

Dual luminophore polystyrene microspheres for pressure-sensitive luminescent imaging

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Abstract

Polystyrene microspheres containing both an oxygen-sensitive platinum porphyrin luminescence and a pressure-insensitive silicon porphyrin luminescence are prepared in high yield. The ratio of these two luminescences responds reversibly in aerodynamic flows over a wide dynamic range of oxygen concentrations, with a response time of <10 ms. These microspheres have been used in a non-intrusive imaging method to potentially obtain the pressure distributions in three-dimensional aerodynamic flows.

Keywords: porphyrin, platinum porphyrin, silicon porphyrin, pressure-sensitive paint, dual luminophor paint, luminescent flow measurement

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Conjugated organic and organometallic molecules such as ruthenium complexes and platinum porphyrins exhibit luminescence quenching by oxygen [1–3]. These oxygen-sensitive luminophores can be used to monitor oxygen concentrations in various environments through luminescence intensity or luminescence decay (lifetime) rate measurements. A number of oxygen sensors based on these luminophores are now commercially available, and are used in a wide variety of applications [4–6]. Our research group was among the first to dissolve these luminophores in oxygen-permeable polymer matrices to form pressure-sensitive paint (PSP). PSP made it possible to obtain high-resolution, two-dimensional pressure distributions over aerodynamic surfaces in wind tunnel environments [7–9]. The use of PSP in this manner is widely accepted in the aerodynamic community [9]. Paint formulations, test equipment and software are now available commercially [10]. With further development, PSP is being employed in a widening variety of applications. For example,

fast responding PSP has been used in unsteady aerodynamic applications, such as airflow over rotor blades [11]. Most recently, PSP for insect flight has been evaluated in our laboratory [12] with the ultimate goal of mapping the pressure distribution over an insect's wings in flight.

A new aerodynamic application of PSP has recently been demonstrated by Abe and co-workers [13]. The method is based on using pressure-sensitive airborne particles that the researchers dubbed 'PSParticles' for combined particle imaging velocimetry (PIV) and pressure measurements in a dynamic flow system. These particles are 0.5 to 25 μm in diameter, fumed silicon dioxide particles with porous outer shells that are loaded with the pressure-sensitive luminophore ($[\text{Ru}(\text{bpy})_3^{2+}]\text{Cl}_2$). The researchers injected the particles into a flow of nitrogen gas that emptied from a jet into an ambient air chamber. The oxygen concentration within the emanating plume of nitrogen was measured through rapid lifetime determination of the PSParticles luminescence. While this experiment demonstrates a proof of concept, the researchers could only make oxygen concentration measurements over

a limited dynamic range (0%–1% (O_2)), and the ruthenium luminophore's high-temperature dependence required careful monitoring of the temperature in the ambient air chamber.

We recently reported the synthesis of oxygen-sensitive polystyrene microspheres (PSBeads) doped with dual luminophores [14]. The first luminophore is an oxygen-sensitive platinum porphyrin (PtOEP, emission at 650 nm), and the second is a silicon porphyrin (SiOEP, emission at 580 nm) whose luminescence is oxygen independent and thus serves as a reference dye. It has been demonstrated that the PSBeads can be made with high uniformity and high synthetic yield. Depending upon synthesis conditions, particles with a narrow range of diameters from 1 to 5 μm can be produced.

While the application of PSP for surface pressure measurements has been well developed, there is no method presently known to the authors to measure pressure globally and non-intrusively within a fluid flow, thereby providing a pressure field. In fact, the understanding of the fluctuating pressure field is important and directly applicable to many engineering applications, such as noise reduction within aircraft, automobiles and turbine engines and prevention of damage to buildings due to large pressure fluctuations about their leading edge. This paper will therefore discuss the development of an accurate imaging method for the PSBeads, allowing for the global mapping of the pressure distribution within a fluid flow. Ultimately, since the full understanding of such flow fields requires knowledge of both the velocity and pressure fields, we plan to use PSBeads in conjunction with digital particle imaging velocimetry (DPIV) to measure pressure and velocity distributions in flow.

2. Dual luminophore PSP

As previously stated, the successful employment of PSP relies on accurate measurement of changes in the paint's luminescent intensity as a function of pressure change, which in turn requires careful control and placement of the light sources and detecting camera, and ensuring that the surface illumination is uniform. Moreover, model motion during measurement leads to systematic errors that are difficult to quantify. To offset these variables, a dual luminophore PSP was developed. The PSP relies upon a pair of dyes that can be excited at the same wavelength, yet emit their luminescence at different wavelengths. Only one of the dyes has a luminescence that is quenched by oxygen. The other dye serves as a reference and corrects for excitation variations and luminescence intensity changes.

The benefits of using two luminophores for intensity-based pressure measurements have previously been realized and reported [15]. The dual luminophore PSP was successfully evaluated using the two-camera system by ISSI of Dayton of Ohio [16] and recently by Mébarki of the NRC of Canada on automotive model testing [17].

The dual luminophore PSP was made from NIR oxygen-sensitive molecule Pt-tetra(pentafluorophenyl) porpholactone (TFPL) which provides I_{sen} , and Mg-tetra(pentafluorophenyl)porphine (TFPP) which provides I_{ref} . The dual luminophore PtTFPL and MgTFPP in the FIB polymer produced near ideal PSP measurements with pressure sensitivity of 4.5% per psi and a temperature dependence of

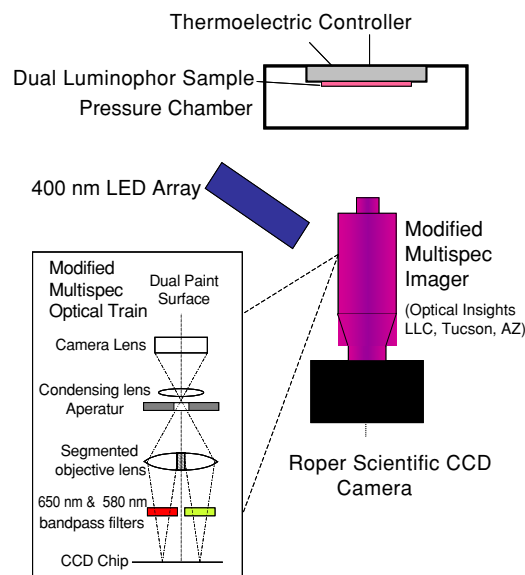


Figure 1. Schematic of two-image multiplexer system.

less than $-0.1\% \text{ } ^\circ\text{C}^{-1}$. The temperature dependence of the dual luminophore intensity ratio ($I_{\text{ref}}/I_{\text{sen}}$) is substantially reduced compared with the use of I (PtTFPP) alone, which has a temperature dependence in FIB of $0.60\% \text{ } ^\circ\text{C}^{-1}$. In general, our experiment suggests that using a ratiometric method of the two intensities will produce a more reliable oxygen/pressure sensor.

Ideally, to take full advantage of a dual luminophore PSP, simultaneous images of the same test surface at the two emission wavelengths of the luminophore would be obtained. We have recently demonstrated this ability through the use of an image multiplexer known as the MultiSpec Imager, built by Optical Insights of Tucson, Arizona [17]. Essentially this device uses a lens that incorporates an internal beam splitter prism and mirrors; the MultiSpec Imager takes one image and splits it into two. The two images are then passed through the desired bandpass filters and refocused onto a single CCD chip. Thus, two simultaneous images are obtained; one displaying the intensity of the pressure-sensitive luminophore and the other displaying the reference intensity.

An example of a pressure measurement using dual luminophore PSP is shown in figures 1 and 2. The dual luminophore PSP was spin coated onto an aluminium sheet and housed in a lab-constructed chamber designed to vary both pressure and temperature using a vacuum pump and thermal modulator. The film was illuminated with a 400 nm LED array. A schematic of this experimental setup is shown in figure 1. The images were collected using MetaFluor imaging software (Universal Imaging Corp.) and image ratios were calculated using MATLAB. The emission ratio (MgTFPP/PtTFPL) images at ten different pressures are shown in figure 2. The normalized ratio mean values and standard deviations for ten pressures are listed in table 1. These results lead us to believe that we currently have the ability to obtain pressure measurements from the dual luminophore PSBeads using a single CCD. As a result, we are confident that the problems arising from the use of a single luminophore pressure sensor or a dual luminophore, two-camera system, can be avoided.

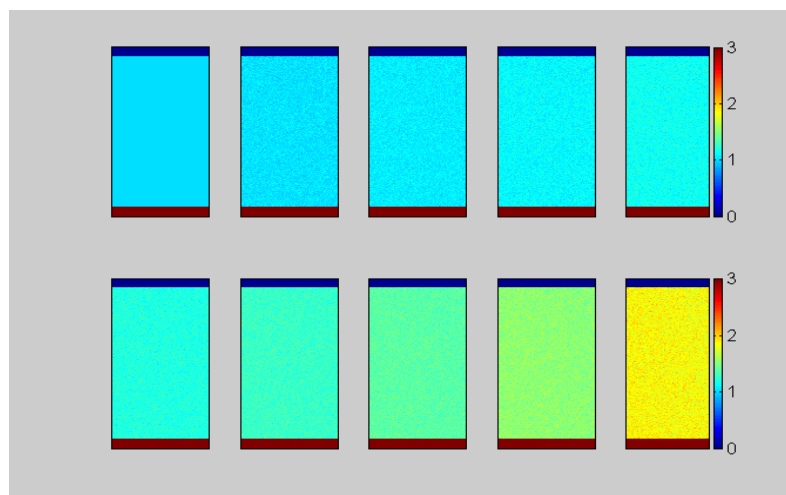


Figure 2. Dual film ratio images for dual film (MgTFPP to PtTFPL) at ten air pressure points (Torr), right to left, decreasing order (760, 675, 591, 506, 422, 338, 253, 169, 84, 0).

Table 1. Mean and standard deviation of the ratio (MgTFPP/PtTFPL) images at ten various pressures.

Pressure (Torr)	Mean value	Standard deviation
760	1.0	–
675	1.0238	0.0526
591	1.0561	0.0539
506	1.0942	0.0558
422	1.1390	0.0573
338	1.1945	0.0601
253	1.2655	0.0634
169	1.3642	0.0675
84	1.5168	0.0741
~0	1.8492	0.0874

3. Experimental details

3.1. Synthesis of dual luminophore polystyrene beads (PSBeads)

In a typical synthesis [14], 45 ml of ethanol and 5 ml of deionized water (18 M Ω) were placed in a three-neck flask (100 ml) equipped with a condenser. The solution was heated at 80 °C for 30 min. Then 0.4 g of poly(vinyl pyrrolidone) (PVP, MW \approx 55 000, Aldrich, the steric stabilizer), 0.009 g of silicon octaethylporphine dichloride, SiOEPCl₂ (Frontier Scientific (formerly Porphyrin Products), Logan, UT, USA), 0.031 g of platinum octaethylporphine, PtOEP (Frontier Scientific), 5 ml of styrene (Aldrich, the monomer) and 0.1 g (12 mM) of 2,2'-azobisisobutyronitrile (AIBN, Aldrich, the initiator) were sequentially added to the solution. The polymerization was allowed to proceed for 24 h at 80 °C and magnetic stirring was applied during the entire synthesis. Finally, the suspension of PSBeads was cooled down to room temperature. The PSBeads were collected via centrifugation at 3900 rpm for 2 min, followed by washing with ethanol three times. To vary the size of the PSBeads, we altered the amount of AIBN from 0.1 g to 0.05 g (6 mM) and 0.2 g (24 mM) keeping all other conditions constant. The monodisperse polystyrene beads were uniform and varied in diameter from 1 to 5 μ m.

3.2. PSBeads characterization

3.2.1. Microscopic images. Dried PSBeads on silicon wafers were imaged with a field emission scanning electron microscope (FEI-SEM, Sirion XL) operated at an accelerating voltage of 5 kV. Optical micrographs of the PSBeads were obtained using a Zeiss Axiovert 200 inverted microscope. The fluorescent images were captured with a Panasonic industrial colour CCD camera (model number GP-KR222) using a cut-off filter of 455 nm to isolate the luminescence light. The PSBeads were excited by a 100 W mercury short arc lamp equipped with a bandpass filter centred at 405 nm.

3.2.2. Response time. The response time to oxygen concentration or pressure change of the PSBeads shown in figure 6 was generated using a special instrument that we call the pressure jump apparatus, which is fully described in Baron *et al* [18]. The system utilizes a solenoid valve, a 2 cm³ airtight chamber, and a gas handling system that creates a pressure jump from 0.1 to 700 Torr in 600 μ s. The chamber is fitted with a pressure transducer for measuring the pressure simultaneously. The optical detection system for measuring PSBeads' response to the pressure change uses a filtered light from a tungsten lamp for excitation, and the emission is detected using a photomultiplier tube. The excitation light is filtered using a 405 nm bandpass filter, and the emitted light was filtered using a bandpass filter centred at 650 nm. The system is capable of simultaneously sampling the optical and the pressure signals. Data analysis using nonlinear least-squares of the luminescent response allows determination of the PSBeads' response time.

3.3. Imaging of the airborne PSBeads

Imaging of the PSBeads in air suspensions of varying oxygen concentrations was performed using the experimental setup as shown in figure 3. The PSBeads were made airborne using an aerosol generator. The aerosol was formed from a water/ethanol suspension by use of a medical nebulizer attached to compressed gas cylinders containing

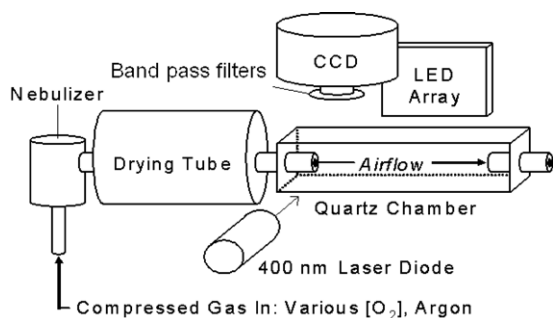


Figure 3. Experimental setup for imaging the air born PSBeads.

various oxygen concentrations. The aerosol then passed through a diffusion dryer (TSI Incorporated, Model 3062) filled with approximately 600 g of silica gel (Wilkerson Corporation, Englewood, CO) and then through a krypton-source neutralizer to minimize deposition of charged aerosol on the test chamber wall. The dried PSBeads emptied into a rectangular 2.5 cm \times 2.5 cm \times 15 cm quartz-walled chamber from an aluminium tube with an inner diameter of 2 mm. The exit velocity was estimated at ~ 1400 ml min^{-1} through the use of a flow meter. This corresponds to an average velocity of 8 m s^{-1} over the cross section of the aluminium tube. An exit tube was held in place at the end of the chamber with a rubber septum, preventing the build up of pressure. The exit tube leads to a water trap to collect any particles that leave the chamber.

To visualize the entire plume of PSBeads, we illuminated the chamber with two LED arrays each containing 80 LEDs (395 nm, ETG Inc., Los Angeles, CA, ETG-5UV395-30) passing through a 400 nm cut-off filter. For the oxygen titration experiment, we replaced the LED arrays with a 404 nm laser diode (Power Technology, Inc., Little Rock, AK, 26 mW max output) as an excitation source. In all cases, intensity images were captured with a MicroMax CCD (1030 \times 1300 pixels, cooled to -20 $^{\circ}\text{C}$, Roper Scientific, Inc.) fitted with a filter

holder containing 650 nm, 50 nm fwhm and 580 nm, 20 nm fwhm bandpass filters. False-coloured images and image ratios were produced using MATLAB (e.g. see figure 7).

4. Results and discussion

Polystyrene microspheres can be readily synthesized in large quantities and can be doped with multiple dyes through various methods. In our laboratory, we have explored two methods of incorporating the sensor (oxygen-sensitive dye) and reference (oxygen-insensitive dye) molecules into the microspheres. In the first, we simply attempted to adsorb the sensor molecules onto the surface of the microspheres by injecting the dyes (in organic solution) into an aqueous suspension of microspheres followed by heating and agitation. It was believed that the dye molecules would incorporate themselves into the microspheres as the organic solvent evaporated. In an effort to maintain uniformly shaped beads, we attempted to control the ratio of aqueous to organic solvents. However, it became evident that a relatively high concentration of organic solvent was necessary to draw the dye into the microspheres. Unfortunately, the organic solvent caused the microspheres to swell, resulting in inconsistently dyed microspheres that exhibited structural defects and irregularities.

The second method, developed by one of us (Xia), was based on the incorporation of the dyes during synthesis of the beads by emulsion polymerization. This process consistently produced uniform monodisperse polystyrene microspheres in high yield. Figure 4 (left) is a luminescence microscopy image of the synthesized microspheres or PSBeads. This image is the 650 nm PtOEP phosphorescence emission from 3.0 μm diameter PSBeads in an aqueous suspension. The PSBeads were excited at a wavelength of 540 nm.

The size of the PSBeads can be readily varied from 1 to 5 μm by adjusting the amount of radical initiator (AIBN) used in the polymerization process. Figure 4 (right) shows SEM images of PSBeads at three initiator (AIBN) concentrations:

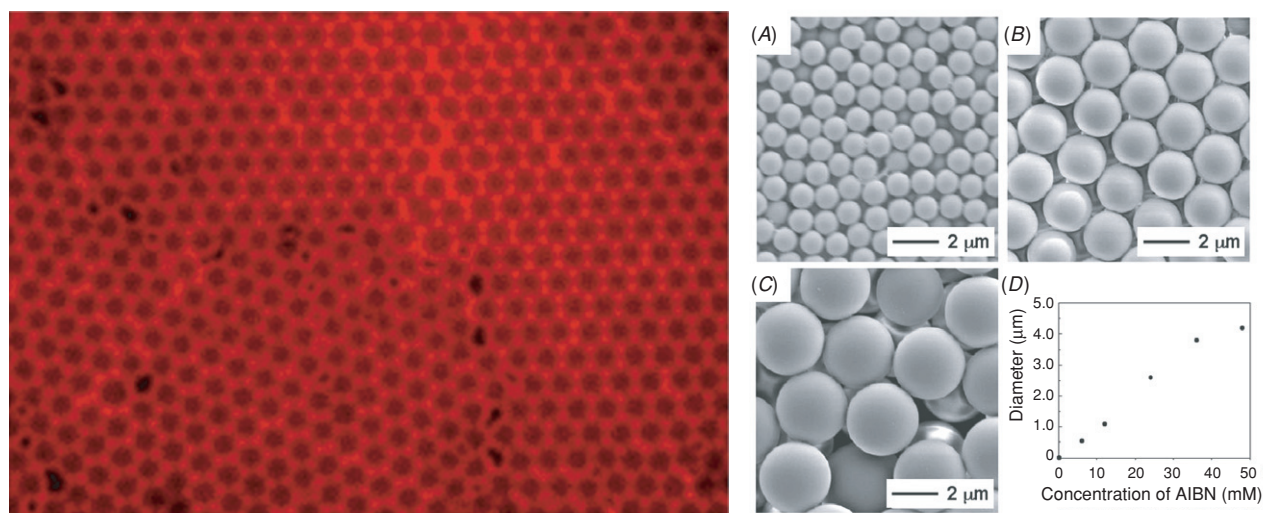


Figure 4. Left: phosphorescence microscopy images of PSBeads 3.0 μm in diameter, right: (A)–(C) SEM images of PSBeads containing SiOEP and PtOEP that were synthesized with different AIBN concentrations.

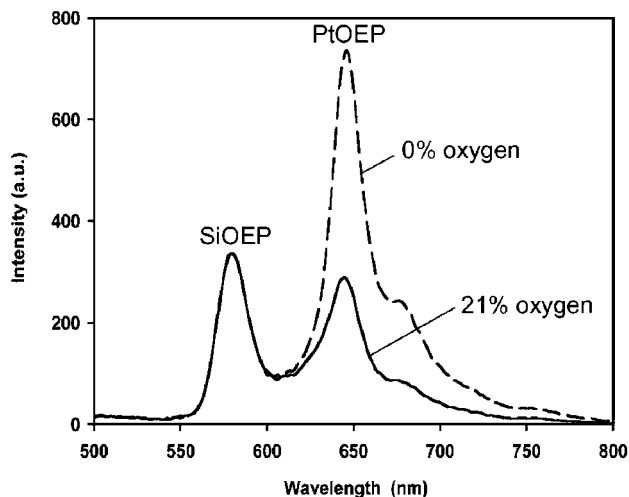


Figure 5. Emission spectra for PSBeads excited at 400 nm and under pure nitrogen (no oxygen) and air (21% oxygen). Labels indicate the predominant emission lines for each luminophore.

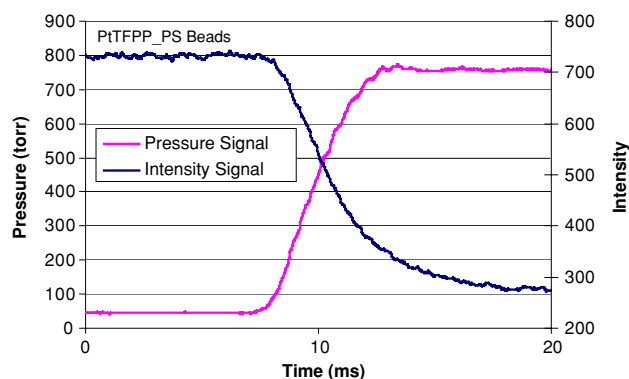


Figure 6. Response time for PSBeads to pressure jump.

(A) 6, (B) 12 and (C) 24 mM. Plot (D) is the correlation between the mean diameter of each sample and the concentration of AIBN.

The emission spectra of an array of PSBeads one bead thick deposited on an aluminium plate are displayed in figure 5. The film is stimulated at 400 nm, a common wavelength for PtOEP and SiOEP, and the intensity dependence of each luminophore as a function of oxygen is revealed. As expected, the intensity of SiOEP at 580 nm did not change with the concentration of oxygen, whereas the intensity of PtOEP at 650 nm was significantly decreased with the concentration of oxygen (inversely proportional to the concentration of oxygen).

For response time measurements, PSBeads are spread on a 1 cm² aluminium plate and inserted into the pressure chamber on our pressure jump apparatus [18]. Figure 6 shows the response of both PSBeads and a pressure transducer plotted on the same time scale. The PSBeads' response to changes in oxygen is so fast that the luminescent intensity changes from initial to final value in the same amount of time as the pressure jump. In fact, the PSBeads' response from a vacuum to 1 atm jump was within the measuring system resolution of 10 ms. We estimate a 1 ms upper limit response time value for the PSBeads.

Pseudocolor 650 nm Emission Intensities of PS microspheres in 0%, 5%, and 10% O₂ flows

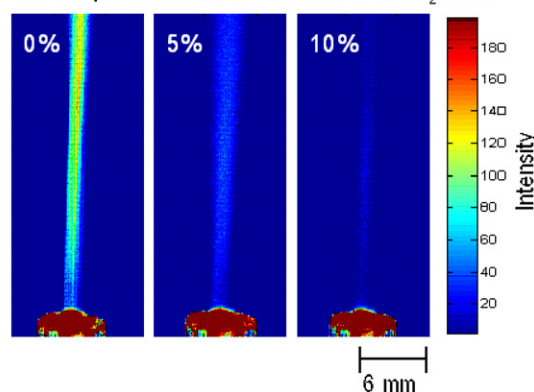


Figure 7. PSBeads particle beam at different oxygen concentrations.

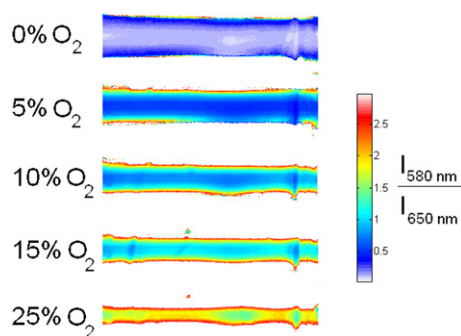


Figure 8. PSBeads ratio of $I_{580\text{ nm}}/I_{650\text{ nm}}$ images excited by a 400 nm laser in 0%, 5%, 10%, 15%, 25% and 30% oxygen concentrations.

McGraw [12] of our laboratory, using the phosphorescence microphone device, measured a response time of <1 ms for the thin pressure-sensitive paint film spotted on a chromatography plate made of micrometre diameter silica particles. It should be noted that previous studies [20] demonstrated that particle size is a major factor affecting response time: the smaller the particle size the faster the response time.

Using the setup described in figure 3, a jet flow of the PSBeads was generated and imaged as they were ejected from the nozzle. The PSBeads flowed from the nozzle tip entrained with carrier gases of varying oxygen concentrations. The entire plume of PSBeads was visualized using two LED arrays to illuminate the spheres. Two images were taken through 580 nm and 650 nm filters at 0%, 5% and 10% O₂ and the ratios of the images are shown in false colour in figure 7.

The PSBeads respond reversibly in aerodynamic flows over a wide dynamic range of oxygen concentrations. Again, using the setup described in figure 3, but with a 404 nm laser diode as the excitation source, the image ratios of the PSBeads at five oxygen concentrations were obtained (figure 8). The intensity image ratios were plotted as a function of per cent oxygen concentration and are shown in figure 9. The plot follows Kavandi's equation [19] and is fitted to a linear relationship of intercept $A = 0.1$ and slope $B = 0.0699$ with a correlation coefficient of $R^2 = 0.9689$.

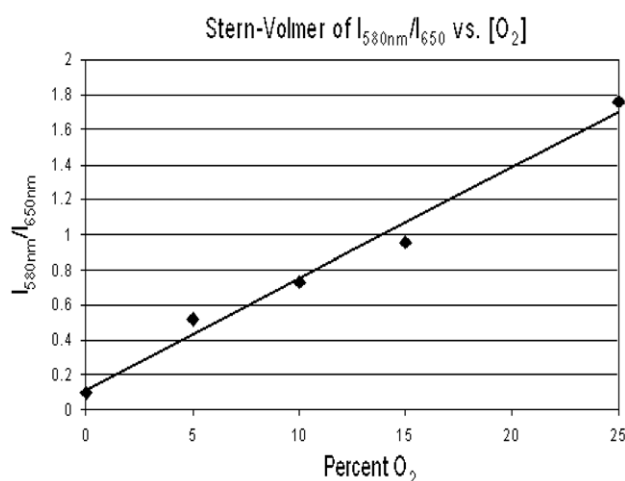


Figure 9. Stern–Volmer plot showing the linear dependence between the intensity ratio of SiOEP to PtOEP and five oxygen concentrations.

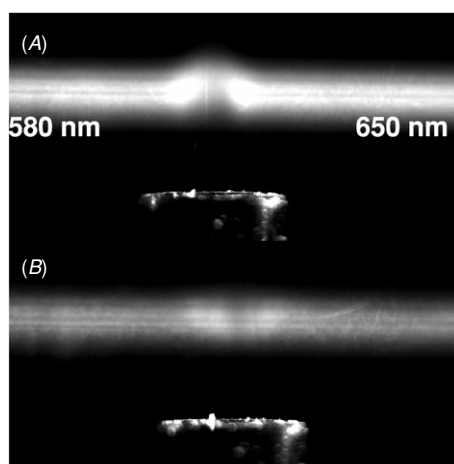


Figure 10. Laser shift images, (A) $I_{650\text{ nm}}$ of PSBeads in argon; (B) $I_{650\text{ nm}}$ of H_2TNMPP -doped silica particles in argon.

During the PSbead titration experiment, a distortion in the laser line was observed for the beads in an argon flow. The distortion appears as a bulge in the laser line where it crosses the stream of beads that are emanating from the drying tube. This distortion is only observable at 650 nm of the PtOEP phosphorescence emission and only for beads in an argon flow, as is shown in figure 10(A). These facts suggest that the distortion is a result of the long lifetime of the PtOEP phosphorescence in the low oxygen concentration environment that is present in the argon flow, leading to image smearing.

The lifetime of the pressure-sensitive luminophore, PtOEP, in argon is $\sim 50\ \mu\text{s}$. The beads are exiting the nozzle at approximately $7.4\ \text{m s}^{-1}$. As a result, from the moment of excitation to the end of luminophore emission, a bead will have travelled 0.37 mm. Theoretically, the observed effect would be a ‘smear’ of emission that was 0.37 mm in length, assuming an infinitely narrow laser excitation line.

To determine the extent of the smear in the experimentally obtained images, the distance from the leftmost edge of the undistorted laser line to the peak of the bulge is measured in

pixels. Using the diameter of the exit nozzle as a reference, the distance in pixels is converted to millimetres. The resulting bulge width was approximately 0.31 mm, a value that is close to the expected smear length.

To further support this hypothesis, the experiment was repeated with fumed silica particles doped with Tetrakis(*N*-methylpyridyl) porphine tetra-*p*-tosylate salt (H_2TNMPP). H_2TNMPP on silica has a 660 nm fluorescence band whose intensity changes with oxygen concentration. The sensor was studied previously by Wan [20] and demonstrated a linear Stern–Volmer with a 60% dynamic range. The lifetime of this luminophore is approximately 10 ns, and as a result, no discernible smearing of the laser line would be expected. As shown in figure 10(B), this is indeed the case.

It should be noted that while this ‘smearing’ effect is detrimental to our application, it has in fact been used successfully by Koochesfahani and co-workers to measure fluid velocity [21]. In fact, a whole field named molecular tagging velocimetry is based on long-lived tracers such as PSBeads.

5. Conclusion

Airborne microspheres made from polystyrene beads are developed for pressure measurement in fluid flow. The beads are loaded with two luminophores; one luminophore has pressure-independent emission and provides an intensity reference. The other exhibits a pressure-dependent emission. The intensity ratio of these two emissions allows for accurate measurement of pressure using airborne beads. The polystyrene bead microspheres (PSBeads) are small enough to follow fluid flow accurately and function simultaneously as pressure-sensitive airborne micro-particles, thus potentially providing an accurate non-intrusive imaging method for mapping the pressure distribution in a two-dimensional flow.

Future research will focus on (i) combining pressure measurement with the DPIV for velocity determination; (ii) synthesizing larger ($> 5\ \mu\text{m}$) polystyrene microspheres and (iii) evaluating a ‘multispec’ device that can resolve four images, for pressure and DPIV measurements simultaneously.

We are especially interested in the work of Dullens *et al* of Utrecht University in the Netherlands [22]. This group has succeeded in synthesizing monodisperse, polymer microspheres made of crosslinked poly(methyl methacrylate) loaded with fluorescent dyes. We believe that in synthesizing similar crosslinked polymer microspheres, we will be able to tune the rate of oxygen diffusion through the polymer by regulating the degree of crosslinking. The goal is to produce pressure-sensitive microspheres, which are much brighter at 1 atm of pressure.

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