

Correcting lifetime measurements for temperature

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Abstract

Typical pressure sensitive paint (PSP) methods use intensity measurements to predict the pressure. Unfortunately, there are a number of difficulties that arise when using intensity measurements, such as: uneven illumination conditions, photodegradation, inhomogeneous paint coatings, and thickness effects. On the other hand, lifetime measurements are free of these problems. In addition, lifetime methods may be able to eliminate the troublesome ‘wind-off’ condition by using the internal reference τ_{vac} (the vacuum lifetime of the sensor). However, both methods require correction due to the temperature dependence of the paint. We propose a method of correcting lifetime measurements for temperature. A non-oxygen quenched, temperature-dependent phosphor is added to the standard UW paint. The temperature is determined from the lifetime of the phosphor. Then, using the lifetime of PtTFPP and the temperature-selected pressure calibration curve, the pressure can be calculated more accurately. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Optical oxygen sensors are gaining in popularity due to their high sensitivity and selectivity as compared with other methods [1]. Additionally, oxygen sensors can be used in aerodynamic imaging to provide a two-dimensional pressure map over a test surface [2]. A typical optical oxygen sensor consists of a luminescent molecule, whose luminescence is quenched by oxygen, embedded in an oxygen permeable polymer film. Ideally, the films should be physically robust, quickly responding, and the oxygen response easily characterized. For a perfect responding film, the Stern–Volmer equation is used to relate either the intensity or the lifetime of the luminescence to the concentration of oxygen in the film:

$$\frac{I_{\text{vac}}}{I} = \frac{\tau_{\text{vac}}}{\tau} = 1 + K_{\text{SV}}[\text{O}_2] \quad (1)$$

where I_{vac} is the intensity of luminescence in the absence of oxygen, τ_{vac} is the lifetime of the molecule in the

absence of oxygen and K_{SV} is the Stern–Volmer constant [3]. Intensity based methods are often plagued by problems such as drift in lamp intensity and variation in sample composition. These problems can be avoided by using a lifetime-based method. However, like the intensity, there is a temperature dependence to the lifetime. Although the temperature dependence of the lifetime is generally less than that of the intensity, the change in lifetime due to temperature can be as large as the change due to pressure. This is especially true at high pressure and at low wind velocities. Temperature dependence has been cited as the largest source of error in these measurements. Clearly, if lifetime imaging is to be a useful technique, a method for correcting for temperature dependence is desirable.

Several methods exist for correcting intensity measurements. However, no such method exists for lifetime-based sensing. The method proposed here consists of a non-oxygen quenched, temperature-dependent phosphor added to the typical pressure-sensitive film. The ideal temperature sensor would have the following characteristics:

- excite in the same spectral region as PtTFPP,
- emit in a different spectral region,
- have a strong temperature dependence, and
- exhibit no pressure dependence.

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The phosphor, $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ has a well-known temperature dependence in the green part (514 nm) of the spectrum [4]. This emission is well separated from the red emission of the pressure sensor, PtTFPP. Hence, by monitoring at two wavelengths, one can determine both the temperature and the pressure of any point on the test surface. Knowledge of the temperature allows for a more accurate determination of the pressure. Previously, there have been problems with using inorganic phosphors in PSP because of the difficulty in achieving a uniform coating of the phosphor across the test surface [5]. However, while non-uniformity of the coating causes serious error for intensity measurements, this should not be a concern for lifetime methods.

2. Materials and methods

2.1. Luminescent molecules

Platinum meso-tetra (pentafluorophenyl) porphyrin (PtTFPP) was purchased from Porphyrin Products (Logan, UT) and used without further purification. VSR provided $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$.

2.2. Polymers

The FIB polymer was synthesized in-house. FIB is a copolymer of heptafluoro-*n*-butyl methacrylate and hexafluoroisopropyl methacrylate (Lancaster Synthesis). Upon receipt, both monomers contain a small amount of inhibitor, which is removed with activated charcoal. The reaction vessel is purged with argon. A solution containing of a 1:1 mole ratio of the monomers and the initiator (0.2% w/w lauroyl peroxide (Aldrich)) in trifluorotoluene is heated to 74°C for 48 h. The temperature is then raised to 100°C for 1 h to decompose any remaining initiator. To

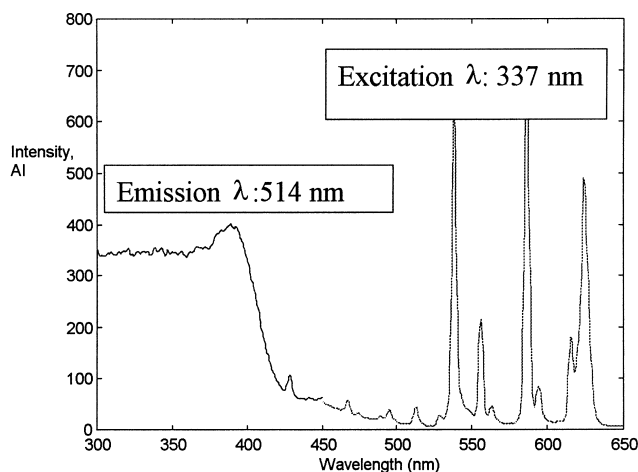


Fig. 2. Fluorescence spectra for solid $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. The curve for $\lambda < 450$ nm is the excitation spectrum monitored at $\lambda_{\text{em}} = 514$ nm. The curve for $\lambda > 450$ nm is the emission spectrum for $\lambda_{\text{ex}} = 337$ nm. Note that the weak emission peak at 514 nm is the temperature-dependent line.

precipitate the polymer, the solution is diluted to three times its volume with trifluorotoluene. This solution is then added dropwise to hexanes (Fisher Chemicals). The precipitate is washed with methanol and hexanes and then transferred to a vacuum pump overnight to remove any residual solvent [6].

2.3. Preparation of films

PtTFPP (10 mg) and $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (0.22 g) were added to separate 1:1 mixtures of trifluorotoluene and acetone. The total solvent used for each solution was about 20 ml. The phosphor mixture was ball-milled for 8 h. After this time, 0.5 g of FIB was added to the solution. This solution was then sprayed using an airbrush onto a 1-in. \times 1-in. piece of aluminum. The plate dried overnight at 50°C, then the solution of PtTFPP in FIB (0.5 g) polymer was sprayed on top of the existing film. The plate was placed in an oven at 50°C overnight prior to measurements. In other experiments, we found no difference if this annealing step was omitted.

2.4. Lifetime measurements

An instrument was built in-house to take intensity measurements with time at a given temperature and pressure. The block diagram of this instrument is shown in Fig. 1. The nitrogen line (337 nm) of an Oriel nitrogen-pumped dye laser (Model 79110) was used as the excitation source. A mirror guides the laser beam to the sample chamber. The sample is enclosed in a pressure- and temperature-controlled chamber. The valve manifold contains four valves to control the pressure in the chamber: a vacuum valve, vent valve, bypass valve, and a proportional valve. The proportional valve was designed in house to achieve pres-

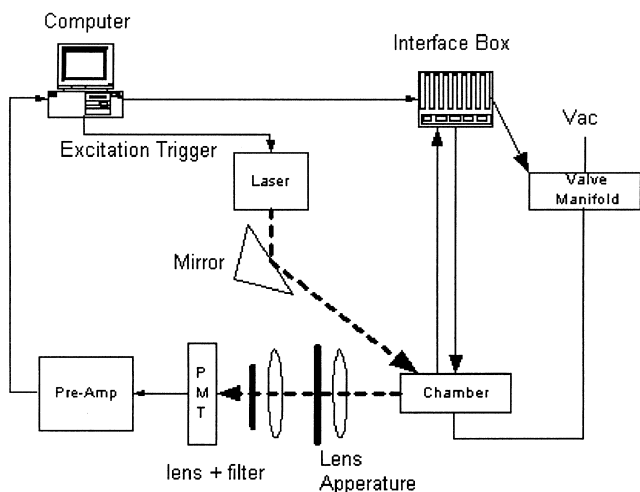


Fig. 1. Block diagram of the lifetime survey apparatus.

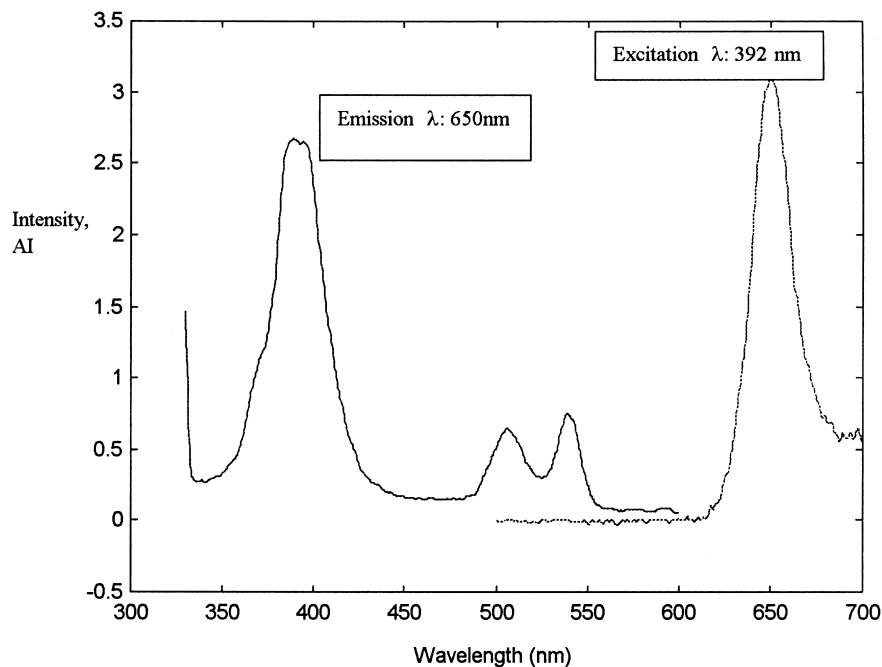


Fig. 3. Fluorescence spectra for PtTFPP in solution. The curve for $\lambda < 600$ nm is the excitation spectrum monitored at $\lambda_{em} = 650$ nm. The curve for $\lambda > 500$ nm is the emission spectrum for $\lambda_{ex} = 392$ nm.

tures between vacuum and 1 atm. The pressure in the chamber is measured with a pressure transducer. The chamber temperature is regulated by a solid state thermoelectric heat pump that is controlled by an integrating proportional temperature controller. The actual temperature inside the chamber is measured using an Analog Devices AD590 temperature sensing IC. The phosphorescence of the film is detected by a red extended photomultiplier tube

(RCA 1P28A). An aperture and appropriate emission filter (centered at 650 nm with a 10 nm FWHM) are placed in front of the PMT. The signal from the PMT tube is sent to a current to voltage preamplifier with a fixed time constant of 90 ns and then to a 10 MHz 8 bit A/D converter board (designed in house) inside the host computer. The computer allows the user to specify the temperature and pressure inside the chamber. The system can scan pressure at

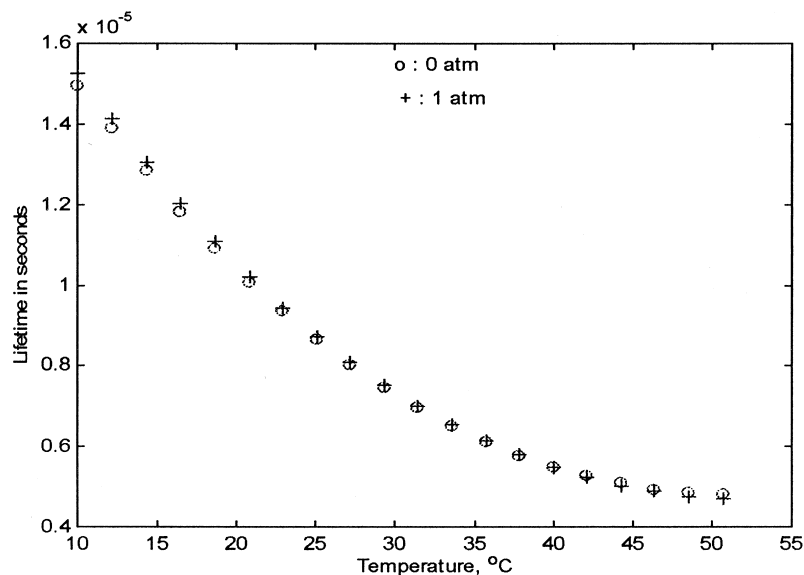
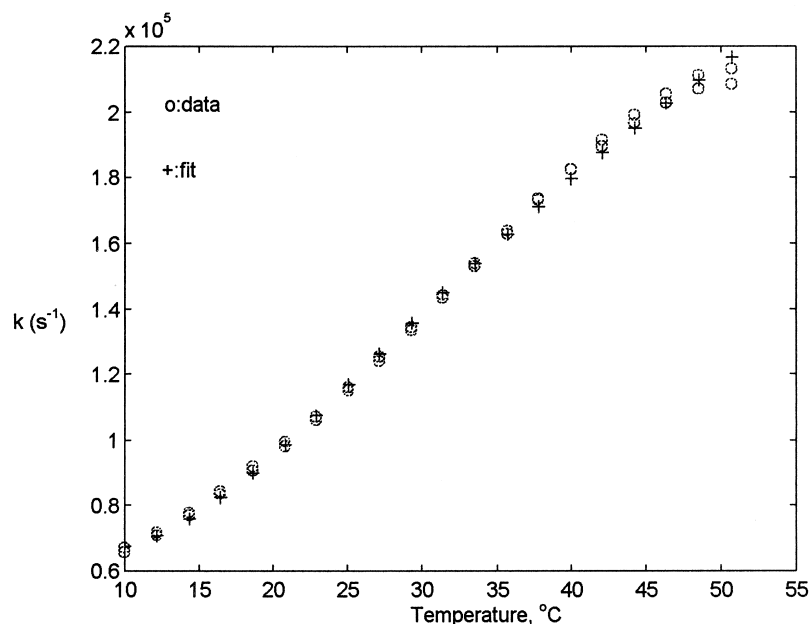


Fig. 4. The lifetime of the 514 nm emission of $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ in dual paint as a function of temperature for two pressures: 1 atm and vacuum.

Fig. 5. Arrhenius type fit to $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ lifetime.

constant temperature (a ‘pressure run’); it can also scan temperature at $P = 1$ atm or $P = \text{vacuum}$ (about 60 mTorr) (‘a temperature run’). Housed in the interface box are the valve drivers, temperature control electronics, pressure transducer signal amplifier and power supply for the thermoelectric module and valve manifold. More details on the instrumentation can be found in Alan Baron’s thesis [7]. Each decay curve analyzed represents the averages of at least 50 time decays. The ‘fmins’ function in MATLAB was used to fit the data to a single exponential. Although at pressures other than vacuum the luminescence decay is

non-exponential, the best single exponential fit provides a lifetime value that correlates well with pressure.

3. Results

3.1. Spectral data

The emission and excitation spectra of $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ are shown in Fig. 2. The spectra for PtTFPP are shown in

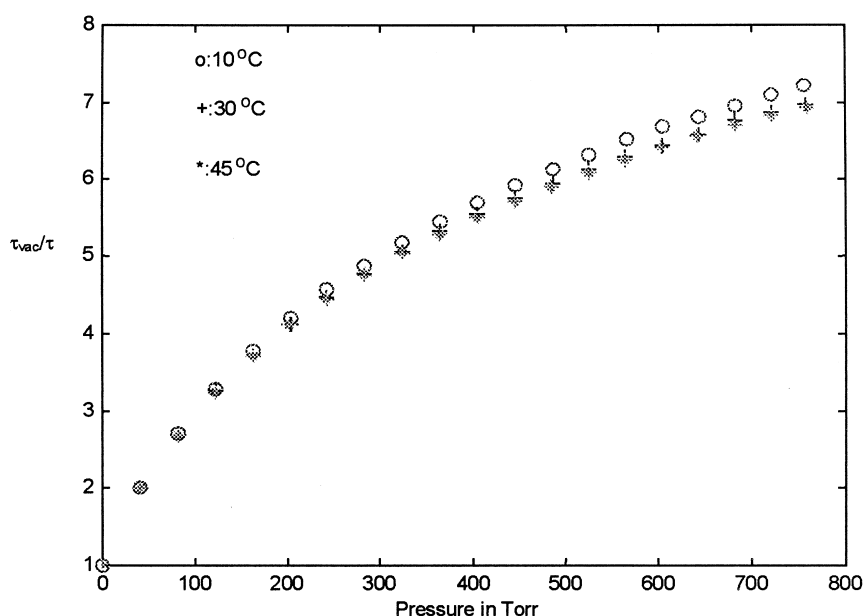


Fig. 6. Lifetime Stern–Volmer plots for the lifetime of PtTFPP at three temperatures in dual paint.

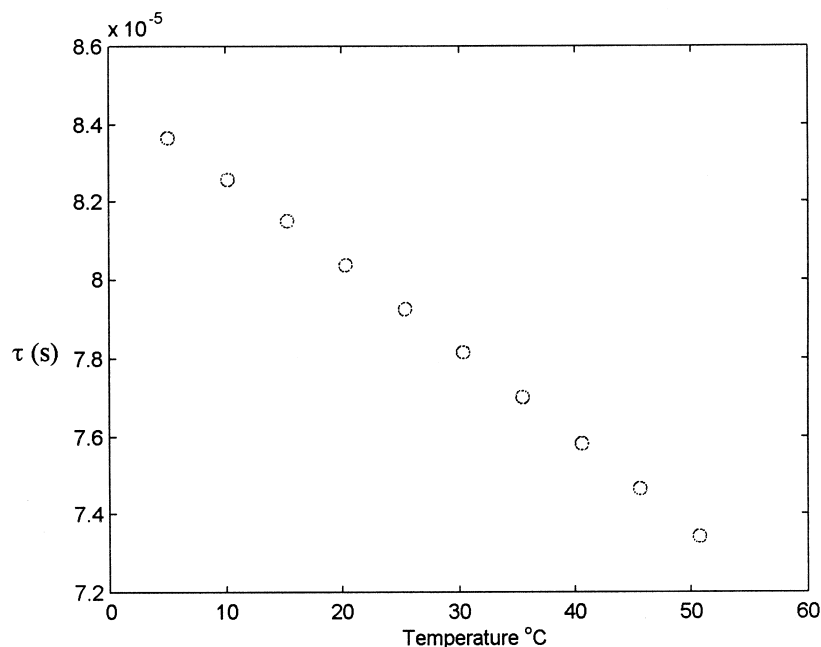


Fig. 7. The vacuum lifetime of PtTFPP as a function of temperature.

Fig. 3. Typically, PtTFPP is excited at 390 nm. Since the temperature-dependent line at 514 nm of $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ is very weak (see Fig. 2), we need a powerful light source. Thus we used the 337 nm line of the N_2 laser for excitation of both sensors. In solution, we find that the absorbance of PtTFPP at 337 nm is about 2% of the absorbance at its peak at 390 nm [8]. Nonetheless, the green emission of the $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ is not as intense as the 650 nm triplet emission of the PtTFPP.

3.2. Predicting temperature from $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ emission

The temperature dependence of the lifetime of $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ at both atmospheric pressure and vacuum is shown in Fig. 4. It is 1.9%/°C and quite independent of pressure. From this data, we will determine temperature. The theoretical relation between lifetime and temperature is expressed as an Arrhenius function:

$$k = \frac{1}{\tau} = k_0 + k_1 e^{-\Delta E/RT} \quad (2)$$

This is shown in Fig. 5. The fit parameters are:

$$k_0 = 5.1 \times 10^4 \text{ s}^{-1}; k_1 = 3.9 \times 10^5 \text{ s}^{-1} \text{ and}$$

$$T^* = \Delta E/R = 43 \text{ K}$$

Eq. (3) can be inverted to give the temperature:

$$T = \frac{T^*}{\ln(k_1/(k - k_0))} \quad (3)$$

The root mean squared prediction error (RMSPE) was calculated for the temperature as predicted by the $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ data using Eq. (3).

$$\text{RMSPE} = \sqrt{\frac{\sum_{n=1}^{20} (T_n^{\text{exp}} - T_n^{\text{pred}})^2}{20}} = 1.11^\circ\text{C} \quad (4)$$

over the range of 10°C–50°C. The RMSPE is calculated by generating a calibration curve, leaving one point off the graph. The resulting calibration curve is then used to predict the temperature of the left-out point. This is repeated for every point of the calibration [9].

3.3. Predicting pressure from PtTFPP emission

We obtained Stern–Volmer plots (Fig. 6) as τ_{vac}/τ vs. pressure in Torr at 10 temperatures: 5°C, 10°C, ... 50°C.

Table 1
Parameters for determination of pressure from PtTFPP lifetime

Temperature (°C)	<i>a</i>	<i>b</i>	<i>c</i>
5	19.18	−46.77	49.94
25	21.11	−54.08	56.03
45	22.78	−61.21	62.29

Table 2

Test runs for $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ /PtTFPP determination of temperature/pressure

Run no.	Temperature (°C)	Pressures
1–3	12.1	760, 587, 394, 196, 7 Torr
4–6	28.4	759, 587, 394, 196, 8 Torr
7–9	44.6	760, 586, 394, 196, 6 Torr

We further plotted τ_{vac} vs. temperature. This is shown in Fig. 7. The temperature dependence of the lifetime is about $-0.3\%/^{\circ}\text{C}$. This is approximately 60% of the temperature dependence of intensity, which is $-0.52\%/^{\circ}\text{C}$ [6]. We attribute this difference to the temperature dependence of the absorbance of PtTFPP [10]. However, since we seek the inverse relation to determine P from τ_{vac}/τ , we used this data to determine parameters for the fit:

$$P = a \left(\frac{\tau_{\text{vac}}}{\tau} \right)^2 + b \frac{\tau_{\text{vac}}}{\tau} + c. \quad (5)$$

It should be noted that in doing this fit we used the measured values of τ_{vac} (T). The parameters a, b, c were determined for each of the 10 temperatures from 5°C to 50°C . Some typical values are shown in Table 1.

3.4. Test measurements

To test our ability to predict pressure given lifetime measurements of $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ and PtTFPP at a particular temperature and pressure, we generated a set of test data. The test data consisted of pressure runs (of five pressures) taken at three different temperatures. Each pressure run was repeated twice: once using a red interference filter to observe the PtTFPP 650 nm emission and once using a green interference filter to observe the $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ 514 nm emission. Three sets of data were obtained. The nine test data runs are shown in Table 2.

Table 3

Temperature determination from the nine test runs

The standard deviation is given in parenthesis for each run and is based on the five pressures studied at each temperature.

Run no.	Real temperature (°C)	Predicted temperature (°C)	Error (°C)
1	12.09 (0.002)	12.7 (0.07)	+0.6
2	12.09 (0.0004)	12.7 (0.06)	+0.6
3	12.09 (0.002)	12.7 (0.06)	+0.6
4	28.36 (0.005)	27.7 (0.06)	−0.9
5	28.36 (0.0009)	27.7 (0.11)	−0.9
6	28.36 (0.001)	27.6 (0.07)	−0.8
7	44.62 (0.003)	47.4 (0.12)	+2.8
8	44.32 (0.002)	47.3 (0.16)	+3.0
9	44.62 (0.002)	47.5 (0.09)	+2.9

The temperature for each run was calculated using Eq. (3) above. The error was determined by the difference between the temperature as measured by the sensor in the sample chamber. Table 3 gives the real temperature, predicted temperature, and error in $^{\circ}\text{C}$ for all test runs.

Having determined temperature, we get pressure from the PtTFPP lifetime using Eq. (5). We determined τ_{vac} , a , b , and c from the closest temperature in the calibration data consisting of 20 pressure at 10 temperatures. In the longer term, these could be corrected using an analytical formula or just a simple interpolation. We found that using the pressure range from about 200 Torr to 760 Torr results in better predictive ability, i.e., smaller differences between the predicted and measured pressure. [We omitted pressures below 200 Torr since the Stern–Volmer is highly curved in this region, which is not of great interest for most wind tunnel work.] Table 4 gives the measured pressure, predicted pressure (using Eq. (5)), and the predicted pressure uncorrected for temperature (using τ_{vac} , a , b , and c for 25°C). The pressure determined from the PtTFPP lifetime is never in error more than 4% if temperature correction is used. Without temperature correction, the error is as high as 16%.

3.5. Comparison with single luminophor paints

In Fig. 8 we show the lifetime of the 514 nm line of $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ in FIB without PtTFPP. It shows a slightly larger temperature dependence when compared with dual-paint formulation (Fig. 4). A Stern–Volmer plot for PtTFPP in FIB without $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ is shown in Fig. 9. When compared with Fig. 6, we note the larger dynamic range of the single dye paint. $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ has an emis-

Table 4

Pressure determination using PtTFPP lifetime

Real pressure	Predicted: temperature corrected	Predicted pressure: temperature not corrected
<i>Run no. 1, $T = 12^{\circ}\text{C}$</i>		
759.99	758.42	709.93
587.84	597.31	573.52
394.74	396.84	391.42
196.88	204.14	173.34
<i>Run no. 4, $T = 28^{\circ}\text{C}$</i>		
758.61	759.06	748.26
587.12	597.75	608.31
394.33	396.47	419.88
196.67	203.30	196.21
<i>Run no. 7, $T = 44^{\circ}\text{C}$</i>		
760.00	756.89	812.68
586.91	590.85	656.83
393.79	396.61	459.92
196.55	204.00	219.08

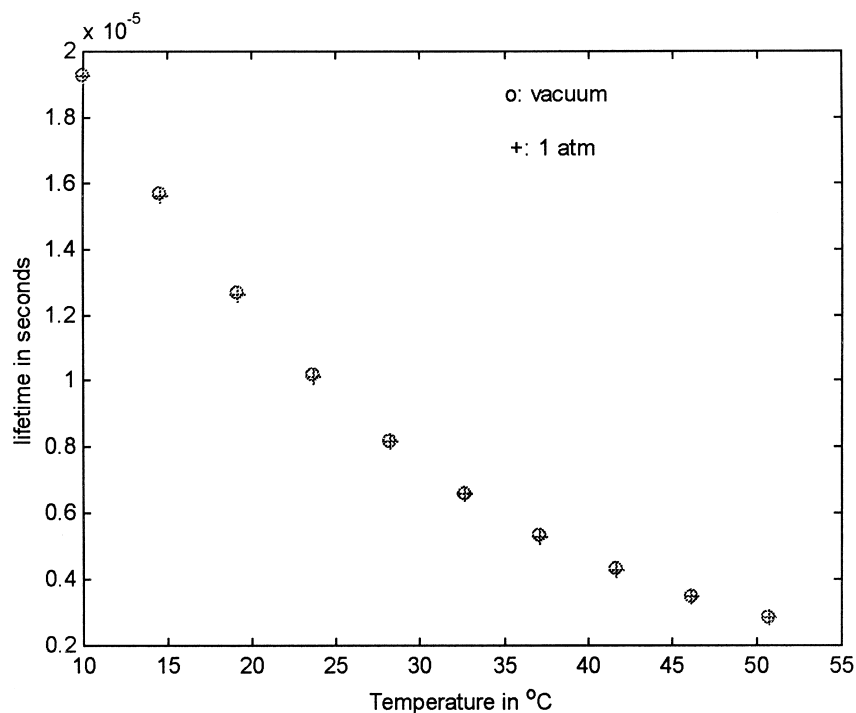


Fig. 8. Temperature dependence of $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ in FIB (without PtTFPP).

sion at 625 nm. We measured this lifetime to be on the order of 400 μs , with very little temperature dependence. The PtTFPP decay curves when fit to a double exponential do not have a 400 μs component. Therefore, the difference

in the dual-paint curves (from the single-paint curves) is not due to the 615 nm emission of the $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. While the exact cause of this difference has not been explored, it does not affect the data analysis or the results.

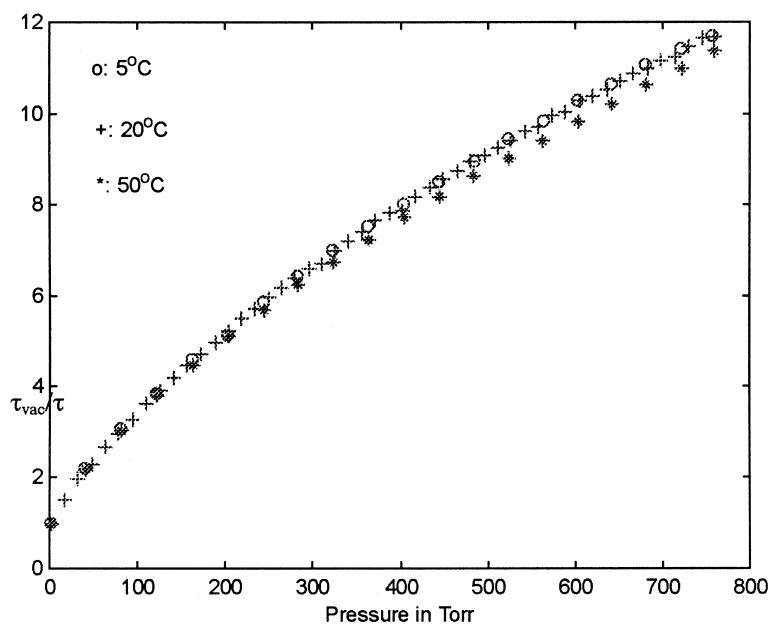


Fig. 9. Lifetime Stern–Volmer plots for PtTFPP in FIB (without $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$) at three temperatures.

4. Conclusion

We have developed a method to correct lifetime measurements for temperature. A paint consisting of PtTFPP and $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ was formulated. The lifetime of $\text{La}_2\text{O}_2\text{S:Eu}^{3+}$ can be used to predict the temperature. From this temperature, the appropriate pressure prediction curve can be selected. Using the lifetime of PtTFPP, the pressure can be determined within about 1%. Refinement of the algorithm may provide better pressure prediction. In the wind tunnel tests, the system would consist of an N_2 laser for excitation and two cameras: one to capture green emission and one for the red emission.

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