In-situ measurement of spectral emissivity of aluminum flame combustion products using saturated atomic lines

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1 Introduction

The combustion of light metals, such as aluminum, is widely employed in propulsion technology, metalized explosives, and recently, as carbon-free energy carriers [1]. Micron-sized aluminum powders are known to burn in vapor phase, and produce billions of condensed phase aluminum oxide (Al_2O_3) nanoparticles per cm^3 [2]. Due to their solid/liquid nature, the metal oxide combustion products emit continuous thermal radiation, in contrast to gaseous flames that typically emit electromagnetic radiation in narrow atomic lines or molecular bands. The strong dependence of the radiative heat transfer rate on temperature ($\sim T^4$), has long inspired the belief that radiation plays an important role in the propagation of metal flames, as they are characterized by extremely high temperatures that greatly exceed typical hydrocarbon flames (3541 K for aluminum-air vs 2236 K for methane-air). This claim has been supported by several modelling studies, many of which predict radiation-driven flames in solid-fuel suspensions [3, 4]. These flames exhibit burning velocities ($\sim$ m/s) that are orders of magnitude larger than flames predominantly driven by molecular heat diffusion ($\sim$ cm/s), due to the excessive radiative preheating of the reactants by the products.

However, despite dating back to the 1920s, there still lacks a direct experimental validation of radiation flame models, or convincing evidence of the existence of radiation-driven flames. Paradoxically, the general agreement in aluminum burning velocity data ($\sim$ 30 cm/s) generated using different burner configurations [1], hints towards an insignificant role of thermal radiation, which is supposed to be highly dependent on the flame geometry and flow characteristics. The apparent disconnect between experiments involving high temperature aluminum flames $\sim$ 3500K, and radiation flame models, suggests that the assumptions commonly adopted about the optical properties of the condensed phase species might not be realistic. The effect of radiation on the combustion of a single aluminum particle was assessed in [5]. While the particle size and emissivity of the aluminum oxide cloud (ϵ = 0.45) was based on *ex-situ* experimental measurements, the latter involved composite aluminized solid propellants, generating highly contaminated aluminum oxide particles with an absorption index orders of magnitude higher than values reported with pure alumina. The influence of thermal radiation on iron flames was assessed in [6]. The emissivity of iron oxide particles (ϵ = 0.7) was based on *ex-situ* experimental measurements conducted on millimetric metal oxide droplets, that are orders of magnitude larger than the particles

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present in the flame. For small particles sizes comparable to the wavelength of light, full Mie scattering effects become important [7], which if not taken into account, result in significantly (orders of magnitude) overestimated emissivities, and thus, exaggerated radiation heat transfer rates.

Despite its high relevance and need to address the gap between radiation flame models and metal flames experiments, reliable *in-situ* absolute emissivity measurements of the hot metal oxide combustion products from aluminum flames are lacking. While some studies have attempted to quantify the emissivity of the exhaust plumes from aluminized propellants, significant scatter in the data is often reported [8], and derived particle emissivities often significantly differ from Mie theory [9], likely due to the uncertainty in fuel and metal oxide composition. Lynch et al. [10] experimentally measured the spectral dependence of emissivity of 40-50 nm pure alumina particles at high temperatures $\sim$ 2800K. However, absolute spectral emissivity was not measured, as doing so using usual radiometry techniques is very challenging, as this requires measurement of absolute values of radiation flux and impractical optical factors calibration procedures against a blackbody emitter.

This paper proposes a novel, calibration-free and instrumentally simple method for measuring the absolute spectral emissivity of high-temperature condensed phase emitters in heterogeneous flames. The proposed method is based on directly comparing the intensity of the continuous spectra emitted by the condensed products with the intensity of saturated alkali metal atomic lines. Aluminum oxide combustion products are considered to address the apparent disconnect between radiation flame models and experimental data of aluminum flames. The McGill Bunsen dust burner is used to produce a fresh bulk flow of alumina nanoparticles, on which spatially resolved emission spectroscopy is performed.

2 Physical basis of the proposed method

Consider the case where a trace amount of micron-size sodium chloride (NaCl) salt is added to the aluminum powder metal fuel. Due to the high flame temperature, the excited sodium will emit strong atomic doublet lines at specific wavelengths of 588.9 and 589.5 nm ($^2\mathrm{S}_{1/2}\rightarrow^2\mathrm{P}_{3/2}$, and $^2\mathrm{S}_{1/2}\rightarrow^2\mathrm{P}_{1/2}$, respectively), which will be superimposed on top of the continuous emission from the condensed phase emitters, as illustrated in Figure 1a). The intensity of the atomic lines emitted from a uniform medium at a given wavelength is given by $I_\lambda = I_{\mathrm{BB},\lambda}[(1-\exp(-\alpha_\lambda)]$, where $I_{\mathrm{BB},\lambda}$ and α_λ are the blackbody emission and the optical thickness, respectively [11]. Since the latter is proportional to the concentration of the emitting species $\alpha_\lambda \sim X_i$ (sodium in this case), the intensity of the Na lines will increase as the concentration of NaCl in the fuel is increased, until the signal becomes saturated at sufficiently large concentrations (Figure 1b-c). Under these conditions, the emission signal becomes equal to blackbody radiation ($\lim_{\alpha_\lambda\rightarrow\infty} I_\lambda = I_{\mathrm{BB},\lambda}$), and is, therefore, independent of the element concentration and only a function of the gas temperature. Thus, the basis of the experimental method proposed herein involves saturating the emission signal by increasing the added alkali metal concentration, yielding blackbody emissions at specific wavelengths against which the continuous emission signal from the condensed phase emitters ($I_{\mathrm{cont},\lambda}$) can be directly compared to determine their emissivity $\epsilon_\lambda = I_{\mathrm{cont},\lambda}/I_{\mathrm{BB},\lambda}$.

Alkali metals, such as sodium, are used since only a trace amount is required to saturate the emission ($<$ 0.0005% for 1 cm optical length, Figure 1b), and because these elements emit strong atomic doublets whose intensity ratios can be used as an indicator for saturation. The line strength (S_i) of the first doublet transition at 588.9 nm is almost double that of the second transition at 589.5 nm. This can be seen from Figure 1a), where emission is optically thin ($\alpha_\lambda <<$), and thus, proportional to the line strength $\lim_{\alpha_\lambda\rightarrow 0} I_\lambda = I_{\mathrm{BB},\lambda}\alpha_\lambda \sim \mathrm{S}_i$. Therefore, an indicator of the first sodium peak saturating is when its ratio relative to the second peak start dropping below 2. At a sufficiently large concentration, both peaks become saturated and emit roughly the same intensities, Figure 1c).

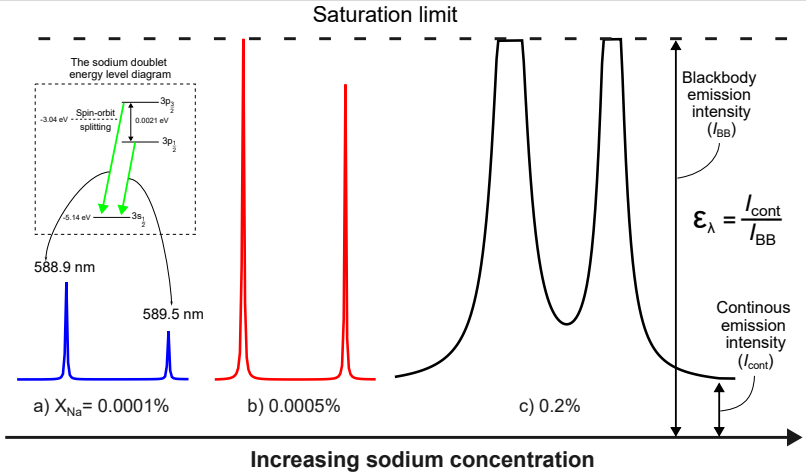

Figure 1: Illustration of the proposed method for measuring absolute spectral emissivity of the particles in suspension that are in thermal equilibrium with the gas by using saturated sodium doublet lines.

To determine the dependence of emissivity on wavelength, a mixture of alkali metals that emit atomic doublets at different wavelengths is used. In addition to Na, the doublets of lithium (Li) 670.77 and 670.79 nm, potassium (K) 766.48 and 769.89 nm, rubidium (Rb) 780.03 and 794.76 nm, and cesium (Cs) at 852.11 and 894.35 nm are incorporated. As shown in Figure 2, the multiple saturated atomic lines can also be used to derive the temperature, by simply fitting the intensities to Planck's law.

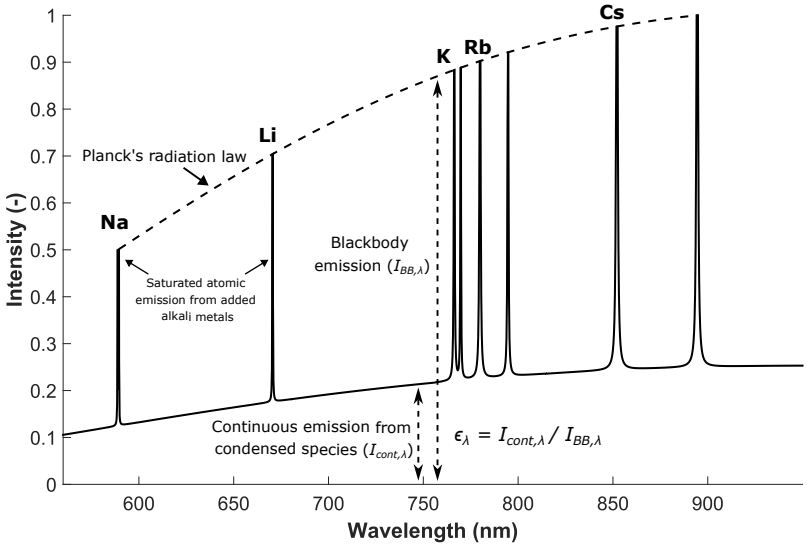

Figure 2: Illustration of spectral emissivity and temperature measurement from saturated atomic lines of alkali metals using a hypothetical theoretical spectrum.

3 Experimental facility

The McGill laminar Bunsen dust burner is used with spherical H-5 aluminum powder manufactured by Valimet Inc. (Stockton, CA) with an arithmetic mean diameter d_{50} of 8 nm and 99.7% purity. Details on the burner design can be found in [1]. The oxidizer is composed of 25-75% O_2-N_2 by volume, and controlled using needle values and Alicat M-series mass flow meters. To adequately saturate the emission signal at different wavelengths, the metal fuel is mixed with 0.6% NaCl, 1% KCl, 1.5% LiCl, 1.5%

RbCl, and 2% CsCl by weight. This has a negligible effect on the flame temperature (less than 0.2%). The alkali metal chlorides (Thermo Fisher Scientific Inc.) with purity exceeding 99% are prepared by first dissolving in water, then boiling the solution at 300°C, then grinding the crystals using a mortar, and finally sieving to 20μm.

Figure 3 shows a schematic of the experimental facility with the scanning system that permits spatially resolved emission spectroscopy. Light from the flame is collected using a 135 mm close focus lens mounted on an SLR camera using macro rings. A fiber optic cable is fixed flush with the film plane of the camera, and is connected to a 550-1000 nm spectrometer (Ocean Optics USB 4000). The latter was intensity calibrated using a NIST-traceable tungsten halogen calibration lamp (StellarNet SL1-CAL) and wavelength calibrated using a mercury argon light source (Ocean Optics HG-1). The SLR camera is mounted on a stepper motor-controlled platform, the position of which is scanned from height above burner (HAB) of 53 to 73 mm for 1D emission spectroscopy in the product zone, as indicated on Figure 3. Nine steps are taken per scan with a total time of 3.5s. At each step, both spectrometers are triggered along with a DSLR camera (Nikon Z8).

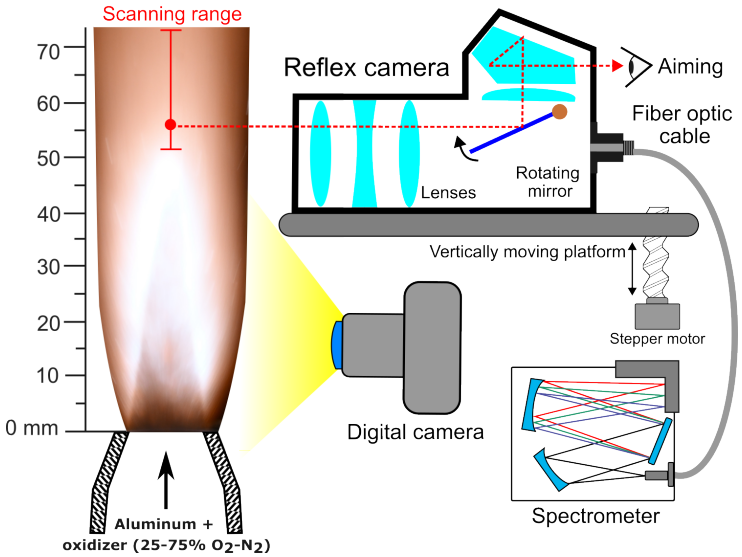

Figure 3: Schematic of the aluminum Bunsen dust burner and the emission spectroscopy diagnostics.

4 Results

Figure 4 shows a sample spectrum acquired at HAB = 73 mm, with the atomic emission lines from the five alkali metals. The ratio of the doublet peaks of all the atomic lines is considerably smaller than their line strength ratio (LSR), and the peak intensities fit very well to Planck's radiation law at T = 2551 K. This suggests that the atomic lines are saturated, and that their peaks are adequately captured by the spectrometer used. Visually, one could immediately notice how insignificant the continuous emission signal is compared to the saturated blackbody emission of the atomic lines. Calculating the emissivity from the ratio of the continuous and atomic emission signals, as reported in Figure 4b), reveals strikingly low values $\epsilon_\lambda \leq 0.025$. Within the considered spectral range, emissivity is also seen to exhibit a power law dependence on wavelength, $\epsilon \sim 1/\lambda^n$, with the exponent being n = 1.2 for this spectrum.

Figure 5 compares the experimental measurements with theoretical emissivity predictions. The latter is based on Mie theory [12], and takes into account the particle size distribution, bulk material, cloud thickness, and temperature. The particle size distribution was determined using a scanning electron

microscope on the collected aluminum oxide products. The particle diameter range is between 20 and 80 nm, with an average of 40 nm. Strong agreement is observed between experiments and theoretical predictions, with calculated emissivities in the vicinity of 0.025 for the average optical length, L = 25 mm. A power law dependence of emissivity on wavelength is also predicted theoretically, consistent with experimental measurements. The small size ($\sim$ 40 nm) of the emitting nanoparticles compared to the wavelength of light ($\sim$ 600 nm) means that particles cannot absorb light efficiently, which by Kirchhoff's law, renders their emissivities low.

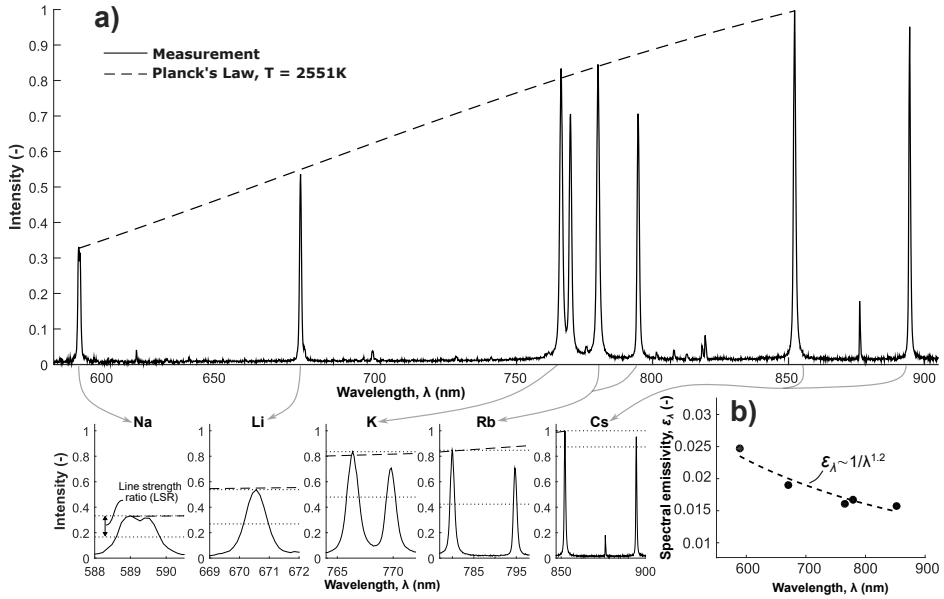

Figure 4: a) Spectrum with saturated atomic lines, and b) measured spectral emissivity at HAB = 73mm.

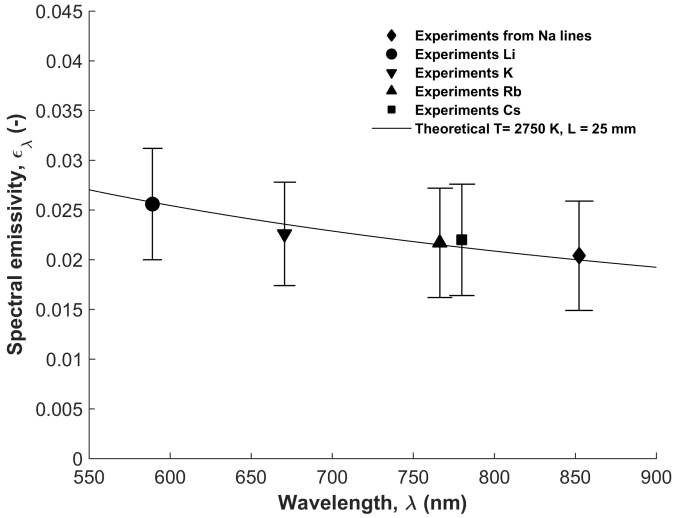

Figure 5: Comparison between experimentally measured and theoretically predicted spectral emissivity.

5 Conclusions

This study introduces a calibration-free diagnostic approach to measure the spectral emissivity of the condensed phase species in heterogeneous flames. The case of Al_2O_3 combustion products in aluminum Bunsen dust flames is considered, to address the apparent disconnect between radiation flame

models and experimental data of metal flames. The proposed method is based on mixing the metal fuel powder with small amounts of alkali metals to saturate the emission signals at specific wavelengths. The saturated signals are blackbody emissions against which the continuous emission signal from the condensed emitters can be directly compared to derive emissivity. Experimental results reveal strikingly low emissivity, $\epsilon_\lambda \sim 0.025$, an order of magnitude smaller than values typically adopted in flame radiation models.

6 Acknowledgments

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