Trends in Food Science & Technology 50 (2016) 85–102

Contents lists available at ScienceDirect

Trends in Food Science & Technology

journal homepage: http://www.journals.elsevier.com/trends-in-food-science-and-technology

Review

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

Swagata Banerjee [a, 1], Caroline Kelly [a, 1], Joseph P. Kerry [b], Dmitri B. Papkovsky [a, *]

[a] School of Biochemistry and Cell Biology, University College Cork, Cavanagh Pharmacy Building, College Road, Cork, Ireland
[b] School of Nutrition and Food Science, University College Cork, Cavanagh Pharmacy Building, College Road, Cork, Ireland

ARTICLE INFO

Article history:
Received 24 September 2015
Received in revised form
20 January 2016
Accepted 28 January 2016
Available online 1 February 2016

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

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 (O_2) are important tools for monitoring of packaged products, new product development and optimisation. They allow fast, reversible, real-time and quantitative monitoring of residual O_2 levels in a non-destructive manner, being superior over alternative systems. In this review, we describe the main types of phosphorescent O_2-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 O_2 in various types of packaged foods and beverages. We also compare commercial O_2 sensing instrumentation and disposable O_2 sensors currently in use.

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, CO_2 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, Miltz, Sonneveld, & Bigger, 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 (N_2, CO_2, O_2) 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 O_2 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 O_2 analysis involves rather expensive analytical instruments like GC, electrochemical sensors (Clark-type O_2 electrode) (Clark, Wolf, Granger, & Taylor, 1953), O_2/CO_2 gas

* Corresponding author.
E-mail address: d.papkovsky@ucc.ie (D.B. Papkovsky).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.tifs.2016.01.021
0924-2244/

analysers (e.g. Dansensor™ (Dansensor A/S)), 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 O_2 sensors is also influenced by gas flow rate, stirring rate, operational temperature, poisoning by other gases (H_2S) and fouling of membranes (Trettnak, Gruber, Reininger, & Klimant, 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, Errico, Gentile, & Volpe, 2011, chap. 53; 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 O_2, 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, 1992; Lawrie, Mills, & Hazafy, 2013; Smolander, Hurme, & Ahvenainen, 1997). The redox indicator can provide qualitative or semi-quantitative information about the O_2 level through oxidation of the dye. Ageless Eye™, one of the commonly used indicators, produced by Mitsubishi Co to check integrity of food packages(Mitsubishi Gas Chemical Company Inc.), is based on the change in colour of methylene blue dye from colourless in the reduced form at $[O_2] \leq 0.1\%$ to blue oxidised form in the presence of O_2 ($\geq$0.5%). The indicator ink, represents irreversible O_2 response (activated by UV light), can be printed on various surfaces. However, its high sensitivity often results in colour change at low O_2 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 H_2S (Smolander et al., 2002), volatile biogenic amines (Kaniou, Samouris, Mouratidou, Eleftheriadou, & Zantopoulos, 2001; Loughran & Diamond, 2000; Rokka, Eerola, Smolander, Alakomi, & Ahvenainen, 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 (3 m), enzymatic (Vitsab International AB) or polymerisation (Temptime Corporation) 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, Narsaiah, Grewal, & Anurag, 2015). RFIDs can be combined with other indicators such as TTIs or sensors and provide real time information in a contactless 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, Kim, Puligundla, & Ko, 2014). Residual O_2 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 O_2 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 O_2 sensors rely on the principle of quenching of luminescence intensity and lifetime of an oxygen-sensitive dye embedded in a polymeric matrix by sample O_2. 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 O_2 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 O_2 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. O_2 sensing by photoluminescence quenching

O_2 sensing using photoluminescent dyes rely on the collisional quenching of an electronically excited dye molecule by O_2 molecules (Fig. 1A) (Lakowicz, 2006). The long-lived emission of phosphorescent dye molecules allows deactivation of their excited state through collisional interactions with O_2 molecules, which decreases the emission intensity and lifetime in a concentration dependent manner. Ground state O_2 molecules (paramagnetic; triplet configuration, $^3O_2$) can accept energy from the excited triplet state of the chromophore, thereby deactivating the chromophore and forming singlet oxygen ($^1O_2$). The short-lived $^1O_2$ usually reverts back to ground state O_2; it can also react with surrounding chemical groups causing photo-oxidation.

2.1. Detection formats

Luminescence spectroscopy allows quantitative monitoring of O_2 concentrations through optical parameters of the sensors. The principal detection formats are measurement of the luminescence intensity (I) and luminescence lifetime (τ) of the O_2 sensitive dye. The theoretical relationship between intensity/lifetime and the concentration of O_2, in the case of purely collisional quenching, can be described by Stern–Volmer equation (Eq. (1)) (Lakowicz, 2006),

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

$$[O_2] = (I_0/I - 1)/K_{SV} \quad \text{or} \quad [O_2] = (\tau_0/\tau - 1)/K_{SV} \quad (2)$$

where I_0 and I, τ_0 and τ are the luminescence intensities and lifetimes in the absence and in the presence of O_2, respectively; k_q is the bimolecular quenching rate constant, which gives a measure of the quenching efficiency or accessibility of the chromophore to O_2; K_{sv} is the Stern–Volmer constant. Classical relationship between luminescent parameters and O_2 concentration (i.e. calibration) and its linearization in Stern–Volmer plots are shown in Fig. 1B–C.