High throughput non-destructive assessment of quality and safety of packaged food products using phosphorescent oxygen sensors

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Abstract

Intelligent and active packaging technologies have gained attention in recent time due to increased demand by the consumers and manufacturers for sustaining the quality and safety of food products, improved shelf-life as well as real time monitoring of the packaging, storage and handling processes. In this context, phosphorescence based sensors for molecular oxygen (O₂) are important tools for monitoring of packaged products, new product development and optimisation. They allow fast, reversible, real-time and quantitative monitoring of residual O₂ levels in a non-destructive manner, being superior over alternative systems. In this review, we describe the main types of phosphorescent O₂-sensitive materials, fabrication methods and general requirements for sensors for food packaging applications. The main developments and representative examples are provided which illustrate the application of such sensors for monitoring of gaseous and dissolved O₂ in various types of packaged foods and beverages. We also compare commercial O₂ sensing instrumentation and disposable O₂ sensors currently in use.

Keywords: Optical oxygen sensors; phosphorescence lifetime based oxygen sensing; disposable sensors; non-destructive analysis; food and beverage packaging, MAP foods, residual oxygen; high throughput analysis; food safety; quality assurance.

1. Introduction

Applications of active and intelligent packaging technologies are gaining significant attention in recent time due to increased concern about the quality, sensory aspects, hygiene and safety of packaged food products, combined with increasing demands to improve the shelf-life of food products in a cost-effective manner, while minimising food waste and impact of packaging on the environment (Kerry, O'Grady, & Hogan, 2006; Mohebi & Marquez, 2015). Active packaging allows incorporation of additives, such as gas scavengers, CO₂ emitters, ethanol emitters, temperature and moisture controllers, antimicrobial agents, to enhance the quality and sensory aspects of packaged foods (Ahvenainen, 2003; Han, 2003; Rooney, 1995; Suppakul, et al., 2003). Use of vacuum and particularly modified atmosphere packaging (MAP) systems is on a rise to store perishable foods in an oxygen free environment in order to maintain their quality and increase the shelf-life (Rooney, 1995). In MAP systems food products are enclosed in packs containing a mixture of natural gases (N₂, CO₂, O₂) in specific proportions, to retard the growth of microorganisms and other degradations processes (Yam, Yam, & Davis, 2010). However, MAP processes themselves do not always guarantee the presence of right gas composition and require reliable control at the packaging site and verification throughout product lifespan. The residual oxygen levels in MAP products can increase due to factors such as gas permeability of the packaging material, gas trapping ability of enclosed food, compromised packaging, inefficient gas flushing, accidental damage during packaging, handling or transportation. Monitoring of MAP composition and particularly O₂ levels in individual packs can therefore provide valuable information about the quality of food, integrity of packing material, efficiency of the packaging machine and process, storage conditions and handling.

Conventional headspace O₂ analysis involves rather expensive analytical instruments like GC, electrochemical sensors (Clark-type O₂ electrode)(Clark, et al., 1953), O₂/CO₂ gas analysers (e.g. DansensorTM (Dansensor)), destructive sampling of the food package headspace and also requires skilled personnel. As well as providing limited sample throughput and creating wastage, these techniques only provide a time of analysis snapshot of the conditions in the selected packs, insufficient to detect all faulty packages and preform periodic rechecks. The operational efficiency of electrochemical O₂ sensors is also influenced by gas flow rate, stirring rate, operational temperature, poisoning by other gases (H₂S) and fouling of membranes (Trettnak, et al., 1995).

Intelligent or 'smart' packaging approaches allow non-destructive monitoring of some properties of the enclosed food or the environment inside the pack and provide information about the current status of the food in such packs (Yam, Takhistov, & Miltz, 2005). Various concepts of intelligent packaging currently exist that include indicators and sensors for different physical, chemical or biological variables which reflect the quality, safety of food products (Avella, et al., 2011; Borchert, Kerry, & Papkovsky, 2013; Kuswandi, et al., 2011; Mills, 2005).

Indicators report presence or absence of a substance through a characteristic change, often the colour of the indicator material. Thus, package integrity is monitored through the incorporation of an optical indicator for O₂, which consists of a redox dye, a strong reducing

agent such as glucose and an alkaline compound to maintain alkaline pH and prevent rapid oxidation of the dye (Ahvenainen, Eilamo, & Hurme, 1997; Krumhar & Karel; Lawrie, Mills, & Hazafy, 2013; Smolander, Hurme, & Ahvenainen, 1997). The redox indicator can provide qualitative or semi-quantitative information about the O₂ level through oxidation of the dye. Ageless Eye™, one of the commonly used indicators, produced by Mitsubishi Co to check integrity of food packages(AgelessEye), is based on the change in colour of methylene blue dye from colourless in the reduced form at [O₂] ≤ 0.1% to blue oxidised form in the presence of O₂ (≥ 0.5%). The indicator ink, represents irreversible O₂ response (activated by UV light), can be printed on various surfaces. However, its high sensitivity often results in colour change at low O₂ levels in MAP foods, giving false readouts.

Freshness indicators can inform about the quality and microbial contamination of the product through the colour change resulting from its interaction with the microbial metabolites (Smolander, 2008), such as the concentration of H₂S (Smolander, et al., 2002), volatile biogenic amines (Kaniou, et al., 2001; Loughran & Diamond, 2000; Rokka, et al., 2004), ethanol (Randell, et al., 1995), lactic acid (Shu, Håkanson, & Mattiasson, 1993). Time-temperature indicators (TTI) provide the temperature history of a food product over a period of time (Taoukis & Labuza, 1989). TTIs can be based on temperature dependent diffusion (3m), enzymatic (Vitsab) or polymerisation (Fresh-Check) reactions, and provide irreversible visual readout of the proper or improper temperature regime (but not the exact profile) to which the food product has been exposed to. Incorporation of radiofrequency identification (RFID) tags allows tracing and identification of faults (Kumari, et al., 2015). RFIDs can be combined with other indicators such as TTIs or sensors and provide real time information in a contact-less manner without being in the direct line-of-sight of a scanner.

Unlike the above indicator systems, optochemical sensors are composed of optically active materials which provide a *reversible* and *quantitative* response against specific parameter (Hugi & Voirol, 2001; Kress-Rogers, 2001). Such sensors for various analytes have gained significant attention for their application in non-destructive monitoring quality of food such as freshness, deterioration due to heat or microbial spoilage, oxidative rancidity, compromised package integrity or barrier properties (Hugi & Voirol, 2001; Kress-Rogers, 2001; Meng, et al., 2014). Residual O₂ in packaged foods is one of the key markers of the quality of the product, the integrity of the packaging material and operation efficiency of the packaging lines. Elevated O₂ levels can result in rapid deterioration of food-quality through lipid oxidation, destruction of citric acid leading to loss of flavour, fast ripening and browning through enzyme catalysed reactions, growth of microorganisms.

Photoluminescence (fluorescence/phosphorescence) based O₂ sensors rely on the principle of quenching of luminescence intensity and lifetime of an oxygen-sensitive dye embedded in a polymeric matrix by sample O₂. They offer several important advantages over the conventional systems including lack of oxygen consumption during measurement, reversible real-time operation, direct quantitative readout, contactless, non-destructive mode of detection, possibilities of miniaturization and up-scaling (Amao, 2003; Papkovsky & Dmitriev, 2013; Wang & Wolfbeis, 2014). Such low-cost, disposable, calibration-free solid-state O₂ sensors can be applied on a large scale to detect package integrity, product

deterioration, microbial growth and monitor quality and safety of food products along the packaging line.

In this review we focus on various applications of luminescent O₂ sensors for quality control and safety assessment of packaged foods and beverages, describing corresponding sensor materials, measurement systems and some core food packaging applications.

2. O₂ Sensing by Photoluminescence Quenching

O₂ sensing using photoluminescent dyes rely on the collisional quenching of an electronically excited dye molecule by O₂ molecules (Figure. 1A) (Lakowicz, 2006). The long-lived emission of phosphorescent dye molecules allows deactivation of their excited state through collisional interactions with O₂ molecules, which decreases the emission intensity and lifetime in a concentration dependent manner. Ground state O₂ molecules (paramagnetic; triplet configuration, ³O₂) can accept energy from the excited triplet state of the chromophore, thereby deactivating the chromophore and forming singlet oxygen (¹O₂). The short-lived ¹O₂ usually reverts back to ground state O₂, it can also react with surrounding chemical groups causing photo-oxidation.

2.1. Detection Formats

Luminescence spectroscopy allows quantitative monitoring of O₂ concentrations through optical parameters of the sensors. The principal detection formats are measurement of the luminescence intensity (I) and luminescence lifetime (τ) of the O₂ sensitive dye. The theoretical relationship between intensity/lifetime and the concentration of O₂, in the case of purely collisional quenching, can be described by Stern-Volmer equation (eq. 1) (Lakowicz, 2006),

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [O_2] = 1 + K_{SV} [O_2] \quad (1)$$

$$[O_2] = (I_0/I - 1)/K_{SV} \quad (2)$$

$$\text{or } [O_2] = (\tau_0/\tau - 1)/K_{SV}$$

where I₀ and I, τ₀ and τ are the luminescence intensities and lifetimes in the absence and in the presence of O₂, respectively; k_q is the bimolecular quenching rate constant, which gives a measure of the quenching efficiency or accessibility of the chromophore to O₂; K_{SV} is the Stern-Volmer constant. Classical relationship between luminescent parameters and O₂ concentration (i.e. calibration) and its linearization in Stern-Volmer plots are shown in Figure1B-C. However in practice and particularly for polymeric sensor materials, the Stern-Volmer plots deviate from the ideal linear nature depicted by equation 1, due to heterogeneous micro-environment of the dye and different O₂ accessibilities. Under such conditions the dependence can be described by more complex (albeit less physically meaningful) models, such as “two-site model” (Carraway, et al., 1991; Demas, DeGraff, & Xu, 1995):

$$\frac{I}{I_0} = \frac{\tau}{\tau_0} = \frac{f}{1 + K_{SV}^1 [O_2]} + \frac{(1 - f)}{1 + K_{SV}^2 [O_2]} \quad (3)$$

where *f* represents the fraction of the first emitting component, K_{SV}¹ and K_{SV}² are the Stern-Volmer constants corresponding to each component. Originally developed for intensity

quenching, Eqn. 3 is also applicable for lifetime based O_2 sensing (Banerjee, Kuznetsova, & Papkovsky, 2015; Borisov, et al., 2014).

Figure 1. Schematic representation of phosphorescence process and its quenching by O_2 (A), dependence of luminescence signal from the sensor (intensity, I or lifetime, τ) on O_2 concentration (B) and its linearisation in Stern-Volmer plots showing the ideal (dotted line) and the more common curved (solid line) cases (C).

Although intensity measurements have been used in some O_2 sensors, this parameter can often be influenced by factors such as positioning of sample, fluctuation in light source, changes in optical path, detector drift, degradation or leaching of dyes. This results in large measurement errors, sensor-to-sensor and batch-to-batch variation, unstable calibration, the need of frequent re-calibrations. A modification of intensity measurements is the ratiometric mode, which measures intensities at two different wavelengths, one of which is sensitive to O_2 and the other is not (the reference dye) (Kondrashina, et al., 2012; Koo Lee, et al., 2010; Napp, et al., 2011; Wang, et al., 2011; Xu, et al., 2001). The intensity ratio gives more stable readout and calibration, however sensor chemistry is more complex and factors such as

detector noise, different extent of photo bleaching of the dyes, scattering and auto-fluorescence can still influence this parameter and affect the accuracy of measurements.

The emission lifetime on the other hand is an intrinsic parameter of a luminescent sensor material. It provides more stable calibration, independence on excitation intensity, detector sensitivity, measurement geometry and concentration of the reporter dye (though self-quenching of the dye at high concentrations can affect lifetime signals). For these reasons, the majority of modern sensors use luminescence lifetime-based detection of O₂. Lifetime based O₂ sensing can be realised either in time domain by tracing the luminescence decay after short-pulse excitation, or in frequency domain by measuring phase shift of the luminescent intensity signal under periodically modulated excitation.

2.2. O₂-Sensitive Dyes

Luminescent O₂ sensors are derived by encapsulating an O₂-sensitive dye in a suitable O₂-permeable matrix such as organic polymer or inorganic sol-gel (Amao, 2003; Papkovsky & Dmitriev, 2013; Quaranta, Borisov, & Klimant, 2012; Wang & Wolfbeis, 2014). Commonly used luminescent dyes include complexes of transition metals and Pt(II)-porphyrins (Amao, 2003; Amao & Okura, 2009), which exhibit relatively long-lived emission at room temperature (τ_0 in the μ s range) quenched by O₂ in a concentration dependent manner (see Table 1).

[Ru(bpy)₃]²⁺ (where bpy = 2,2'-bipyridine), represents an early example of Ru(II) based dye used for sensor fabrication (Cook, et al., 1984; Lippitsch, et al., 1988; Mills, Graham, & O'Rourke, 2014; Wang & Wolfbeis, 2014; Wolfbeis, Leiner, & Posch, 1986). It was later replaced by [Ru(dpp)₃]²⁺ dye series, where dpp stands for tris(4,7-diphenyl-1,10-phenanthroline). [Ru(dpp)₃]²⁺ dyes display moderately intense absorption and a broad MLCT emission in the visible region with an unquenched lifetime τ_0 of $\sim 6.4 \mu$ s and quantum yield ϕ of ~ 0.3 (Table 1) (Alford, et al., 1985). [Ru(dpp)₃]²⁺ has been studied in various O₂-sensitive matrices including sol-gel (MacCraith, et al., 1993; Xu, et al., 2001), organically modified silicate (ormosil) (Badocco, Mondin, & Pastore, 2012; Chen, et al., 2002; Klimant, et al., 1999; McDonagh, et al., 2001; Tang, et al., 2003), organic polymers such as polystyrene (PS) (Hartmann, Leiner, & Lippitsch, 1995; Klimant, et al., 1997), polysulfone (PSu) (Badocco & Pastore, 2008), ethyl cellulose (EC) (Draxler, et al., 1995), polydimethyl siloxane (PDMS) (Xu, et al., 1994). Ionic complexes such as [Ru(dpp)₃]²⁺ suffer from poor solubility in hydrophobic polymers. To overcome this, such dyes can be adsorbed on SiO₂ or TiO₂ particles and then incorporated into hydrophobic polymeric binder (Mills & Graham, 2013; Wolfbeis, et al., 1986), or they can be ion-paired with lipophilic anions such as dodecyl sulphate, trimethylsilylpropanesulfonate, tetraphenyl borate (Klimant & Wolfbeis, 1995; Mills & Thomas, 1997). Thus, O₂xyDotTM sensor produced by Oxysense uses [Ru(dpp)₃](ClO₄)₂ incorporated in silicone rubber. Ru(II) dyes are excitable with blue LEDs (Oxysense), but their disadvantages are moderate brightness, relatively short lifetimes and excitation wavelengths, high temperature sensitivity of the triplet state (Alford, et al., 1985; Forster, 2002).

Pt(II)-porphyrins (Amao & Okura, 2009) display strong absorption in the UV region ($\lambda_{\max} \sim 390-420$ nm - Soret band), weaker absorption Q bands in the visible region, strong

room temperature phosphorescence with large Stokes shift and emission lifetime around 50-100 μ s strongly quenched by O₂. Pd(II)-porphyrins display 5-10 times longer lifetime and correspondingly higher sensitivity towards O₂ compared to their Pt(II) analogues (Eastwood & Gouterman, 1970). Such dyes are useful for trace O₂ analysis, while at ambient O₂ levels (~15-25 kPa) they are strongly quenched producing weak phosphorescent signals and poor resolution in O₂ measurements.

Pt(II)-octaethylporphyrin was initially used in O₂ sensing (Amao, et al., 2002; Douglas & Eaton, 2002; Lee & Okura, 1997a; Papkovsky, 1995; Papkovsky, et al., 1992), but it has modest photostability and undergoes rapid photobleaching in polymeric matrices (Puklin, et al., 2000). In Pt(II)-tetrakis-(pentafluorophenyl)porphyrin (PtTFPP) dye contain the electron-withdrawing perfluorinated substituents which lower its oxidation potential and improve photostability (Amao, Miyashita, & Okura, 2001; Lee & Okura, 1997b; Puklin, et al., 2000). This dye has been extensively used in various polymers including PS (Amao, et al., 2001; Lee & Okura, 1997b), PSu (Badocco, et al., 2012; Xue, et al., 2015), sol-gel matrices (Chu & Chuang, 2015; Chu & Lin, 2014; Chu & Lo, 2011) and co-polymers. O₂ sensors have been developed by covalently linking PtTFPP to poly(2-hydroxyethyl methacrylate)-copolyacrylamide (Tian, Shumway, & Meldrum, 2010), co-polymers of styrene and pentafluorostyrene (Koren, Borisov, & Klimant, 2012), polyfluorene co-polymer (Dmitriev, et al., 2015). Such sensor materials overcome the problems of migration and leaching of dye from polymeric matrix, while retaining the O₂ sensitivity and photostability. One major limitation with PtTFPP is that high brightness can only be achieved upon excitation at ~400 nm (Soret band), while under visible light excitation (Q-bands 500-520 nm) it has moderate brightness and therefore less favourable for O₂ sensing.

Dyes absorbing in the red region and emitting in the far-red/NIR region are preferred over the UV and visible light excitable dyes, due to minimal interference from sample autofluorescence, background from support media and reduced effects of excitation on light-sensitive products. Compared to the parent porphyrins, Pt(II) complexes of porphyrin-ketones (Papkovsky, et al., 1995) and porphyrin-lactones (Khalil, et al., 2002), synthesised by oxidation of the porphyrin ring, display red-shifted Q-bands and enhanced absorption. The PtOEPK displays phosphorescence around 759 nm with unquenched lifetime of ~61 μ s in polystyrene (Papkovsky, et al., 1995), excitable with bright and low-cost yellow LEDs. While studied in several different polymers (Klimant, et al., 1997; Kolle, et al., 1997) and used extensively in packaging applications (see Section 3 below), PtOEPK dye has relatively low emission yield (resulting in moderate brightness of sensors) and high cost.

Porphyrins with extended π -conjugation such as tetrabenzoporphyrins (TBPs), tetranaphtho[2,3]porphyrins (TNPs) also exhibit red absorption and bright emission (Rogers, et al., 2003; Vinogradov & Wilson, 1997; Vinogradov & Wilson, 1995). Thus, the Pt(II)-tetraphenyltetrabenzoporphyrin (PtTPTBP) in toluene has a strong absorption at Q band at 614 nm ($\epsilon = 13.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and strong phosphorescence with $\lambda_{\text{max}} = 770 \text{ nm}$ and quantum yield ~0.5 (Borisov S. M., et al., 2009). The bright, photostable and longwave Pt-TBP dyes have been used to produce robust optical sensors, including those with O₂ reporter dye covalently conjugated to silicone (Müller, et al., 2015). They are excitable with orange-red LEDs.

Several other dyes including cyclometalated iridium (Borisov & Klimant, 2009; Borisov & Klimant, 2007; Köse, et al., 2005; Li, et al., 2015), lanthanide (Borisov & Klimant, 2012; Borisov, et al., 2014; Law, et al., 2009; Songzhu, et al., 2010) and other metal complexes (Medina-Rodriguez, et al., 2015) have also been described for O₂ sensing. Noble or rare metal free organic chromophores such as, camphorquinone (Charlesworth, 1994), erythrosine B (Gillanders, et al., 2004; Lam, Chan, & Lo, 2001), BODIPY derivatives (Banerjee, et al., 2015; Ermolina, et al., 2014) also exhibit phosphorescence at room temperature effectively quenched by O₂, but these dyes are associated with lower wavelength excitation, low brightness, considerable photodecomposition. For more details see the recent reviews (Amao, 2003; Quaranta, et al., 2012; Wang & Wolfbeis, 2014).

Table 1. Summary of photophysical properties of the commonly used O₂-sensitive dyes

Dye	$\lambda_{\max}^{\text{Abs}}/\text{nm}$ (ϵ)	$\lambda_{\max}^{\text{Em}}/\text{nm}$	ϕ^a	τ (μs) ^a	Brightness in PS ^b	Ref.
[Ru(dpp) ₃] ²⁺	463 (2.86×10^4)	618	0.366	6.4	10467	(Alford, et al., 1985)
PtTFPP	394 (32.3×10^4) 504 (2.32×10^4) 538 (2.94×10^4)	647 710 (shoulder)	0.088	60	92000 5600 7600	(Lai, et al., 2004) (Borisov, Nuss, & Klimant, 2008)
Pt-OEPK	398 (8.62×10^4) 592 (5.51×10^4)	758	0.12 ^c	60 ^c	19000 12000	(Papkovsky, et al., 1995)

PtTPTBPF	430 (21.2×10^4), 615 (14.6×10^4)	773	0.60	50	149000 102000	(Borisov S. M., et al., 2009)
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^a Quantum yield, Φ and lifetime τ values refer to O₂-free solution. ^b For brightness, values were taken from Ref (Borisov, et al., 2008), calculated using, ϕ of Ir(Cs)₂(acac) in PS as 1; ^c in micellar sulphite solution

2.3. Polymeric Host

In a sensor, an O₂-sensitive dye is encapsulated in a polymeric host, which provides it the desired quenching by O₂ and additional shielding from other quenchers in the surrounding medium/test sample. The polymer is usually chosen such that it has good compatibility and solubility for the dye, optimal quenching by O₂ and eliminates dye aggregation and leaching (Korotcenkov, 2014). The polymer should possess high chemical, mechanical and thermal stability and not change its microstructure over time. The permeability of O₂ through the polymer and the lifetime of the dye determine the sensitivity of the sensor. Dyes with short emission lifetime such as [Ru(dpp)₃]²⁺ require polymers with high O₂ permeability, such as silicones and fluorinated copolymers. Pt-porphyrins having longer lifetimes are compatible with a broader range of plastics including PS, PSu, food-grade polymers polyethylene (PE) and polypropylene (PP), special and biodegradable polymers such as polylactic acid (PLA) and polyphenylidene sulphide (PPS).

PS, PSu and silicones are commonly used in O₂ sensors, due to their moderate to high gas permeability, high chemical and mechanical stability, and ability to form transparent coatings (Wang & Wolfbeis, 2014). Alternatively dyes can be adsorbed on SiO₂ or TiO₂ beads and then incorporated in the polymer (Mills & Graham, 2013; Wolfbeis, et al., 1986), but such sensor materials tend to be more heterogeneous. To achieve fast response to O₂, sensor materials are usually prepared as thin film coatings. For easier handling and improved mechanical stability sensor coatings are applied on solid support material such as tip of optical fibre, glass slide, or more commonly on polyester film (Mylar®) (Klimant & Wolfbeis, 1995; Moreno-Bondi, et al., 1990) or microporous membranes (Papkovsky, O'Riordan, & Guilbault, 1999; Papkovsky, et al., 1998). The latter facilitate production of uniform coatings, enhance phosphorescent signals, prevent delamination of sensor material, facilitate handling, and still retain fast response to O₂. Fluorinated and other co-polymers are actively used in O₂ sensors (Amao, et al., 1999; Amao, Miyashita, & Okura, 2000; Ishiji, Kudo, & Kaneko, 1994; Morin, et al., 2000; Puklin, et al., 2000) due to their high chemical and photostability and O₂ permeability.

Hydrophilic host polymers such as polyurethane, polyacrylamide, poly(ethylene glycol), show lower O₂ permeability and are less suited for fabrication of O₂ sensors. Due to

presence of H-bonding groups (hydroxyl, amino, carboxyl, carboxamide), hydrophilic polymers undergo swelling in water, which affects the O₂ calibration under dry/humid conditions (some degree of cross-sensitivity to humidity has also been noted for certain hydrophobic polymeric materials (Kelly, et al., 2014b)). On the other hand, polyurethane hydrogels have been used as binder polymers for incorporating microparticle sensors (Fischer, et al., 2012; Stich, Schaeferling, & Wolfbeis, 2009). Due to high biocompatibility they also have potential for development of enzyme biosensors based on O₂ transducers (Pospiskova, et al., 2013; Schrenkhammer & Wolfbeis, 2008).

2.4. Sensor Fabrication Methods

To ensure fast response and easy access of sample O₂ to the dye, the O₂ sensing material is usually prepared as thin film coating on a suitable substrate or support material, or integrated directly into food package. The resulting sensor should be stable, produce robust, reproducible and easily measurable luminescent signals and response to O₂ concentration. There are several ways through which an O₂-sensitive dye can be incorporated in a polymeric matrix.

Commonly, the dye is dissolved in a suitable organic solvent, mixed with a polymer of choice to form a sensor cocktail (or O₂-sensitive luminescent ink (Mills, 2005)), which is then applied on a support (polyester film, glass slide, optical fiber tip, etc.) and dried to form solid-state sensor coating. Such method is relatively simple and works satisfactory when the dye and the polymer have similar polarity. However, ‘cocktail’ methods are associated with large changes in the volume of sensor coating during drying (1:5-1:100), resulting in tension, prominent micro-heterogeneity and relaxation processes within the polymer matrix. Interaction of sensor material with support material and formation of mixed polymer phases can also take place. The processes of coating and drying from a volatile organic solvent are difficult to control precisely, and this leads to significant variability between batches, shift and drift of calibration and compromised analytical performance. These limitations are critical when the sensors are intended for use on a large scale, disposable and calibration-free basis, which is required in many packaging applications. Solvent-based incorporation in hydrophobic polymers does not fully prevent migration and leaching of the dye into the sample and support material (especially for microporous supports with very high contact area). Such undesirable effects can be overcome by covalent coupling of the dye and polymer through functional groups including amine (Borisov, Lehner, & Klimant, 2011; Wang, et al., 2002; Xavier, et al., 1998), alkene (DeRosa, et al., 2003; Tian, et al., 2010), siloxane (Malins, et al., 1999). Thus, covalent linkage of PtTFPP by ‘click’ chemistry (Koren, et al., 2012) prevented leakage and migration, while retaining high stability and homogeneous distribution of the dye. The downside of this is increased cost of sensor material.

As alternatives to polymeric cocktail coatings, several other methods and host materials exist for fabrication of O₂ sensors. Bulk PE and PP exhibit excellent mechanical properties and moderate O₂ permeability. They are widely used in packaging laminates as inner heat-sealable layers (*Plastic Films in Food Packaging: Materials, Technology and Applications*, 2012). However these polymers are less explored in O₂ sensors due to poor compatibility with established fabrication methods (solvent cocktails). Nonetheless, O₂

sensors have been fabricated from PP and HDPE films by solvent-crazing process, which creates well-developed nanoporous structures within the polymer, which can physically trap various cargo such as O₂-sensitive dye molecules (Gillanders, et al., 2010). The resulting sensors based on ordinary polyolefin and phosphorescent porphyrins exhibited useful sensing performance, high brightness, chemical and mechanical stability. More recently, discrete sensor spots were fabricated by localised spot-crazing of HDPE films (Toncelli Claudio, et al., 2014) and PPS film (Kelly, et al., 2015; Toncelli C., et al., 2014), which exhibited linear Stern-Volmer plot in the range of 0-21 kPa O₂, mild temperature dependence and cross-sensitivity to humidity. Non-woven polyolefin materials (microfibrous PP membranes) were also impregnated with phosphorescent dyes (PtTBP) by swelling in an organic solvent to produce usable sensors showing good sensitivity to O₂ ($\tau_0 \sim 50\text{-}60 \mu\text{s}$, $\tau_{21} \sim 22\text{-}30 \mu\text{s}$), fast response, wide O₂ range (0-100 kPa), brightness and no cross-sensitivity to humidity (Kelly, et al., 2014b).

Incorporation of an O₂-sensitive dye into micro and nanoparticles such as cross-linked PS beads has also been explored (Borisov, et al., 2014; Borisov Sergey M., et al., 2009; Chojnacki, Mistlberger, & Klimant, 2007; Stich, Fischer, & Wolfbeis, 2010). Such precursor sensor materials can be fabricated by simple and scalable solution method in a powder form, which is then incorporated in a 'binding' polymer (e.g. silicone) to produce sensor coatings. SiO₂/TiO₂ microparticles with adsorbed O₂-sensitive dye were also extruded into flexible films of common packaging polymers, such as LDPE (Mills & Graham, 2013). This approach and sensor materials are attractive, as they are compatible with standard industrial processes and facilitate sensor integration in packaging materials.

Sol-gel matrices synthesised through hydrolysis of silane precursors allow encapsulating O₂ sensitive dyes and provide optical transparency, good mechanical and chemical stability (Jerónimo, Araújo, & Conceição B.S.M. Montenegro, 2007). Porosity and O₂ sensitivity of the sol-gel can be tuned by parameters such as pH, aging time, water and precursor silane ratio, etc. (McEvoy, McDonagh, & MacCraith, 1997). Sol-gels can alter their network structure over time, thus affecting sensor calibration and response time. Ormosils containing higher amount of alkyl and aryl groups and exhibiting high oxygen permeability have been used to fabricate Ru(II)-polypyridyl and Pt(II)-porphyrin based sensors (Basu, 2007; Chu & Chuang, 2015; Korzeniowska, et al., 2015; McDonagh, MacCraith, & McEvoy, 1998). The limitations of sol-gel technology are its reliance on the many ingredients and process parameters, slow speed of polymerisation/setting and the need for 'annealing'.

For packaging applications, fabricated O₂-sensors should be incorporated into the packages with foods or integrated in particular packaging materials which are then used on a packaging line. Sensor incorporation and integration options include free-standing sensor inserts placed in containers with food, sensor labels of adhesive stickers attached to or printed on the inner side of the packaging tray or lidding material, sensors laminated inside the packaging material between the barrier and inner heat-sealable layers. The main requirements for the integration are easy access of sample O₂ from headspace, liquid or bulk food to the sensor and optical contact with the particular luminescent detector/reader to interrogate with the sensor from a certain distance (usually a few mm) and produce reliable readings of O₂ concentration. Sensor contact with atmospheric O₂ should be avoided, as this will skew the O₂ measurements.

Another role of sensor integration process is to protect sensor material from direct physical contact with the product, and *vice versa*. This is because some food components (e.g. meat juice, fat, flavours, etc.) can affect sensor characteristics (reduced signals due to colouration, shift calibration due to plasticisation) and thus lead to erroneous O₂ readings. A gas-permeable film (PE or PP) laminated on top of the sensor can prevent migration of sensor components (dye, polymer matrix) into food and product contamination with debris which can be accidentally delaminated and ingested. This can improve sensor safety.

2.5. Sensor Selection and Characterisation

Many luminescent dyes and O₂ sensing materials have been described so far, but only a small number of these (Table 1) have been actually used in packaging applications, i.e. with real food samples and under industrial settings. These materials usually have advantageous O₂ sensing performance, spectroscopic properties, availability, costs, scalability of raw materials and manufacturing processes, and compatibility with existing packaging materials and commercial detection instrumentation. The other candidates failed in one or more of these selection criteria, like attrition of leads in drug discovery.

By now Pt(II)-benzoporphyrin dyes excitable at 580-630 nm and exhibiting near infrared emission at 730-850 nm look most promising. High brightness, good separation of excitation and emission (Stokes shift >100nm), narrow bands, moderate quenching by O₂ due to relatively short lifetimes (~65 µs unquenched) are their advantages. These dyes are excitable with powerful orange-red LEDs and detectable with silicon photodiodes, which makes the development of lifetime-based O₂ sensing instrumentation relatively easy and inexpensive. Their chemical, photo stability and solubility in polymeric matrices are good, synthesis is relatively inexpensive, although more costly than for PtTFPP or sensor dyes without noble metals (Borisov S. M., et al., 2009). Low intrinsic toxicity of these dyes and minute quantities used per sensor (<1 µg) make them affordable and safe to use in packaging and with food products. A number of sensor materials based on these dyes have been described, which have simple chemical composition (two-component composites) and fabrication procedure, good analytical performance and reproducibility, general convenience and robustness (Mills, 2005). These materials are suitable for large scale manufacturing and integration in existing packaging systems.

However to implement up-scaling and sizeable deployment in food packaging, prototype O₂ sensors should undergo a detailed characterisation of their operational performance, with rigorous testing and comprehensive validation under real-life conditions. Initially, sensor calibration is performed in laboratory settings, measuring lifetime signals from several individual sensors from a batch at different O₂ concentrations and temperatures. For general food packaging applications, sensors should normally show stable and reproducible calibrations in the concentration range 0-25 kPa (0-100 kPa for raw red meat). Most of the solid-state sensors showed dependence on the temperature and sensitivity usually decreases at low temperature, which should be factored in to ensure accurate O₂ readings over a wide temperature range (~-20° C to +30°C for food). Unfortunately, only a few studies have been performed over this temperature range (Papkovsky, et al., 2000). Sensor response time is another critical factor. Use of thin film coatings, microporous membranes with low gas

diffusion barrier and fast response time are generally desired, especially for on-line monitoring of packaging integrity for a large number of samples (Douglas & Eaton, 2002; Kolle, et al., 1997). High photostability and long storage and shelf-life stability are other important parameters.

2.6. Measurement Instrumentation and Commercial Systems

Several companies currently produce optical O₂ sensors and measurement instruments for different industrial applications. Not all of these are usable in core packaging applications, which demand a number of special requirements for the sensors, instrument and measurement mode(s). The main requirements for food packaging applications are:

1) Robust operation with detached O₂ sensors. This feature, in turn, implies: i) insensitivity to geometrical alignment of the sensor and the instrument during the measurement; ii) insensitivity to attenuation of the luminescence intensity signal from the sensor by the packaging material and food matrix (sensor staining, sample autofluorescence, light absorption and scattering); iii) ability to measure optical signals at a certain (variable) distance (usually 0–15 mm) by hand; iv) ability to measure sensors in packages of variable size and shape, irregular geometry.

2) Use of disposable sensors with large number of test samples under different conditions. This implies: i) adequate sensitivity and range of O₂ concentrations: typically 0.03 – 25 kPa (0.03-25% O₂ at normal pressure) or preferably 0.01-100 kPa; ii) calibration-free measurements (factory or batch-calibration, stable to the factors listed in 1); iii) high reproducibility with a typical variation across the whole O₂ range of ± 2 -3% of reading or 150 ppm in the low O₂ range; iv) rapid (<1 min) and robust changes in sensor signal in response to changes in sample O₂ concentration.

3) Broad range of working temperatures (-20°C - +50°C for the sensors and 0-50°C for the instrument). This necessitates automatic compensation of luminescence measurements for variation of sample temperature (by means of a contactless IR T-sensor built in the instrument), and barometric pressure (for flexible packages and readout in % O₂ scale). No cross-sensitivity to humidity (identical calibration in gas and liquid phase), no interference by other species that may be present in samples being measured.

4) Light-weight, portable device - handheld reader, with user-friendly design and software, external data communication and on-site performance validation tools (reference sensors). Fast measurement and signal processing (<1s per reading), data logging and ID tagging (e.g. bar-coding). Affordable price: \$1-2k for an instrument (currently \$4k–\$10k) and <10 cent for a disposable sensor (currently >\$1).

5) High level of validation of the sensors and measurement device with different types of packaging materials and packaged products tested and independently verified. High safety of the sensor material, its ingredients and processes involved. High storage and operational stability (months-years).

Currently, several commercial systems on the market a large degree fulfil these requirements and are suitable for robust O₂ monitoring in food packaging. Their main characteristics are summarised in Table 2. Examples of O₂ sensors and measurement instruments are shown in Figures 2 and 3.

Table 2 Examples of commercial O₂ sensor systems

Company	Mocon Inc & Luxcel Ltd.	Oxysense	PreSens GmbH
Sensor	OpTech™-O ₂ Platinum	O ₂ xydots®	Pst3
Dyes	PtTBP	[Ru(dpp) ₃]Cl ₂	PtTFPP
Forms	Adhesive stickers (peelable from a card)	Sensor dots applied with silicon glue	Sensor dots applied with silicon glue
Measuring range	0.001- 30% permeation mode (g) 0.015%-25% headspace mode (g) (0.006-10.5 mg/L (l))	0-30%	0-100% (g) (0-45 mg/L (l))
Accuracy	± 2% or ± 150 ppm (whichever is greatest)	5% of reading	± 0.4 % @ 20.9 % O ₂ ± 0.05 % @ 0.2 % O ₂
Detection limit	0.03 % (0.03 kPa)	0.03 % (gas) 15 ppm (liquid)	0.03% (gas) 15 ppm (liquid)
Compensation	Automatic temperature (contactless IR sensor) and pressure compensation	Integrated temperature and pressure probes	Integrated temperature, and pressure probes
Operating temperature	5-40°C	0°C - 70°C	0-50°C
Response time	< 3 sec (gas) <30 sec (liquid)	< 30 sec	<6 sec (gas) <40 sec (liquid)
Price per sensor	\$3	\$4.30	\$33

Figure 2. Images of various types of O₂ sensors: A) Presens Sensor spots; B) Oxysense sensor spots glued to the bottle; C) Mocon Optech®-O₂ Platinum adhesive stickers on a card and CalCard for system validation, D) sheet of extruded sensor film, E) Mocon needle-type and ImPULSE™ sensors for Optech®. A, B and E are reproduced from manufacturer's website. D is reproduced from (Mills & Graham, 2013), with permission from Royal Society of Chemistry.

Figure 3. Images of O₂ sensing instrumentation: A) One of the first prototypes - fibre-optic phosphorescence phase detector; B) PreSens' Fibox 4; C) OxySense Oxygen analyser; D) Mocon OpTech™ handheld reader. B-D are reproduced with permission from the manufacturers.

Several other sensor modifications are also offered by these companies. Thus, PreSens provides Pst6 sensors for trace O₂ analysis, as well as the dipping fibre optic probe for use in fermentors. The free-standing dOxybead™ sensors developed by Luxcel are simply dispensed in packs, food samples and beverage bottles, their characteristics are similar to Mocon sensors (Table 2).

The needle-type sensors (PreSens, Mocon, OxySense) and ImPulse™ sensor pins (Mocon) are designed for destructive measurements. Although less advantageous, this could be the only option for non-transparent packages, such as metal-coated or pigmented film packaging, paper cartons. These sensors are usually used for end-point O₂ measurements when package integrity is no longer important, however special rubber septa for the needle probe or adhesive coating on ImPulse™ sensors allow repetitive measurements, although not over long time periods.

Some sensors require quick re-calibration before use to ensure their accuracy, others are supplied pre-calibrated in batches. PreSens recommend a two point calibration with 0 kPa and 21 kPa O₂ gas mixtures for their sensors (Ps3 and others). OxySense O₂xydot® sensors come with factory calibration, however the user may need to carry out re-calibrations at various conditions, if deemed necessary. The OpTech™ sensors come factory-calibrated. Very often sensor characteristics specified on company web site relate to pre-calibrated sensors or one batch of sensors rather than for different batches. In this case, sensor type has to be specified and its calibration parameters loaded in the instrument software. In our experience to date, Mocon sensors provide best reproducibility for disposable sensors, with

sensor-to-sensor and batch-to-batch variability of <2%. High reproducibility of sensors also allow Mocon to offer “CalCardTM” for validation of the sensor stickers and instrument performance on-site, and simple re-calibration of the system with complex samples such as non-transparent packs or highly absorbing samples or vessels.

Temperature compensation is also realised differently - by independent measurement of temperature and subsequent manual compensation of readings in the software, with a contact T-probe connected to the instrument or by contactless measurement of local temperature at the sensor with a built-in infrared T-sensor. The latter approach is the most accurate, it allows automatic compensation and processing large number of samples which have significant variation in temperature (e.g. refrigerated samples measured at ambient temperature).

Barometric sensors built into the instrument allow compensation of optical readings for variation of atmospheric pressure. This enables conversion of primary O₂ readings (sensor normally measures kPa or μ M of O₂) into % O₂, which more common for food industry. Measurement of % O₂ in pressurised containers (wine bottles) still remains challenging.

Easy incorporation of the sensors into food packaging is a must. Pst3 and Oxydot[®] sensors must be adhered to the packaging with silicone glue, which can often be pernickety and adds to experimental set-up time. In contrast, OpTechTM sensors come as self-adhesive stickers on a card, which are easy to handle and attach. The adaptability of O₂ sensors and flexible handheld instrumentation allow their use in various applications, including monitoring O₂ during processing, transportation and storage. Although useful and fit-for-purpose, the above sensors still have the drawback of being quite expensive, limiting their inclusion and use in mass scale manufacturing. To be viable for routine packaging applications, each sensor must cost less than 10 cent (Mills, 2005).

To address these challenges, many studies are carried out to create less expensive O₂ sensor solutions. We believe that this can be realised on the basis of existing phosphorescent dyes, O₂-sensing materials, fabrication processes, integration approaches and reading equipment. High demand in non-destructive O₂ sensing and packaging applications may also lead to the creation of entirely new O₂ sensor materials and systems.

3. Applications of O₂ Sensors in Food Packaging

3.1. Monitoring residual (headspace) O₂ in packaged foods

The proof of concept work on the non-destructive luminescence based O₂ sensing in food packaging was done in 2000s. Prior to the appearance of commercial O₂ sensor systems such as Fibox (PreSens), Oxygen analyser (OxySense) and OptechTM (Mocon), more primitive though well performing O₂ sensors and instruments (phosphorescence phase detector – see Figure. 3 (Ogurtsov & Papkovsky, 1998)) were mainly used.

Initially, sensors comprised of phosphorescent PtOEPK dye dissolved in polystyrene and spotted on polymeric membrane or filter paper were used to track O₂ levels in vacuum packed chicken meat (Papkovsky, et al., 2000) and in MAP chicken, beef and ham samples (Papkovsky, et al., 2002; Smiddy, et al., 2002). In both the vacuum and MA packaged samples, when the sensors were placed on top, in direct contact with the product, reliable optical signals and quantitative measurements of O₂ were obtained for the food samples they

were exposed to. However, for vacuum packaged samples the sensor was seen to provide inadequate information about global O₂ levels and package integrity, because in such shrunken packs without any headspace, diffusion of O₂ laterally and from the bulk of the product is largely reduced. As a result, unless some air was able to enter and swell the pack, the sensor could not detect compromised integrity (cuts or punctures in packaging materials at distant sites from the sensor, >1 cm). Therefore, wider use of O₂ sensor dots in vacuum packaged products as a QA tool was hardly justifiable.

In contrast, for MAP products the use of disposable O₂ sensors in individual packs was found to be very useful and informative. The sensors placed on top of the food or underneath the lidding and exposed to package headspace were able to: i) quickly scan for residual O₂ levels medium and large batches (10s - 100s of packs, each measured in 1-5 s); ii) reliably quantify actual O₂ concentration in each pack, determine mean values and variability within the batch; iii) detect outliers and faulty packs with headspace O₂ exceeding predicted values for this product; iv) monitor dynamics of headspace O₂ concentration over product shelf life; v) pick up the appearance of new faulty packs by repetitive measurements (Figure 4); vi) assure general compliance (or not) to product specifications of each pack, whole tested batch and corresponding products and manufacturing processes used.

Figure 4. Representative results of screening of a batch of MAP food product with disposable O₂ sensors (top) and changes in headspace O₂ in MAP ham packs over storage at 4°C (bottom).

This sensing approach was subsequently applied to many other MAP food types including raw and cooked meat, smoked fish, bread, convenience foods (lasagne)(Fitzgerald, et al., 2001). Samples of MAP cheddar cheese (high fat product) were also checked for integrity via Pt-OEPK sensors which revealed a number of faults in the process and packaging material and allowed their troubleshooting and optimisation (O'Mahony, et al., 2006). The need for leak checking in such products was evident, as the study found ~5% faulty packs (three out of 70). Otherwise, poor quality of packaging may lead a large amount of waste, financial losses and loss of reputation for the manufacturing companies.

These initial studies have also demonstrated the applicability of the O₂ sensors in industrial settings on production lines with commercial products (sliced MAP hams), and the need for repetitive testing of MAP packages (Papkovsky, et al., 2002). Although the products were packaged under anoxic atmosphere, residual O₂ levels in packs were significantly higher (0.1-1%) and gradually increased during storage. This is due to the factors such as O₂ trapping by the food product, exchange with headspace, permeability of the packaging materials to atmospheric O₂ and imperfect sealing. Screening showed multiple failures in packaging (1-5 bad packs in each batch) which could be easily missed using the traditional headspace analysers with random once-off destructive measurements throughout a batch. Commercially, early discovery of these failures could reduce waste and financial losses, as when the leakage is discovered the food could be repackaged without harmful effects on its quality. Thus the O₂ sensors potentially allow 100% quality control in sizeable batches of products and (where feasible and justifiable commercially) integration in each MAP pack. More thorough testing with O₂ sensors can help avoid massive product recalls.

3.2. Food research and quality assessment

After initial food packaging tests were proven successful, researchers began to use O₂ sensors to monitor and characterise various products, assess their quality, shelf-life behaviour and troubleshoot problems with packaging. Thus, OpTechTM sensors have been used to measure the depletion of O₂ in raw beef and chicken fillets (Morsy, April 2014) packaged under 21% O₂ in the headspace. The beef and chicken showed a depletion of oxygen over a 9 day and 10 day period respectively, which corresponded to the food spoilage by aerobic bacteria, which consumed the headspace O₂. PtOEPK sensors were used to chart the O₂ profile of a faulty package of cheddar cheese, showing its compromised resistance to microbial spoilage and mould growth (Figure 5A) (O'Mahony, et al., 2006).

Fresh produce, such as vegetables and salads, are highly perishable and 'breathable' products. Since these products are alive and respiring after harvesting, they require quick processing, customised packaging and storage (Borchert, et al., 2012) in order to maintain acceptable quality and shelf life. A specific O₂ content in MAP and perforation of the lidding are required for the respiration to occur and to maintain low enough O₂ levels that discourage the growth of microorganisms. High throughput non-destructive O₂ sensing with Mocon OpTechTM system successfully addressed these issues and accelerated the development of improved packaged products (Hempel Andreas, et al., 2013). It provided accurate and reliable checking of O₂ levels within packaged fresh salad leaves and generation of respiration

profiles (Figure. 5B). Different lettuce types showed different respiration and O₂ requirements in MAP to achieve a shelf-life of seven days.

PtOEPK sensors were used during the testing of different ethanol based atmosphere modifiers on MAP bread (Hempel AW, et al., 2013). The purpose was to prolong shelf life of commercial ciabatta bread without compromising palatability. The sensors showed that although the products were packaged with an O₂-free atmosphere, their O₂ levels rose to approximately 14% as a result of the diffusion of O₂ stored in the bread structure. This encouraged the growth of mould, seen by day 12 of storage. The use of ethanol spray offset the physical appearance of mould, but only for one day and also imparting a disagreeable flavour to the product. In contrast, the ethanol-emitting LDPE sachet delayed mould growth onset up until day 30 of storage, without imparting undesirable aromas and flavours onto the product. This study with O₂ sensors showed promise of ethanol emitters for the prolongation of shelf-life.

Colour, taste and aroma are important parameters on which food is evaluated by producers and consumers. Residual O₂ can have a major effect on these parameters and the quality of the finished product. Therefore, the monitoring of O₂ and correlation with the degradative processes occurring in foods is vital in predicting shelf-life and ensuring quality aspects. In a study on the lipid oxidation, samples of raw and cooked vacuum-packaged and MAP beef were assessed with O₂ sensors (Smiddy, et al., 2002). Figure 5C-D show that vacuum-packed raw and cooked meats were stable to oxidation until day 35, while MAP meat which had a higher level of O₂, had an oxidative stability of 12 days. The oxidation in the MAP cooked beef was slightly lower than that in the vacuum-packed cooked beef, implying that although some O₂ is needed for lipid oxidation, it is not the driving factor. The cooked meats showed higher lipid oxidation than the raw meat, showing that high temperatures drive the oxidation procedure. Thus, efforts must be made to limit O₂ exposure in the period between cooking and packaging.

Figure 5. Representative O₂ profiles: A) an improperly packaged cheese sample (arrow shows appearance of mould), B) mean O₂ levels ($n = 12$) in commercial packages with salad leaves, C) and D) O₂ content and lipid oxidation in raw vacuum packed meat and cooked vacuum packed meat respectively. (□) represents the % of O₂ and (●) - lipid oxidation in mg MDA/kg meat. A) Reproduced from (O'Mahony, et al., 2006) with permission from Elsevier B) from (Hempel Andreas, et al., 2013) with permission from MDPI. C and D Reproduced from (Smiddy, et al., 2002) with permission from Elsevier.

Packaging of food products under MAP conditions with right composition of O₂ and CO₂ gases in combination with refrigeration temperature appears an efficient approach to decrease microbial contamination and preserve the quality of food products. Recent studies have suggested (Amanatidou, Smid, & Gorris, 1999; Van der Steen, et al., 2002), MAP should have elevated levels of O₂ (>70%) and CO₂ (10-20%) to reduce the growth of spoilage microorganisms, prevent various anoxic processes and maintain the natural freshness, taste and appearance of green produce (salads, vegetable or fresh cut fruits). In this context, parallel analysis of headspace O₂ and microbial load in MAP products can provide valuable information. This was demonstrated by the combined use of OptechTM O₂ sensor system for non-destructive headspace O₂ measurement and GreenLight® system (Mocon-Luxcel, also based on the optical O₂ transducer) for rapid determination microbial load in the various ready-to-eat MAP salad samples (Borchert, et al., 2012). The GreenLight test provided monitoring of microbial load over the period of storage by destructive sampling, which is a convenient replacement to the tedious agar plating technique (ISO4833:2003). The combined use of OptechTM and GreenLightTM O₂ sensor technologies provide a versatile platform for high throughput assessment of microbial safety and quality of food products, optimisation of packaging and shelf-life studies of MAP products.

3.3. O₂ sensing in liquid products and beverages

As well as controlling some chemical reactions in foods, dissolved O₂ plays a key part in liquid products and beverages. In particular, many chemical reactions occur during maturation of red wine and O₂ has either beneficial or negative effect on final wine characteristics. Therefore, O₂ content in the wine must be controlled and optimized. In a

proof of concept study, PtTBP based sensors were applied to green and brown coloured wine bottles to detect O₂ leaks (Müller, et al., 2015), which showed that they can monitor integrity of capped bottles and track the ingress of O₂ via their closures.

Many wine-makers are adding O₂ in a controlled manner in order to optimize the maturation. The influence of different O₂ exposures on the evolution of volatile sulphur compounds (VSCs), including H₂S, methyl mercaptan (MeSH) and ethyl mercaptan (EtSH), during maturation of Shiraz Red wines was investigated with the aim to control O₂ procedures and the development of VSC in the wines (Ugliano, et al., 2012). In another study, the bottles were fitted with two Pst3 sensors to measure dissolved and headspace O₂. It showed that O₂ had a direct effect on the H₂S and MeSH levels, which in turn affected the odour of the wine. This data revealed a relationship between O₂ levels and accumulation of VSCs.

To combat oxidative degradation ascorbic acid is added to white wine (Wallington, et al., 2013), which has been shown to improve flavour and colour. The undesirable by-products from the ascorbic acid are usually scavenged by the sulphur dioxide present in the wine, preventing their effects on wine quality (Bradshaw, et al., 2011). If not controlled, these processes can potentially deplete sulphur dioxide which provides antimicrobial protection to the wine and extends shelf-life.

The PreSens PSt3 and PSt6 sensors were used to measure headspace and dissolved O₂, respectively, and gather kinetic data on the non-oxidative degradation of ascorbic acid. Although conditions were not pure anoxic, O₂ concentrations were maintained < 50 µg/L, i.e. below quality control capabilities of the wine industry and the limit of detection of the PSt3 sensors (V. O'Brien, 2009). The results showed that lower temperatures were more effective at inhibiting ascorbic acid degradation. Therefore, the storage and transport of wines should not expose them to elevated temperatures. Other studies with PSt3 and PSt6 sensors and the Fibox 3 were to ascertain the routes of O₂ ingress and the main chemicals reactions affecting the character of wines. If O₂ is too low, aroma defects such as dominant smell of egg, rotten vegetables accompanied by fruity undertones (Mestres, Busto, & Guasch, 2000) can occur. On the other hand, excess of O₂ can enhance oxidation and discoloration of the wine (Salmon, 2006).

PreSens optical dipping probe was also used to assess dissolved O₂ concentrations influenced by the pump-over operations during wine production (Moenne, et al., 2014). As expected the closed pump-over systems showed no increase in O₂ while for the open set-ups extra O₂ was integrated into the wine. In addition, depending on the depth at which the reading was taken, the O₂ concentrations in production vats varied greatly, which implies that uneven oxygenation during processing can lead to a heterogeneous product.

Excessive O₂ added to wine can also detrimentally change its colour (white wine can turn brown and red wine can turn an orange-red hue), and controlled oxygenation can help to control this (McRae, et al., 2015). O₂ is normally added after fermentation, however O₂ sensors were used to monitor the O₂ concentration of Shiraz wines made with rotary fermenters and treated with different oxygen levels (McRae, et al., 2015). From this data, correlations were made between higher O₂ concentrations and more stable wine colour and a

lower tannin concentration which in turn leads to lower wine astringency. Both parameters increase the desirability of wines to consumers.

Like wine, flavour and visual appearance of beer are dependent on oxidation during processing and packaging (Hempel A., et al., 2013). The lower the oxidation, the more stable the beer flavour. After fermentation, beer should be completely free of O₂, however it is most prone to oxidation at this point. Bottles are filled up to the top with carbonated beer and then capped aiming to minimise O₂ trapped in the bottles. However, the bottling process is affected by the different foam structures formed in bottle necks which trap some O₂. As shown by monitoring of O₂ in bottles of pasteurised beer with O₂ sensors, high residual O₂ levels in headspace lead to higher levels of carbonyls and development of undesirable taste during storage (Hempel A., et al., 2013). The study also showed that pasteurization caused headspace O₂ to diffuse into the product and then release back. Sensory analysis showed that beers with an initially high headspace O₂ (>1%) were deemed unacceptable by the beer tasting panel. Therefore, O₂ sensors can be used as quality check and to set up a QC tolerance level for headspace O₂ in bottled and pasteurised beer.

Packaged juices are also highly perishable and O₂ sensitive products, and their residual O₂ is an important quality factor in the production and storage. Thus, orange juice contains high amounts of ascorbic acid (AA, or vitamin C) as stabilising anti-oxidant, which is oxidized over time into L-dehydroascorbic acid which has an 5 times lower antioxidant activity (Nkhili & Brat, 2011). The residual O₂ and the permeability of the packaging have an impact on the nutritional qualities of the juice and its oxidative browning. Oxydot[®] sensors were used to link headspace O₂ levels to the degradation of AA (Van Bree, et al., 2012; Wibowo, et al., 2015), showing that DHA was formed more rapidly and at greater quantities at higher O₂ levels. Therefore, O₂ should be controlled during processing and packaging of orange juice to ensure that undue degradation does not occur.

The connection of storage temperature and lipid oxidation in rapeseed oils was examined using Oxydot[®] sensors. They showed that elevated temperatures increase O₂ consumption leading to higher levels of peroxide formation in oil stored under air headspace (Kozak & Samotyja, 2013), whereas samples stored with nitrogen headspace showed little peroxide formation. Thus, the O₂ measurement could be applied to work out optimal storage conditions for oils.

3.4. O₂ permeation measurements

In MAP systems a gradient of the gas is created between the inner compartment with food and external atmosphere (usually air). The permeation of packaging materials, even with high-barrier properties, is still significant and passes atmospheric O₂ into the product. Therefore, measurement of gas permeability of packaging materials is of critical importance for the food and packaging industry.

The O₂ permeability of films and other materials is measured on special instruments such as Mocon's Ox-Tran[®] Model 2/21 system and Oxsense's Oxysperm OTR System. In the Ox-Tran[®], films are placed in a diffusion chamber, purged with nitrogen, and then permeation of O₂ through the film from the outside of the cell (air or O₂ atmosphere) is monitored (MOCON). Although very accurate, this method is slow, has low sample

throughput and usually operates with planar unprocessed samples and in gas/gas phase system.

Introduction of disposable O₂ sensors and non-destructive contact-less optical measurements can address these shortcomings and enable an extended panel of gas permeation tests. The sensors can be adhered to almost any surface of the pack, be used to measure O₂ permeability of packaging materials which were stressed on the packaging line (whole chain of steps: thermoforming, filling, sealing, labelling/printing and mechanical handling, etc.). Flexible and versatile O₂ sensor technology allows permeation measurements in various shapes of packs, including whole composite material (e.g. trays with sealed lidding, bottles with closures, package filled with liquid or food simulant. Also gas exchange can occur between the headspace and food products (see above).

In our early study with the phase detector and PtOEPK-PS sensors, we compared O₂ permeation of commercial PE/PP yoghurt bottles having different size (Figure 6). PET carboys used in home winemaking and brewing were evaluated for O₂ permeability using a OpTechTM instrument (Gibbs, 2013). The OpTechTM stickers were adhered to the neck of each carboy and scanned regularly for O₂ content. The study affirmed the suitability of BetterBottle PET carboys for home-brewing as they allowed minimal oxygen transfer. A similar study was carried out using PreSens Fibox 3 oxygen meter and PSt6 sensors which were adhered to the glass bottle with silicone glue, and used to compare the O₂ ingress into the bottles with different Normacorc closures co-extruded from low density polyethylene over 250 days (Diéval, Vidal, & Aagaard, 2011). For comparison, the bottle necks were cut, corked and permeability was measured by the Mocon Ox-Tran[®] instrument. The O₂ sensor performed well against the Ox-Trans and was shown to be a viable simple-to-use alternative for O₂ permeability measurements. The Oxyperm System has been adapted for measuring O₂ permeability of PET bottles, but the instrument is expensive and requires training to use (Oxysense).

Figure 6. O₂ ingress kinetics through plastic yoghurt bottles (top, our unpublished data) and the Classic and Premium Normacore closures (bottom, reproduced from (Diéval, et al., 2011) with permission from Wiley), measured with optical O₂ sensors.

O₂ has been shown to enter wine products by way of their closures. The effect of different types of closures and different storage conditions (i.e. glass bottles vs. stainless steel drums) on the coloration of Grénache rosé wines were studied (Wirth, et al., 2012), in which the samples were monitored with Fibox instrument and Pst3 and Pst6 sensors fitted inside the wine bottles (Ugliano, et al., 2011).

A study on the permeation levels of different multilayer packaging compositions, has led to the development of simulation software to predict the optimum headspace O₂ concentration in different packaging configurations and storage conditions (Van Bree, et al., 2010). Validation of this software was achieved with the assistance of Oxydots[®]. This software could help to eliminate some of the testing of packaging materials needed for new food products.

3.5. Validation of O₂ sensors, stability and safety in contact with food products

Despite the existence of several commercial O₂ sensor systems and significant number of studies and publications with disposable O₂ sensors, the level of their validation and benchmarking against alternative methods (also against each other) is far from being comprehensive. Mocon OpTech[™] system, which has a manufacturer's range of 0-30% oxygen was compared to the destructive headspace analyser Dansensor which has a range of

0-100% oxygen and carbon dioxide and punctures the package through a septum in order to analyse the headspace (Borchert, et al., 2012). The study showed good agreement of values even up to 40% O₂, after which the OpTech™ started to show inaccurate readings. However Optech performed better in the low O₂ range showing sensitivity of 0.03% as opposed to 0.1% for the Dansensor (Dansensor).

The existing O₂ sensors are generally stable. However, very few studies have looked in detail at possible changes in sensor behaviour and calibration upon its exposure to food products of liquid samples in packs. In many cases, sensor stability, accuracy of O₂ readings, robustness in conditions of real life operation with different types of packaged foods and beverages remain open questions. This knowledge is particularly important when sensors are operating in direct physical contact with food product that may have high content of fat (plasticisation by oil), strong flavours (cross-sensitivity to gaseous quenchers), variable water content (dry/humid conditions), or long-term experiments with liquid samples. There are multiple reports that package environment and food matrix can negatively affect sensor calibration (shift or drift) and this, if not compensated, may lead to significant errors in O₂ readings (Eaton & Douglas, 2002; Kelly, et al., 2014a). Even if the sensor is protected from contact with the product by an O₂ permeable coating (e.g. PE lamination), this does not guarantee the absence of interferences, since water vapour, flavours and gaseous metabolites can still penetrate. Some examples of ‘bad’ and ‘good’ sensors are shown in Figure 8.

Figure 7. Effect of contact with food (MAP meat) on the calibration of the PtOEPK-PS sensors (top) and cross-sensitivity of a PtTBP-PP sensor to humidity (bottom). Reproduced from (Kelly, et al., 2014a) with permission from Elsevier.

Quite often operational performance and specifications of disposable O₂ sensors provided by the manufacturers, especially limits of detection, accuracy, temperature effects, potential interferences, do not match the actual values achieved in packaging applications. As stated above, these specifications often relate to sensors calibrated *in situ* by an operator, rather than to batches of factory-calibrated sensors. Head to head comparison of different types of commercial O₂ sensors and instruments with the same packaged products and conditions frequently reveals significant differences in O₂ values that they produce (our unpublished data). Some of the published data on the absolute O₂ levels in certain MAP food products and beverages can also be questioned. This situation raises concerns about accuracy and validity of measurements with such sensors. On the other hand, relative O₂ values between different conditions/products, O₂ trends and profiles measured with different O₂ sensor systems are more trustful.

The ever increasing use of disposable sensors and non-destructive O₂ measurements necessitate more rigorous testing, validation and benchmarking of the existing commercial instruments and new prototypes developed by researchers or companies. More comprehensive testing of sensor performance with different products and packaging processes and comparison of the different sensors systems with each other should be carried out more comprehensively. So far, very few such studies were conducted and published.

4. Conclusions and Outlook

The above sections illustrate the utility of photoluminescence based O₂ sensing approach for non-destructive high-throughput monitoring of quality and safety of packaged foods, efficiency of active packaging materials, systems and particular food products. Disposable O₂ sensors can provide robust response, fast and reliable measurement of dissolved and gaseous O₂ level in a reversible, non-destructive, real-time manner and repetitively. They have been used with many different types of packaged foods and beverages, packaging materials and conditions. Existing O₂ sensors have proven themselves as very useful and powerful tools for food quality and safety assurance, throughout the whole production, processing and distribution chain. They are actively used in food research and packaging, new product development and troubleshooting, in quality control tasks.

Food packaging with its huge market size (millions and billions of packs) has long been seen as the holy grail for O₂ sensors, with potential to incorporate sensor in every commercial MAP pack. Unfortunately this has not materialised yet. Over the last decade, the O₂ sensor technology has become mature, disposable calibration-free sensors are now produced commercially and their usage in food industry went up from dozens to hundreds (maybe thousands) per trial. However, this is far away from the anticipated scale (many millions). Sensors are still considered as useful research tools rather than necessity which can improve food safety and quality and attract new customers.

The main challenges here are very low profit margins in the food industry (every cent is counted) and the diversity of packaged products, for many of which packaging materials and sensor materials should be individually tailored. This is augmented by a significant disconnect between the packaging companies, who are expected to incorporate O₂ sensors in their packaging materials, and food processing companies who can use such 'smart' materials with their products. The former have to take the risk and invest heavily in sensor technology, while the latter - provide technical specifications, clear economic justification and solid commitment to use these smart materials on a large scale. The latter step implies a large (several orders of magnitude) spike in the number of sensors produced and used by the industry.

The high costs of existing sensors, relative complexity, general lack of flexibility and integration options make most of them unsuitable and unaffordable for large scale use in the food industry. Several critical issues need to be addressed. To be commercially viable, the disposable sensors should cost <10 cents (current cost >\$1), analytical performance, robustness and flexibility should further improve. The sensor materials should be made more compatible with the industrial packaging systems and facilitate integration of *discrete* O₂ sensors in individual packs, which measurement instrumentation should become more convenient and less expensive. When developing new and improved O₂ sensors, interactions between the sensor and food components, stability, cross-sensitivity, safety and ethical aspects should be assessed comprehensively. We anticipate that advanced sensor systems for packaging applications which embed these features will emerge in the near future.

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6. References

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