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Simultaneous sensing of dissolved oxygen and probe temperature using a ruby insert and compact photon counting photon counting receiver

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ABSTRACT

We present a new sensor capable of real-time simultaneous determination of dissolved oxygen and temperature sensor. The measurements are achieved by essentially simultaneous interrogation of fluorescence lifetime of both an oxygen sensing Ru^{2+} pO_2 sensor membrane impregnated in silicone, and a Cr^{3+} - doped sapphire crystal (Ruby). The presence of the ruby crystal provides several advantages

- It acts as a thermal sensor at the probe tip, that is illuminated by the same LED as the Ru^{2+} sensing layer.
- As the ruby crystal is mounted at the distal end of the optical fibre probe, it provides a reference signal to indicate mechanical damage or membrane detachment problems.
- By providing a reasonably constant fluorescence intensity, more significant, yet gradual changes in fluorescence light output from the membrane (e.g. due to photo-degradation) may be detected.

1. INTRODUCTION

Fluorescence lifetime interrogation is now employed in many commercial chemical sensors, many of them involving an Ru^{2+} -based dye for oxygen sensing. Such sensors offer many well researched advantages over traditional electro-chemical sensors (firstly, they do not consume oxygen, secondly, the probe tip has a very low cost, and thirdly they are immune to electromagnetic interference).

One of the biggest problems with such dissolved oxygen ~~sensors~~ chemical sensors is that their sensitivity, varies significantly with temperature. This dependence occurs with most fluorescent-lifetime-based chemical probes, as the occupancy and hence decay rates of electronic levels vary considerably with temperature. It is therefore desirable to mount a temperature sensor at the probe tip to monitor this parameter to correct for thermal changes. Clearly, a simple thermocouple could be used, but this requires a separate interrogator and throws away one of the major attractions of the probe, its non- electrical nature. It would be highly desirable to use an optical temperature probe that can be interrogated via the same optical lead as the chemical sensor, and use the same opto-electronic interrogation system as is used to detect the chemical measurand, giving an almost ideal solution.

An earlier optical temperature compensation system used an alexandrite crystal to monitor the temperature of a platinum tetraphenylporphyrin indicator, and an interrogation system which measured the frequency spectrum of the detected fluorescent signal (ref 1). Although this worked in practice, it required a complicated high frequency signal processing scheme, which would be expected to give an inferior signal/noise ratio due to the high frequency detection circuits.

We now report results from our new, real-time temperature-compensation system that uses the same LED source, same photo-multiplier detector and even the same digital detection hardware as the Ru^{2+} dye chemical probe, and uses Ruby as a thermal indicator. Our combination has a far greater ratio of crystal fluorescent lifetime to that of the Ru^{2+} dye and ruby, unlike alexandrite, is non toxic. The ruby crystal also provides a fluorescence intensity reference for on-line calibration of the interrogation hardware, and, by examining the relative intensities from ruby and membrane, mechanical damage or detachment of the sensing membrane may be recognised.

We now report the first real-time results, of our combined temperature and dissolved oxygenation system proving its practical viability.

Common Ru^{2+} chemical sensors usually measure fluorescent lifetime by monitoring the phase delay between incident blue light from an excitation LED and, by means of a photodiode, the detected fluorescent signal returning from the probe. Photon-counting fluorescence detection works by observing the rate of arrival of