Two-line atomic fluorescence as a temperature probe for highly sooting flames

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We investigate the applicability of two-line atomic fluorescence (TLAF) from seeded indium atoms for temperature measurements in highly sooting flames. The results show that TLAF holds promise for two-dimensional temperature measurements in sooting and fuel-rich flames under conditions in which other thermometry techniques fail, a result that is attributed to the superior characteristics of the indium atomization process. Furthermore, no native species was found to interfere spectrally with the detected TLAF wavelengths. Advantages of and problems with the technique are discussed. © 2000 Optical Society of America

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For the development of soot formation models, detailed knowledge of conditions that prevail in sooting and fuel-rich flames is of fundamental importance. Laser diagnostics play a vital role in this task. Several laser techniques for temperature measurement were employed in the past; see Ref. 1 and references therein. However, these techniques are not easily applied in strongly sooting flames owing to the strong absorption, spectral interference from particulate scattering, and large molecular fluorescence that occur in such flames. Rotational coherent anti-Stokes Raman scattering (CARS) is an effective technique for point measurements at low to moderate temperatures.[2] For two-dimensional temperature measurements, however, a novel approach based on filtered Rayleigh scattering has been applied successfully in fuel-rich combustion.[3] Furthermore, various laser-induced fluorescence strategies for thermometry have been tried, based either on naturally occurring species such as OH (Ref. 4) and NO (Ref. 5) or on seeded atoms.[6] However, the use of OH and NO in sooting flames is limited because of the low species concentrations, the absorption at the excitation wavelengths, and the emission induced by interfering species that are attributable to those flames. These problems can be partially overcome by seeding the combustion process with suitable atoms as thermometry markers. Experiments in fuel-rich flames were performed based on thermally assisted fluorescence of gallium (Ga) atoms.[7] The disadvantage of both filtered Rayleigh scattering and thermally assisted fluorescence is that knowledge of collisional cross sections of all involved species is required. In highly sooting, turbulent flames this parameter is difficult to assess.

In this context, two-line atomic fluorescence (TLAF) is an attractive alternative because the technique is not affected by molecular collisions.[8] TLAF involves sequentially measuring the Stokes and anti-Stokes direct-line fluorescence produced by optical excitation in a three-level system. Temperature T is then evaluated from the ratio of the corresponding fluorescence signals. As the excitation is to the same upper state for each fluorescence process, the effects of quenching in the linear excitation regime are exactly the same and cancel out in the expression for T. Two-dimensional application of TLAF has been demonstrated and successfully applied in practical turbulent combustion processes under lean conditions.[9,10] In the research reported in Ref. 10 it was shown that indium is particularly suitable as a tracer because its T sensitivity covers nearly the entire range of temperatures encountered in practical combustion. Here we assess the feasibility of performing measurements in highly sooting environments.

The experiments were performed in a slot burner fitted with a standard analytical flame atomizer assembly (Perkin-Elmer). Atmospheric-pressure premixed acetylene (C_2H_2)/air flames were seeded with aqueous solutions of indium chloride ($InCl_3$). The data presented here correspond to fuel equivalence ratios $\Phi = 1.0$, $\Phi = 2.5$, and $\Phi = 3.5$. The flame flows were maintained by mass-flow controllers with 7.50 standard liters (sl)/min for the main air flow, 4.0 sl/m for the seeding flow, and a C_2H_2 flow that varied from 0.965 to 3.38 sl/m. The experimental setup is shown in Fig. 1. To investigate the effect of Φ on the production of indium atoms, we directly imaged flame emission onto the entrance slit of a 150-mm spectrograph. Figure 2 shows emission spectra for the three stoichiometries used; clearly, a marked signal increase is observed in fuel-rich flames. It seems that the process by which indium atoms are produced is more efficient in rich ($\Phi > 1$) than in lean flames because the rate of indium oxidation is lower in rich flames. In lean-combustion processes and in the reaction zone, where OH and O_2 concentrations are excessive, more indium oxides are produced, thus reducing the amount of indium atoms available. The correspondingly lower fluorescence signal in this case is a manifestation of this fact.

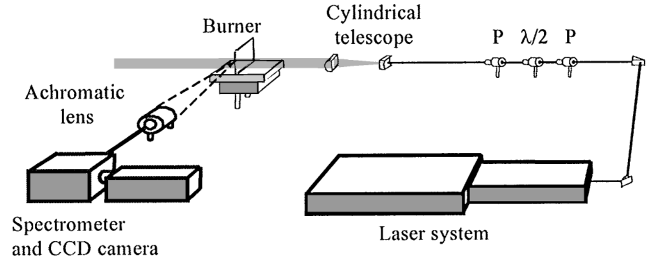

Fig. 1. Experimental setup.

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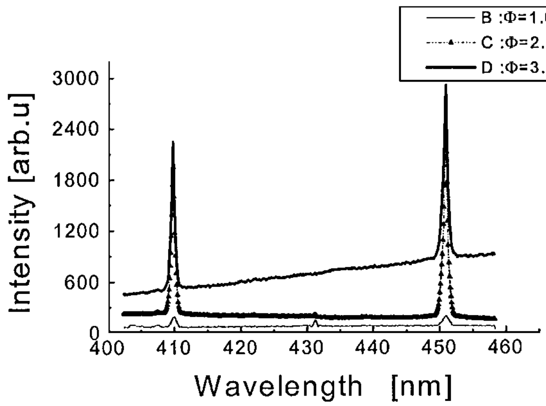

Fig. 2. Emission spectra from three C_2H_2 flames seeded with the same indium concentration, collected through a spectrometer. The detected indium emission increases with Φ. The increasing background originated from the soot particle emission.

Pressure and collisions also affect the rate of indium atom production. In fuel-rich flames a larger number of $C_nH_m{}^+$ ions are present, increasing the rate of ionization of indium. Species with ionization potentials that are >10 eV are not normally ionized by such species under combustion conditions.[11] Indium has an ionization potential of 5.8 eV, and therefore the production of indium ions has to be considered, especially in the reaction zone of the flame, where most of the ions are produced.

However, the dramatic increase in signal at larger Φ suggests that oxidation is the limiting step in indium atom production and that ionization is of subordinate importance. For TLAF in fuel-rich flames this is a major advantage because a lower seeding concentration can be used to reach a sufficient signal-to-noise ratio, minimizing effects of the seeder species on the combustion chemistry. In Fig. 2, increasing background radiation from heated soot particles is also seen, which increases with Φ (camera exposure time, 900 μs). At the short gate time used for TLAF, however, soot emission did not pose a problem.

For the TLAF experiments we used a Nd:YAG pumped optical parametric oscillator laser (Spectra-Physics) to obtain the required wavelengths (410 and 451 nm). Initially excitation scans were performed over indium absorption lines and fluorescence was collected as before, but here time gates of 200 ns were used. The results revealed that, because of the low laser intensity required as a result of the atoms' high oscillator strength, no laser-induced incandescence (LII) from soot particles or laser-induced fluorescence from polycyclic aromatic hydrocarbons (PAH) or other interfering species could be detected. The low laser energy required for TLAF ($3 \pm 1 \times 10^3$ W/cm^2 cm^{-1}) is a tremendous advantage over other techniques, where much higher laser intensities are needed, giving rise to LII from soot particles or LIF from PAH. Such interference is difficult to account for by background subtraction, particularly in fluctuating and turbulent flames, causing uncertainties in evaluated temperatures.

It is essential that the use of tracer species has minimal influence on the combustion process. It has been shown that metallic additives may either decrease soot formation or increase the rate of soot oxidation.[12–14] The metallic ions are thought to increase the soot nucleation rate. Furthermore, they lead to smaller individual particles for a given carbon yield and therefore to higher chemical rates of oxidation. The effect of a given metal is shown to depend almost exclusively on temperature, seeding concentration, and ionization potential. Higher temperatures, higher concentrations, and lower ionization potential cause removal of a greater amount of soot.[14] To investigate whether seeded indium influences these parameters, we measured the soot volume fraction and particle size, using LII, for various stoichiometries and seeding concentrations. Details of the LII technique are described in Refs. 15 and 16.

The two flames investigated had Φ values of 2.5 and 3.5, and the area studied was 10–25 mm above the burner head. Measurements were performed both with and without indium atoms present. Seeding concentrations were increased from 4.5×10^{-4} to 1.0×10^{-2} M of an $InCl_3$ aqueous solution. For unseeded flames, the solution was replaced by distilled water. It is understood that the addition of H_2O in the seeding system under discussion may reduce the flame's temperature by as much as 100–150 K and affect soot production (e.g., by means of a reduction of the soot oxidation rate), but this is of no importance in the present context in which the feasibility of the technique is assessed. However, in practical situations, in which this reduction is not acceptable, one could employ a different method of indium seeding in which this problem does not arise (see, e.g., Ref. 9). The result showed a homogeneous distribution of soot in the measured area. For $\Phi = 0.25$ the measured soot volume fraction was 1.0×10^{-6} and the particle size was ~17 nm. For $\Phi = 3.5$ the fraction increased to 3.0×10^{-6} and the particle size to 20 nm (precision, 30%). Within the measurement uncertainties no influence or changes, either of the soot volume fraction or of the particle size, could be seen when the seeding concentration was increased. These results agree with earlier results[12] obtained for seeded species with similar ionization potential at similar concentrations. Typically a seeding concentration of 25×10^{-4} M of $InCl_3$ solution for TLAF measurements is used.

Finally, temperatures were evaluated for stoichiometries that rose from $\Phi = 1.0$ to $\Phi = 3.5$ (Fig. 3). The temperature was calculated from a region in the center of the flame (indicated by the rectangles in the fluorescence images in Fig. 3) and correspond to an average of 50 single-shot images for each fluorescence signal. Each individual image was normalized by its laser profile to account for intensity variations across the laser sheet. The average fluorescence images were then processed by the method described in Ref. 10.

To obtain the calibration constant C and to provide a measure against which TLAF temperatures could be compared, we made rotational CARS temperature measures at various heights in the flame. Two such measurements are included in Fig. 3. Error bars for the TLAF temperatures that were evaluated

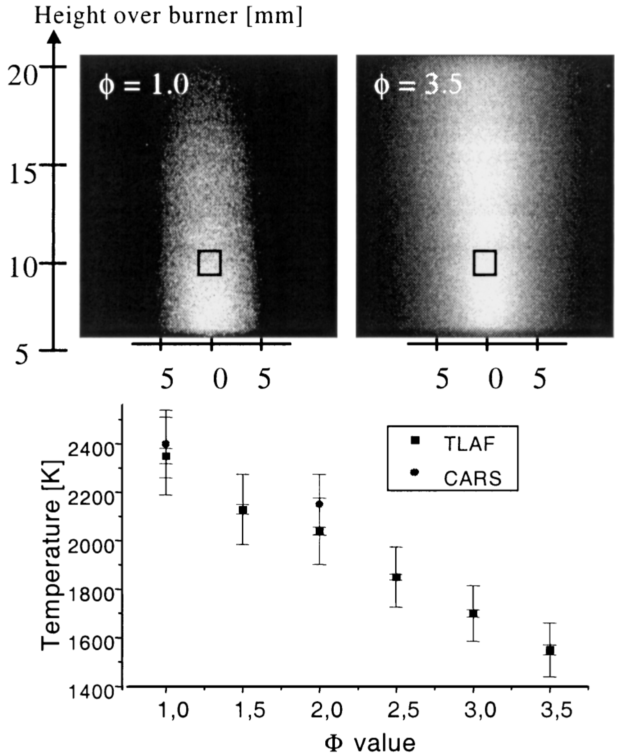

Fig. 3. Mean TLAF temperatures and two CARS reference temperatures for several Φ values in a C_2H_2/air flame (bottom). Top, the 410-nm TLAF signals for $\Phi = 1$ and $\Phi = 3.5$. The temperatures were calculated in the regions indicated by the rectangles shown in the fluorescence images.

correspond to the standard deviation of the temperatures evaluated for each pixel in the rectangles shown. The large temperature drop that is evident in Fig. 3 is a consequence of the change in flame chemistry but is also caused by the fact that the measurement location was kept fixed while the flame's shape changed significantly over the displayed range of ϕ. The accuracy of TLAF point measurements was the subject of a previous publication.[17] Although the discussion in Ref. 17 applies in principle also to the present technique, an accuracy assessment in the present case must take into account the flame and seeding stabilities and the fact that the two TLAF signal components were measured sequentially (i.e., with a long time delay between). On all measurements the TLAF signals were well within the error bars of the CARS reference measurements (see Fig. 3). We estimate an accuracy of 7% for the present technique, although some part of the inaccuracy might stem from actual variations in the seeded flames. The top of Fig. 3 shows the TLAF signal at 410 nm for $\Phi = 1$ and $\Phi = 3.5$. The change in the indium signal profiles with increasing Φ is clearly seen. We found that oxidation plays a major role in the efficiency of the TLAF process. In a fuel-rich flame, in which less oxygen is available, the seeding efficiency is increased owing to the particular characteristics of the indium atomization process.

Our results show that TLAF thermometry performs well over a large range of Φ values, despite the drastic drop in temperature and the high concentration of soot particles associated with large Φ values. Furthermore, indium is an attractive seed species because both the excitation and detection wavelengths are in the visible range (410 and 451 nm), where absorption by hydrocarbons and other native combustion species were found to be negligible. The large oscillator strength of indium means that low laser energies and low seeding concentrations can be used. At the present concentrations no interferences at the TLAF wavelengths were found from LII of soot. Futhermore, we did not measure any effect of indium on the soot production rate. All these facts make In:TLAF attractive for thermometry applications in fuel-rich combustion processes.

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References

1. A. C. Eckbreth, *Laser Diagnostics for Combustion Temperature and Species*, 2nd ed. (Gordon & Breach, Amsterdam, 1996).
2. P.-E. Bengtsson, L. Martinsson, M. Aldén, and S. Kröll, Combust. Sci. Technol. **81,** 129 (1992).
3. D. Hoffman, K.-U. Münch, and A. Leipertz, Opt. Lett. **21,** 525 (1996).
4. U. E. Meier, D. Wolff-Gassmann, J. Heinze, M. Frodermann, I. Magnusson, and G. Josefsson, presented at the 18th International Conference on Instrumentation in Aerospace Simulation Facilities, Toulouse, France, June 14–17, 1999.
5. K. Kohse-Höinghause, Prog. Energy Combust. Sci. **20,** 203 (1994).
6. H. Haraguchi and J. D. Winefordner, Appl. Spectrosc. **31,** 330 (1977).
7. R. G. Joklik, J. J. Horvath, and H. G. Semerjian, Appl. Opt. **30,** 1497 (1991).
8. J. W. Daily, Prog. Energy Combust. Sci. **23,** 133 (1997).
9. C. F. Kaminski, J. Engström, and M. Aldén, Proc. Combust. Inst. **27,** 85 (1998).
10. J. Engström, C. F. Kaminski, M. Aldén, G. Josefsson, and I. Magnusson, in *1999 SAE International Congress and Exposition* (Society of Automotive Engineers, Warrendale, Pa., 1999), paper 1999-01-3541.
11. C. Th. J. Alkemade, *Flame Emission and Atomic Absorption Spectrometry*, Vol. 1 of Fundamental Aspects of Decomposition, Atomization, and Excitation of the Sample in the Flame, J. A. Dean and T. C. Rains, eds. (Marcel Dekker, New York, 1972), pp. 101–150.
12. B. S. Haynes, H. Jander, and H. G. Wagner, Proc. Combust. Inst. **17,** 1365 (1979).
13. U. Wieschnowsky, H. Bockhorn, and F. Fetting, Proc. Combust. Inst. **22,** 343 (1988).
14. P. A. Bonczyk, Fuel **70,** 1403 (1991).
15. R. L. Vander Wal and K. J. Wieland, Appl. Phys. B **59,** 445 (1994).
16. B. Mewes and J. M. Sietzman, Appl. Opt. **36,** 709 (1997).
17. G. Zizak, N. Omenetto, and J. D. Winefordner, Opt. Eng. **23,** 749 (1984).