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Establishing calibration-free pyrometry in reactive systems and demonstrating its advanced capabilities

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ABSTRACT

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A calibration-free multi-color pyrometry data analysis approach for determining the temporal change in the reciprocal temperature by only comparing the photomultiplier tube (PMT) responses to the system light emission is introduced. For Arrhenius reactions, analyzing the reciprocal temperature is particularly relevant for evaluating reactivity. The high accuracy of the proposed method is provided by eliminating the calibration step, which is made possible by considering the ratio of PMT signals as a function of time. The developed methodology is applicable to systems with continuous light emission spectra of the thermal nature that originate from condensed particulates. A demonstration of the data analysis approach was performed using aluminum powder burning in air. Four PMTs detected light emission during combustion that enabled analysis of six detector combinations to obtain a time-dependent signal ratio. Based on the temperature-dependent nature of light emission, the PMT response ratio provided the value of the reciprocal temperature change. All six detector combinations generated precisely coinciding results within time periods where the light emission trace behavior was relatively smooth that validated the data processing approach. It was also found that a non-smooth behavior of light emission led to significant deviations between outputs of different PMT combinations. This inconsistency between outputs was an indication of multi-temperature light emission whereas consistency between outputs corresponds to the single-temperature emission behavior. Using the calibration-free data processing approach, we isolated time periods where multi-temperature radiation is essential. Then, we further decoupled contributions from nonmonotonic light emission signals and resolved two distinct temperatures responsible for observed radiation peculiarities.

1. Introduction

Originally developed as a method to characterize the surface of molten metals [1,2], currently pyrometry has become a powerful tool for inferring temperatures of reactive systems such as metal flames [3–8] and thermites [9–12] from their light emission. The major assumption which enables data analyses is that radiation is emitted by a single-temperature source, which is undoubtedly valid in optically thick (metallurgy) systems [1,2]. Then, the recorded spectrum can be fitted to the Planck's function to infer the graybody temperature. On the contrary, in optically thin systems, in which emitters inside the system contribute to irradiance together with the surface sources, a single-temperature approximation is flawed [13,14]. In particular, the detected light emission in an aluminum (Al) dust flame is a

superposition of radiation emitted by burning metal particles and formed nano-oxides [15] that have substantially different temperatures. Also, temperatures of the nano-oxides generated in flames depend on the stage of the nanoparticle growth [16]. Then, the implied single-temperature concept for determining an average temperature is misleading since it does not correspond to any system component. Analyzing data in a way that allows for distinguishing of single- and multi- temperature emission will provide more meaningful understanding of the burning system's behavior. Specifically, data validating the applicability of the graybody assumption can be quantitatively determined.

An essential step to advance pyrometry is acknowledging the coincidence of multi-temperature emitters contributing to the system's radiation. Improved process comprehension requires decoupling spectra

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of different temperatures to more thoroughly inform the underlying physics of the reacting system. At the same time, demonstrating the limitations of single-temperature pyrometry justifies the need for considering a multi-temperature system.

Common pyrometry measurements require accurate detector calibration. Associated errors [17–19] reduce the resolution that complicates data interpretation, in particular, making it nearly impossible to distinguish between the validity of the single-temperature assumption and the need to consider the multi-temperature system. In this paper, we introduce calibration-free pyrometry, which enables direct measurements of the reciprocal temperatures. Eliminating the calibration step significantly improves the resolution of data analysis, and the resulting error that originates from neglecting different light emitter temperatures can be quantified. The data analysis approach is applicable to systems with continuous light emission spectra of the thermal nature that originate from condensed particulates. Those systems include but are not limited to metal flames generating nano-oxides as well as sooting hydrocarbon flames.

In the traditional pyrometry data processing approach, only a snapshot, i.e., a light emission spectrum at a given time, is analyzed to infer some temperature based on the single-temperature assumption. The validity of this single-temperature assumption cannot be verified from the snapshot alone. In the data analysis approach introduced in the current paper, the temporal behavior of light emission spectra is utilized instead. An analysis of the time-dependent ratios of photomultiplier tube (PMT) signals allows for demonstrating whether a one-temperature emitter contributes to detected light or multi-temperature emission should be considered. Existing data analyses approaches do not consider this issue (i.e., existing approaches do not distinguish between singletemperature and multi-temperature emission) nor can address it since the temporal behavior of light emission spectra are not used for interpretation.

The introduced data processing approach was utilized in a demonstration with Al powder combustion in air. Deviations in the graybody assumption resulting from multi-temperature emission were observed from the detected light traces and depended on the combustion stage. The observed temporal emission spikes confirmed the multitemperature radiation nature and justified decoupling light emission at corresponding time periods. The temperatures inferred after decoupling were about 500 K higher than the values obtained based on the single-temperature assumption. A 500 K discrepancy serves as additional evidence for the need of advanced data analytics in pyrometry diagnostics.

2. Light emission from double-temperature system

Comprehending the nature of radiation is essential for an accurate analysis of pyrometry data. In particular, neglecting differences in spectral behavior that originate from multi-temperature light emitters can contribute to misinterpretation of the recorded signal.

To understand an effect of multi-temperature emitters on the pyrometry data interpretation, a numerical example analysis was carried out in a double-temperature system similarly to that described in Ref. [8]. Note, that a transition from a single-temperature to a double-temperature concept is an essential path in comprehending the multi-temperature system radiation. The following analysis allows for elucidating major anomalies in data related to pyrometry interpretation and appear in non-isothermal systems only.

At the chosen graybody temperatures and relative fractions of light emitters, the double-temperature system irradiance was calculated. Then, the modeled signals were used as the data for common pyrometry processing. The graybody temperature was inferred by using either the Wien plot approach that utilizes data points at all wavelengths or by the two-color pyrometry approach based on the irradiance ratio at two given wavelengths. The Wien plot approach is detailed in Ref. [8]. In data processing, the Wien logarithms are plotted against wavenumbers and the linear fitting provides the temperature.

Four wavelengths were chosen for the example analysis as shown in Table 1. Those wavelengths correspond to bandpass filters of PMTs used in the aluminum powder burning demonstration described below.

Fig. 1 demonstrates the Wien plots for two systems, namely, 1) the single-temperature emitters at 2500 K; 2) a double-temperature emitter with 96.678 % of emitters at 2000 K and 3.322 % of emitters at 3000 K. The relative fractions of emitters in the second case were chosen such that the graybody temperature of the double-temperature system inferred from the Wien plot is equal to 2500 K, i.e., to the value in the single-temperature system. Thus, the considered example illustrates that an isolated multi-color pyrometry measurement is not capable of distinguishing single- and double-temperature systems. Furthermore, in the case of the double-temperature system, the apparent graybody temperature (2500 K) does not represent the actual temperatures of cold (2000 K) and hot (3000 K) emitters.

At the same time, a difference between those systems can be found using two-color pyrometry. Table 2 presents temperatures obtained for the double-temperature system at different wavelength combinations. It is worth noting that in the single-temperature system all temperatures are equal to 2500 K regardless of the pair of wavelengths. Then, the scatter in graybody temperatures depending on the wavelengths is an indication of non-isothermal light emitters. Also, since the relative contribution of hot emitters to radiation increases at short wavelengths, the two-color temperature is higher when the short-wavelength region is used for detection. The corresponding trend in the two-color temperature dependence upon wavelengths of detection, if it is seen in a real experiment, is an indication that the coincidence of multi-temperature emitters must be considered.

Fig. 2 presents results of the two-color pyrometry example analysis in the system that consists of 96.678 % cold emitters at 2000 K and 3.322 %of hot emitters at varying temperatures shown in Table 2. The shaded region represents the temperature measurement uncertainties. The trend in the two-color pyrometry temperature scatter depends on wavelengths of light detection, which is seen in the example analysis (Table 2), and can be concluded only in the case of the relatively high temperatures of hot emitters, i.e., >2600 K. At low temperatures in Fig. 2, calibration-related uncertainties make the difference, if any, unreliable. Thus, uncertainties in pyrometry temperatures related to the instrument calibration, which are ~ 2 % of the inferred value [19], can prevent the accurate interpretation of the real experiment by not distinguishing the coincidence of multi-temperature light emitters. Those uncertainties would naturally disappear if the calibration step were eliminated and enable an extension of pyrometry for studying non-isothermal systems. The example analysis in Fig. 2 supports the necessity of a calibration-free approach to processing light emission data that can provide highly accurate resolution and is worth establishing.

3. Fundamentals of calibration-free pyrometry

The validity of pyrometry is based on the quality of fitting measured light emission to the Planck's blackbody function. In other words, only the graybody radiation spectrum may allow for inferring temperature. The common belief is that the graybody spectrum stems from the wavelength-independent emissivity of a radiation source [20]. However, although detected spectra of metal flames are well-described by the Planck's law, wavelength-independent emissivity is very unlikely in the case of the dominant radiation emitted by nano-oxides generated during metal combustion [14].

A deep discussion on the nature of light emission from nano-oxides

Table 1

Wavelengths used in the numerical example analysis.

	А	В	С	D
Wavelength, nm	850	660	600	500



Fig. 1. Wien plots for modeled light emission from the single-temperature emitters at 2500 K and double-temperature emitters at 2000 K, 96.678 % and 3000 K, 3.322 %. The slopes of linear fitting lines are the same and equal to $-5.7552 \mu m$ providing the same graybody temperature of 2500 K for both systems.

Table 2

Temperatures obtained by two-color pyrometry for the double-temperature emitter system at 2000 K, 96.678 % and 3000 K, 3.322 % using different wavelength combinations as defined in Table 1.

Wavelength combination	AB	AC	AD	BC	BD	CD
Temperature, K	2367	2409	2500	2509	2603	2647



Fig. 2. Two-color temperatures in the numerical example analysis with 96.678 % cold emitters at 2000 K and 3.322 % of hot emitters at varying temperatures obtained at different pairs of detection wavelengths as defined in Table 1. The average temperature is also presented. The shaded band represents the temperature interval related to calibration uncertainties that can be ~ 2 % in a real experiment [19].

[21] is beyond the scope of this paper, but the possibility of their graybody spectra, which are seen in experiments, is addressed here. Metal oxides are wide-bandgap materials [22], their optical properties in the visible light are determined by defect states in the forbidden band [23,24]. Relatively fast processes of nanoparticle formation in flames

leads to extremely high defect concentrations that result in the emissivity obeying the Urbach rule with the Urbach energy on the order of single eV [25,26]. Being an exponential function of energy, nanoparticle specific emissivity can also preserve the graybody spectral behavior of radiation [27]. Thus, light emission from flame-generated nanoparticles is coincidentally favorable to pyrometry.

A signal from a photomultiplier tube (PMT), which detects light emission, is a product of the radiation source's irradiance, its solid angle seen by the collection optics, the optic's transmittance, and the detector's sensitivity. In the case of the graybody flame radiation, its irradiance, *I*, obeys the Planck's law [28], according to Eq. (1).

$$I \propto \frac{1}{\lambda^5 \left[\exp\left(\frac{C}{\lambda T}\right) - 1 \right]}$$
(1)

Then, the PMT signal can be expressed as shown in Eq. (2).

$$PMT = \frac{K}{\exp\left(\frac{c}{\lambda T}\right) - 1} \approx K \exp\left(-\frac{c}{\lambda T}\right)$$
(2)

Here, $C = 14,388 \ \mu\text{m}$ K is the second radiation constant, λ is the wavelength of a PMT bandpass filter, *T* is the temperature, and *K* is the PMT-dependent constant. The second expression in the right-hand side (RHS) of Eq. (2) is deduced from the Wien's approximation of the Planck's law in the visible light that is valid at typical combustion temperatures. Note that the factor λ^{-5} that enters the Planck's function is included in the PMT-dependent constant *K*.

Considering Eq. (2) for two different PMTs with bandpass filters at wavelengths of λ_1 and λ_2 , which detect radiation emitted by the same source, the reciprocal temperature can be obtained as shown in Eq. (3).

$$\frac{1}{T} = \ln \frac{K_1}{K_2} - \frac{\ln \frac{PMT_1}{PMT_2}}{\frac{C}{\lambda_1} - \frac{C}{\lambda_2}} \equiv A_{12} - B_{12} \ln \frac{PMT_1}{PMT_2}$$
(3)

In Eq. (3), constants A_{12} and B_{12} are characteristics of a given pair of PMTs (e.g., as in Table 2). The normalization constant B_{12} can be exactly calculated according to its definition by Eq. (4).

$$B_{12} \equiv \frac{1}{\frac{C}{\lambda_1} - \frac{C}{\lambda_2}} \tag{4}$$

The offset constant A_{12} , which is required to determine the actual temperature, can be obtained as a result of calibration in common pyrometry. As further detailed, eliminating the offset constant, which cancels as a result of the suggested data processing approach, allows one to infer the reciprocal temperature change instead of the absolute value. We coin the corresponding procedure as "calibration-free pyrometry" since it uses only the ratio of PMT signals that are directly measured and calibration is unneeded for calculating that ratio. Moreover, the elimination of the calibration-based offset constant enables a statistical analysis of the single-temperature assumption validity. That analysis is free of calibration-related uncertainties, which makes its interpretation highly accurate.

According to Eq. (3), the temporal behavior of the reciprocal temperature is described by the time-dependent logarithm of the ratio of two PMT signals. Then, in the case of single-temperature radiation, the behavior of the normalized logarithm of the PMT signal ratio, i.e., $B_{ij} \ln \frac{PMT_i}{PMT_j}$ as a function of time should exactly coincide regardless of the combination (*i*, *j*) of PMTs. The corresponding plots are offset by A_{ij} values (from Eq. (3)), as sketched in Fig. 3.

In the case of exact coincidence of the temporal behavior, at any combination (i, j) of PMTs the variation of the ordinate in the corresponding graphs (shown in Eq. (5)) should be the same.

$$\Delta\left(B_{ij}\ln\frac{PMT_{i}}{PMT_{j}}\right) \equiv B_{ij}\ln\frac{PMT_{i}}{PMT_{j}} - \left(B_{ij}\ln\frac{PMT_{i}}{PMT_{j}}\right)_{0}$$
(5)



Fig. 3. Sketch illustrating exactly the same temporal behavior of the normalized logarithms of the PMT signal ratios regardless of PMT combinations (shown in parentheses) that is valid only in the case of the single-temperature light emission. Corresponding plots are offset by calibration-based constants.

And that ordinate variation is equal to the reciprocal temperature change, ΔT^{-1} , defined by Eq. (6).

$$\Delta T^{-1} \equiv \left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{6}$$

The subscript "0" corresponds to an arbitrary time, from which the ordinate variation is calculated, and T_0 is the temperature at that time.

However, in the actual experiment, the plots would not coincide exactly. Then, the standard deviation, $\delta(\Delta T^{-1})$, can be considered that is defined in Eq. (7).

$$\delta(\Delta T^{-1}) \equiv \left[\frac{\sum_{i(7)$$

In Eq. (7), the average reciprocal temperature, $\overline{\Delta T^{-1}}$, is calculated using Eq. (8).

$$\overline{\Delta T^{-1}} \equiv \frac{\sum_{i < j} \Delta T_{i,j}^{-1}}{N} = \frac{\sum_{i < j} \Delta B_{ij} \ln \frac{PMT_i}{PMT_j}}{N}$$
(8)

N is the number of all possible PMT combinations (i < j) over which summation in Eqs. (7) and (8) is carried out. It is worth noting that for data processing purposes, it might be convenient to offset the signal data such that $\left(B_{ij}\ln\frac{PMT_i}{PMT_j}\right)_0 = 0$. In that case, $\Delta\left(B_{ij}\ln\frac{PMT_i}{PMT_j}\right) = B_{ij}\ln\frac{PMT_i}{PMT_j}$, and, therefore, $\Delta T_{i,j}^{-1} = B_{ij}\ln\frac{PMT_i}{PMT_j}$. An analysis of the time-dependent standard deviation calculated based on Eq. (7) is essential to validate the single-temperature radiation assumption. A discussion regarding the standard deviation is advanced below in the Results and Discussion section.

It should be emphasized again that in the introduced data processing approach, only ratios of PMT signals are utilized. Then, the approach's significant advantage is that no system calibration is required, which eliminates all associated errors. A probable drawback of the approach is related to a seeming impossibility to infer actual temperatures, although the reciprocal temperature changes can be accurately determined. The issue is, however, not that serious as could be perceived at first glance. Based on Eq. (6), the actual time-dependent temperature, T, can be found from Eq. (9).

$$T = \frac{T_0}{1 - T_0 \overline{\Delta T^{-1}}}$$
(9)

Thus, if the temperature, T_0 , at a certain moment is known (or can be accurately assumed), Eq. (9) provides the absolute temperature at any

time, at which the average reciprocal temperature, $\overline{\Delta T^{-1}}$, is obtained from PMT measurements. Also, any uncertainty in choosing the value of T_0 does not affect the relation between the absolute temperature change, $\Delta T \equiv (T - T_0)$, and the reciprocal temperature change, as can be concluded from Eq. (10).

$$\Delta T = \overline{\Delta T^{-1}} \frac{T_0^2}{1 - T_0 \overline{\Delta T^{-1}}}$$
(10)

Both the absolute temperature change and reciprocal temperature change are nearly proportional to each other and allow for a qualitative analysis regardless of the exact value of T_0 .

Knowledge of the reciprocal temperature change instead of the absolute temperature value can be enough for a description of the reactive system behavior. For example, the temperature-dependent reaction rate, R, obeys the Arrhenius law with the activation energy E_A [29].

$$R(T) \propto \exp\left(-\frac{E_A}{T}\right) \tag{11}$$

Then, the change in the reaction rate due to temperature variations, ξ , is ultimately governed by the reciprocal temperature change.

$$\xi \equiv \frac{R(T_2)}{R(T_1)} = \exp\left[-E_A\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$
(12)

Thus, besides the application of calibration-free pyrometry as a tool of justifying multi-temperature light emission, the capability of the established data processing approach to directly provide desired temperature values at high accuracy makes the technique attractive.

4. Demonstration method

A demonstration with Al powder combustion in air was performed to illustrate analysis of light emission during a real burning process. This application was selected because it demonstrates that the singletemperature light emission source assumption is only valid at clearly definite moments in the burning process. The aluminum burning demonstration shows the capabilities and usefulness of the calibrationfree pyrometry data analysis approach by considering recorded signals without extensive discussion of the light emission origins. It is important to understand that exactly the same steps applied to this demonstration could be performed in any particulate-containing system (including a sooting flame).

The aluminum powder burning set-up is sketched in Fig. 4. Aluminum powder of 100 nm nominal particle size (Product Number US1043, US-Research Nanomaterials, Houston, TX, USA) and 50 mg quantity was placed in a 70-microliter crucible (Product Number DSC72001, DSC Consumables, Austin, MN, USA) open at the top to air. The powder was irradiated by a 400 Watt CO₂ laser (10 μ m wavelength band, Firestar TI-Series, Synrad, Mukilteo, WA, USA) that initiated powder oxidation. The firing mechanism was controlled by a waveform generator (SDG 1032X, Siglent, Shenzhen, China).

Light emission from the reaction zone was detected by a set of four PMTs (PMT1001, Thorlabs, Newton, NJ, USA). Those PMTs were arranged together as a device used for 4-color pyrometry and detailed in previous work [12]. The PMTs were equipped with four bandpass filters with 10 nm pass widths and are indicated in Table 2. As it was addressed the choice of PMT wavelengths for pyrometry is compatible with light emission peculiarities during Al combustion [11,12]. Light emission from the aluminum powder reaction was collected using a reflective collimator (RC12SMA-P01, Thorlabs, Newton, NJ, USA) that passed through the 200 µm optical fiber and was sent to the PMTs where Al combustion radiation was recorded for further analysis.

5. Results and discussion

The PMT signals that were used for data processing are presented in



Fig. 4. Sketch of the aluminum powder burning set-up. Wavelengths of PMT bandpass filters are provided for reference. Circle inset provides a picture of inside chamber with crucible containing powder.



Fig. 5. Four discrete PMT signals labeled as A–D from a representative aluminum powder oxidation run.

Fig. 5. The initial light intensity increase corresponds to powder heating by the laser, which initiated metal combustion.

By choosing different PMT combinations (6 in total), the timedependent signal ratio logarithms were calculated. Then, based on Eqs. (5) and (6), the obtained logarithms are just the reciprocal temperature changes with respect to T_0 , the temperature achieved by the system at the moment of the maximum value of the logarithm. Inferred reciprocal temperature changes are presented in Fig. 6 for all PMT combination. The corresponding data were offset such that the maximum value is set at zero for each PMT pair (see Fig. 6a). Corresponding graphs visually coincide that might validate the singletemperature emission assumption. Then, reporting the average reciprocal temperature change would be in-line with common pyrometry capabilities yet a strong pivot from reporting temperature explicitly. The reciprocal temperature does not require instrument calibration and, therefore, can be more accurately obtained in any experiment. Additionally, the graphs were offset by varied values (see Fig. 6b) in order to demonstrate identical dynamics of graphs and the coincidence of periods of unsmooth behavior regardless of PMT pairs.

To extend the capabilities of our data processing approach and allow for an advanced interpretation, we not only calculated the average reciprocal temperature change (see Eq. (8)), but also compared it with



Fig. 6. Reciprocal temperature change for different PMT pairs. The different line widths in panel (a) are shown in order to visually demonstrate that the graphs overlap. The same graphs are shown offset in panel (b) to demonstrate identical dynamics. The varied offset constants are reported in the panel (b) caption.

the standard deviation (see Eq. (7)). Both time-dependent values are presented in Fig. 7.

Within time periods of smaller standard deviations, the average reciprocal temperature change behaves smoother (i.e., >2 s in Fig. 7). On the contrary, within periods of strongest variations of the average reciprocal temperature, spikes in the standard deviation by more than one order of magnitude are evident. Based on the numerical example analysis (Fig. 2), the spikes in the standard deviation are an indication of an additional light emission source that has a significantly different spectral behavior within those periods. Spikes in the standard deviation originate from a different temperature associated with additional light emitters. Thus, the single-temperature assumption is not valid within time periods that correspond with standard deviation spikes. A close inspection of the detected light shows that the PMT signal spikes coincide with the standard deviation spikes (see Fig. 7). Fig. 8 demonstrates the corresponding signal behavior of PMT A. Then, although the standard deviation spike is the indicator of the single-temperature irrelevance, a noticeably unsmooth temporal behavior of the light emission is the actual reason the single-temperature assumption is not valid.

The simplest explanation of an invalid single-temperature assumption is that at the spike onset, an additional light source of a different temperature begins contributing to the detected system radiation. That contribution can be inferred by subtracting the local background value (see the inset in Fig. 8) from the total signal value around the local minimum. Performing the subtraction for all PMT signals and processing results as a new data set, we can find the reciprocal temperature change for any PMT combination (and its average and standard deviation) similarly to what was done with the original data set in Fig. 7. Fig. 9 presents the obtained values for all PMT combinations together with corresponding results for the original (non-subtracted) data. Note that the time period between 1.26 s and 1.30 s was chosen for the analysis based on the behavior of the standard deviation (see Fig. 7) that reaches the greatest value in this time period. Then, the strongest effect from multi-temperature emitters on the data analysis approach can be seen with greatest clarity. It is noted that any PMT signal spike leads to noncoincidence of the reciprocal temperature curves. However, spikes corresponding to a higher standard deviation are better examples for demonstrating the analysis (due to the strongest contributions of additional radiation sources).

A divergence of reciprocal temperature change curves for different PMT combinations and the corresponding spike of the standard deviation seen in Fig. 9a were discussed as indicators of the irrelevance of the single-temperature emitters. A good coincidence of reciprocal temperature change plots with a relatively low value of the standard deviation



Fig. 8. Signal detected by PMT A. The circle shows the time period of noticeable light trace variations that correspond to the standard deviation spike presented in Fig. 7b. The horizontal line in the inset illustrates a local background.

presented in Fig. 9b indicates the single temperature approximation might be valid for subtracted signals. For those subtracted signals, the accurately inferred reciprocal temperature change is a characteristic of the second radiation source.

In order to illustrate a possible misinterpretation in the case of ignoring the occurrence of the second light source of a different temperature, results of different data processing scenarios are presented in Fig. 10 within the time period of interest, i.e., between 1.26 s and 1.30 s. Actual temperatures were restored using Eq. (9) at two arbitrary temperatures, T_0 , i.e., 2500 K and 3000 K, chosen for comparison. Fig. 10 comparison confirms that the choice of the arbitrary temperature, which is required to relate the reciprocal temperature change to the actual value, does not affect the temporal behavior trend.

In Fig. 10, the temperature denoted as "original" corresponds to the reciprocal temperature change inferred from the measured data presented in Fig. 9a. The "subtracted" temperature was calculated using the results shown in Fig. 9b for the second radiation source, which occurs only after the spike onset. The comparison in Fig. 10 shows clearly that the data processing approach is crucial. In the case of the single-temperature assumption, the obtained ("original") temperature is about 500 K lower than the ("subtracted") temperature of the second



Fig. 7. Time-dependent (a) average reciprocal temperature change, and (b) standard deviation of the reciprocal temperature change. The insets show the time period between dotted vertical lines, where strongest variations are evident.



Fig. 9. Reciprocal temperature change for different PMT combinations and its average value with the inset showing the standard deviation. The panel (a) corresponds to the total light emission and panel (b) presents results for the subtracted signal as described in the text (i.e., local background value subtracted from the total signal). The time range in panel (a) is extended to earlier times to demonstrate how the standard deviation spike develops with time. Note that the insets for the standard deviation have different scaling in panels (a) and (b) to provide fine resolution of the temporal behavior of standard deviation, and the significantly reduced standard deviation associated with the subtracted signal.



Fig. 10. Actual temperatures restored from reciprocal temperature changes at two different arbitrary parameters $T_0 = 2500$ K and $T_0 = 3000$ K. The time period around the standard deviation spike is shown. Results for the original data processing and subtracted signals (that are available only after the spike onset at about 1.28 s) are presented.

light source. That temperature of the second radiation source is only justified in the case of the calibration-free approach, after the singletemperature assumption has been demonstrated invalid. This huge difference challenges reliability of the common pyrometry data analysis approach and corresponding results. The calibration free approach applied to reciprocal temperature more accurately represents emission behavior without the need for assumptions.

6. Concluding remarks

Calibration-free pyrometry developed in the current work allows for the accurate inference of the reciprocal temperature change being the actual parameter entering the Arrhenius reaction rate equations. Accurate means there are no calibration-related uncertainties that are associated with conventional pyrometry.

Common pyrometry-based data processing approaches are based on a single-temperature source assumption. The impact of the calibrationfree data processing approach is that it allows analyses of the validity of the single-temperature assumption. Anomalies in the detected light signal's temporal behavior, i.e., spikes in the standard deviation, were demonstrated to be indicators of light sources with different temperatures. The temperature obtained by isolating the corresponding light emission is substantially higher than the common pyrometry methods could infer. The introduced reciprocal temperature data analysis approach enables multiple perspectives of radiant emission and identification of anomalies associated with the single-temperature assumption and graybody approximation.

Our data processing method is free of erroneous assumptions, since calculating the standard deviation and its analysis is a natural part of the suggested procedure. Justifying the need to consider multi-temperature light emission sources and providing the capability to decouple those, the approach we detailed here establishes a path to advance pyrometry in reactive systems and make the outcomes more reliable.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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