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(54) Title: ALKALI METAL SPECTROSCOPY FOR IMAGING OF PARAMETERS IN A COMBUSTION CHAMBER OF AN INTERNAL COMBUSTION ENGINE

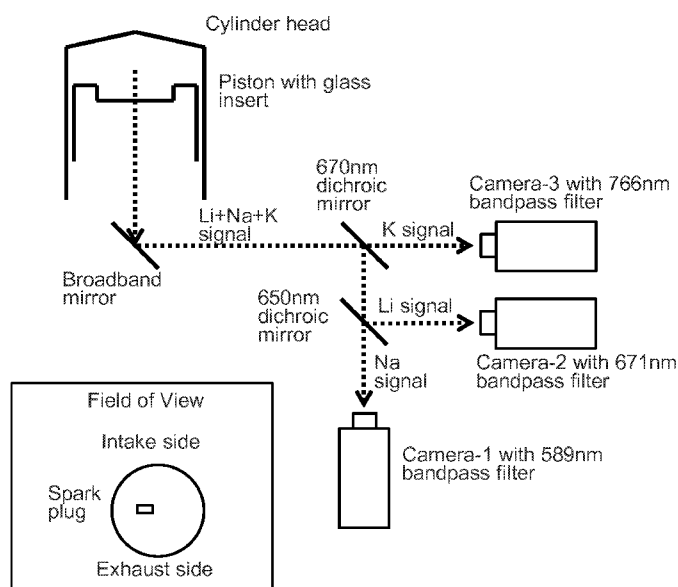


Figure 1

(57) Abstract: A diagnostic tool and method of spectroscopic analysis of fuel combustion in a combustion chamber of an internal combustion engine. The method carried out by the diagnostic tool includes the steps of: (a) introducing a mixture of fuel, air, and a plurality of different alkali metal dopants into a combustion chamber of an internal combustion engine; (b) igniting the mixture; (c) optically recording spectral data associated with fluorescence of each of the alkali metal dopants during combustion of the mixture; and (d) determining burned gas temperature by analysis of the spectral data. Equivalence ratio and mass fraction burned can also be determined. Example dopants include sodium, either lithium or cesium, and either potassium or rubidium.



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ALKALI METAL SPECTROSCOPY FOR IMAGING OF PARAMETERS
IN A COMBUSTION CHAMBER OF AN INTERNAL COMBUSTION ENGINE

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TECHNICAL FIELD

This invention relates optical detection of burned gas temperature, equivalence ratio, and mass fraction burned in an internal combustion engine.

BACKGROUND

10 During the past decades the most common gasoline combustion concept was the spark ignited, port fuel injected (SI-PFI) gasoline engine. For this engine, the fuel is injected into the air intake port just upstream the intake valve, where it evaporates and the gaseous air-fuel mixture enters the combustion chamber. Because the air-fuel mixture is only ignitable by spark within a narrow range of nearly stoichiometric equivalence ratios,
15 engine load must be controlled by choking the air flow. A great benefit from stoichiometric engine operation is that it allows for the use of a three way catalyst downstream the exhaust port to chemically convert harmful emissions of carbon monoxide, nitrogen oxides and unburned hydrocarbons into carbon dioxide, nitrogen and water. However, the need for a stoichiometric equivalence ratio causes the SI-PFI engine
20 to have low combustion efficiency particularly at low load operating conditions.¹

In recent years the SI-PFI has partly been replaced by the introduction of the spark ignited, direct injected (SIDI) gasoline engine. This engine injects the fuel directly into the combustion chamber where it evaporates and mixes with the air. This method allows for load control by controlling only the amount of fuel injected whereas the air
25 flow remains unrestricted. To overcome the issue of ignitability of the very lean air fuel ratios at low load operating conditions, various fuel stratification methods have been developed to create a cloud of near stoichiometric equivalence ratio at or in close proximity to the spark plug while the overall equivalence ratio remains lean. These methods encompass wall and air guided injection systems, where the injector typically
30 sits far from the spark plug and the fuel cloud is transported to the spark plug by proper

design of the piston wall or the flow field inside the engine to transport the fuel cloud close to the spark plug. Spray guided systems have the injector positioned close to the spark plug spraying the fuel onto or close to the spark plug.

5 A downside of stratified SIDI engine operation is the need for a much more complex exhaust gas after-treatment system in comparison to the three-way catalyst. The need for reduction of nitrogen oxides to meet emission regulations may necessitate the use of expensive lean NO_x traps or selective catalytic reduction catalysts. A better solution would be to prevent the formation of nitrogen oxides in the engine in the first place. This can be achieved by lowering the combustion temperature by recirculating
10 exhaust gas (EGR) back into the air intake, because the formation of nitrogen oxides in the flame strongly depends on temperature. The higher specific heat of carbon dioxide and water contained in the exhaust gas helps reduce peak combustion temperatures and reduce the formation of nitrogen oxides.

Especially with high rates of EGR, stratified SIDI engine combustion suffers from
15 occasional, random misfires and partial burns. These pose a large problem for both engine efficiency and emissions, because large amounts of hydrocarbons from the fuel exit the engine unburned. Up to date there is no comprehensive understanding of what causes these cycle to cycle variations and how to avoid them effectively.

Double or multiple injections per engine cycle can improve combustion stability
20 and lower tailpipe emissions and can be utilized as an exhaust gas heating strategy for cold start operation. Increased soot formation when injecting into the flame poses a potential limitation to this strategy, because the emission of particulate matter is regulated by legislation.

Quantitative knowledge of local temperature and equivalence ratio is often
25 desired to optimize engine operating parameters and combustion chamber design. The global equivalence ratio can be obtained from a carbon and oxygen analysis of exhaust species such as CO, CO₂, H₂O, O₂, NO_x or the use of wide-range exhaust oxygen sensors. However, these devices cannot provide the spatial and temporal resolution that is necessary in the highly dynamic and spatially stratified environment of direct injection

engines. The fast response sampling of gas from the cylinder can provide better temporal resolution but no spatial resolution. Various studies have attempted the one or two dimensionally resolved measurement of fuel concentration or air/fuel ratio in the cylinder of operating engines using optical diagnostics. These techniques include infrared absorption spectroscopy, ion-current sensing at the spark plug, chemiluminescence imaging of combustion radicals such as OH, CH, C₂ and CN, laser induced fluorescence (LIF) and laser Raman scattering. The experimental uncertainty of these tools is typically near $\pm 10\%$. Fansler et al. summarize the specific advantages and disadvantages of each technique with respect to spatial and temporal measurement resolution, potential for quantifying the local equivalence ratio and limitation to certain areas of interest such as the spark plug.

The application of optical diagnostics in engines is often limited by costly and sensitive equipment such as lasers and image intensifiers (LIF, Raman spectroscopy), the limitation to flame front processes (OH, CH and C₂ chemiluminescence) or restriction to areas near the spark plug (ion current sensing, CN chemiluminescence). Infrared absorption techniques can only provide measurements that are averaged along the line of sight, while LIF and Raman spectroscopy are limited to two dimensional planar measurements. Despite the large advances in our understanding of engine combustion in the past, there is still strong demand for reliable measurement techniques that can overcome some of the limitations of currently available tools. It is desirable to extend the toolset of optical diagnostics toward lower hardware requirements so it can be used reliably in industrial research and product development environments.

Alkali metals can be introduced into the combustion chamber as air seeding or fuel dopants. The high temperatures in the flame and burned gas region excite the alkali atoms and the subsequent fluorescence can be strong enough to be captured with standard, high-speed cameras without the need for image intensifiers or a laser. The intensity of the alkali fluorescence light in the burned gas region mainly depends on the number of alkali atoms present, the fraction of the atoms that are present in an excited electronic state, the transition probability between excited state and ground state as well as the reabsorption of emitted light by ground-state alkali atoms. The total number of

atoms can vary as a function of the air to fuel ratio, because an increased availability of oxygen and hydroxyl radicals will affect the chemical reactions that bind the free atoms into various molecules. The fraction of the atoms that are present in an excited state depends on the gas temperature, while the transition probability is a constant of nature and cannot be manipulated. The self-absorption of the fluorescence mainly depends on the number density of ground-state alkali atoms, the absorption path length and the spectral absorptivity, which is strongly influenced by various ways of absorption line broadening.

Sodium luminescence has first been utilized in engine experiments for combustion analysis in 1935-1940 by Rassweiler et al., Withrow et al. and Breevoort, where the intake air of a spark-ignited gasoline engine was seeded with sodium salt to visualize flame propagation and measure combustion temperature using the sodium line reversal method. Drake et al. and Zeng et al. utilized sodium luminosity in a spray-guided, spark ignited, direct injection gasoline engine to visualize early flame propagation. Most recently, Beck et al. and Reissing et al. doped the fuel with sodium and potassium and utilized the temperature dependence of the sodium to potassium fluorescence ratio to calculate burned gas temperature. In all studies the influence of the chemical environment, the collisional environment as well as self-absorption of the fluorescence light was not considered. The applicability of this tool was therefore limited to a narrow range of operating conditions.

SUMMARY

In accordance with an embodiment of the invention there is provided a method of spectroscopic analysis of fuel combustion in a combustion chamber of an internal combustion engine. The method includes the steps of: (a) introducing a mixture of fuel, air, and a plurality of different alkali metal dopants into a combustion chamber of an internal combustion engine; (b) igniting the mixture; (c) optically recording spectral data associated with fluorescence of each of the alkali metal dopants during combustion of the mixture; and (d) determining burned gas temperature by analysis of the spectral data.

Specific embodiments use intensity ratios of the spectral data for two or more of the dopants to determine burned gas temperature as well as an equivalence ratio for combustion of the mixture. In some embodiments, mass fraction burned can be determined using a spatially integrated fluorescence intensity along with a correction that is based on the burned gas temperature and equivalence ratio. In some embodiments, three dopants are used which may include sodium (Na), either lithium (Li) or cesium (Cs), and either potassium (K) or rubidium (Rb).

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred exemplary embodiments of the invention will hereinafter be described in conjunction with the appended drawings, wherein like designations denote like elements, and wherein:

Figure 1 is a block diagram of an optical measurement system of a diagnostic tool constructed and operated in accordance with an embodiment of the invention;

Figure 2 depicts the transmission characteristics of bandpass filters used in the optical measurement system of FIG. 1;

Figure 3 includes graphs showing the dependency of various alkali dopant fluorescence intensity ratios on temperature and equivalence ratio at a constant pressure;

Figure 4 includes graphs showing the dependency of various alkali dopant fluorescence intensity ratios on pressure at a constant equivalency ratio;

Figure 5 is a series of combustion chamber images showing the fluorescence intensity of three alkali dopants under a homogenous operating condition and at a specified equivalence ratio;

Figure 6 shows certain specified intensity ratios determined from the dopant spectral intensities of FIG. 5;

Figure 7 is a graph showing spatial profiles of various dopant fluorescence intensities and intensity ratios;

Figure 8 includes graphs showing the spatial and 5-cycle ensemble average of the images of FIGS. 5 and 6 as a function of temperature for various equivalence ratios;

Figure 9 shows the same intensity ratios as that of FIG. 6 after the recorded alkali fluorescence intensity ratios are post-processed and converted into a temperature and equivalence ratio scale;

Figure 10 is a graph comparing the fluorescence based temperature measurement with a GT-Power two-zone temperature calculation;

Figure 11 shows calculated equivalence ratio for the same cycle as that of FIG. 9;

Figure 12 shows a 5-cycle ensemble average of sodium fluorescence images for various engine crank angles and mass fraction burned at a specified equivalence ratio;

Figure 13a is a graph showing spatially integrated sodium fluorescence intensity data extracted from the images of FIG. 12 and plotted as a function of calculated mass fraction burned for various equivalence ratios;

Figure 13b is a graph as in FIG. 13a corrected for its dependence on temperature, pressure, equivalence ratio, and self absorption;

Figure 14a is a series of images showing a well burning engine cycle during spray-guided, stratified operation;

Figure 14b is a series of images showing a poorly burning engine cycle during spray-guided, stratified operation;

Figure 15 depicts the transmission characteristics of bandpass filters used in an alternative embodiment of the optical measurement system of FIG. 1;

Figure 16 shows images from a spray-guided engine operation using double injection; and

Figure 17 shows a comparison of images of a 100-cycle ensemble average of identical engine operating conditions with different injectors.

DESCRIPTION OF THE ILLUSTRATED EMBODIMENTS

Disclosed herein is a system and method that enables determination of local burned gas temperature, equivalence ratio and mass fraction burned in an internal combustion engine under a wide range of operating conditions. The system and method
5 utilizes the effect of various physical and chemical processes occurring during combustion on the fluorescence intensities of various alkali metals that are introduced into the combustion chamber along with the air and fuel.

System Setup

Fig. 1 depicts an overview of an optical measurement system that can be used to
10 carry out the alkali metal fluorescence spectrometry in accordance with one embodiment of the invention. This embodiment will be described as it was used for prototype testing of the system and method described herein. A direct injected, 500 cm³ single-cylinder gasoline engine with optical access through a piston window was used and run at 2000 rpm at various equivalence ratios with 8.8 ± 0.2 mg of fuel injected in each cycle at 290
15 degrees before combustion top dead center. The cylinder pressure was measured with crank-angle resolution using a pressure transducer (Kistler 6125A). A throttle plate in one of the two intake ports was used to generate a high swirl motion in the combustion chamber. The air intake system allows for diluting the air with additional amounts of nitrogen to simulate the effects of exhaust gas recirculation on engine combustion. The
20 air/fuel ratio was obtained by metering intake air flow with a critical orifice and the fuel using a Coriolis (Micro Motion Elite CMF010) mass flow meter, via the oxygen and carbon balance of the emissions bench, as well as via an oxygen sensor in the exhaust manifold. The air/fuel ratio obtained by the Coriolis meter was used in the calculation, and the accuracy uncertainty of $\pm 1.3\%$ was determined by comparisons to the emissions
25 bench readings. The precision error of the Coriolis meter was determined as $\pm 2.7\%$ via the comparison of measured fuel mass flow from multiple engine experiments with identical injector pulse width. The total uncertainty of the measured equivalence ratio is therefore less than 3.0%. Isooctane served as the fuel instead of commercial gasoline and was doped with two alkali containing additives dissolved in heavy oil (75 cst). One of the
30 additives contained a combination of lithium carbonate, sodium carbonate and potassium

nitrate. The manufacturer specification of the lithium, sodium and potassium mass fractions in this additive was 3500 ppm, 1000 ppm and 1500 ppm. An additional, lithium (5000 ppm) carbonate containing fuel additive was used to enhance the lithium fluorescence intensity. 50ml of the combined fuel additive and 15ml of the additional lithium fuel additive were mixed into one liter of isooctane. The mole fractions of lithium, sodium and potassium in the fuel were 5340 ppm, 322 ppm and 284 ppm, respectively.

Three CMOS high-speed cameras (Vision Research Phantom V7.1) were used to record the fluorescence of lithium, sodium and potassium, respectively. The quantum efficiency of the cameras reported by the manufacturer was 33%, 27% and 22% near 589nm, 671nm and 767nm, respectively. The optical path of the emitted lithium, sodium and potassium light from the engine was split using two dichroic filters. The first dichroic filter (Edmund Optics NT43-962) with 99% reflectivity near 589 nm, 40% reflectivity near 671 nm and 98% transmission near 767 nm was used to separate the potassium fluorescence from lithium and sodium fluorescence. The second dichroic filter was custom designed by Rocky Mountain Instrument Co. with 94% transmission at 589 nm and 99.5% reflectivity near 671 nm to split sodium and lithium fluorescence. This arrangement allows the cameras to share an identical line of sight into the combustion chamber to ensure good spatial overlap of the images. Determination of the various combustion parameters discussed herein (including burned gas temperature, equivalence ratio, and mass fraction burned) can be carried out using a computer (not shown) programmed with the proper models, calibration data, constants, and mathematical relationships needed to implement the methods described herein. Such programming and details are within the level of skill in the art and not further detailed herein.

Band-pass filters on each camera lens with center wavelength of 671.0 nm (FWHM 10 nm, 90% peak transmission, 50mm diameter), 589.0 nm (FWHM 10 nm, 100% peak transmission, 50mm diameter) and 766.5 nm (FWHM 10 nm, 50% peak transmission, 50mm diameter), respectively, ensured that any soot or combustion luminosity other than alkali fluorescence did not interfere with the recorded signal.

Transmission spectra of the bandpass filters were measured using an Ocean Optics (Model USB2000) absorption spectrometer and are displayed in Fig. 2.

Before discussing the results of the experimental setup described above, the particular selection of the three alkali metals used, namely, lithium, sodium and potassium, will be described, along with the model prediction of the alkali fluorescence intensity in the engine that is expected from the experiment.

Alkali Metal Selection

A thorough analysis was carried out to select the three most promising alkali elements for this study. Sodium was selected due its thermodynamic equilibrium most strongly favoring the atomic state, which promises good fluorescence signals under a wide range of temperatures and equivalence ratios. Ionization was calculated to be negligible under the observed temperature range of up to 2700 K. Its emission near 589.0 and 589.6 nm is close to the sensitivity peak of the camera and both emission lines can be captured simultaneously with a spectrally narrow bandpass filter. The only downside is that the sodium's excited state energy is the highest of all alkali elements resulting in the lowest excited state population over the entire temperature range.

Potassium and rubidium are expected to behave very similarly in the flame with regards to temperature and equivalence ratio dependence due to the very small difference in excited state energy and almost identical thermodynamic properties. Only one of the two elements can be selected since the K/Rb fluorescence ratio would not be sensitive to temperature or equivalence ratio changes. The thermodynamic equilibrium of potassium and rubidium and their respective hydroxides favor the atomic state more than in the case of cesium or lithium. Their excited state energies are lower than the lithium's and only slightly higher than in the case of cesium. Ionization of both elements becomes relevant at elevated temperature above 2500 K and must be accounted for. Potassium is preferred over rubidium because its emission lines at 766.5 and 769.9 nm are much closer than the 780.0 and 794.8 nm lines of rubidium and can therefore be captured simultaneous with a narrower bandpass filter.

Cesium differs from the selected sodium and potassium in both its temperature dependence and thermodynamic equilibrium. Its excited state population is the highest of all alkali elements over the entire temperature range due to its low excited state energy. Cesium is most prone to ionization, but this would only become important at the high end of the observed temperature range, where the fluorescence signal is strong due to the high excited state population and the thermodynamic equilibrium favoring the atomic state. Fluorescence intensity loss due to high temperature ionization is therefore no experimental concern and can be accounted for quantitatively. Although the emission lines of cesium at 852.1 and 894.4 nm are separated too far to capture them both simultaneously with a narrow bandpass filter, the camera chip sensitivity is still sufficient for the stronger line at 852.1 nm. Although the camera is more sensitive to the lithium emission lines near 670.8 nm and a narrow bandpass filter can capture both lithium lines, the thermodynamic equilibrium of lithium is most strongly shifted toward the hydroxide. Particularly at low temperature and lean operating conditions, the cesium signal is expected to be stronger than the lithium fluorescence. However, no commercially available, cesium containing, organic fuel additive could be identified and therefore lithium was used as the third alkali element in this study rather than the preferred cesium.

Model Prediction of the Alkali Metal Fluorescence in the Engine

With the dependences of alkali fluorescence intensity on the collisional energy exchange environment, the chemical equilibrium and the effect of self-absorption understood, the expected measured fluorescence intensities of lithium, sodium and potassium and the intensity ratios of Na/Li, Li/K, Na/K and $\text{Na} \cdot \text{Li}/\text{K}^2$ can be predicted. The mole fractions of lithium, sodium and potassium in the fuel used in the subsequent experiments were 5340ppm, 322ppm and 284ppm, respectively, and these values were used in the following calculations. The three combustion parameters affecting the fluorescence intensity are temperature, pressure and equivalence ratio. Fig. 3 shows the dependence of the Na/Li, Li/K, Na/K and $\text{Na} \cdot \text{Li}/\text{K}^2$ fluorescence intensity ratios on temperature and equivalence ratio for a constant pressure of 10 bar. The Na/Li, Li/K and Na/K fluorescence intensity ratios each show strong dependences on temperature. The signal ratios are most strongly affected by equivalence ratio between $\Phi=0.9$ to $\Phi=1.1$ and

at temperatures less than 2100K. While the equivalence ratio dependences continue in a less sensitive way in the fuel rich equivalence ratio regime, the fluorescence intensity ratios are nearly independent on equivalence ratio between $\Phi=0.5$ to $\Phi=0.9$. It is apparent that the equivalence ratio dependence of the predicted Li/K fluorescence intensity ratio is nearly the inverse of the Na/K ratio. The product of both ratios to form the quantity $\text{Na}\cdot\text{Li}/\text{K}^2$ is therefore nearly independent on equivalence ratio but shows a strong dependence on temperature. $\text{Na}\cdot\text{Li}/\text{K}^2$ shows only a small equivalence ratio dependence in the rich regime and at high temperature.

Fig. 4 illustrates the dependence of the Na/Li, Li/K, Na/K and $\text{Na}\cdot\text{Li}/\text{K}^2$ fluorescence intensity ratios on pressure at a constant equivalence ratio of $\Phi=1.0$. While the Na/Li, Li/K and Na/K ratios are significantly affected by pressure, it is observed that the pressure dependence of the Na/K and Li/K ratios are opposite but nearly equal in magnitude. The $\text{Na}\cdot\text{Li}/\text{K}^2$ fluorescence intensity ratio remains therefore nearly unaffected by pressure over the entire temperature range of interest.

While any of the two-component ratios could be used for temperature measurements in homogeneous combustion environments, where both cylinder pressure and equivalence ratio are known, the combination of three alkali components to form the $\text{Na}\cdot\text{Li}/\text{K}^2$ fluorescence ratio is preferred due to its independence on pressure and equivalence ratio. In stratified combustion environments, where both temperature and local equivalence ratio are unknown, the $\text{Na}\cdot\text{Li}/\text{K}^2$ fluorescence intensity ratio can be used as a direct marker for burned gas temperature independently of cylinder pressure and equivalence ratio. It is the preferred choice for temperature measurements in both homogeneous and stratified combustion environments. When the temperature is measured using the $\text{Na}\cdot\text{Li}/\text{K}^2$ fluorescence intensity ratio, any of the two-component ratios Na/Li, Li/K or Na/K can be used for the simultaneous measurement of local equivalence ratio. The Na/K signal ratio is expected to yield the highest signal to noise ratio due to the very faint fluorescence intensity of lithium in cold and lean zones.

Burned Gas Temperature and Equivalence Ratio Imaging and Analysis

Fig. 5 shows an example of a series of images with the fluorescence intensity of the three alkali components simultaneously recorded under homogeneous operating condition and an equivalence ratio of $\Phi=1.06$. The images look qualitatively similar, because the three cameras share an identical view and the alkali metal fluorescence depends on the same parameters for all three components. The fluorescence intensities, however, differ quantitatively in their dependence on burned gas temperature, cylinder pressure and equivalence ratio. This becomes apparent in Fig. 6, where the ratios of the Na·Li/K² and Na/K fluorescence intensities are illustrated after the recorded images in Fig. 5 were normalized by their respective camera exposure time. The spatial and temporal intensity gradients of the fluorescence intensity ratio images are much more homogeneous than in Fig. 5, because the Na/K ratio only depends on burned gas temperature, pressure and equivalence ratio and the Na·Li/K² ratio is only temperature dependent. Because the fuel was injected early in the cycle at 290° bTDC, neither temperature nor equivalence ratio are expected to substantially differ spatially.

Fig. 7 shows spatial profiles of the Li, Na, K, Na·Li/K² and Na/K fluorescence images to illustrate the spatial heterogeneities of the Li, Na and K fluorescence intensities. The profiles are taken in vertical (from intake to exhaust side) direction immediately to the right of the masked out spark plug at 2° aTDC. The Li, Na and K fluorescence intensities show large spatial gradients due to their strong dependence on the depth of the burned gas zone, which differs spatially due to the pent-roof shaped cylinder head. While the spatially averaged fluorescence intensities can be compared to the model predictions as a function of temperature, pressure and equivalence ratio, it is not possible to utilize these signals directly for spatially resolved burned gas temperature measurements in the engine. The fluorescence intensity ratios are nearly homogeneous, because they only depend on temperature, pressure and equivalence ratio and neither of these scalars is expected to differ substantially in space due to the nearly homogeneous engine operating condition.

The spatial and 5-cycle ensemble average of the images in Fig. 5 and Fig. 6 is extracted and plotted as a function of burned gas temperature for various equivalence

ratios in Fig. 8. Using the fundamental physical and chemical properties of the alkali metals, the lithium, sodium and potassium fluorescence intensity dependence on burned gas temperature, pressure and equivalence ratio can be calculated. These predictions are compared to the measured fluorescence data in Fig. 8 to validate the predicted temperature, pressure and equivalence ratio dependence of these alkali metals. The model calculation does not account for the solid angle of the camera lens, and therefore the calculated Li, Na, K deviates from the measurement by a constant factor. The Na/K and Na·Li/K² fluorescence intensity ratios are of great interest in this study, because they are independent of the solid angle of the camera lens as well as less dependent on mass fraction burned and depth of the burned gas volume. The temperature and equivalence ratio dependences agree well with the measurement. The quantity Na·Li/K² shows a strong temperature dependence but is nearly independent on equivalence ratio. It can therefore be used for burned gas temperature measurements in stratified engine environments. The Na/K ratio can be used in combination with the Na·Li/K² ratio to simultaneously calculate equivalence ratio and temperature from the recorded alkali fluorescence. All data points were extracted late in the cycle after peak burned gas temperature was reached, where combustion is nearly complete and the burned gas zone is fully expanded.

The cylinder pressure changes throughout the cycle and for different engine operating conditions. The apparent temperature and equivalence ratio dependences are therefore partly caused by pressure dependences. Unfortunately, the burned gas temperature, pressure and equivalence ratio cannot be changed independently in engine experiments. Therefore, the model predictions must be validated with the recorded fluorescence intensities and intensity ratios for the few combinations of temperature, pressure and equivalence ratios that could be achieved in the experiments. The precision uncertainty in the recorded Na/K and Na·Li/K² fluorescence intensity ratios is estimate via the standard deviation of the 5-cycle ensemble average at crank angle 20° aTDC as ±0.007 and ±0.009, resulting in a 95% confidence interval of ±0.014 and ±0.018, respectively. The plotted data range covers the expansion stroke (372° - 430° CA aTDC) after peak temperature had been reached and combustion was nearly complete. The burned gas temperature is calculated using the two-zone 'GT-Power' engine combustion

model, as is known to those skilled in the art. The predicted Na/K fluorescence intensity ratio had to be divided by the constant 1.08 to agree with the measured values. This is believed to be due to uncertainty in the transmission of the filters and the quantum efficiency of the cameras. The predicted Na/K ratios show a strong dependence on temperature, pressure and equivalence ratio that is in close agreement with the measurements. The quantity $\text{Na} \cdot \text{Li} / \text{K}^2$ shows the expected temperature dependence and both the predicted and measured data are nearly independent on equivalence ratio and pressure within an uncertainty of ± 50 K. Given the accuracy uncertainty in the calculated burned gas temperature of ± 100 K, both fluorescence intensity ratios are in quantitative agreement with the model predictions over the entire range of observed temperatures, pressures and equivalence ratios. With the model predictions calibrated with measurement data from known, well controlled engine operating conditions, it can subsequently be used to measure spatially resolved burned gas temperature and equivalence ratio without the help of temperature calculation in GT-Power or equivalence ratio measurements via the metering of intake air and fuel or the emissions bench. Fig. 9 shows the same data set as Fig. 6 after the recorded alkali fluorescence intensity ratios were post-processed and converted into a temperature and equivalence ratio scale.

The calibration curves from Fig. 8 were generated for data points late in the cycle where combustion was nearly complete, the burned gas zone was fully expanded and the absorption path length was large. The equivalence ratio images early in the cycle and around the perimeter of the burned gas zone in Fig. 9 appear richer than expected, but once the burned gas zone in Fig. 9 has expanded further, the calculated local equivalence ratios are in good agreement with the global equivalence ratio of $\Phi = 1.06$ measured by the emissions bench and the fuel and air metering systems. The measured equivalence ratio late in the cycle appears richer than expected. This is largely attributed to very low fluorescence intensity at the low temperature late in the cycle, which decreases the signal to noise ratio of the images. The images show some spatial stratification with the local equivalence ratio in the center region being richer than in the outer regions of the piston bowl. The equivalence ratio is also measured to be leaner at the bottom (exhaust) side of the piston bowl than at the top (intake) side. This stratification was not expected due to the early injection of fuel at 290° bTDC, but the spatial RMS of ± 0.08 lies within the

reported measurement uncertainty of $\pm 10\%$ of previously used tools such as LIF, which could explain why it has not been detected before.

The fluorescence based temperature measurement is compared to the GT-Power two-zone temperature calculation in Fig. 10. The measured data agree with the calculation within ± 15 K between 370-430 °CA aTDC, where the burned gas zone is fully expanded and combustion is nearly complete, but deviate by up to 90 K early in the combustion cycle at -10° aTDC. The fluorescence based temperature measurement is therefore expected to very accurately capture local temperature differences, but the overall accuracy of the absolute temperature values is coupled to the GT-Power accuracy uncertainty of ± 100 K.

The large temperature deviation early in the cycle, in combination with the equivalence ratio being measured too rich, indicates that the burned gas temperature obtained from the alkali fluorescence early in the cycle and around the perimeter of the burned gas zone is systematically biased towards lower values.

Mainly two reasons could potentially explain the inaccuracy in these regions: (1) The burned gas zone is not fully expanded in the direction of the cameras' line of sight for small flame kernels and near the outer regions of the burned gas zone, which impacts the magnitude of self-absorption of the fluorescence intensity. However, the calculations that lead to temperatures and equivalence ratios displayed in Fig. 9 assumed a fully expanded burned gas zone. (2) The assumption of a complete chemical equilibrium may not be valid for regions in or near the flame front. Both effects are included in the following discussion of measurement uncertainties.

Measurement Uncertainty

The product of alkali atom number density and absorption path length is independent of crank angle position under the assumption that the burned gas zone spans over the entire height of the cylinder volume. While this is the case late in the cycle where combustion is nearly complete, it may not be a valid assumption for early flame kernels. With only the bottom view of the cameras into the cylinder, it is not possible to

obtain a measure of the height of the burned gas zone. Assuming spherical flame propagation the depth of the early burned gas zone is nearly zero around its perimeter and radiation trapping should be negligible in this area. The model was modified to assume no self-absorption and re-applied to the early flame images to improve the accuracy of the temperature and equivalence ratio measurement. Fig. 11 shows the calculated equivalence ratio at -10° aTDC for the same cycle as Fig. 9, where the two limiting cases of absorption paths lengths are compared. The equivalence ratio in part (a) was calculated assuming the depths of the burned gas cloud being fully expanded, which is most appropriate for the center region of the image. The spatially averaged burned gas temperature was calculated as 2463 K, as shown in Fig. 8. Part (b) assumes the complete absence of absorption, which would be the limiting case for the perimeter of the burned gas zone assuming spherical flame propagation. In the limit of the assumed absence of self-absorption, the measured equivalence ratio is richer than in case (a) even around the perimeter of the burned gas zone. The spatially averaged burned gas temperature for this case is 2375 K, which deviates even stronger from the GT-Power calculation. The comparison shows that the correct assumption of the depths of the burned gas zone is important for the imaging of early flame kernels, but it does not explain the observed discrepancies in the measured burned gas temperature and equivalence ratio.

The calculated dependences of the fluorescence intensities on temperature, pressure and equivalence ratio assume all combustion species to be in a state of total thermal equilibrium. While this is nearly the case in the burned gas zone, where combustion is complete, it is not necessarily a valid assumption near the flame front, which forms the perimeter of the early flame kernel where the measured temperatures and equivalence ratios deviate substantially from the known values. Previous studies have reported super-equilibria of hydroxyl and hydrogen radicals that would affect the chemical balance between alkali atoms and their hydroxides and lead to a deviation from the assumed chemical equilibrium between the alkali atoms and their oxidation products. A potential solution to this problem would be the inclusion of reaction kinetics in the model instead of the assumption of thermodynamic equilibrium. However, not enough information is available with regards to the exact composition of the alkali metal fuel additives and their reaction pathways and reaction rates in the flame. In addition, no

alkali reaction mechanism is available for engine combustion environments using isooctane or gasoline-like fuels. The reaction mechanisms that were developed in $H_2/O_2/N_2$ flames differ largely in their reported reaction rate constants. It is therefore currently not possible to include reaction kinetics into the model calculations to improve the alkali fluorescence based temperature and equivalence ratio measurements in or near the flame front.

Uncertainty is introduced by the assumption of a homogeneous burned gas temperature in the combustion chamber, which is required for the two-zone GT-Power combustion model. Since the lithium, sodium and potassium fluorescence intensities depend exponentially on burned gas temperature, a thermal stratification along the cameras' line of sight causes the integrated fluorescence to correspond to a temperature higher than the calculated mean. This effect would be less pronounced for the Na·Li/K² and Na/K fluorescence ratios, because their exponent in the Boltzmann term is much smaller, but still poses a limitation to the quantitative application of this tool to stratified combustion environments.

Similarly, the integration of the recorded fluorescence intensity along the cameras' line of sight in a stratified combustion environment would generally bias the measured equivalence ratio towards values that are richer than the line of sight average, because the fluorescence intensity is generally higher in richer zones. Additionally, in cases where self-absorption of the alkali fluorescence is significant, the temperature and equivalence ratio measurement will be biased to areas closer to the cameras (in this study the piston top), because photons originating from this region are more likely to escape the cylinder due to their shorter path length. Self-absorption of the alkali fluorescence could be minimized to less than 2% of the emitted light under most engine conditions, if the alkali mole fractions in the fuel were reduced by a factor of approximately 500. This would reduce the recorded fluorescence intensity by a factor of approximately 100 and necessitate the use of image intensifiers.

The assessment of the precision error of the temperature and equivalence ratio imaging in the engine is complicated by the fact that combustion cycles are not truly repeatable. At a stable, nearly stoichiometric engine operating condition, the temperature

and equivalence ratio was measured of 50 consecutive, individual cycles at crank angle 20° aTDC. The 50 cycles were sorted by their IMEP, and the five cycles with the highest IMEP were selected. The coefficient of variance of the IMEP of these five cycles was 0.008. Due to the almost identical engine performance, it is assumed that the burned gas temperature is identical among these five cycles. The standard deviation of the spatially averaged temperature and equivalence ratio measurement was 9.2 K and 0.01, resulting in a 95% confidence interval of $\pm 18\text{K}$ and ± 0.02 , respectively.

The accuracy uncertainty of the temperature calculation in the zero dimensional GT-Power model cannot be fully quantified because of the required estimation of various software parameters. However, systematic variations of the major parameters influencing the burned gas temperature calculation in the engine lead to an estimate of $T \pm 100\text{K}$ in this study. The accuracy of the alkali fluorescence based temperature measurement is therefore also limited to an uncertainty of $\pm 100\text{K}$, since the calculated temperature from GT-Power is used for the calibration of the alkali fluorescence tool. To improve the accuracy of the fluorescence imaging tool, a more reliable calibration methodology would need to be identified. Any spatial or temporal temperature differences observed with this tool are not affected by this, but the absolute temperature values are affected by an estimated accuracy uncertainty of $\pm 100\text{K}$.

Accuracy uncertainty in the imaging of equivalence ratio is not affected by the uncertainty in the calculated burned gas temperature, because the equivalence ratio obtained from the Na/K fluorescence intensity ratio is calibrated using the calculated burned gas temperature of GT-Power and the measured equivalence ratio obtained from the fuel and air metering system. The calibration decoupled the accuracy of the equivalence ratio obtained from the alkali fluorescence from the accuracy uncertainty of the burned gas temperature. Accuracy uncertainty in the equivalence ratio calculated from the alkali fluorescence ratio Na/K is introduced by the $\pm 3.0\%$ uncertainty in the equivalence ratio obtained from the fuel and air metering system, which is used for the calibration of the fluorescence tool. This could be improved by performing the calibration in a more controlled environment such as a premixed flame burner. The equivalence ratio measurement via alkali fluorescence imaging generally has the best sensitivity near

stoichiometric equivalence ratio and low temperature, but generally no sensitivity for $\Phi \leq 0.9$.

Mass Fraction Burned Imaging Using the Spatially Integrated Sodium Fluorescence

The integrated sodium fluorescence intensity depends on pressure, temperature, equivalence ratio, absorption and mass fraction burned. Once the temperature and equivalence ratio have been obtained through the $\text{Na}\cdot\text{Li}/\text{K}^2$ and Na/K fluorescence intensity ratios, the spatially integrated sodium fluorescence intensity can be corrected for the effects of pressure, temperature, equivalence ratio and self-absorption on the sodium fluorescence intensity using model calculations. After the correction has been applied, the spatially integrated sodium fluorescence intensity is expected to show linear dependence on mass fraction burned. With the current experimental setup this correlation can only be performed early in the cycle before the burned gas zone has spread beyond the field of view of the cameras. Sodium fluorescence images that were ensemble averaged over five engine cycles in the range from -24° to -2° CA aTDC and mass fraction burned 0.005 to 0.163, respectively, are shown in Fig. 12 for engine operation and equivalence ratio $\Phi=1.06$. The spark plug electrode is not masked out in the center of these images to minimize error in the spatial integration of the fluorescence intensity. It must be noted, however, that the spark plug ground strap itself covers the view into the spark plug gap between ground strap and electrode.

The spatially integrated sodium fluorescence is extracted from the images and plotted in Fig. 13a as a function of calculated mass fraction burned for equivalence ratios ranging between 0.72 and 1.23. The sodium fluorescence intensities differ largely at any given mass fraction burned depending on the engine operating condition. This is expected because the recorded sodium fluorescence intensity also depends on the burned gas temperature, pressure, equivalence ratio and self-absorption, which differ for each operating condition. The integrated fluorescence signal is subsequently corrected for its dependence on temperature, pressure, equivalence ratio and absorption and the corrected fluorescence intensities are plotted in Fig. 13b. The data show a linear correlation with mass fraction burned and nearly collapse onto the same curve for the various engine operating conditions. This shows that the spatially integrated sodium fluorescence

intensity can be used to measure mass fraction burned within an experimental uncertainty of ± 0.02 provided the burned gas temperature and equivalence ratio are known from the three component fluorescence intensity ratios.

Various limitations exist that introduce error to the plotted data. (1) The ground strap of the spark plug is partially covering the view. If the early flame kernel exists mainly in the gap between ground strap and spark plug electrode, the measured sodium signal for early crank angles may not be visible to the camera. (2) The spark is occasionally carried with the in-cylinder air flow and the arc becomes visible to the camera for early crank angles despite the bandpass filters. This will cause interference with the recorded sodium signal, since the camera cannot distinguish between the two. The use of filters with even narrower spectral bandwidths could help avoid interference from the spark arc. (3) At the very onset of combustion the relative uncertainty in the mass fraction burned values calculated by the heat release analysis tool is highest. The mass fraction burned is calculated as 0.005 even before the start of combustion. (4) The sodium fluorescence was corrected for self-absorption using the burned zone diameter as the absorption length assuming spherical flame propagation. However, this will still introduce error in the outer regions of the burned gas zone, where the burned zone thickness is smaller. However, with the current view it is not possible to know the depth of the burned gas zone accurately at each point. Imaging from multiple directions would yield more accurate knowledge of the thickness of the burned gas zone.

Alkali Metal Fluorescence Imaging of a Complex Combustion Process

Fig. 14 shows a comparison of a well burning (Fig. 14a - IMEP 151 kPa) and poorly burning (Fig. 14b - IMEP 70 kPa) engine cycle during spray-guided, stratified engine operating. The injector used was an 8-hole injector with 60° spray angle and a length over diameter (L/D) ratio of the injector holes of 2.0. The engine speed was 800 rpm and the intake air was diluted with 32% nitrogen to simulate the effect of high exhaust gas recirculation (EGR). Injection and spark timing were set to -24° and -22° aTDC, respectively, and the total amount of fuel injected was 6.0 mg/cycle. Fig. 14 shows a side by side comparison of the recorded burned gas temperature and equivalence ratio of the two cycles. Combustion in the well burning cycle in part (a) seems to start in

a much larger area and quickly extends in several directions simultaneously. It is generally observed that large parts of the flame perimeter are stoichiometric or rich, and the burned gas zone expands the quickest in these directions. The burned gas eventually fills most of the piston bowl indicating all the fuel was combusted. This is confirmed by an independent heat release analysis that computed a final mass fraction burned of 95%. In contrast, combustion in the poorly burning cycle in part (b) is very slow initially and expands out only in the left and downward (towards exhaust side) direction. The burned gas zone becomes lean around most of its perimeter and stops expanding indicating that the initial flame did not get exposed to any more fuel and combustion stopped prematurely. The fuel in the upper (intake side) half of the piston bowl never ignites, which is confirmed by a total mass fraction burned of only 50%. It must be emphasized that alkali fluorescence originates from the entire burned gas volume and the images are merely a two dimensional projection integrated along the line of sight of the camera. In a spray guided engine environment with large stratification of equivalence ratio and burned gas temperature along the cameras' line of sight, the recorded values of temperature and equivalence ratio are generally skewed toward higher than average temperature and richer than average equivalence ratio due to the thermodynamic and spectroscopic properties of the alkali metals, as well as to areas closer to the piston bowl surface due to self-absorption of the alkali fluorescence. Formation of soot particles is possible in this stratified environment and broad banded soot luminosity may be transmitted through the bandpass filters and consequently get misinterpreted as alkali fluorescence. This would predominantly affect the potassium channel, because the wavelength of the potassium fluorescence is longer than lithium or sodium fluorescence. As a consequence, the $\text{Na}\cdot\text{Li}/\text{K}^2$ and Na/K intensity ratios would appear too low on the images, leading to systematic shift in the calculated temperature towards lower values and richer equivalence ratio. In addition, it was observed in homogeneous engine environments that equivalence ratios are generally measured too high near the flame front due to suspected super-equilibrium OH concentrations in these areas. This will also affect the measurement under spray-guided conditions leading to inaccuracy in the measured temperature and equivalence ratio that can currently not be quantified.

The three camera setup shown in Fig. 1 was modified to improve the signal to noise ratio of the lithium fluorescence in cold and lean burned gas zones and to better suppress soot luminosity. Two Phantom V7.1 cameras recorded the sodium fluorescence at 589.0 and 589.6 nm and potassium fluorescence at 766.5 nm, respectively. A Vision Research Phantom V710 with a higher quantum efficiency of 35% near 671 nm was used to record both lithium fluorescence lines. The lens mounted filters were replaced by customized narrow-banded filters purchased from Omega Optical with center wavelengths at 589.0 nm (FWHM 2.0 nm, 50% peak transmission, 50 mm diameter), 670.8 nm (FWHM 1.0 nm, 30% peak transmission, 50 mm diameter) and 766.5 nm (FWHM 1.0 nm, 40% peak transmission, 50 mm diameter). Experiments in stratified engine environments without alkali fuel additives showed a total suppression of the soot luminosity even under high-sooting operating conditions. The measured transmission spectra of the narrow banded bandpass filters are shown in Fig. 15.

A spray-guided engine operating condition with double injection was recorded and is displayed in Fig. 16. Engine speed was 800 rpm, the end of the first (EOI-1) and second injection (EOI-2) were set to -21° and -12° aTDC, respectively, and the spark timing was set to -19° aTDC. The total amount of fuel injected was 4.2 mg/cycle resulting in an IMEP of 112 kPa. The fuel metering system was not instrumented to measure the amount of fuel injected individually for the first and second injection. The images are ensemble averaged over 30 cycles and show the initial expansion of the burned gas cloud after the first injection and the leaning out of this zone as more oxygen is entrained from the surrounding zones. As the second injection event takes place at -12° aTDC, the local equivalence ratio in the center region becomes rich while the local burned gas temperature cools off due to the evaporation of the liquid fuel. Further entrainment of oxygen from unburned areas during the course of the combustion cycle leans out the burned gas zone. Generally the equivalence ratio remains higher around the perimeter of the visible cylinder bowl.

Fig. 17 shows a comparison of a 100-cycle ensemble average of identical engine operating conditions with different injectors. The engine was run at 2000 rpm with 20% dilution of the intake air with nitrogen. Both injection and ignition timing were set to -36°

aTDC with 7.7 mg of fuel injected per cycle. Both injectors are 8-hole injectors of the same manufacturer and model generation with 60° spray angle. The length over diameter ratio of the injector used in Fig. 17a was $L/D=2.4$ and in Fig. 17b $L/D=2.0$. This small parameter variation has a very minor impact on engine performance with the average
5 IMEP being 240 kPa for the $L/D=2.4$ injector and 235kPa for the $L/D=2.0$ injector. Previous studies have shown that a variation of the L/D ratio can significantly influence the spray plume angle and change the spray and fuel-air mixing characteristics. Larger L/D ratios generally produce a narrower cone angle with better plume separation, while smaller L/D ratios produce wider cone angles that can lead to plume interaction and the
10 total collapse of the spray. The burned gas temperature of the $L/D=2.0$ injector is approximately 200K lower than for the $L/D=2.4$ injector, which could be due to the delayed evaporation of the fuel drawing heat from the burned gas zone. The equivalence ratio is initially measured richer for the $L/D=2.0$ injector in the observed piston bowl area. Toward the end of combustion the area near perimeter of the piston bowl is
15 significantly richer than the center region. This is in good agreement with the assumption that the spray of the $L/D=2.0$ injector might have collapsed hitting the piston and the possibility of liquid fuel accumulating in the corner of the piston bowl, where it might not sufficiently mix with air and consequently burn at very rich equivalence ratio. Simultaneous imaging of the injector spray can provide additional insight and help
20 develop a better understanding of the relation of injector spray characteristics to combustion characteristics.

Modifications and Alternative Embodiments

The diagnostic tool and method described above is useful for alkali metal spectroscopy of the combustion process in the combustion chamber of an internal
25 combustion engine such as is commonly used in vehicles.

An accuracy limitation for stratified engine operation stems from the fact that each camera only sees a 2D projection of the 3D burned gas zone and the measured temperatures and equivalence ratios are therefore merely weighted averages along the camera's line of sight. Unknown depth and stratification of the burned gas cloud
30 therefore limit the quantitative applicability of this measurement technique in stratified

combustion environments. This could be improved by imaging from multiple views to allow for valid approximations of the stratification of these two quantities. Useful applications of this tool are the investigation of partial burns and cyclic variability under stratified engine operation as well as comparing the effects of engine hardware or design changes on the combustion process. In combination with spray and soot imaging, this tool can be used for injector and combustion chamber geometry optimization.

The quantitative examination of small flame kernels is limited by the unknown absorption length. Imaging from multiple views could in part lift this limitation. It is possible to fully avoid self-absorption of the alkali fluorescence by reducing the alkali fuel concentration by a factor of approximately 500. In this case less than 2% of the emitted fluorescence would get reabsorbed. Overall, this would result in measured fluorescence intensities being lower by a factor of 100, which is too weak to record the fluorescence with the existing imaging setup. The use of high speed image intensifiers would be required to amplify the light sufficiently. While the use of image intensifiers introduces additional shot noise to the images, the overall accuracy of the equivalence ratio and temperature measurement of small flame kernels might still be improved substantially by avoiding self-absorption.

In addition, the mismatch of recorded burned gas temperature and equivalence ratio in the early flame kernel and near the perimeter of the burned gas zone indicate that the assumption of perfect chemical equilibrium in burned gas zone is not valid near the flame front. Previous studies have shown super-equilibrium concentrations of hydroxyl and hydrogen radicals in these areas, which would affect the equilibration of alkali atom concentration and consequently result in inaccuracies in the obtained temperature and equivalence ratio. A quantitative investigation of the reaction kinetics would be required to improve accuracy of this tool near the flame front region. Unfortunately, not enough literature data is currently available to attempt the inclusion of reaction kinetics for alkali containing isooctane fuel in engine combustion.

The experimental approach of this technique could be simplified further by replacing the three high-speed cameras that were used in this study by relatively inexpensive photo multipliers. This would remove the capability of two dimensional

spatial resolution of burned gas temperature and equivalence ratio that was demonstrated in this study. However, in cases where spatial resolution is not required, this approach would significantly reduce experimental complexity and cost. This approach could be combined with a fiber optics imaging system to allow for data collection in all metal engines with little optical access. The model that was developed in this study to quantify the temperature, pressure and equivalence ratio dependence of the alkali fluorescence intensity could be integrated in a simple machine that acquires the fluorescence intensity using photo-multipliers and fiber optics and automates the conversion of recorded fluorescence intensities into burned gas temperature and equivalence ratio with little requirement for user input. Such a device could be of high interest for the use in industrial engine development environments, where fast and reliable results and hence reduction of experimental complexity are of high importance.

The diagnostic tools and methods described above can be used for analysis of any of a variety of direct injection engines, including automotive (car/truck/motorcycle) as well as smaller engines used, for example, in lawn care.

It is to be understood that the foregoing description is of one or more embodiments of the invention. The invention is not limited to the particular embodiment(s) disclosed herein, but rather is defined solely by the claims below. Furthermore, the statements contained in the foregoing description relate to the disclosed embodiment(s) and are not to be construed as limitations on the scope of the invention or on the definition of terms used in the claims, except where a term or phrase is expressly defined above. Various other embodiments and various changes and modifications to the disclosed embodiment(s) will become apparent to those skilled in the art.

As used in this specification and claims, the terms "e.g.," "for example," "for instance," "such as," and "like," and the verbs "comprising," "having," "including," and their other verb forms, when used in conjunction with a listing of one or more components or other items, are each to be construed as open-ended, meaning that the listing is not to be considered as excluding other, additional components or items. Other terms are to be construed using their broadest reasonable meaning unless they are used in a context that requires a different interpretation.

CLAIMS

1. A method of spectroscopic analysis of fuel combustion in a combustion chamber of an internal combustion engine, comprising the steps of:

- (a) introducing a mixture of fuel, air, and a plurality of different alkali metal dopants into a combustion chamber of an internal combustion engine;
- (b) igniting the mixture;
- (c) optically recording spectral data associated with fluorescence of each of the alkali metal dopants during combustion of the mixture; and
- (d) determining burned gas temperature by analysis of the spectral data.

2. The method set forth in claim 1, wherein step (d) further comprises determining burned gas temperature based on an intensity ratio determined using the spectral data for at least some of the dopants.

3. The method set forth in claim 2, wherein the dopants include three dopants (a, b, c), and wherein step (d) further comprises determining the burned gas temperature using the following ratio of spectral intensities: $a \cdot b / c^2$.

4. The method set forth in claim 3, wherein dopant a comprises sodium (Na), dopant b comprises lithium (Li) or cesium (Cs), and dopant c comprises potassium (K) or rubidium (Rb).

5. The method set forth in claim 3, further comprising the step: (e) determining equivalence ratio for the combustion of the mixture using an intensity ratio of a/c .

6. The method set forth in claim 5, further comprising the step: (f) determining mass fraction burned for the combustion using the burned gas temperature and equivalence ratio.

7. The method set forth in claim 6, wherein step (f) further comprises determining the mass fraction burned using a spatially integrated fluorescence intensity obtained from the spectral data for one of the dopants and correcting the integrated fluorescence intensity using the burned gas temperature and equivalence ratio.

8. The method set forth in claim 1, wherein step (a) further comprises introducing the following three alkali metal dopants into the combustion chamber: sodium (Na), lithium (Li) and potassium (K), and wherein step (d) further comprises determining burned gas temperature using an intensity ratio of $\text{Na} \cdot \text{Li} / \text{K}^2$.

5 9. The method set forth in claim 8, further comprising the step: (e) determining equivalence ratio for the combustion of the mixture using an intensity ratio of Na / K .

10. The method set forth in claim 1, further comprising the step: (e) determining equivalence ratio for the combustion of the mixture after determining the burned gas temperature.

10 11. The method set forth in claim 2, further comprising the step: (f) determining mass fraction burned for the combustion of the mixture after determining the burned gas temperature and the equivalence ratio.

12. The method set forth in claim 1, wherein step (c) further comprises recording the spectral data using a different image sensing device for each of the dopants.

15 13. The method set forth in claim 12, further comprising optically separating the spectral data associated with each of the dopants prior to recording the spectral data.

14. A diagnostic tool that carries out the method of claim 1.

15. A method of spectroscopic analysis of fuel combustion in a combustion chamber of an internal combustion engine, comprising the steps of:

- 20 (a) introducing a mixture of fuel, air, and a plurality of different alkali metal dopants into a combustion chamber of an internal combustion engine;
- (b) igniting the mixture;
- (c) optically recording spectral data associated with fluorescence of each of the alkali metal dopants during combustion of the mixture;
- 25 (d) determining burned gas temperature and equivalence ratio for the combustion of the mixture by analysis of the spectral data;

- (e) determining a spatially integrated fluorescence intensity for one of the dopants;
- (f) determining a correction to the integrated fluorescence intensity based on the burned gas temperature and equivalence ratio; and
- 5 (g) determining mass fraction burned for the combustion using at least the integrated fluorescence intensity and correction.

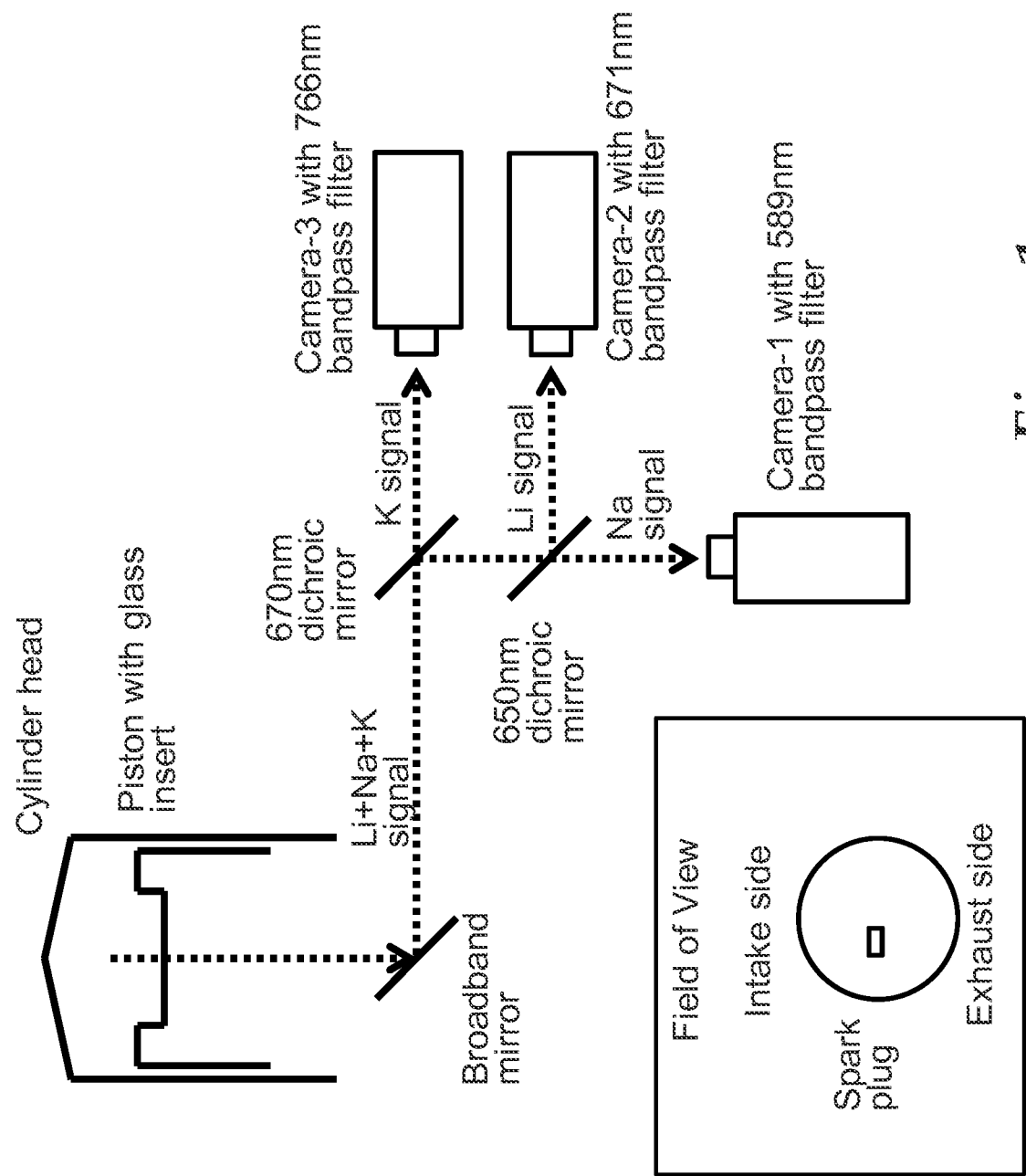
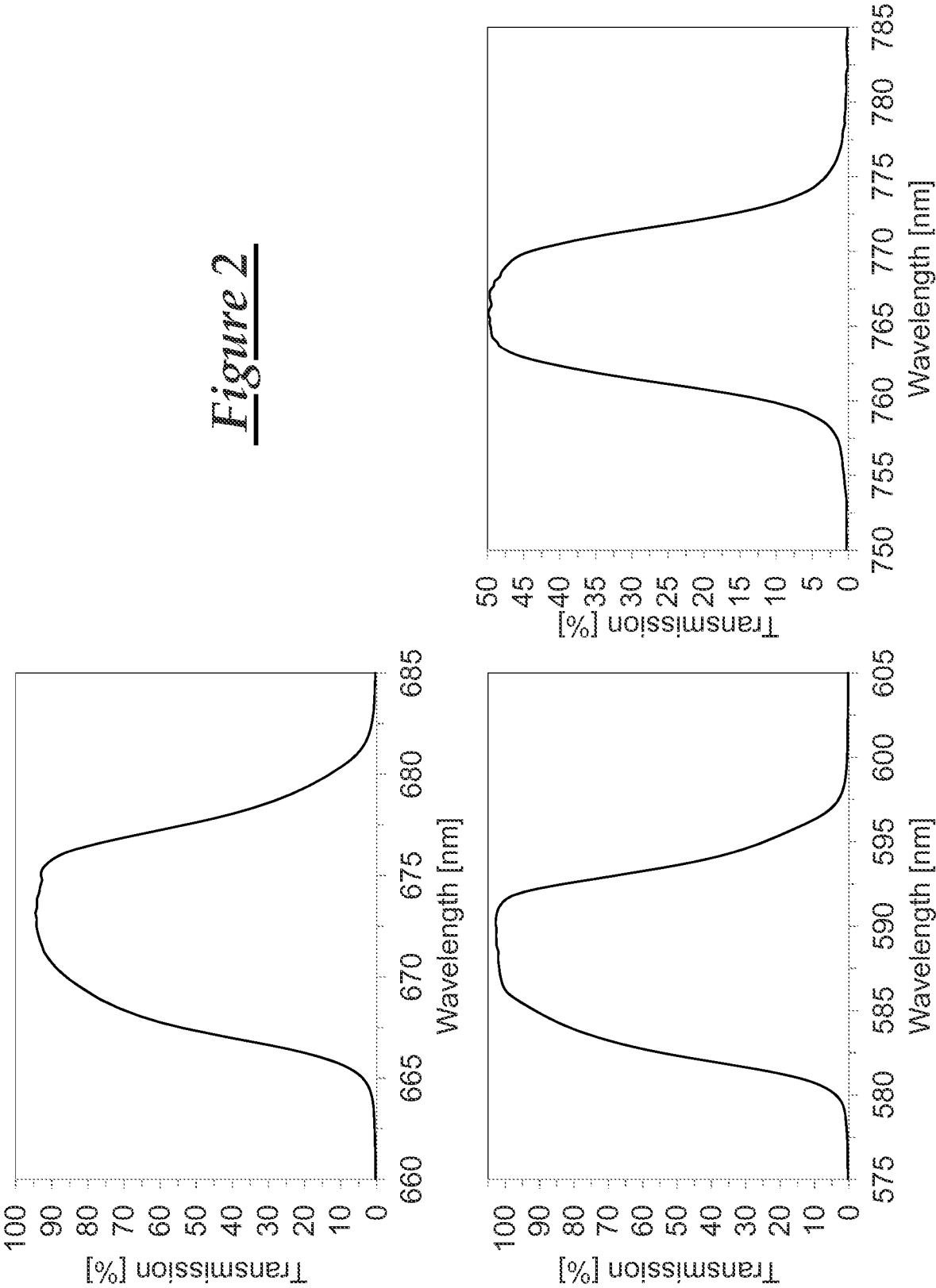


Figure 1

Figure 2



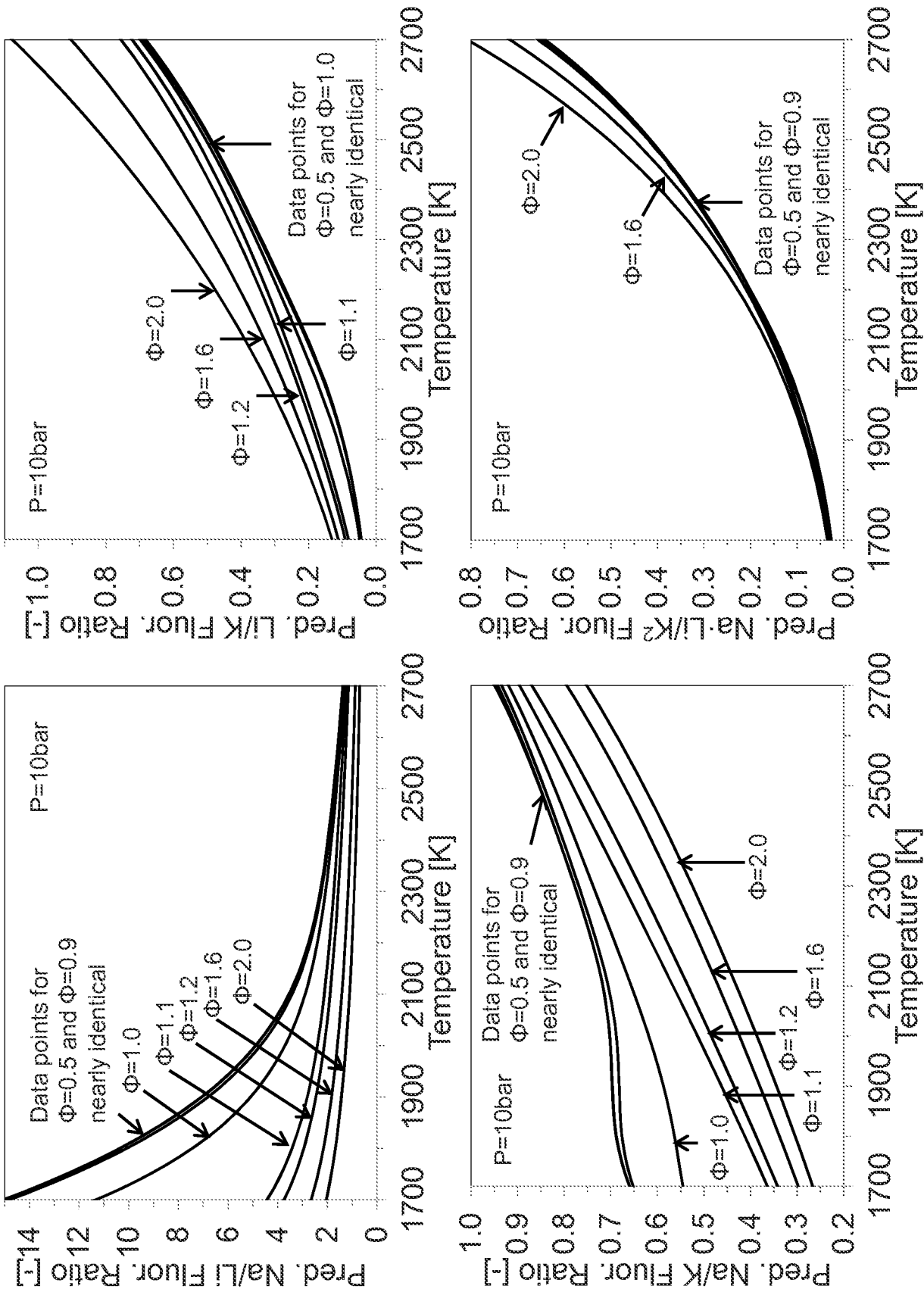


Figure 3

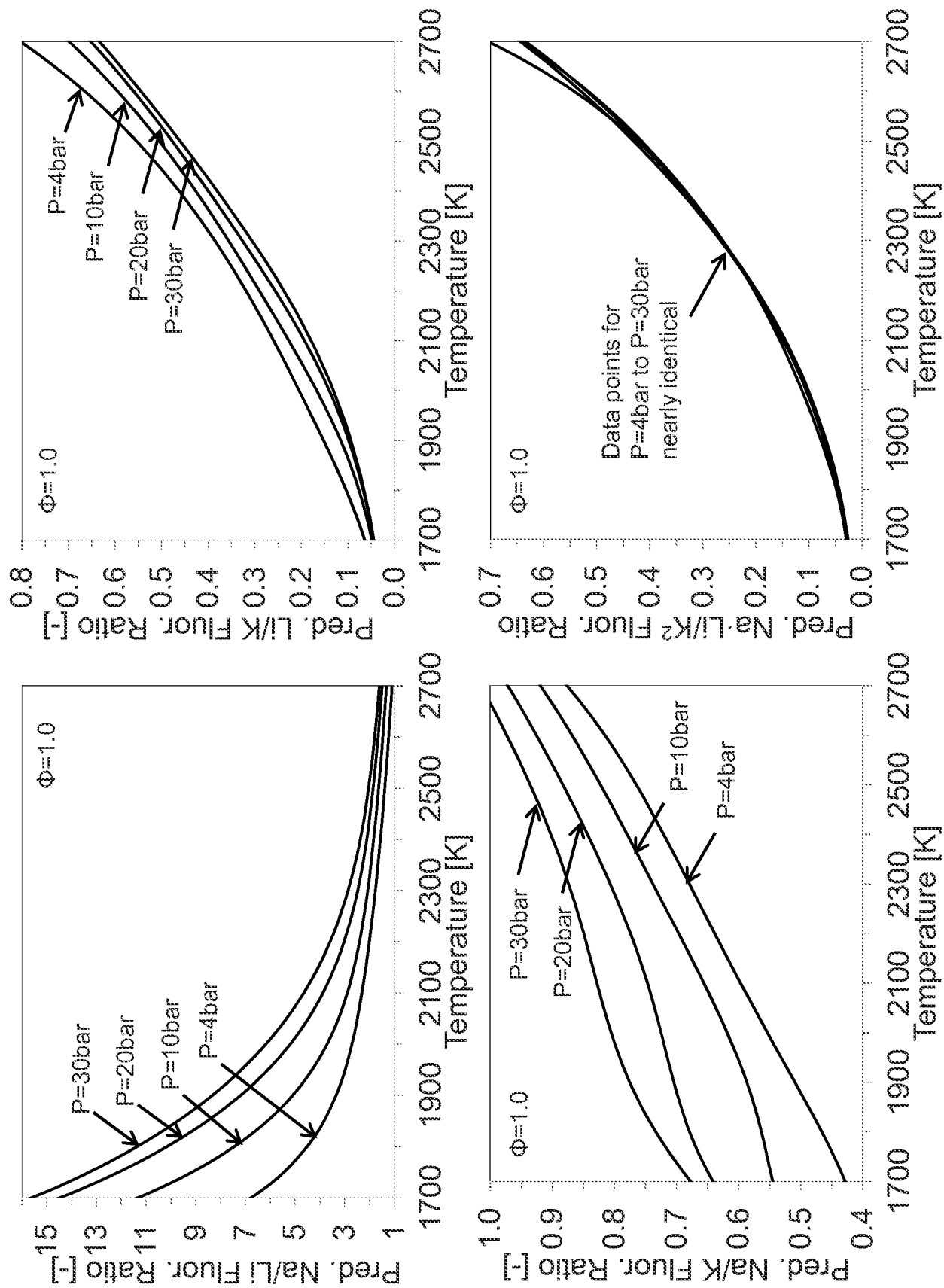
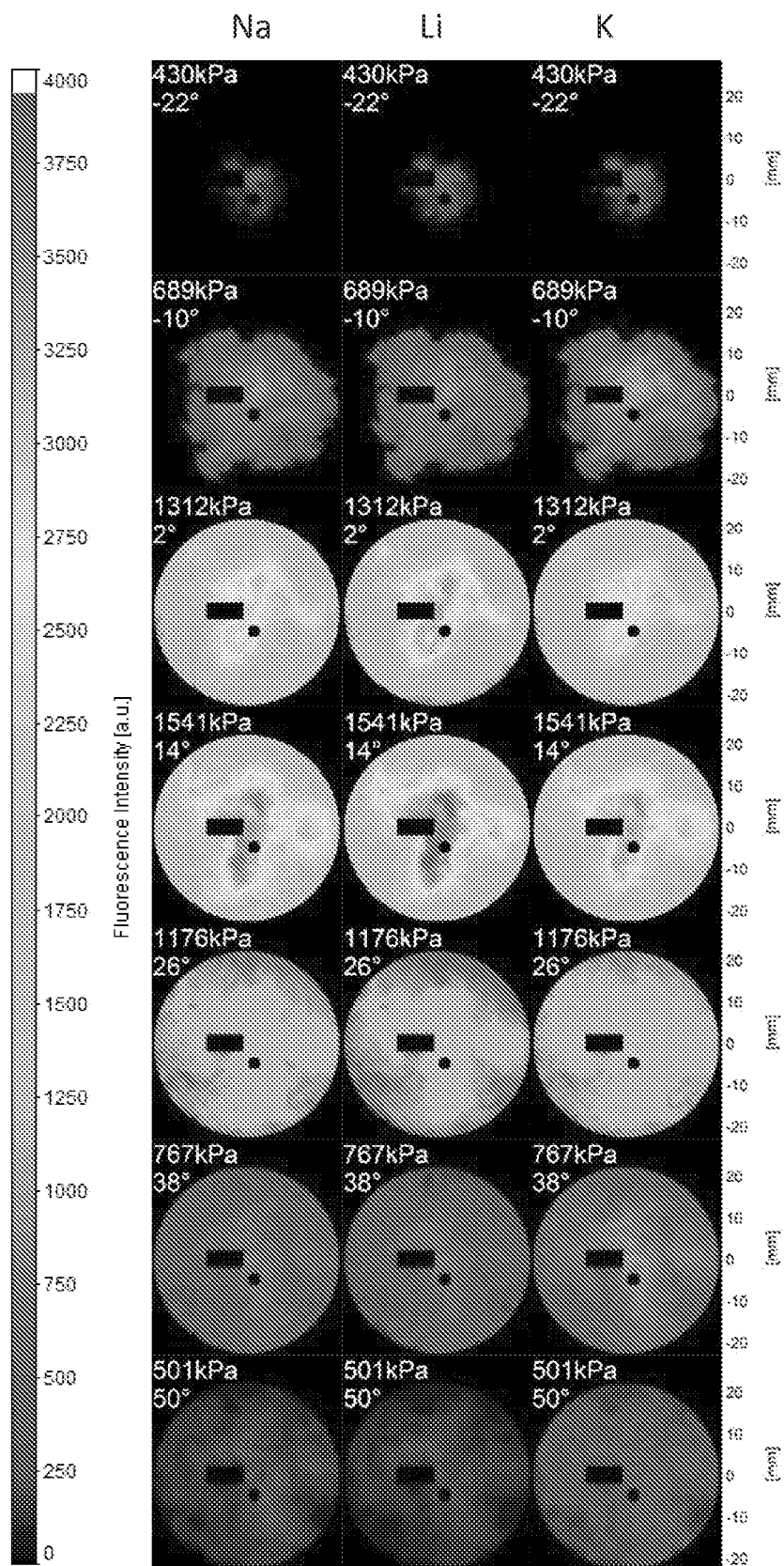
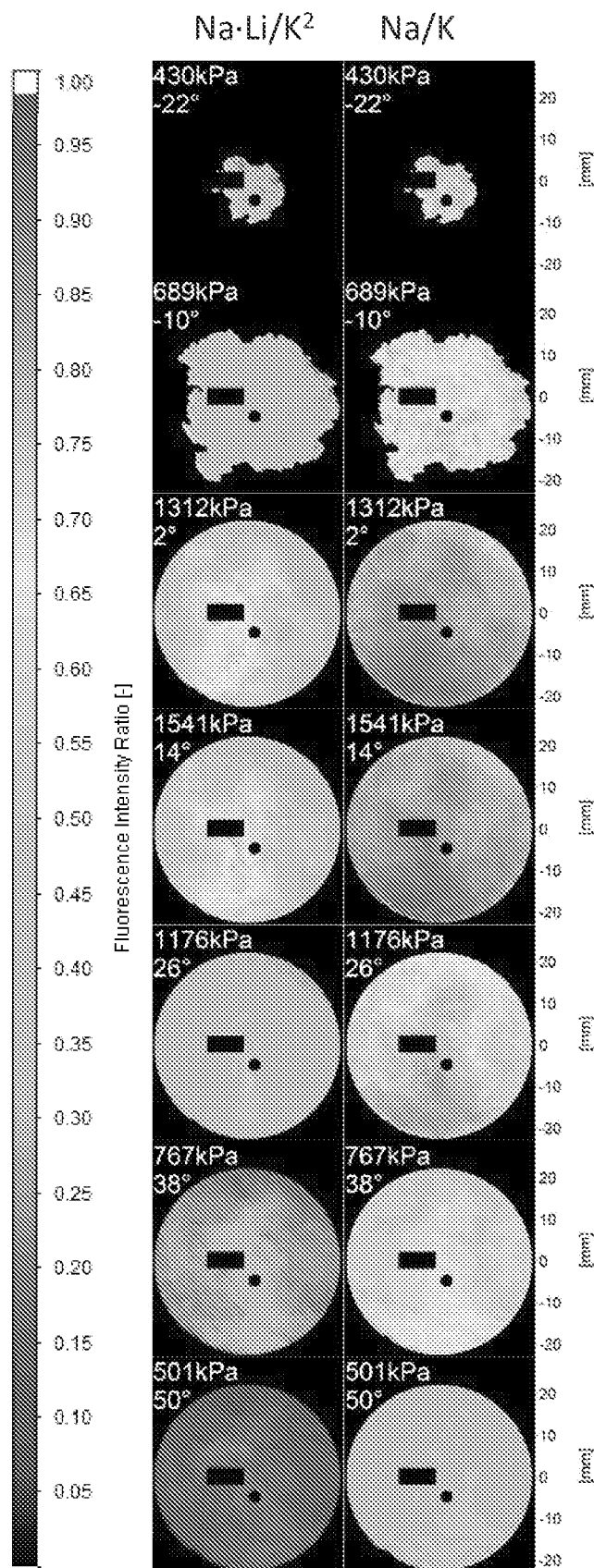


Figure 4

*Figure 5*

Figure 6

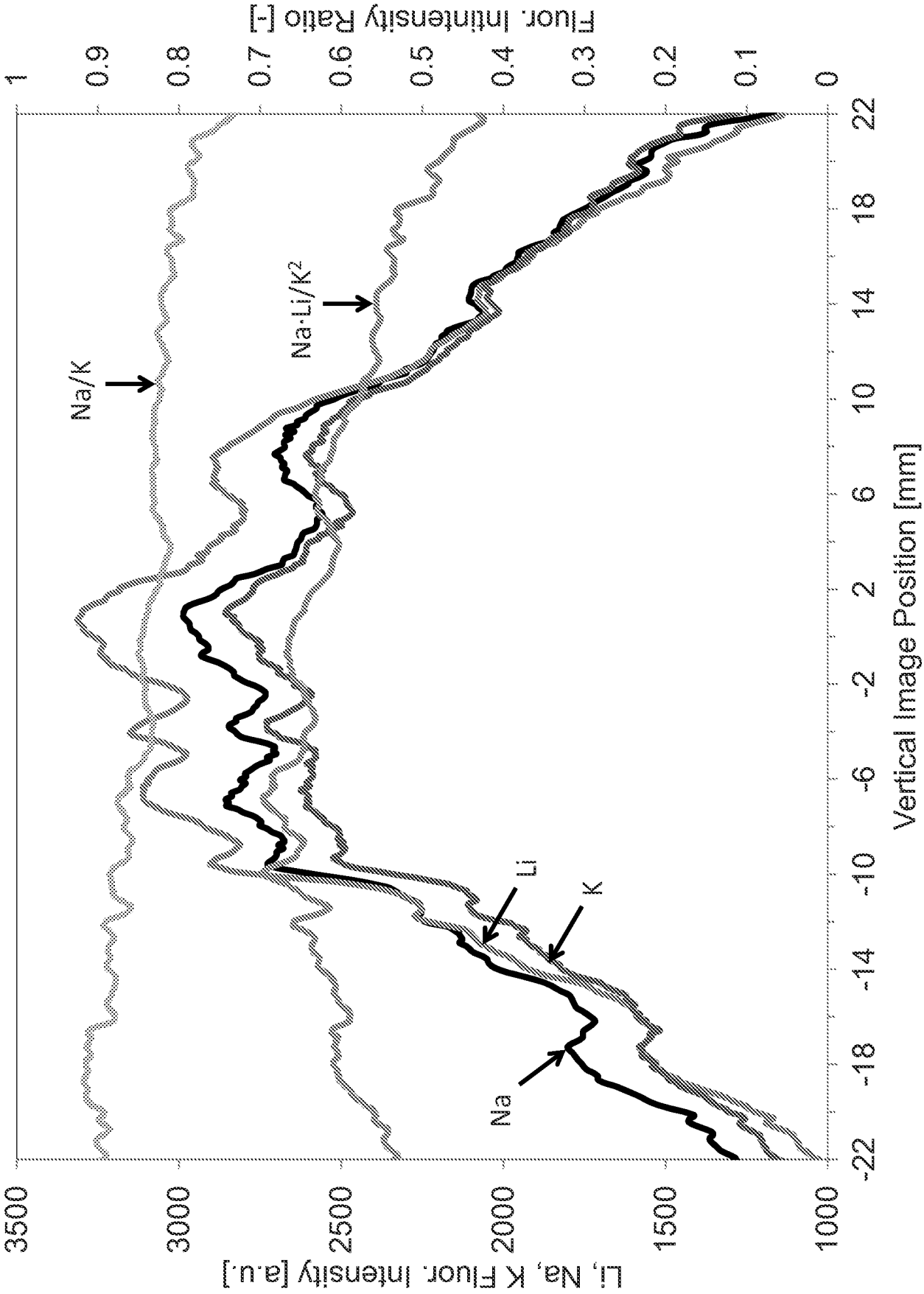
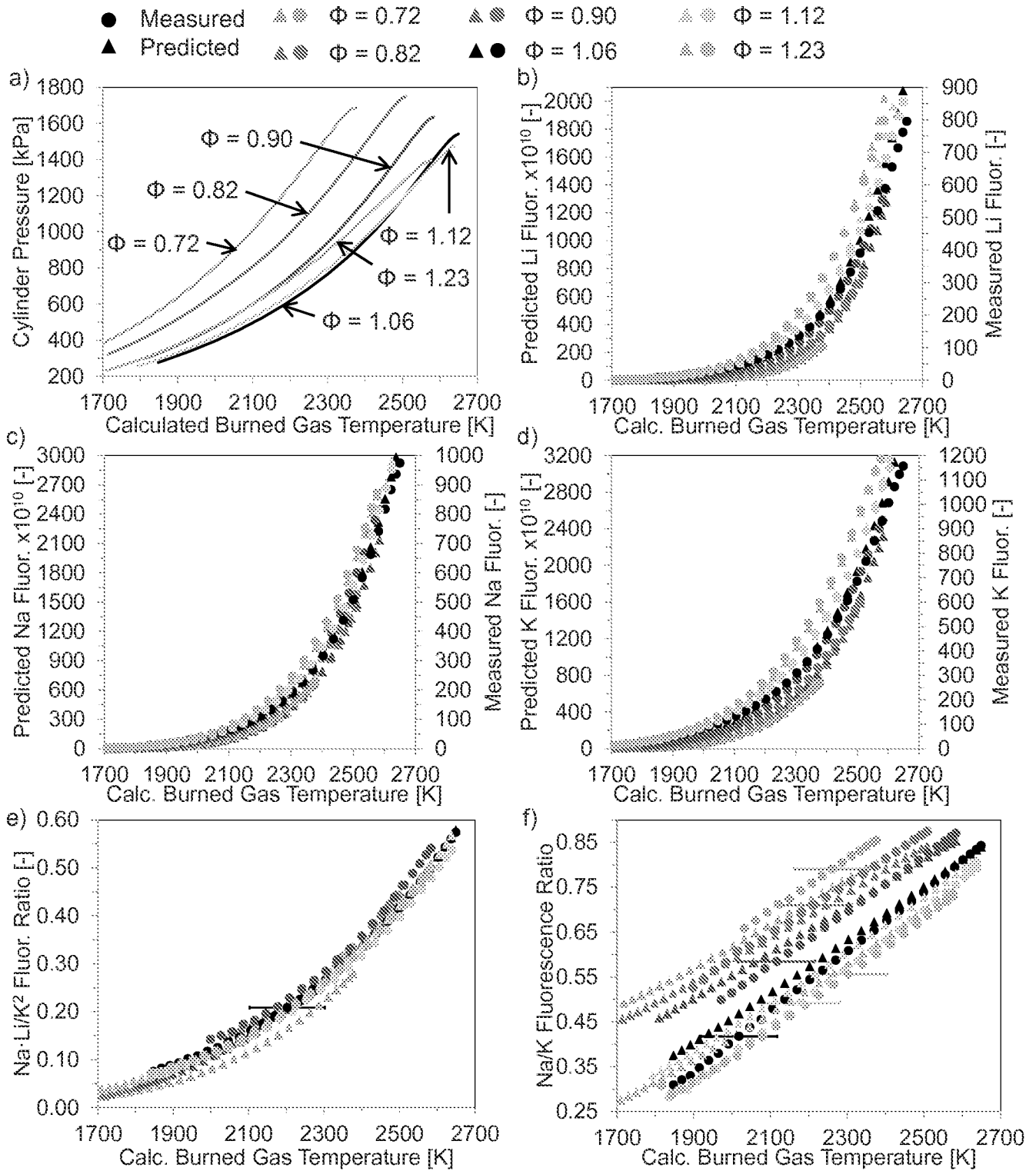
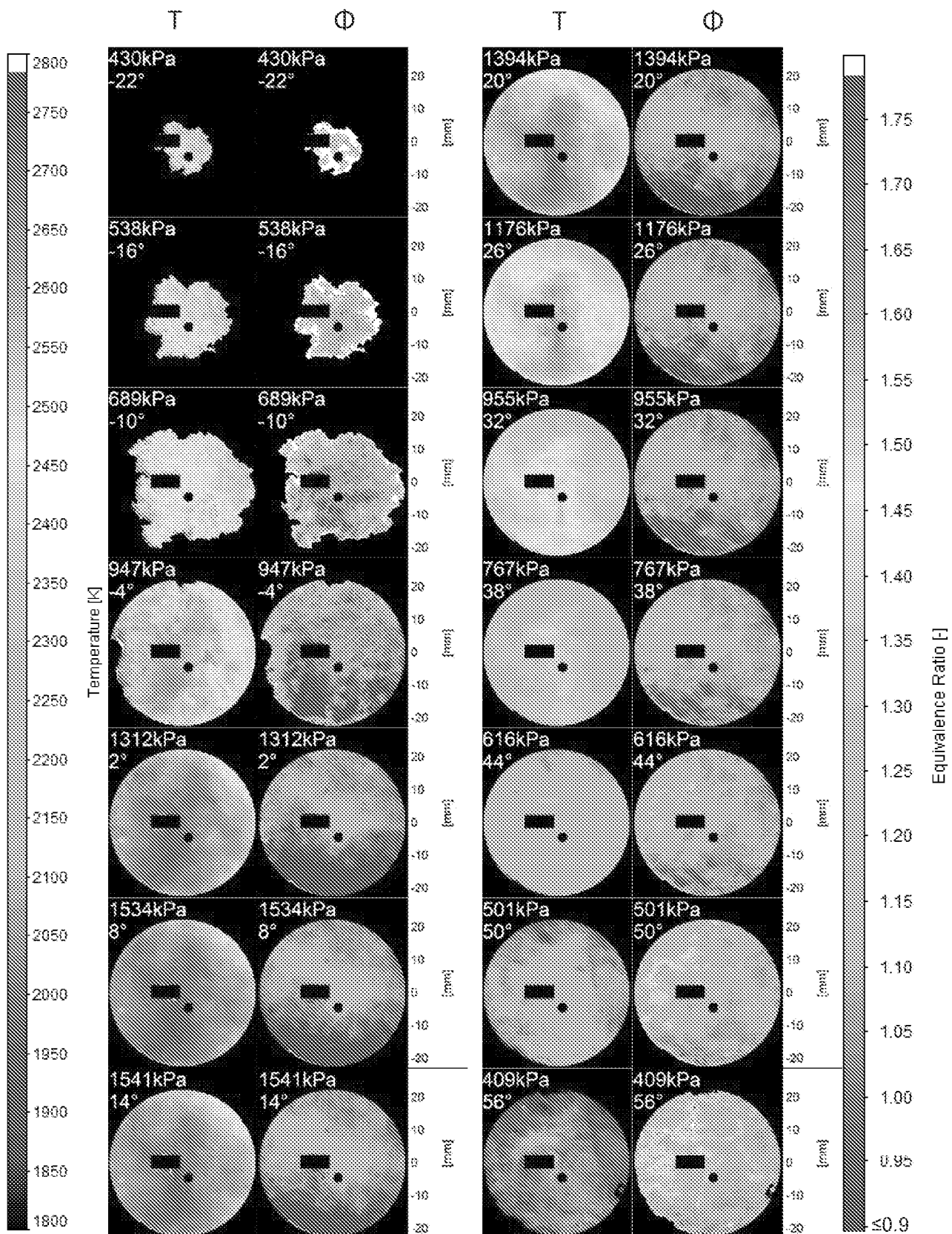


Figure 7

Figure 8

*Figure 9*

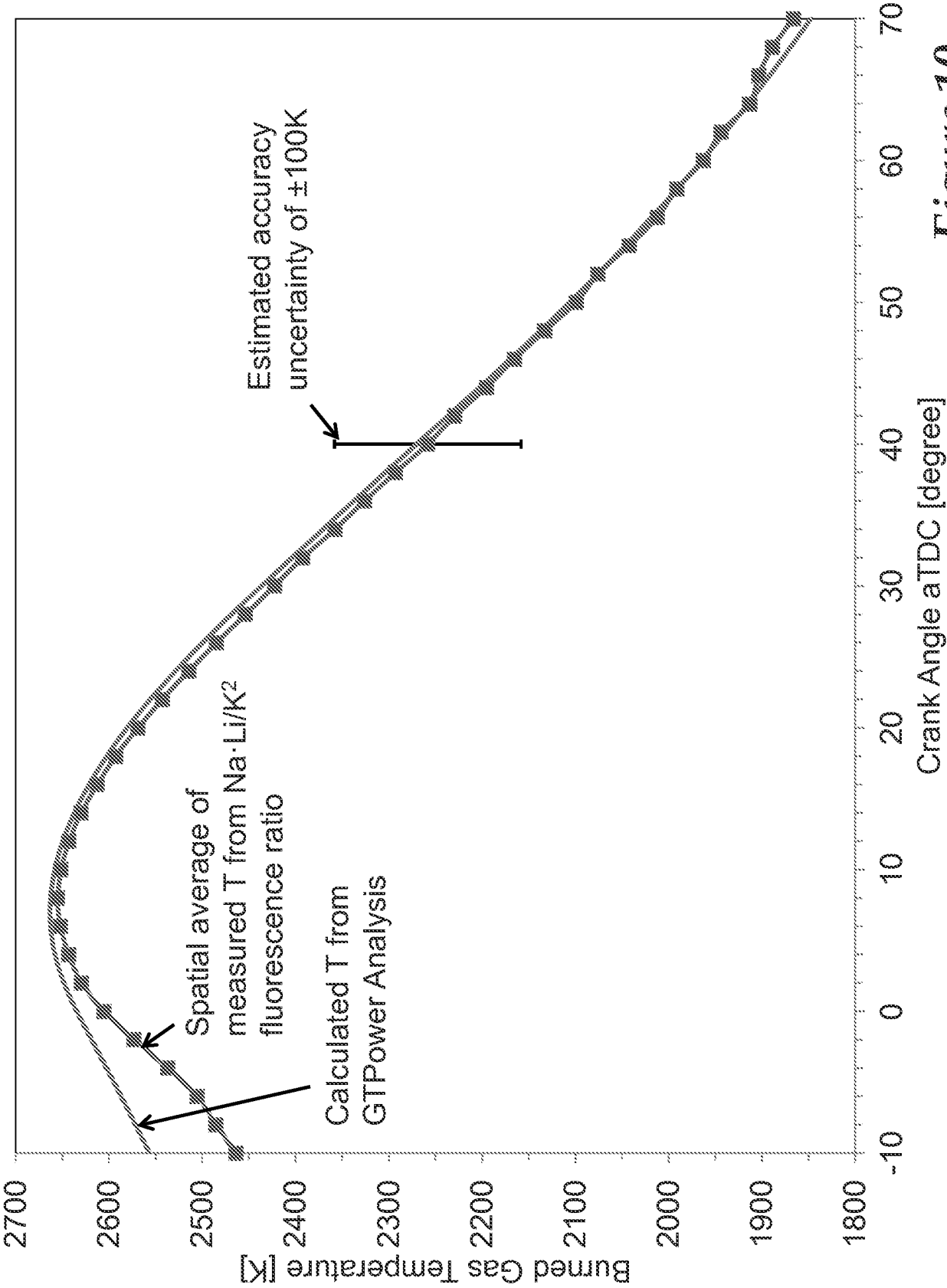


Figure 10

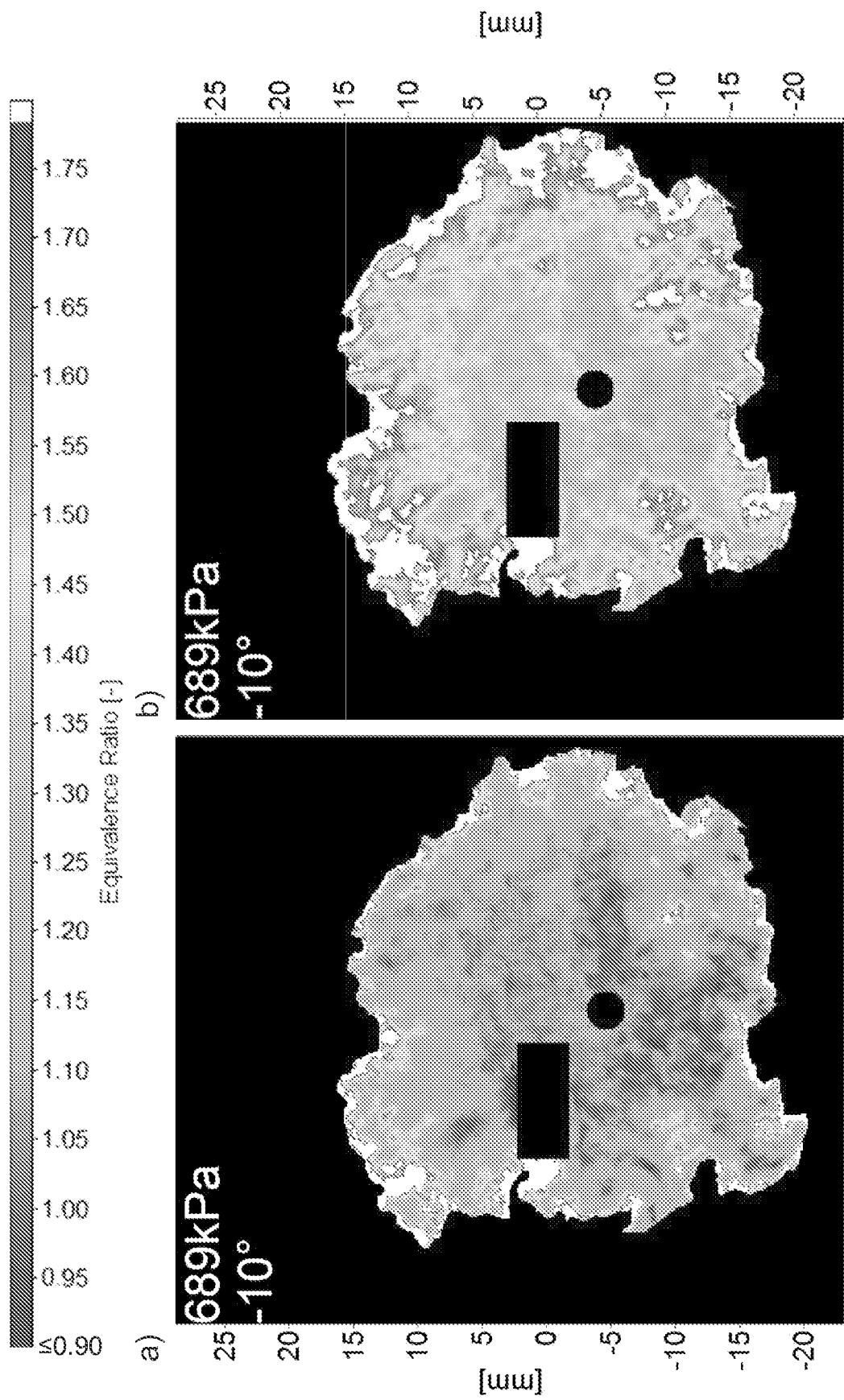


Figure 11

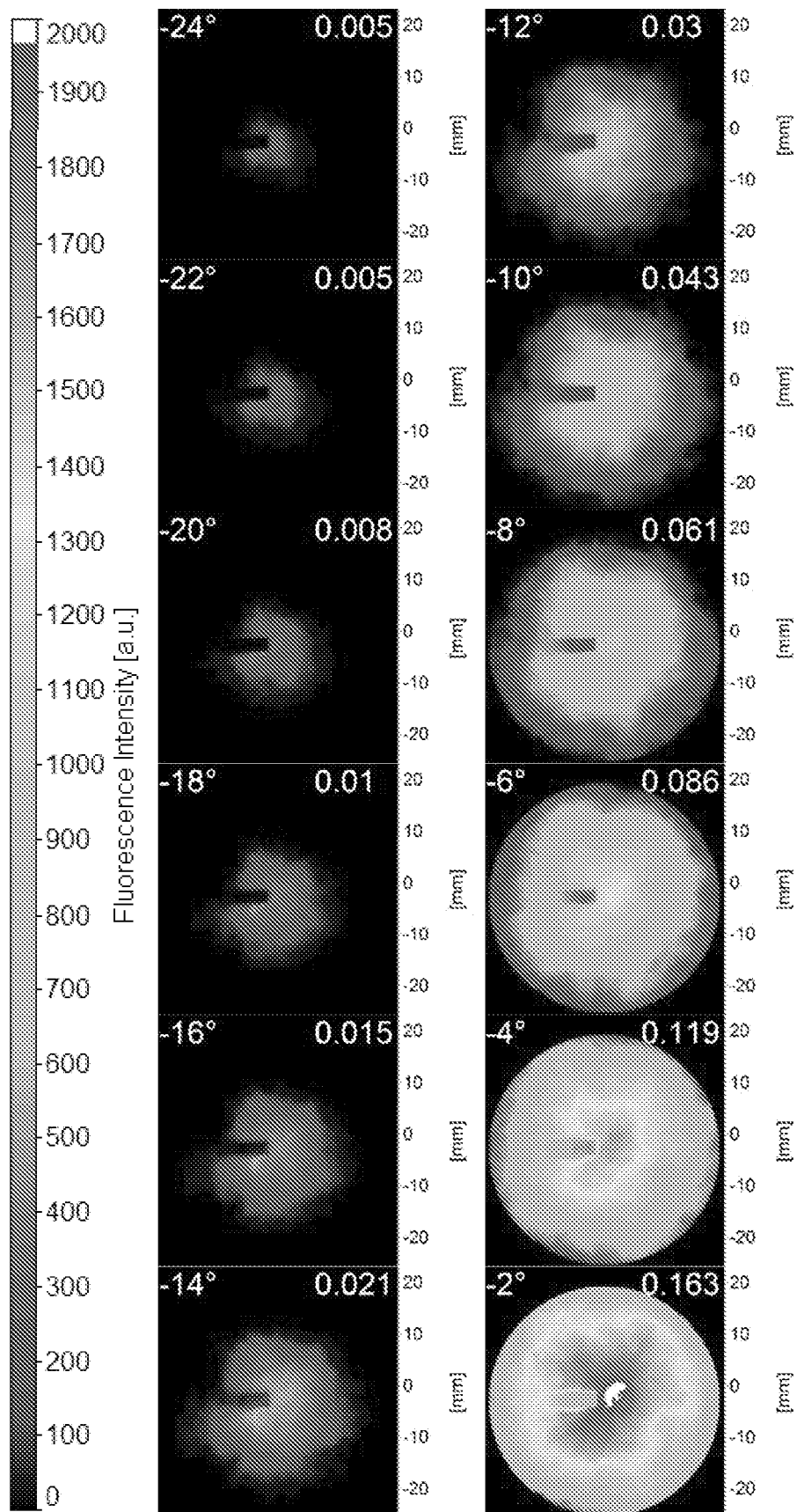


Figure 12

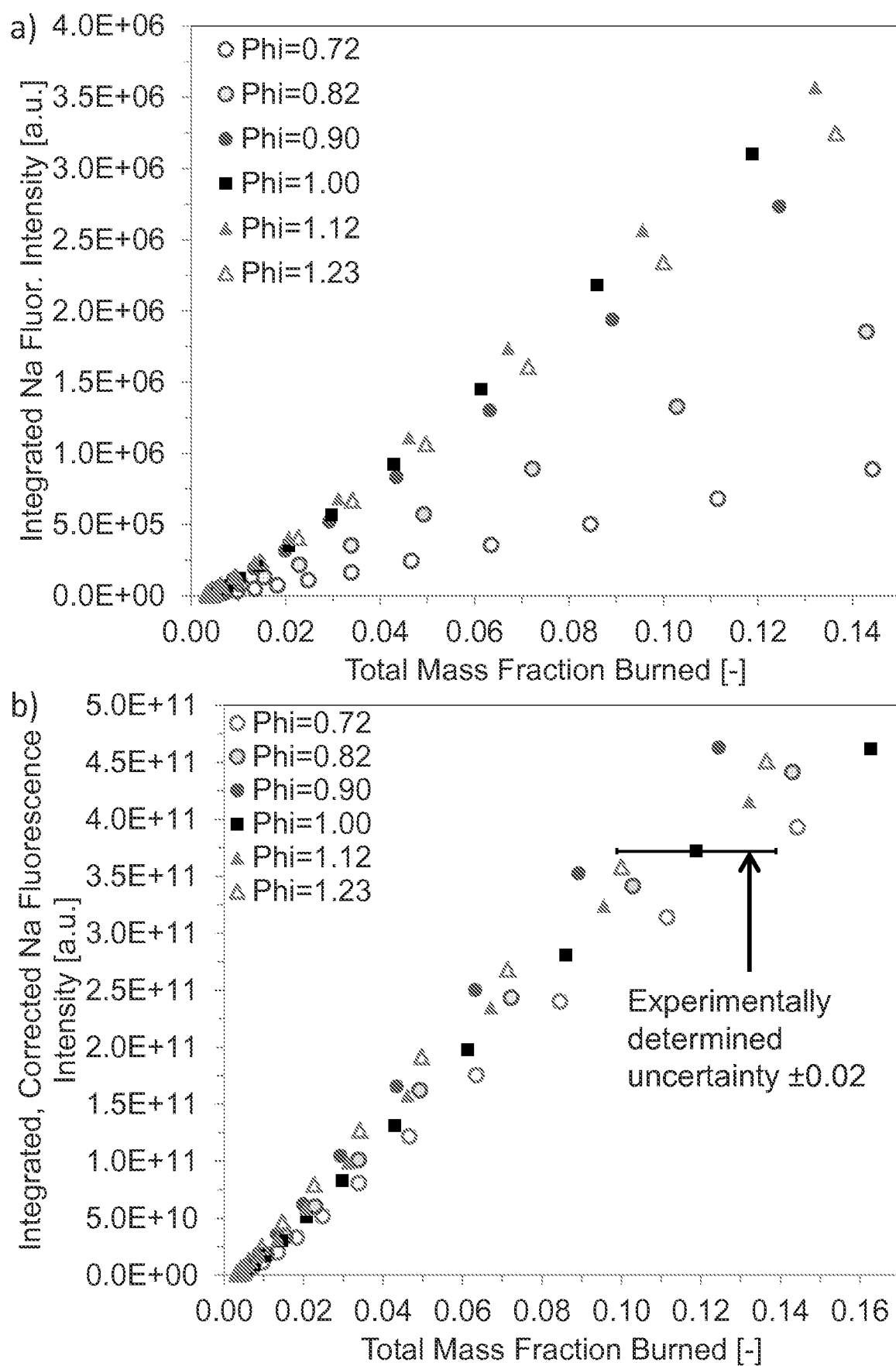


Figure 13

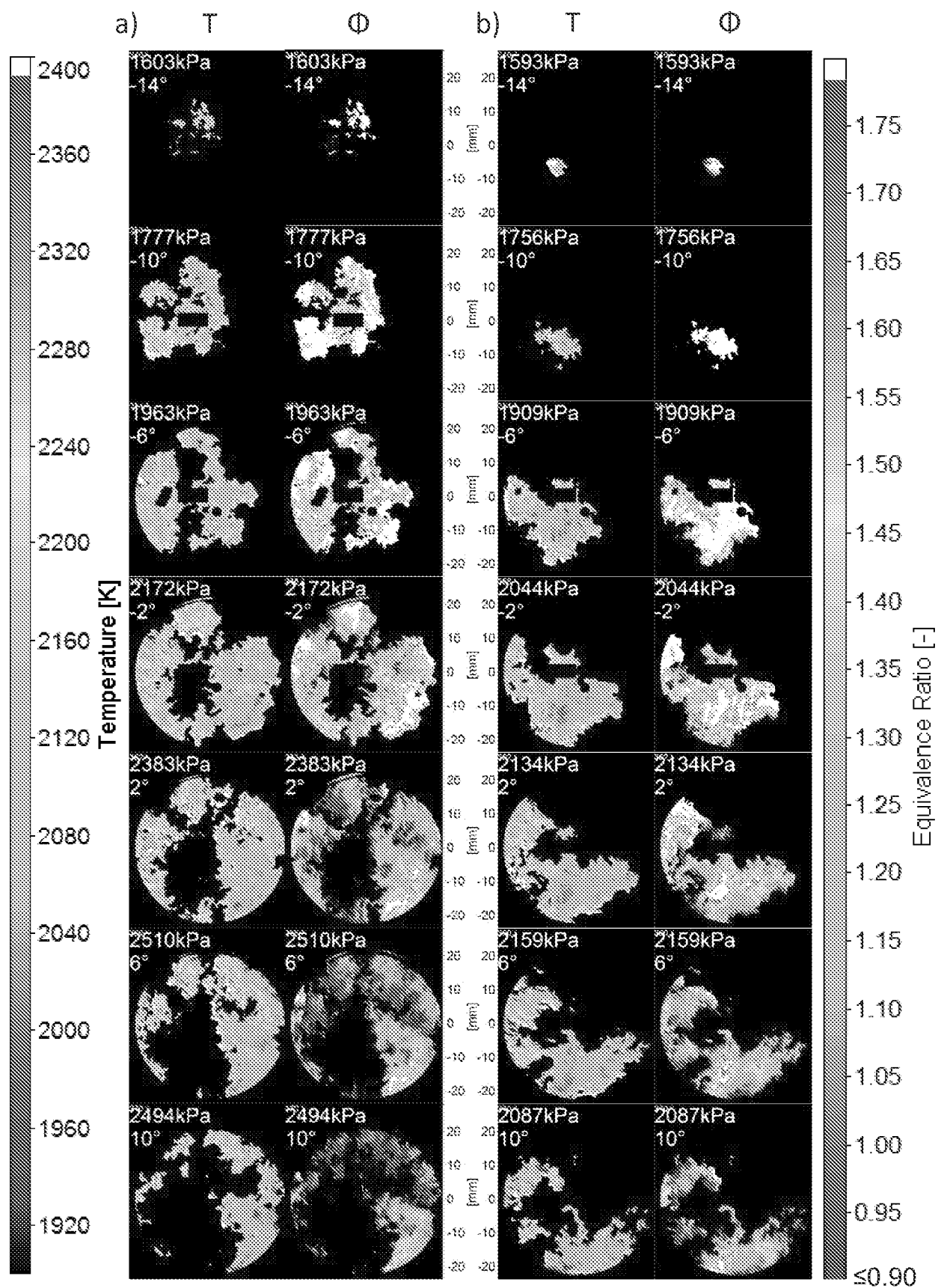
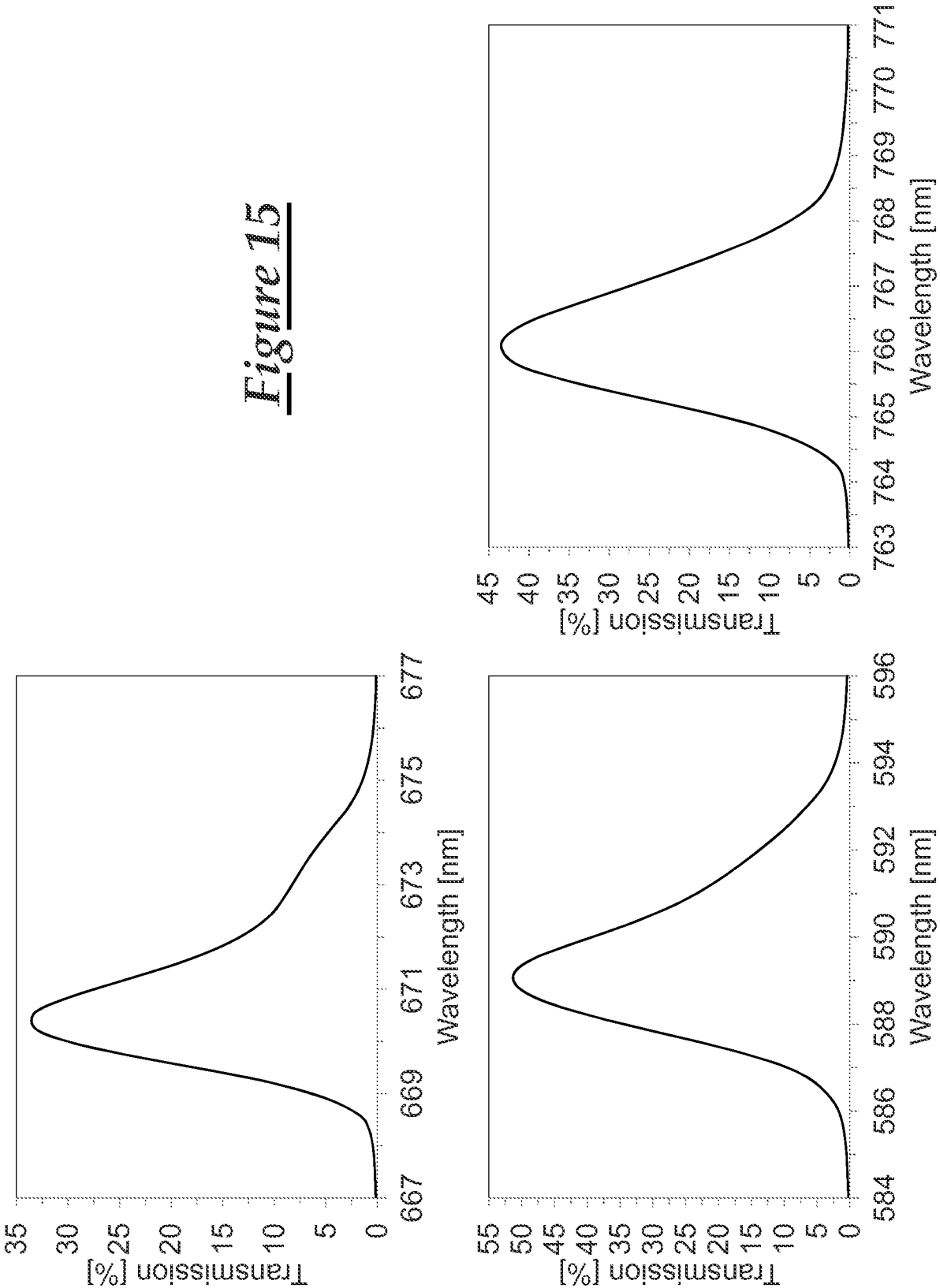
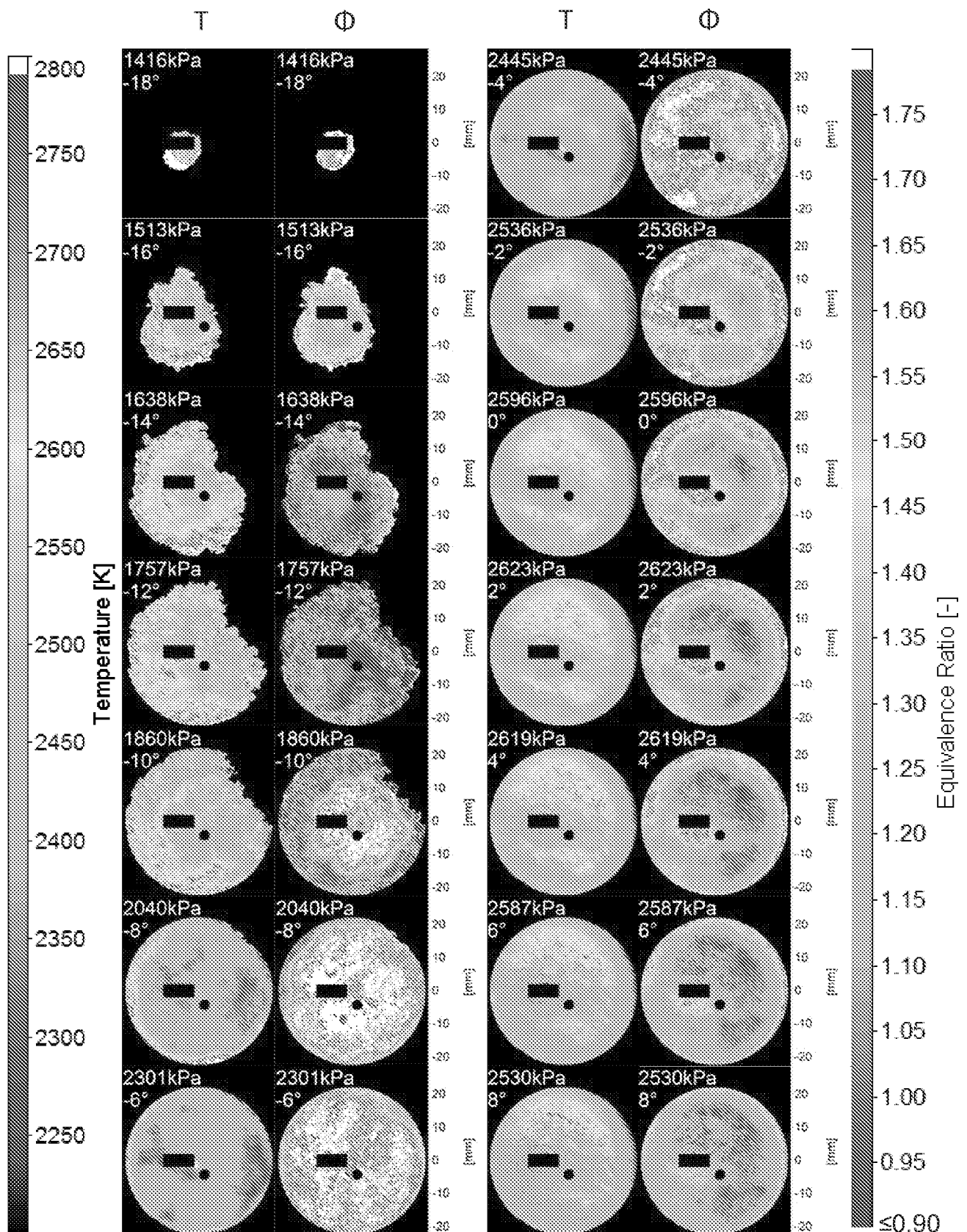
Figure 14

Figure 15



Figure 16

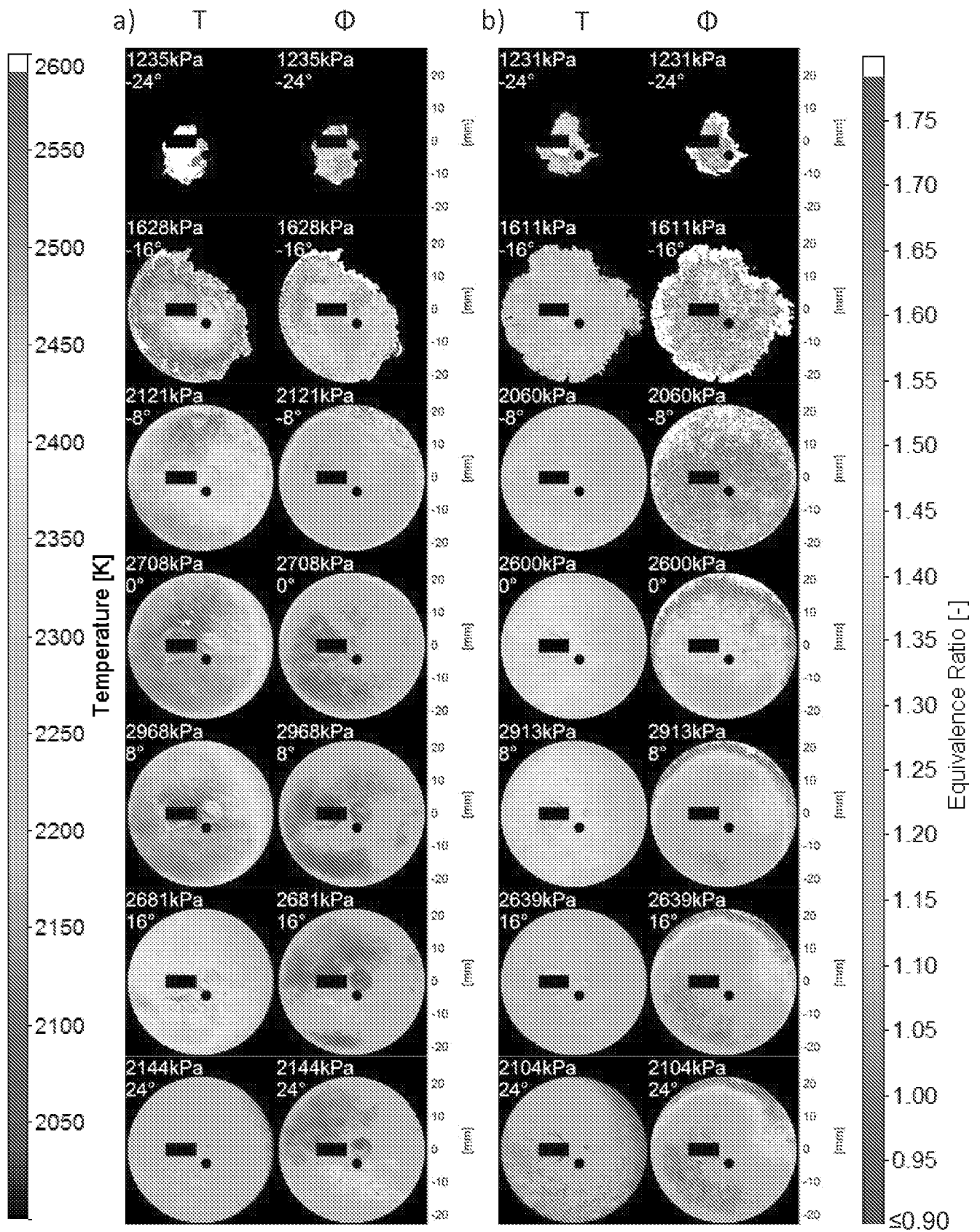


Figure 17

A. CLASSIFICATION OF SUBJECT MATTER**F23N 5/08(2006.01)i, F23M 11/04(2006.01)i, G01N 21/71(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

F23N 5/08; G01N 21/64; G01N 21/65; G01N 21/39; F23M 11/04; G01N 21/71

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: combustion, fluoresce, alkali metal, spectroscopy, optical, temperature, and equivalence

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 05-149877 A (TOYOTA MOTOR CORP et al.) 15 June 1993 See abstract, paragraphs [0002], [0003], [0014], [0016], [0021]; figures 1,3.	1-15
A	WO 95-00833 A1 (ANDRESEN, PETER) 05 January 1995 See abstract; figures 1-6.	1-15
A	WO 2012-121654 A1 (VATTENFALL AB et al.) 13 September 2012 See abstract; page 8, line 6 - page 11, line 25; figures 2,3a,3b,4,5.	1-15
A	SCHULZ et al., `Laser-Induced-Fluorescence Detection of Nitric Oxide in High-Pressure Flames with A-X(0, 2) Excitation`, APPLIED OPTICS, 20 May 1997, Volume 36, No. 15, pages 3227-3232. See the whole document.	1-15
A	EBERT et al., `Laser Diagnostics of Combustion Processes: From Chemical Dynamics to Technical Devices`, Israel Journal of Chemistry, 1999, Volume 39, Issue 1, pages 1-24. See the whole document.	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

05 February 2014 (05.02.2014)

Date of mailing of the international search report

06 February 2014 (06.02.2014)

Name and mailing address of the ISA/KR

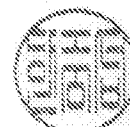
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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