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RECENT ADVANCES ON INTELLIGENT PACKAGING AS TOOLS TO REDUCE FOOD WASTE

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ABSTRACT

Food waste is one of the main issues for international organisms. It is not only an ethical and economic issue but it also depletes the environment of limited natural resources. Among strategies suitable for fighting such challenge, intelligent packaging is an interesting tool to reduce waste derived from households and retailers. A revision of 45 recent advances in the area of optical systems for freshness monitoring is reported herein. The study covers fruits, vegetables, fish products and meat since they are the most representative fields of application. Furthermore, a discussion about the main research challenges and opportunities that will be faced by intelligent packaging in the coming years is included.

Keywords: food freshness, intelligent packaging, optoelectronic nose, chromogenic array

1. INTRODUCTION

Food waste is one of the main issues for international organisation such as FAO and the interest is growing in most of the countries, in particular in industrialized ones. Wasting food is not only an ethical and economic issue but it also depletes the environment of limited natural resources (i.e. water, energy, chemical substances and materials). This topic is expected gain attention in the coming years since the world population is projected to increase by almost one billion people within the next decade to reach 9.6 billion by 2050 (Alexandratos & Bruinsma, 2012). Such population will not only demand further calories, but also is expected that the consumption of animal protein will growth as the middle class increases. This kind of food is much more perishable than cereals and demands more resources in order to generate an equivalent number of calories.

According to FAO 1.3 billion tonnes of food are being wasted annually (FAO, SAVE FOOD initiative). In the UE and USA food waste reaches 88 million tonnes (FUSION, 2016) and 133 billion pounds (USDA's Economic Research Service) respectively, with percentages between 20 y 40% of global production. Similar percentages can be found in developing countries. The percentage of waste is strongly dependent of the kind of food with values from 20% for beef meat to 35% for fishery products or 45% for fruits and vegetables (FAO, SAVE FOOD initiative). However, the part of the value chain responsible for main losses depends on each country. While in industrialized countries the sectors contributing the most to food waste are households, in developing countries most of the waste is generated during the production and processing steps (FUSION, 2016; FAO, SAVE FOOD initiative).

Although all actors in the food chain have a role to play in preventing and reducing food waste, from producers and processors of food to retailers and consumers, the relevance of household waste suggest that advances in packaging can be an essential tool to reduce food waste. Packaging has become an essential technology to ensure safety in the food chain, avoid undesired reactions, satisfy consumer expectations and increase food shelf-live. Yet, despite major developments in packaging materials and systems, the fundamental principles of packaging products remain the same. Among the tendencies, active packaging and intelligent packaging systems offer a huge potential to reduce food wastes.

The FREEDONIA group (2015) in its report about active & intelligent packaging forecasts an expansion of the demand for active or intelligent packaging in the US of 7.3 percent annually to $4.0 billion in 2019. Intelligent packaging demand will see the faster growth, advancing at a double-digit rate and reaching $1.5 billion in 2019 as products such as time-temperature indicators and smart labels and tags become more common. Moreover, FOODDRINK EUROPE, that represents the European food and drink industry has included, in the 2016 Strategic Research and Innovation Agenda of Food for Life (the food industry European Technology Platform), the recommendation to research in smart intelligent/communicative packaging solutions to reduce cold/frozen chain use for fresh foods, which would consequently reduce energy consumption, carbon emissions, preservatives intake and food waste.

One main issue related with the use of chemical substances that could be in contact with food is regulation. Normative in this topic is a complex issue and, in general, the legislators are very conservative to preserve food safety and health of the consumers. Currently, in the European Union there is no specific regulation regarding which dyes can become in contact with foods. However, this issue is treated partially in other regulations. In absence of European directives, guidelines defined by national or regional entities or certain reference organisms or associations must be followed. Regarding European regulations we can cite regulation EU No 10/2011 about plastics, that includes definitions about authorized substances and migration limits or the EU No 1935/2004 on materials and articles intended to come into contact with food. Also are of relevance the European Parliament and Council Directive 94/36/EC of 30 June 1994 on colours for use in foodstuffs which include a lists of authorized substances that could be used as indicators in arrays or other smart sensors. Other regulations include Council of Europe resolutions ResAp(2004) 1 and ResAP (96)2 on coatings, the Code of Practice for Coated Articles Where the Food Contact Layer Is a Coating of the European Council of the Paint, Printing Ink and Artists' Colours Industry, or the 2011 Inventory List of the European Printing Ink Association. Thus, it is of great importance that substances present in intelligent packaging are part of the positive lists and in its absence, that the application system (i.e. with diverse coatings) guarantees that there is no contact nor migration of the substances to the food over the limits. It is also important that the substances used do not induce changes in flavour or appearance of the food.

Due to their novelty and specificity, relevant regulation at European level can be found at the regulation EC/450/2009 about active and intelligent materials. According to EC/450/2009, intelligent materials and articles means materials and articles which monitor the condition of packaged food or the environment surrounding the food. Intelligent packaging systems are those that possess enhanced function with respect to communication and marketing functions, such as to provide dynamic feedback to the consumer on the actual quality of the product. The indicator can interact with internal (food components and metabolites in the headspace) and/or external factors (environmental). As a result of this interaction, the indicator generates a response (i.e., colour change, electrical signal) that correlate with the state of the food product. The information generated is not only useful for communication with the consumers by informing them about safety and quality of the products, but can also be a powerful tool to reduce food waste. Currently, the static “Best Before” and “Use By” dating approach is the standard in the food industry. However, this is a generic approach that must be conservative in order to minimize the risks derived of the logistic processes, thus reducing the effective shelf-live of foods and increasing the consumer disposal. It does not inform about the particular state of every package, and proves invalid to report improper meat treatment during distribution or differences in end users handling. If we bear this particular aspect in mind, the development of "dynamic shelf-life systems" based on disposable systems capable of being incorporated into the package to offer individual easy-to-interpret information on freshness by end users may be of much importance to reduce food waste.

Advanced packaging is useful to increase the efficacy of the information transfer during the product distribution chain and in the house of the consumer through innovative communication methods such as radiofrequency identity tags, time-temperature indicators, integrity sensors, and freshness indicators. Although there are several developments of electrochemical sensors, e-tongues and e-noses for food freshness monitoring (Zou et al., 2015), in general this kind of systems are complex, need expensive instrumentation and are usually not suitable to be incorporated in packaging. Among the techniques to develop easy handling disposable systems, the use of chromogenic chemosensors is, perhaps, one of the most promising, since they are usually cheap, versatile, can be printed on the package, colour changes can be easily measured using cameras or other image capturing systems, or they may allow the naked eye detection of colour changes through transparent films. Few technologies are as advanced or as inexpensive as visual imaging.

The use of single chromogenic indicators have the advantage of their simplicity but have some limitations such as lack of specificity (offering false positives or false negatives). Additionally, the presence of certain target metabolites is not necessarily an indication of poor quality and careful correlations among concentration of metabolites and organoleptic quality and safety are necessary. The existence of false negatives is likely to dissuade producers from adopting indicators unless specific indications of actual spoilage can be guaranteed. Some others innovative chromogenic indicators are time temperature indicators (TTI) (Kerry et al., 2006), such devices show time temperature dependent change that reflect the full or partial temperature history of a food product. Operation of TTIs is based usually on a visible response to mechanical, chemical, electrochemical, enzymatic or microbiological changes. The visible response to temperature is cumulative and although some correlations can be established between temperature and freshness, it does not really provide information about biochemical processes occurring in food.

Another approach is the use of optoelectronic noses, built by an array of dyes able to offer information through suitable colour changes. Indeed, in the last few years, the use of arrays of non-specific colorimetric probes has proved a suitable approach to analyse complex systems.

The issue of intelligent packaging is of great relevance and some compilations can be found in the literature. Nevertheless, in general the topic is analysed in reviews together with other concepts about packaging or focused in a specific area i.e. meat (Kerry et al. 2006; Realini & Marcos, 2014), nanoparticles in packaging (Mihindukulasuriya & Lim, 2014; Fuertes et al., 2016) or smart packaging (Biji et al., 2015). Intelligent packaging is a very dynamic field with continuous advancements and reported reviews do not generally focus in remarking the possibilities of intelligent packaging as a tool to reduce food waste.

Based on the above issues the purpose of this review is to offer a compilation of recent advances in intelligent packaging systems, with a particular focus in the possibilities of these technologies to reduce food waste and a prospective of future research challenges.

2. MATERIAL AND METHODS

2.1 Establishment of the literature base

According to the objective of developing a structured literature review, articles were selected using Web of Science and PubMed databases. In a search for publications,key words related to the theme of indicators and freshness in food (using the search terms “indicator” AND “freshness” AND “food”) in the article title, abstract or keywords, and with the option “all years” were selected. A total of 484 results were found. Publications were excluded in which: (i) the full text was not found in English, or (ii) albeit relevant, the two themes were unrelated to each other, or (iii) the terms “freshness” or “indicator” were used with a different meaning, or not related to packaging applications. With this, the literature base was redefined with 114 publications. Finally, in line with the purpose of the present review, only recent publications were finally selected.

2.2 Classification of publications

Each publication was read and classified according to the food it was about The main reason of such classification is the diverse nature of metabolites generated during spoilage in different foods. For example, fish degrades faster than meat and the nature of the metabolites generated by protein based foods are basically different to those found in fruits. Finally, since some publications described freshness indicators but they were not tested in a particular food, a miscellaneous section has been included to host such results.

2.3 Analysis

The analysis of the publications comprised two steps. The first step consisted in the identification of the quality parameters (such as microbial growth or the presence of certain metabolites) used to correlate with the colour changes. In a second step, the nature of the array was taken into account, with particular interest in dyes and supports used and their implementation in packaging.

3. ANALYSIS AND DISCUSSION

3.1 Commercial RFID, TTI and integrity indicators

Although there is a large amount of information available, documentation about smart or intelligent packaging and their commercial implementation is still reduced (see table 1) (Realini & Marcos, 2014; Fuertes et al., 2016; Mohebi & Marquez, 2015). Apart of freshness indicators, it can be found three main families of indicators for intelligent packaging: radio frequency identification (RFID) tags, time–temperature indicators (TTIs) and integrity indicators (usually gas sensors).

RFID tags use electromagnetic fields to store and communicate real-time information of the product for automatic product identification and traceability (Lee & Rahman, 2014). The tags consist of an integrated circuit built into an antenna for the transmission of information stored in the chip to a reader that permits multiple items to be monitored at the same time and to store diverse information (origin, process parameters, commercial information, etc.) In addition, RFID allows a remote control because line-of-sight is usually not required, and allow a unique identification of the product (Realini & Marcos, 2014; Kuswandi et al, 2011). Easy2log, TempTRIP, Intelligent box or Intelligent fish box (as a response to EU traceability regulations) are examples of reusable RFID systems.

TTIs are tools designed for continuously monitoring the temperature in refrigerated and frozen product along the distribution chain. As can be seen in Table 1, TTIs are today the most common systems used in packaging, since they are simple and their response do not depend on the nature of the food or the concentration of chemical substances but on temperature variations. They offer visual changes that are accelerated with increasing temperature based on physical (MonitorMark), chemical (Keep-it, Fresh-Check, OnVu, FreshCode), enzymatic (VITSAB) or microbiological processes. As can be seen in Figure 1, this kind of systems show to the consumer friendly approaches on the way that the information is displayed. It includes barcodes that disappear, labels that advance in the stick or indicators sited next to a reference to follow colour change to the naked eye.

Integrity indicators provide information about how long a packaging has been opened or give a signal proportional to the gases inside. Their use is associated with the use of modified atmospheres in packaging (MAP), that usually replaces oxygen by other gases (i.e. carbon dioxide or nitrogen) increasing the product shelf life. Commercial examples include Ageless Eye, Tell-Tab and O_2Sense (table 1), which offer diverse changes of colour upon exposition to oxygen, being able to detect to the naked eye concentrations of oxygen as low as 0.5%.

3.2 Freshness indicators

Freshness indicators monitor the quality of packed foods by reacting in one way or another to metabolites generated in the fresh food product as a result of microbial growth or metabolism (Realini & Marcos, 2014). Chemical changes occurring in food products during storage are indicators of freshness. Changes in the concentration of metabolites such as glucose, organic acids (e.g. l-lactic acid), ethanol, carbon dioxide, biogenic amines, volatile nitrogen compounds or sulphur derivatives during storage indicate microbial growth and therefore open the possibility of using their presence as freshness indicators (Arvanitoyannis & Stratakos, 2012). Smart packaging with systems that monitor food freshness through the detection of these metabolites has been described, however in most cases successful commercialization is still rare. Table 1 contains some examples of commercial sticks for fish and poultry.

SensorQ™ was a pH-sensing technology based on anthocyanines able to inform about the formation of biogenic amines from microbiological origin in packed meat and poultry (figure 2a) (DSM, 2007). However this freshness indicator did not achieve a successful commercialization (Fuertes et al., 2016). Additionally, the authors in (Morsy et al. 2016) developed a new colorimetric sensor for monitoring the deterioration of fish meat. Also for poultry, Raflatac is a freshness indicator based on a nanolayer of silver that reacts with hydrogen sulphide, a breakdown product of cysteine. The indicator is opaque light brown at the moment of packaging, but as silver sulphide is formed the colour of the layer is converted to transparent (figure 2b) (Smolander, 2008).

The following three examples are also commercial products currently discontinued. FreshTag® was a colorimetric indicator that informed about the formation of volatile amines in fish products (Kerry, 2014). Toxin Guard™, was based on the incorporation of antibodies into plastic films (figure 2c) (Yam et al., 2005). Finally, Food Sentinel System™ was a biosensor developed to detect food pathogens with a specific-pathogen antibody attached to a membrane forming part of a barcode (Goldsmith et al., 1999). The presence of contaminating bacteria caused the formation of a localized dark bar, rendering the barcode unreadable upon scanning (figure 2d) (Yam et al., 2005).

Apart of naked eye detection, imaging techniques offer particular advantages in non-destructive detection of food quality and safety. This technology is based on the use of colorimetric sensor array to obtain an "odour" fingerprint (Chen et al, 2013). Most of the published results are focused in the monitoring of species in the packaging headspace and food spoilage of perishable and high value products such as vegetables and fruits, meat and fish.

3.2.1 Fruits and vegetables

Among the applications of optoelectronic noses, studies applied to fruits and vegetables have shown that this can be an effective non-destructive technology for sensing spoilage processes. As can be seen in table 2, the number of studies in this filed of application is still reduced in comparison with muscle food, but a growth can be expected in the following years. For example, Hong & Park have developed several sensors to monitor quality of Kimchi, which is a traditional fermented vegetable food and one of the most popular side dishes in Korea. In a first work (Hong & Park, 1999), a colour indicator film consisting of polypropylene resin (using $Ca(OH)_2$ as a CO_2 absorbent) was impregnated with two indicators (i.e. bromocresol purple and methyl red) attached to the lid of kimchi packed in MAP. During kimchi fermentation at different temperatures, pH lowers from 5.8 to 3.5 and titrable acidity increases from 0.25% to 1.1%. These values were correlated with Hunter colour values of the indicators. Colour of the dyes turned from blue to light green (bromocresol purple) and from light orange to red (methyl red). Thus, colour changes of the indicators represented the extent of ripeness of packaged kimchi products.

In a second work (Hong, 2002), a sensing ink was printed on nylon films and the resulting nylon layer was laminated with white-coloured low-density polyethylene to form a double-layered structure with gravure-printed colour indicators. Films contained bromocresol purple and methyl red as chemical dyes.

Nopwinyuwong et al. (2010) described a colorimetric mixed pH dye-based on-package indicator that responds through visible colour changes to carbon dioxide (CO_2) as a spoilage metabolite in trials on golden drop, a typical intermediate-moisture Thai dessert. The label was obtained by casting indicator coating onto nylon/LLDPE film where the indicator solution was an ethanol solution prepared by mixing bromothymol blue and methyl red. Changes in colour in the label from bright light green to orange-red correlate with microbial growth patterns in dessert samples, thus enabling real-time monitoring of spoilage (figure 3).

A system to monitor guava (*Psidium guajava L.*) freshness was developed by Kuswandi et al. (2013) based on bromophenol blue. The dye was immobilized onto a cellulose membrane by absorption, and changes from blue to green were observed when the pH decreased as consequence of the over-ripping of guava due to the production of volatile organic compounds. This indicator could be used to determine the freshness of the guava at ambient temperature (28–30 °C). Another work (Kuswandi et al., 2014) described a naked-eye ethanol biosensor based on alcohol oxidase (AOX) immobilised onto a polyaniline (PANI) film that was used for halal verification of fermented beverages. Changes from green to blue were due to the enzymatic reaction of AOX with ethanol, which produces hydrogen peroxide and acetaldehyde.

Silver-based yellow-coloured colloidal nanoparticle (AgY) was proposed by *Sachdev et al.* (2016) as visual sensor for organo-sulfur compounds released in onions spoilage. The visual changes were monitored along ten days, and the original yellow colour of the AgY colloidal solution changed with time to orange, pink and finally colourless.

3.2.2 Fish products

Due to the interest of the fishery industry to develop rapid methods to evaluate real-time freshness of fish and seafood products, several studies have been focused on the development of “smart packaging” in recent years able to monitor microbial breakdown products in the headspace of packaged fish (table 3). When spoiled, fish releases a variety of basic volatile metabolites, which are detectable with appropriate indicating sensors.

In this field, Pacquit et al. (2007) presented a fast and sensitive detection of spoilage compounds in fish by a non-invasive colorimetric method. The sensor response was found to correlate with bacterial growth patterns in cod and whiting fish samples thus enabling real-time monitoring of spoilage. Sensors were prepared by entrapping within a polymer matrix a pH sensitive dye (Bromocresol green) that responds, through visible colour changes (from yellow to blue) to spoilage volatile compounds (Figure 4a).

An alternative method for detection of fish freshness was proposed by Kuswandi et al. (2012). The authors used a novel colorimetric method based on a PANI film as a chemical sensor for real-time monitoring of microbial breakdown products in the headspace of packaged fish. PANI films responded through visible colour changes (from green to blue) to a variety of basic volatile amines released during fish spoilage (Kuswandi et al. 2012). Moreover, trials on milkfish sample (Chanos chanos) verified that the response of the PANI films also correlated well with microbial growth patterns in fish samples (figure 4d).

Sun et al. (2015), developed a method to improve the sensitivity of the pH indicator bromophenol blue through adding certain amounts of organic acid or alkali to the indicator solution in order to adjust the pH to the colour transition point. With the aim of inspecting whether the sensitivity of the indicator was enhanced after regulating the pH, the authors used the sensor to detect $C_2H_8N_2$ and HCl gases. Besides, a colorimetric sensor array consisting of two indicators (cresol red and metanil yellow), in their respective original and pH-adjusted to the colour transition point forms, was set up to determine fish freshness of Spanish mackerel, through the detection of the volatile organic chemicals (VOCs) released from the rotten fish muscle.

Following the optoelectronic nose patented by Suslick et al. (2000) in which pH indicators and metalloporphyrins are used for the detection of volatile organic compounds, Huang et al. (2011) designed a colorimetric sensor array by printing nine selected dyes (three pH sensitive - bromocresol green, bromocresol purple, and cresol red- and six metalloporphyrins) on a reverse phase silica gel plate to detect volatile compounds typically occurring during fish spoilage (i.e. fish of chub -Figure 4c).

In another work (Zaragoza et al., 2013), an array prepared using five indicators containing pH, Lewis acids and an oxidation–reduction indicators and two different inorganic supports (i.e. aluminium oxide and silica gel) giving eight sensing materials was used for the shelf-life assessment of freshness of sea bream in cold storage. The colour change of the dyes selected in the study (Resorufin, bromocresol purple, bromophenol blue, phenol red and a dinuclear complex of rhodium) were correlated with physicochemical and microbiological variations, thus demonstrating the feasibility of this system to help develop optoelectronic noses for fish freshness monitoring (figure 4b). In a further study (Zaragoza et al., 2014), a similar array based on eight sensing materials and including m-cresolsulfonphthalein was tested for monitoring Atlantic salmon (Salmo salar) spoilage. The authors found that changes in the chromogenic array were correlated with changes in TVB-N and microbial (mesophilic, psychrotrophic and H_2S-producing bacteria counts) parameters characteristics of salmon spoilage. Zaragoza et al. (2015), also developed an optoelectronic nose, which consisted of an array containing six sensing materials prepared by combining different dyes (thymol blue, bromocresol purple, bromothymol blue sodium salt, bromophenol blue and a dinuclear rhodium complex) and two inorganic supports, to evaluate the shelf-life of squid in cold storage. The array was able to discriminate between fresh squid fit for consumption and spoiled squid.

It is also possible to find optoelectronic nose systems designed to detect spoilage of both fish and meat samples (Lin et al. 2015). The authors developed a sensor in food packages of ground meat and salmon to detect the appearance of biogenic amines produced by the degrading food products. The system, based on 4-(dioctylamino)-4’-(trifluoroacetyl)azobenzene, presented distinct optical and electrochemical responses to ammonia, tetramethylammonium hydroxide, ethylamine, cadaverine and putrescine. Spin coated dye films on PET substrates proved to be feasible in a food package to detect spoilage of ground meat and salmon fish using digital camera and image processing.

Silva-Pereira et al. (2015) reported a system for pH monitoring based on Corn Starch, Chitosan and red cabbage extract. The sensor was tested in presence of fish samples and during fish spoilage, the colour changed from colourless to blue at the first steps of degradation and finally to yellow when the samples were completely spoiled.

A colorimetric sensor array of seven indicators ($CoCl_2/SiO_2$; 7-diethylamino-4’-dimethylaminoflavylium/perchlorate/κ-carrageenan; thionine/ κ –carrageenan; 5-dimethylamino-1-naphthalenesulfonic acid/hydroxypropyl cellulose (HPC); 5-dimethylamino-1-naphthalenesulfonamide/HPC; methylene blue/HPC; methylene blue/urea/hydroxyethyl cellulose) was prepared by Morsy et al. (2016) for the control of fish spoilage at room temperature for up to 24 h and at 4 °C for 9 days. The authors found a linear correlation between changes in pH, biogenic amines and other parameters with the colorimetric response of the array over time. The authors also observed that the sensitivity of the different dyes was dependent on the temperature.

3.2.3 Meat

Most colorimetric indicators used in meat have been applied in chicken and pork (table 4). For example, Chen et al. (2013) describe an optoelectronic nose composed by pH indicators and metalloporphyrins that offers good results for the analysis of chicken meat (Chen et al., 2014a; Chen et al., 2014b, Chen et al., 2016). The authors developed a system by printing chemically responsive dyes (9 metalloporphyrins and 3 pH indicators (bromocresol green, bromocresol purple, and neutral red)) on a C2 reverse silica-gel flat plate to evaluate chicken freshness. Colourful difference image, by subtracting the “initial” image from the “final” image, provided a colourful changing profile that was a characteristic fingerprint of volatile compounds in chicken samples. A similar experimental system was used by Urmila et al. (2015) to quantify TVB-N content after exposure to VOCs released from chicken breast fillets in a sealed plastic bag and stored in a refrigerator at 4 °C. In another work (Khulal et al., 2016), researchers of the same group compared for the same colorimetric sensor array the predictive performances of calibration models established by linear (PLSR) and non linear (BP-ANN, AdaBoost BPANN, and SVMR) regression models.

Rukchon et al. (2014) developed a colorimetric mixed-pH dye-based indicator for monitoring skinless chicken breast spoilage during chill storage under aerobic and MAP conditions. CO_2 was used as a spoilage metabolite correlating with microorganisms. They found a greater increase in CO_2 than TVB-N during the storage period. The package indicator contained two groups of pH-sensitive dyes, one of which was a mixture of bromothymol blue and methyl red, while the other was a mixture of bromothymol blue, bromocresol green and phenol red. Characteristics of the two groups of indicator solutions were studied, as well as their response to CO_2. Colour changes correlated well with CO_2 levels of skinless chicken breast and microbial growth patterns.

Related to chicken meat packed in MAP (30% CO_2- 70%N_2) Salinas et al. (2012), developed an array composed of 16 sensing materials using the combination of different dyes (pH indicators, Lewis acids, hydrogen-bonding derivatives, selective probes to certain analytes and natural dyes (phenol red, dimethyl yellow, malachite green, carminic acid, m-cresol purple, curcumin, phenolphthalein, litmus and a dinuclear rhodium complex among others)) with inorganic materials (UVM-7, silica and alumina). Colour changes of the array were characteristics of chicken meat ageing in MAP.

In addition, the same authors also explored the monitoring of processed food. They studied boiled marinated turkey meat (Salinas et al., 2014a) packed in MAP using an array composed of 16 sensing materials based on 13 indicators (dimethyl yellow, malachite green, metanil yellow, carminic acid, brilliant yellow, m-cresol purple, bromocresol purple, thymol blue, phenolphthalein and a dinuclear rhodium complex among others). For the detection of fresh pork sausages spoilage (Salinas et al., 2014b) packed in MAP, the authors developed an array composed of seven sensing materials prepared by the incorporation of pH indicators and chromogenic reagents (malachite green, m-cresol purple, br-cresol purple, squaraine salt and a pyrilium salt) into inorganic materials (UVM-7 and alumina). A good correlation of colour changes with mesophilic bacteria and the sensory score was found demonstrating that the system was able to monitor the sausage spoilage process.

Following with chicken samples *Chen et al.* (2016) developed an optoelectronic nose using a low-cost colorimetric sensor array printed on a C2 reverse silica-gel flat plate. The array was composed by 9 metalloporphyrins and 3 pH indicators (bromocresol green, bromocresol purple and neutral red). The array gave a specific colour fingerprint for the detection of volatile compounds from chicken during spoilage. *Kim et al*. (2016) made a study in order to develop a simple and rapid method for the evaluation of warmed-over flavour (WOF) in cooked chicken. Their method was based on a colorimetric sensor array made by mixing 2,4- dinitrophenylhydrazine (DNPH) with 9 different pH indicators (i.e. bromothymol blue, bromocresol green, bromocresol purple, neutral red, bromoxylenol blue, malachite green chloride, methyl violet, bromophenol blue and chlorophenol red). The array was sensible to pentanal, hexanal, or heptanal associated with the reheating of the meat, and the results demonstrate that the sensor array was able to predict WOF and to distinguish between the different times of samples' storage.

In pork samples, using the same methodology of Chen and collaborators (Li et al. 2014 & 2015) two studies for monitoring pork meat freshness were published. The sensor array was fabricated by printing 12 chemically responsive dyes (3 pH indicators and 9 metalloporphyrin) on a silica-gel flat plate. It was found a correlation of the presence of spoilage metabolites with colour changes of the dyes obtained by difference images before and after exposure. Differences between the studies were found in the classification model and parameter optimization in the analysis of data. In both studies the authors concluded that the method has high potential in evaluating pork freshness. Huang et al. (2014) developed an optoelectronic nose for pork freshness evaluation based on an array with four natural pigments (extracted from spinach, red radish, winter jasmine, and black rice). Colour change profiles were correlated with the total viable count (TVC) per gram of pork and with the presence of biogenic amines.

With the combination of two non-destructive sensing tools, an artificial olfaction system based on a colorimetric sensor array made by 9 metalloporphyrins and 3 pH indicators (bromocresol purple, bromocresol green, and neutral red) and hyperspectral imaging (HSI), Li et al (2016) were able to quantify the TVC content in pork meat. The individual variables were extracted from each sensor and analysed by multivariate analysis.

Choi et al. (2017) elaborated a colorimetric sensing systems using agar, potato starch, and natural dyes (anthocyanins) extracted from purple sweet potato. Agar and potato starch acted as matrices for the immobilization of the anthocyanins. The pH variations were registered as changes at the ultraviolet-visible (UV-vis) spectrum of anthocyanins, and colour variations of the dye from red to green were observed due spoilage of pork samples.

Huang et al. (2014) studied spoilage of Yao-meat (a salted pork in jelly) in vacuum packaging. In a first study, in order to monitor Yao-meat freshness the authors developed an array consisting in eight porphyrins or metalloporphyrins and eight pH indicators (gentian violet, leucomalachite green, thymol, methyl yellow, bromophenol blue, congo red, methyl orange and screened methyl orange) and were able to correlate colour changes with TVB-N, TVC, and residual nitrite (RN). In a second study (Xiaowei, 2016), also for Yao-meat spoilage detection, some indicators were incorporated into TiO_2 in order to obtain a nanoporous sensor array able to detect the trimethylamine (TMA). The sensor enabled the visual detection of TMA gas from 10 to 60 ppm with significant response. Besides, the same authors (Xiaowei et al., 2015) developed a colorimetric sensor array made by printing nine natural pigments (from *Rosa chinensis, Roselle, Camellia japónica*, *Rose*, *Carnation, Myosotis sylvatica, Zhaoshui plum blossom, Lve plum blossom* and *Red plum blossom*) on a hydrophobic nanoporous film sensors for

Yao-meat freshness evaluation and biogenic amines detection vapours concentrations over the range 10–30 ppm). They found that *Rosa chinensis* extract possessed the highest sensitivity and the highest anthocyanin contents. This work suggested that anthocyanin pigments maybe a useful colorimetric sensor for quality evaluation of meat products.

Related to the application of sensors to buffalo meat, Shukla et al.'s (2015) developed a colorimetric sensor sensitive to TVB-N released during 9 days of meat storage under refrigeration at 4 °C without modified atmosphere. The indicator sensor was fabricated by coating filter paper with bromophenol blue via centrifugation. The indicator was attached to the cling film inner side facing towards the meat. The colour of the sensor changed from yellow to blue indicating deterioration in meat quality based on an increase in concentration of TVB-N produced gradually in the package headspace, which was easily visible to the naked eye. The results also indicated that the sensor response correlated well with microbial load, thus enabling the sensor for real-time monitoring of buffalo meat spoilage during refrigeration storage.

More recently, Pablos et al. (2015) developed a method for the preparation of polymers with trinitrobenzene (TNB) derivatives. This method permits to obtain tractable transparent films and coated fibres that are able to react with amine vapours changing colour. Sensing phenomenon was produced when amines in the atmosphere react with TNB derivatives forming highly coloured Meisenheimer complexes distinguishable to the naked eye. In order to test this concept in a more realistic environment a study was carried out with packaged fresh fish (tuna) and meat (beef) both under and without refrigeration, at 3 and 25 °C respectively. Experiments were performed placing sensory discs in the tray without physical contact with the food and the colour evolution along time was followed using a reference disc outside the packaging film. Food spoilage was accompanied by the darkening of the yellow sensing discs to orange in meat (reddish in tuna) after 12 days at 25 ºC.

A much simpler and more immediate sensor was constructed by Kuswandi et al. (2015) to detect beef freshness packaged in polyethylene trays covered with a plastic film in a conventional atmosphere. The sensor was based on colour changes of litmus paper from red to blue (pH 5.7 to 6.0) when in contact with the atmosphere inside the package. Such pH changes were driven by the concentration of biogenic amines due to the microbial growth of the packaged fresh meat. A sticker sensor was placed inside a package without beef sample as control. Colour modulations were also effective for monitoring the microbial quality of the packaged meat and TVC.

A disposable colorimetric sensor array was prepared by *Li et al.* (2016) by printing various responsive dyes combined with a hand-held device for monitoring freshness of different products: i.e. chicken, pork, beef, fish and shrimp. The array was made with 20 different chemical mixtures: (1) 1-[4-[[4-(dimethylamino)phenyl]azo]phenyl]-2,2,2-trifluoro- + TsOH; (2) Ethanone; (3)Naphthyl Red + TsOH; (4) Bromocresol Green; (5) 5, 10, 15, 20-tetrakis(2, 4, 6-trimethylphenyl)porphyrinato zinc (II); (6) Fluorescein; (7) Tetraiodophenolsulfonephthalein; (8) Methyl Red; (9) Bromocresol Purple; (10) Rosolic Acid ; (11) Bromophenol Red; (12) Bromopyrogallol Red; (13) Pyrocatechol Violet; (14) $LiNO_3$ + Cresol Red; (15) 4-[2-[4-(dimethylamino)phenyl]ethenyl]-2,6-dimethylpyrylium tetrafluoroborate; (16) $Pb(OAc)_2$ + Disperse Red; (17) $AgNO_3$ + Bromophenol Blue; (18) $AgNO_3$ + Bromocresol Green; (19) $Zn(OAc)_2$ + m-Cresol Purple + TBAH; $HgCl_2$ + Bromophenol Blue + TBAH; (20) $HgCl_2$ + Bromocresol Green + TBAH. The dispositive enabled real-time collection of colorimetric data, and showed excellent sensitivity to gaseous analytes, especially sulfides and amines at low ppb levels together with excellent discrimination among meat types and storage time.

In order to senseTVB-N produced during chicken meat spoilage, *Khulal et al.* (2017) used an array made of 9 metalloporphyrins and 3 pH indicators (bromothymol blue, bromocresol green and neutral red) whose colour changes were correlated with classical analytical tools (i.e. spectral and textural data). The authors found that this approach reduced data variables but not the original information and improved the model performance to evaluate chicken meat freshness.

3.2.4 Miscellaneous

Although not specifically prepared for freshness monitoring, we include here recent optoelectronic noses that could potentially be used as freshness indicators due to the substances they monitor; mainly amines or gaseous ammonia (table 5). *Soga et al.* (2013) described the development of a sensor made by combining two functional elements: a sensing dye with selectivity for amines and polymer nanoparticles with different polarities destined to encapsulate the dye. The mixing two nanoparticles of different polarity in different mixture ratios with the dye resulted in a six colorimetric array with a polarity gradient. This mixture had the ability to distinguish between closely related amines, relying on a polarity-based approach. Seven primary amines with decreasing polarities were tested to demonstrate the performance of the sensor array. The authors found a good discrimination ability and high reproducibility to amine concentrations as low as 50 ppm, even in the presence of a relative humidity between 10% and 80%. Furthermore, the sensor array showed no significant response to common volatile organic compounds, thus confirming the high selectivity toward amines.

Lin et al. (2016) explored a simple but effective strategy for visual monitoring of biogenic amines based on multiple colour changes originated by a metallization reaction of Au nanorods (NRs). The reaction of NRs and biogenic amines tuned the localized surface plasmon resonance (LSPR) adsorption, resulting in a naked-eye colour change related to the concentration of the biogenic amines. This strategy may provide a simple and user-friendly platform for *in situ* evaluation of foodstuffs freshness.

By combining electrospinning and sol-gel technologies, Geltmeyer et al. (2016) prepared silicon oxide nanofibrous membranes for the immobilization of pH-indicator dyes (methyl yellow and methyl red) with covalent bonds. This support displayed a high sensitivity for pH-changes in water with a fast response time. The covalent bond between the dyes and the sol-gel network appeared to be essential to obtain a reusable pH-sensor in aqueous environment. The authors found a high sensitivity when sensing HCl, NH_3 and biogenic amines.

Hoang et al. (2016) described a highly sensitive colorimetric method for the detection of gaseous ammonia. The authors prepared bromocresol green-impregnated polyacrylonitrile (BCG-PAN) nanofibers to create a porous nanofibrous structure, which exhibited durable structural stability under different conditions with a better colour uniformity than porous paper. Upon exposure to 25 ppm ammonia, it was found a quickly change of the BCG-PAN material from yellow to blue within 1 min. Furthermore, the sensor had a detection limit by the naked-eye for ammonia of less than 1 ppm, good selectivity against common volatile organic solvents and reversible colour change in ambient conditions.

Khattab et al. (2016) developed a fast and sensitive bacterial recognition method by using tricyanofuran hydrazine as molecular indicator. Bacterial proliferation produces ammonia gas, which basifies the environment and induced colour changes in the tricyanofuran hydrazone probe.

A colorimetric sensor for application in intelligent packaging was developed by Shukla et al. (2016) using natural dyes extracted from red cabbage and the rose flower. The extracts were immobilization on filter paper. The natural flavonoids (anthocyanins) present on red cabbage and rose act as natural pH sensors changing their colour from red to green when the pH increases. This sensor showed short response time, reproducibility, reversibility and was stable towards light and storage.

Mills et al. (2017) prepared a colorimetric indicator with a colour change based on the aggregation of thiazine dyes (methylene blue, MB) encapsulated within hydroxypropyl cellulose (HPC). The initially purple MB/HPC film was activated by heat treatment at 370 °C for 4 s, at which point the film becomes blue. The heat-treated MB/HPC films (blue) responded to an environmental humidity exceeding 70% at 21 °C within seconds, coming back to their initial purple colour. When exposed to a lower relative humidity, the film was stable in its blue form; but a MB/HPC film treated at 220 °C for 15 s turned blue and gradually returned to its purple form in an environmental humidity between 37-50%. This indicator may find applications in packaging of products that cannot tolerate high humidity levels, such as dry foods.

4. CHALLENGES FOR FUTURE RESEARCH.

As noted in the introduction, research in intelligent packaging is expected to continue in the coming years. It is an emerging market with initiatives all over the world that can play a relevant role to reduce food waste. A crucial aspect in this area is the change of the generic “Best Before” and “Use By” dating to a "dynamic" system. This change of paradigm would offer information about the state of every package in real time, avoiding waste of safe food that is discarded just because the date has expired. Moreover, it must be considered that such generic dates are fixed in a conservative way, circumstance that even increases food waste.

Although the household are the most relevant player, a large percentage of loss takes place in the supply chain. Food distribution chains trend to discard products even before the "best before" date in order to avoid selling a product close to expire. Also, a great amount of food is destroyed unnecessarily simply because a random sample has shown signs of spoiling, discarding the entire batch.

The clear advantages of a dynamic dating system together with the monitoring of all the samples, induced not only the development of research in this area but also the launching of diverse commercial products. Unfortunately, for freshness indicators, the number of commercial products is really scarce and in several cases their commercialization has been discontinued.

One of the main issues that must be considered by researchers and companies is the fact that food safety cannot be compromised by these indicators. Sensing systems must be robust and avoid any false negative (samples that seem safe but are dangerous). Moreover, in order to maximise their efficiency in relation to food waste, they should have as few false positive (samples that seem unsafe but are healthy) as possible. Thus, further validation studies should include large amounts of samples and be tested in as much conditions as possible. In this sense, developing standard testing assays and protocols would help in the development of freshness indicators and their future transfer into industrial products.

Other relevant limitations that could hamper research in the coming years is the legislation regarding the substances that can be in contact with food and the cost of the labels. Current regulation limits seriously the number of substances that can be used in labelling and this issue offers a serious barrier regarding the development of new labels. The authorization of a new substance for food contact is a long, complex and expensive procedure. In this framework, a research opportunity is available in the incorporation of the labels to materials that allow the permeation of the gaseous o liquid metabolites, but avoid the migration of the chemical substances.

Moreover, the fact that the labels must have a very low cost can limit their commercial implantation, in particular if the added value is not perceived by the consumer. Regardless, the fact that the material should be ideally disposable also impose limitations to the types of supports that can be used. Fortunately, for optical systems, the elimination of specialized electronic readers in favour of smartphones may allow them to enter the mainstream.

In case of expensive systems, one possibility is the use of the labels as tracers in order to determine the points of risk and analyse the behaviour of the food on the way from the factory to the consumer houses. Such studies will increase the knowledge of the consumer behaviour to fix "use by" dates more realistic, less conservative, expand the nominal shelf life and reduce food waste while increasing the quality control within the supply chain.

In most of the examples reviewed, sensors are applied separately and they are not part of the packaging. However, those indicators can also be printed directly onto the packaging foil, and it is also possible to print full electronic systems offering packaging new functionalities. Printed electronics on flexible substrates using electrically functional inks is an emerging technology. The unique properties of printed electronic sensors include lightweight, bendable, rollable, portable and foldable. Flexible printed chemical sensors would contain a receptor printed on top of a printed transducer. This offers the possibility of creating sensors on a variety of substrates each shaped and individually tailored to operate uniquely (Vanderroost et al., 2014). Such an approach would increase the functionality (i.e. in line with the tendency of Internet of Things sensors could transmit data to internet or to our smartphone) and reduce the cost tremendously.

Apart of the limitations, most of the reported systems have been designed for follow meat and fish spoilage, and less examples have been described for fruits and vegetables. This tendency can be explained due to the perishable nature of such products and their added value. However similar percentages of food loss can be found also in other products of high relevance such as cereals, dairy products, oilseed, pulses, roots and tubers with more than 300 millions of tonnes per year (FAO, SAVE THE FOOD). These products have not been objective of studies in relation to intelligent labelling, being this area an opportunity for researchers in the coming years.

Finally, most of the research reported by now has been devoted to active or intelligent packaging, but the design of more advanced packaging can also be envisioned. Interactive packaging, which monitors the quality of the product and generates a signal that should lead to a particular response is still in its infancy. Recent advances in nanotechnologies such as the encapsulation of active substances in gated supports (Aznar et al., 2016) able to deliver target substances triggered by predefined stimuli, can offer interesting opportunities for multidisciplinary research teams.

5. CONCLUSIONS

In conclusion, intelligent packaging can be a fundamental tool to front future challenges and reach a more sustainable society by reducing food waste. The change from the standard "use by" date to a dynamic system able to inform about the real state of food will reduce food loses while maintaining food safety. Moreover, the adoption of intelligent packaging can increase the knowledge of the distribution chain and design tailored systems more efficient and sustainable. Currently most of reported results are focused on muscle food (meat and fish) and the number and variety of sensing strategies is relatively limited, with a strong presence of pH indicators supported in diverse materials. This kind of systems due to their unspecific character may lack of enough selectivity and the consequent robustness. Optoelectronic arrays based on the combination of a diversity indicators can be a more effective approach. This tactic may sacrifice simplicity, however the wide use of smartphones offers a relevant opportunity to use them as optical detection devices and data processor. Technologic advances together with an increasing market demand is expected to impulse the adoption of intelligent packaging by food industries decreasing food waste and offering a more sustainable world in the coming years.

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TABLE CAPTION

Table 1: Examples of commercial intelligent packaging products

Table 2: Summary of the freshness indicators for fruits and vegetables analysed in the review with indication of the chemical composition of the indicator and the food.

Table 3: Summary of the freshness indicators for fish products analysed in the review with indication of the chemical composition of the indicator and the food.

Table 4: Summary of the freshness indicators for meat analysed in the review with indication of the chemical composition of the indicator and the food.

Table 5: Summary of other potential freshness indicators analysed in the review with indication of the chemical composition of the indicator and the metabolite monitored.

FIGURE CAPTION

Figure 1. Time–temperature indicators. a) 3M Monitor Mark, b) VITSAB, c)FreshCode, d) TopCryo, e) OnVu, f) Fresh-Check.

Figura 2. Freshness indicators and sensors. a) SensorQ, b) Raflatac, c) Toxin Guard, d) Food Sentinel System.

Figure 3. Images from Nopwinyuwong et al. (2010) in which spoilage process was monitored. Upper side shows changes in color of indicator label in response to CO_2. Bottom side packaged golden drop with food spoilage indicator label. Reprinted with permission from Elsevier.

Figure 4. a) Pacquit et al. (2007), sensor response to a spoiling whiting sample. b) Zaragozá et al. (2013), scheme of a tray with a sea bream sample and the chromogenic array. c) Huang et al. (2011), color variations of the sensor array after exposure to a fish sample at days 1, 4 and 7, respectively. d) Kuswandi et al. (2012), sensor design (left) and its application as smart packaging for milkfish (right). Reprinted with permission from Elsevier.

TABLE 1:

Technology	Commercial name	Supplier
Radiofrequency identification tags (RFID)	Easy2log®	CAEN RFID Srl
	CS8304	Convergence Systems Ltd.
	TempTRIP	TempTRIP LLC
	Intelligent box	Mondi Plc
	Intelligent fish box	Craemer Group GmbH
Time temperature indicators	3M Monitor Mark™	3M company
	Keep -it®	Keep-it Technologies
	Fresh-Check®	Temptime Corp.
	VITSAB®	VITSAB International AB
	OnVu™	Freshpoint and Ciba
	TopCryo®	TRACEO
	FreshCode®	Varcode Ltd.
	Tempix®	Temptix AB
	Cook-Chex	Pymah Corp.
	Timestrip® PLUS™	Timestrip Plc
	Colour-Therm	Colour-Therm
	Thermax®	Thermografic Measurements Ltd
	Novas®	Insignia Technologies Ltd
	Best-by®	FreshPoint Lab
	CheckPoint®	VITSAB
Integrity indicators	Ageless Eye®	Mitshubishi Gas Chemical
	Tell-Tab	IMPAK
	O_2Sense™	FreshPoint Lab
Freshness indicators	Fresh Tag®	COX Technologies
	SensorQ®	DSM NV nd Food Quality Sensor International Inc.
	Raflatac	VTT and UPM Raflatac
	Food Sentinel System	SIRA Technologies Inc.

	Toxin Guard	Toxin Alert Inc.
	RipeSense	RipeSense

TABLE 2

Sensor - support	Application	Reference
Bromocresol purple and methyl red - polypropylene resin	Kimchi	Hong and Park, 1999
Bromocresol purple and methyl red – nylon films	Kimchi	Hong, 2002
Bromothymol blue and methyl red - nylon/LLDPE film	Golden drop	Nopwinyuwong et al., 2010
Bromophenol blue – cellulose membrane	Guava	Kuswandi et al., 2013
Alcohol oxidase (AOX) - polyaniline (PANI) film	Halal fermented beverages	Kuswandi et al., 2014
Silver based yellow colored colloidal nanoparticle	Onion	Sachdev et al., 2016

TABLE 3

Sensor - support	Application	Reference
Bromocresol green – polymer matrix	Fish	Pacquit et al., 2007
Polyaniline (PANI) film	Milkfish	Kuswandi et al., 2012
Ph indicators (bromophenol blue, cresol red and metanil yellow) improved by ph regulation	Spanish mackerel (fish)	Sun et al., 2015
6 metalloporphyrins and 3 ph indicators – reverse phase silica gel	Chub	Huang et al., 2011
Resorufin, bromocresol purple, bromophenol blue, phenol red and a dinuclear complex of rhodium – silica and alumina	Sea bream	Zaragozá et al., 2013
Bromocresol purple, bromothymol blue sodium salt, m-cresolsulfonphthalein, resorufin and a dinuclear rhodium complex – silica and alumina	Atlantic salmon	Zaragozá et al., 2014
Thymol blue, bromocresol purple, bromothymol blue sodium salt, bromophenol blue and a dinuclear rhodium complex – aluminium oxide and silica gel	Squid	Zaragozá et al., 2015
4-(dioctylamino)-4'-(trifluoroacetyl)azobenzene – PET films	Ground meat and salmon	Lin et al., 2015
Corn Starch, Chitosan and red cabbage extract	Fish	Silva-Pereira et al., 2015
Ph indicators and others	Fish	Morsy et al., 2016

TABLE 4

Sensor - support	Application	Reference
9 metalloporphyrins and 3 ph indicators – C2 reverse silica-gel flat plate	Chicken	Chen et al., 2014
9 metalloporphyrins and 3 ph indicators – C2 reverse silica-gel flat plate	Chicken	Chen et al., 2014b
9 metalloporphyrins and 3 ph indicators – C2 reverse silica-gel flat plate	Chicken breast fillets	Urmila et al., 2015
9 porphyrins/ metalloporphyrins and 3 ph indicators	Chicken	Khulal et al., 2016
Two groups of ph-sensitive dyes	Skinless chicken breast	Rukchon et al., 2014
Ph indicators, Lewis acids, hydrogen-bonding derivatives, selective probes and natural dyes – UVM-7, silica and alumina	Chicken	Salinas et al., 2012
13 indicators – silica and alumina	Boiled marinated turkey meat	Salinas et al., 2014a
Malachite green, m-cresol purple, br-cresol purple, squaraine salt and a pyrilium salt – UVM-7 and alumina	Pork sausages	Salinas et al., 2014b
9 metalloporphyrins and 3 ph indicators	Chicken	Chen et al., 2016
9 ph indicators – 2,4- dinitrophenylhydrazine (DNPH)	Cooked chicken	Kim et al., 2016
		Li et al., 2014
9 metalloporphyrins and 3 ph indicators – silica-gel flat plate	Pork	Li et al., 2015
Natural pigments (spinach, red radish, winter jasmine and black rice)	Pork	Huang et al., 2014
9 metalloporphyrins and 3 ph indicators	Pork	Li et al., 2016
Anthocyanins – agar and potato starch	Pork	Choi et al., 2017
8 porphyrins /metalloporphyrins and 8 ph indicators	Yao-meat pork	Huang et al., 2014
8 porphyrins /metalloporphyrins and 8 ph indicators – tio2	Yao-meat pork	Xiao-Wei et al., 2016
9 natural pigments –hydrophobic nanoporous film	Yao-meat pork	Xiaowei et al., 2015

Bromophenol blue – filter paper	Buffalo meat	Shukla et al., 2015
Trinitrobenzene derivatives – transparent films and fibres	Tuna and beef	Pablos et al., 2015
Litmus paper	Beef	Kuswandi et al., 2015
20 different chemical mixtures	Chicken, pork, beef, fish and shrimp	Li et al., 2016
9 metalloporphyrins and 3 ph indicators	Chicken	Khulal et al., 2017

TABLE 5

Sensor - support	Application	Reference
Sensing dye – different polarity nanoparticles (in different ratios)	Amines	Soga et al., 2013
Metallization reaction of Au nanorods (nrs) induced by silver	Biogenic amines	Lin et al., 2016
Ph indicators – nanofibrous membranes	Ammonia, biogenic amines	Geltmeyer et al., 2016
Bromocresol green – polyacrylonitrile nanofibers	Ammonia	Hoang et al., 2016
Tricyanofuran hydrazine	Ammonia	Khattab et al., 2016
Natural dyes (red cabbage and flower of rose) – filter paper	pH changes	Shukla et al., 2016
Methylene blue – hydroxypropyl cellulose	Time	Mills et al., 2017

FIGURE 1

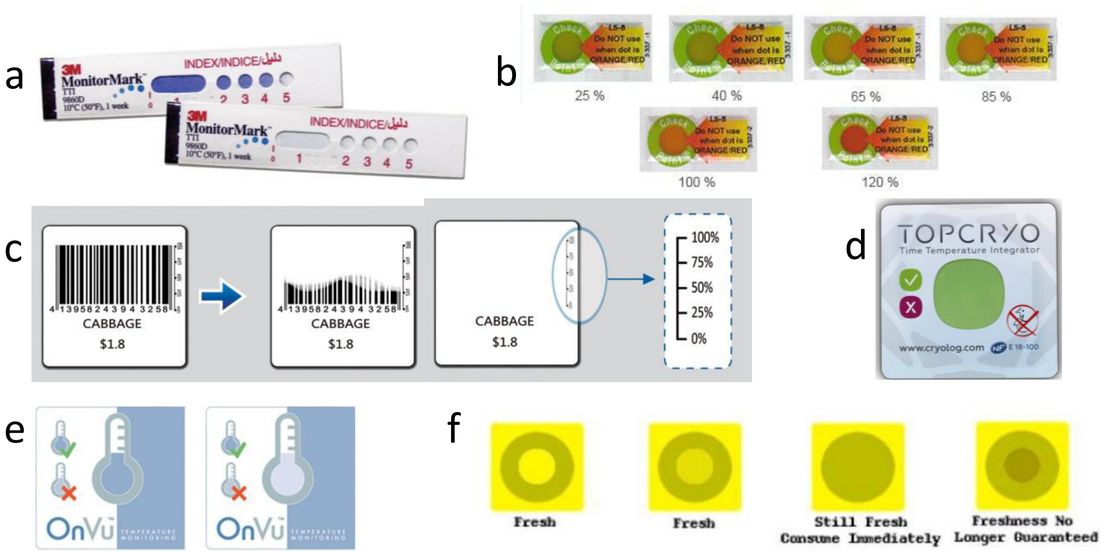

a
3M MonitorMark TTI 9860D 10°C (50°F), 1 week
INDEX/INDICE/دليل
1 2 3 4 5
b
Check Point
Do NOT use when dot is ORANGE/RED
25 %
40 %
65 %
85 %
100 %
120 %
c
CABBAGE
$1.8
100%
75%
50%
25%
0%
d
TOPCRYO
Time Temperature Integrator
www.cryolog.com
e
OnVu
TEMPERATURE MONITORING
f
Fresh
Fresh
Still Fresh Consume Immediately
Freshness No Longer Guaranteed

FIGURE 2

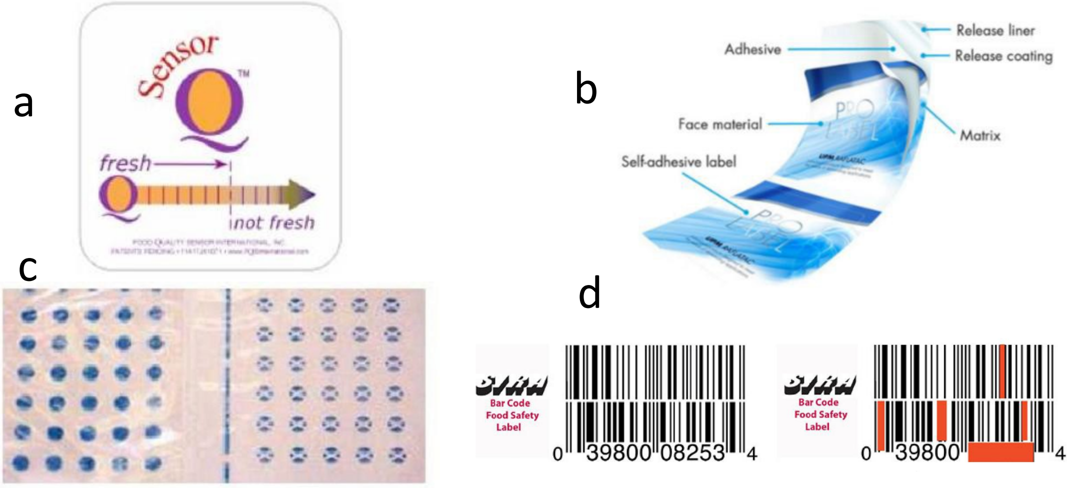

a
Sensor
Q
TM
fresh
not fresh
b
Release liner
Adhesive
Release coating
Face material
Matrix
Self-adhesive label
PRO LABEL
UPM RAFLATAC
c
d
SIRA
Bar Code
Food Safety
Label
0 39800 08253 4
SIRA
Bar Code
Food Safety
Label
0 39800 4

FIGURE 3

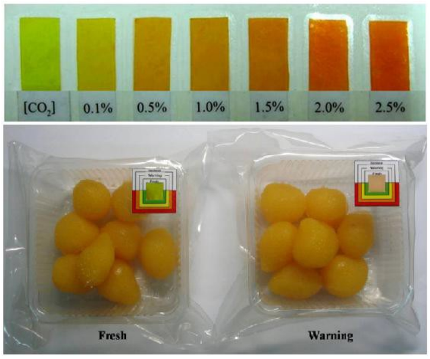
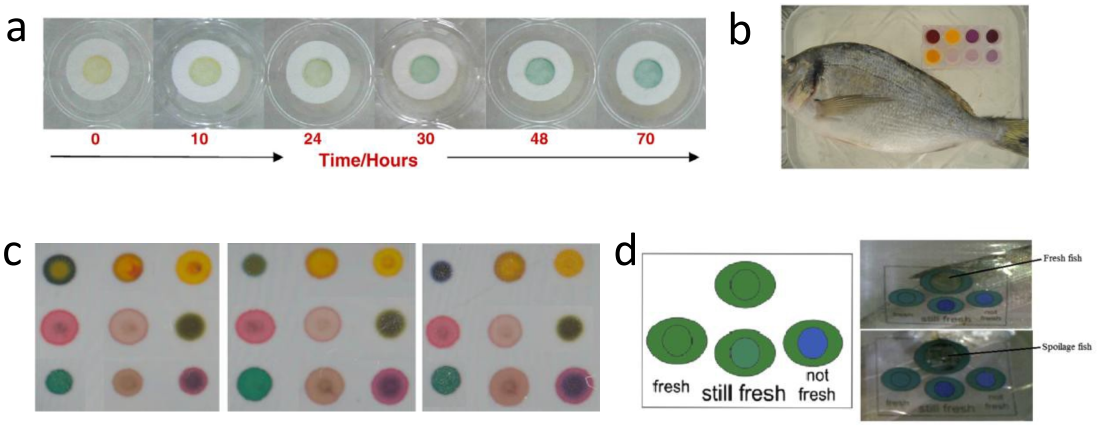


FIGURE 4


a
0
10
24
30
48
70
Time/Hours
b
c
d
fresh
still fresh
not fresh
Fresh fish
Spoilage fish