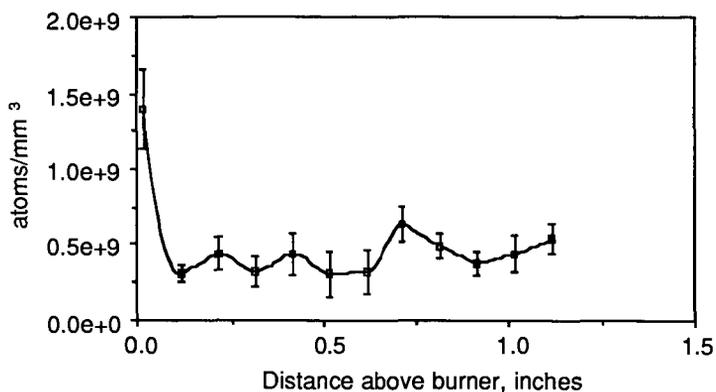


Figure 2. Vertical fluorescence profile of Beulah lignite at the flame center.

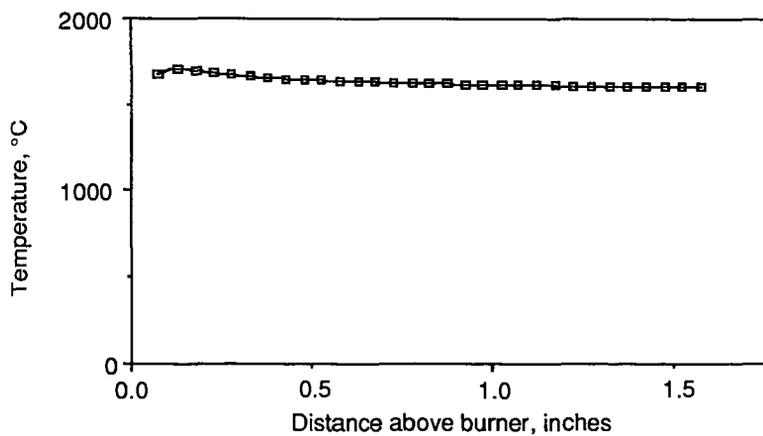


Figure 3. Vertical temperature profile of Beulah lignite at a horizontal position of 0.175 inch.

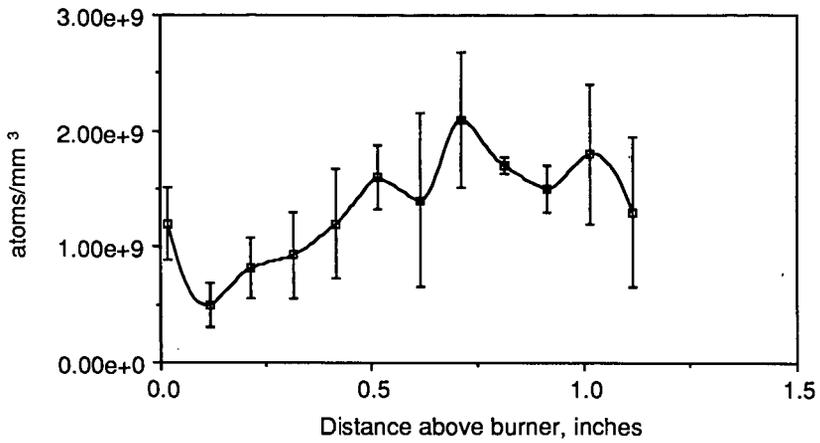


Figure 4. Vertical fluorescence profile of Beulah lignite at a horizontal position of 0.35 inch..

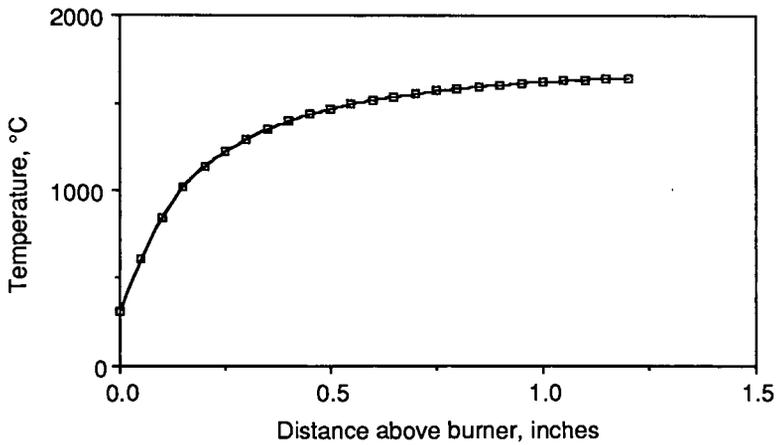


Figure 5. Vertical temperature profile of Beulah lignite at a horizontal position of 0.35 inch.