

Smart Packaging Technologies for Fast Moving Consumer Goods

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3

Smart Packaging of Meat and Poultry Products

S.A. Hogan and J.P. Kerry

3.1 Introduction

The role of preservative packaging, as applied to meat products, is to maintain acceptable appearance, odour and flavour, stabilise product composition and delay the onset of microbial spoilage. A variety of packaging systems and technologies is currently available for muscle foods, specifically fresh and cooked meats and meat products. Fresh red meats may simply be placed on trays and over-wrapped with an oxygen permeable film or placed within a static gaseous modified atmosphere packaging (MAP) environment containing approximately 70–80 % oxygen and 20–30 % carbon dioxide. Fresh poultry products may again be retailed in an overwrap or a MAP format comprising approximately 65–75 % nitrogen and 25–35 % carbon dioxide. MAP is an extremely important packaging technology used extensively for the distribution, storage and display of meat and poultry products throughout the cold distribution chain (Sivertsvik *et al.*, 2002). While described as static, the atmosphere within an MAP pack is far from being static and gas content levels may alter during storage due to reactions between components of the atmosphere and the product and/or due to transmission of gases in or out of the pack through the packaging film (Stiles, 1991). Processed or cooked meats and poultry or cook-chill convenience-style, muscle-based, foods are described as being oxygen sensitive and for this reason, these products are usually stored under some form of vacuum or in MAP using 60–80 % N₂ : 20–40 % CO₂.

The function of carbon dioxide in MAP is to inhibit growth of spoilage bacteria (Seideman and Durland, 1984). Nitrogen is used in MAP as an inert filler gas in order to reduce the proportions of the other gases or to maintain pack shape (Bell and Bourke, 1996). The

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major function of oxygen is to maintain the muscle pigment myoglobin in its oxygenated form, oxymyoglobin, in red meats.

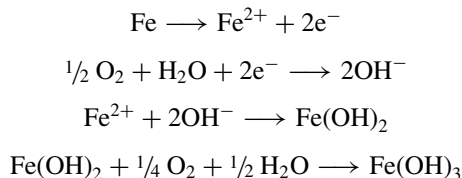
Important properties by which consumers judge meat are appearance, texture and flavour (Faustman and Cassens, 1990). Appearance, specifically colour, is a critical quality attribute in influencing the consumer's decision to purchase. In fresh red meats, myoglobin can exist in one of three chemical forms. Deoxymyoglobin, which is purple, is rapidly oxygenated to cherry red oxymyoglobin on exposure to air. Over time, oxymyoglobin is oxidised to metmyoglobin which results in a brown discoloration associated with a lack of freshness (Faustman and Cassens, 1990). Low oxygen concentrations favour oxidation of oxymyoglobin to metmyoglobin (Ledward, 1970). In order to minimise metmyoglobin formation in fresh red meats, oxygen must be excluded from the packaging environment to below 0.05 % or be present at saturating levels (Faustman and Cassens, 1990). High oxygen levels within MAP also promote oxidation of muscle lipids over time with deleterious effect on fresh meat colour (Kerry *et al.*, 2000). Lipid oxidation is a major quality deteriorative process in meat, resulting in a variety of breakdown products that produce undesirable off-odours and flavours.

In cured, cooked, packaged meat products, factors such as percentage residual oxygen, product to headspace volume ratio, oxygen transmission rate of the packaging material, storage temperature, light intensity and product composition are critical factors affecting colour stability and ultimately consumer acceptance (Møller *et al.*, 2003). Nitrosylmyoglobin, formed from a reaction between myoglobin and nitrite is denatured, upon cooking, to nitrosylmyochrome which gives the characteristic pink colour to cooked, cured ham (Juncher *et al.*, 2003). Exposure to light in combination with oxygen is of critical importance to the colour stability of cooked cured ham as light exposure, even at low oxygen levels, can cause oxidation of nitrosylmyochrome to denatured metmyoglobin, which imposes an undesirable greyness to the meat surface (Møller *et al.*, 2000). Commercially, discoloration in pre-packed, cooked, cured ham is associated with low residual oxygen levels and is overcome with the use of oxygen scavengers or an oxygen scavenging film. Also, with respect to fresh red meats, oxygen scavengers used in conjunction with a carbon dioxide/nitrogen gas mixture extends the colour shelf-life of fresh beef (Allen *et al.*, 1996). Oxygen scavengers are some of the best known examples of smart packaging devices used with oxygen sensitive meat-based products.

3.2 Oxygen Scavengers

High levels of oxygen present in packs containing meat and poultry facilitate microbial growth, off-flavour and off-odour development, colour changes and nutritional losses, thereby causing significant reduction in the quality, safety and overall shelf life stability of these muscle foods. This problem is further compounded in muscle-based food products where clean labelling requirements and minimal processing procedures are being used to satisfy retailer, and ultimately consumer, concerns and demands for fresher and less processed muscle food products. Control of oxygen levels in oxygen-sensitive food packs is critical in order to limit the rate of such deteriorative and spoilage reactions. Oxygen absorbing systems provide an alternative to vacuum and gas flushing technologies as a means of improving product quality and shelf life (Ozdemir and Floros, 2004), while helping

to circumvent problems created by 'chemical or preservative free' minimally processed muscle foods. Vacuum packaging and MAP techniques do not always facilitate complete removal of oxygen. Oxygen that permeates through the packaging film or is trapped within the meat or between meat slices cannot be removed by these techniques. Quality changes in oxygen-sensitive foods can be minimised through the use of oxygen scavengers, which absorb residual oxygen following packaging (Vermeiren *et al.*, 1999). Existing oxygen scavenging technologies utilise one or more of the following concepts: iron powder oxidation, ascorbic acid oxidation, photosensitive dye oxidation, enzymatic oxidation (e.g. glucose oxidase and alcohol oxidase), unsaturated fatty acids (e.g. oleic or linolenic acid), rice extract or immobilised yeast on a solid substrate (Floros *et al.*, 1997; Vermeiren *et al.*, 1999). Structurally, the oxygen scavenging component of a package can take the form of a sachet, label, film (incorporation of scavenging agent into packaging film), card, closure liner or concentrate (Suppakul *et al.*, 2003). The majority of commercially available oxygen scavengers are based on the principle of iron oxidation (Smith *et al.*, 1990):



Comprehensive details on a variety of commercially available oxygen scavengers are presented by Suppakul *et al.* (2003). Ageless[®] (Mitsubishi Gas Chemical Co., Japan) is the most common oxygen scavenging system based on iron oxidation (Figure 3.1). These scavengers are designed to reduce oxygen levels to less than 0.1 %. Other examples of oxygen absorbing sachets include ATCO[®] (used commercially as oxygen scavengers in pre-packed, cooked and cooked, sliced meat products – Emco Packaging Systems, UK;



Figure 3.1 Ageless[®] Label Mitsubishi Gas Chemical Co. Reproduced with permission from Ageless Sales, Mitsubishi Gas Chemical Co. Japan.

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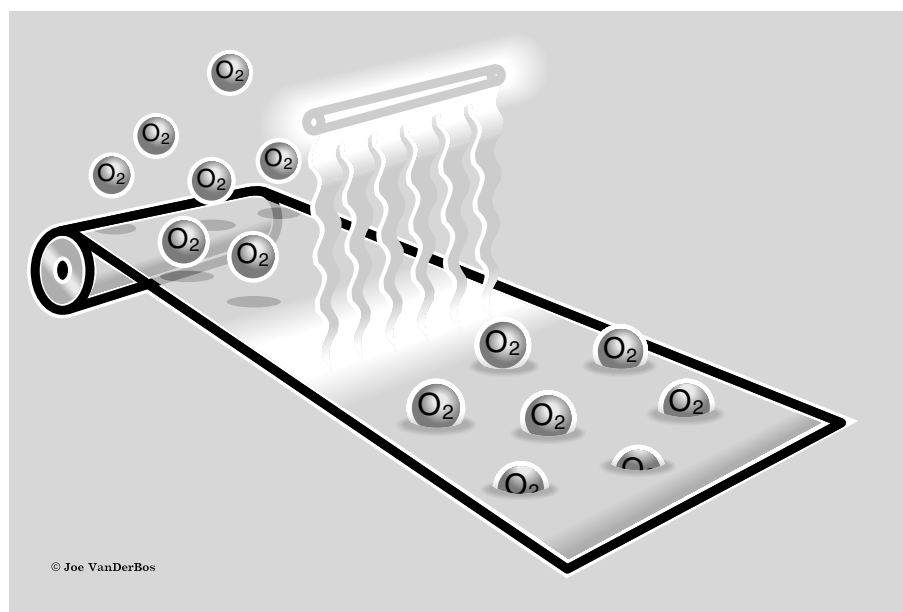


Figure 3.2 Light-activated oxygen scavenging films Cryovac® OS Films. Reproduced with permission from Cryovac Food Packaging, Sealed Air Corporation, USA.

Standa Industrie, France), FreshPax® (Multisorb Technologies, Inc., USA) and Oxsorb® (Pillsbury Co., USA).

The scientific literature contains a number of references to studies that examine the influence of oxygen scavenger sachets on meat quality and these have been reviewed by Kerry *et al.* (2006).

An alternative to sachets involves the incorporation of the oxygen scavenger into the packaging structure itself. This minimizes negative consumer response and offers a potential economic advantage through increased outputs. It also eliminates the risk of accidental rupture of the sachets and inadvertent consumption of their contents (Suppakul *et al.*, 2003). Cryovac® OS2000™ polymer based oxygen scavenging film has been developed by Cryovac Div., Sealed Air Corporation, USA. This UV light-activated oxygen scavenging film (Figure 3.2), composed of an oxygen scavenger layer extruded into a multilayer film, can reduce headspace oxygen levels from 1 % to ppm levels in 4–10 days and is comparable in effectiveness with oxygen scavenging sachets. The OS2000™ scavenging films have applications in a variety of food products including dried or smoked meat products and processed meats (Butler, 2002). A similar UV light-activated oxygen scavenging polymer ZERO₂®, developed by CSIRO, Division of Food Science Australia in collaboration with VisyPak Food Packaging, Visy Industries, Australia, forms a layer in a multilayer package structure and can be used to reduce discoloration of sliced meats. Another successful commercial example for use with meat is the OSP™ system (Chevron Philips Chemical Company, USA). The active substances of OSP™ systems are ethylene methacrylate and cyclohexene methacrylate, which need to be blended with a catalyst or photoinitiator in order to activate the oxygen scavenging mechanism.

3.3 Carbon Dioxide Scavengers and Emitters

As stated previously, the function of carbon dioxide within a packaging environment is to suppress microbial growth. Therefore a carbon dioxide generating system can be viewed as a technique complementary to oxygen scavenging (Suppakul *et al.*, 2003). Since the permeability of carbon dioxide is three-to five-times higher than that of oxygen in most plastic films, it must be continuously generated to maintain desired concentration within the package (Ozdemir and Floros, 2004). High carbon dioxide levels (10–80 %) are desirable for foods such as meat and poultry in order to inhibit surface microbial growth and extend shelf life. Removal of oxygen from the package creates a partial vacuum which may result in the collapse of flexible packaging. Also, when a package is flushed with a mixture of gases including carbon dioxide, the carbon dioxide may dissolve in the product and create a partial vacuum. In such cases, the simultaneous release of carbon dioxide from oxygen-consuming sachets is desirable. Such systems are based on either ferrous carbonate or a mixture of ascorbic acid and sodium bicarbonate (Rooney, 1995). Examples of commercially available dual action combined carbon dioxide generators/oxygen scavengers are Ageless® G (Mitsubishi Gas Chemical Co., Japan) and FreshPax® M (Multisorb Technologies, Inc, USA). Carbon dioxide emitting sachets or labels can also be used alone. The Verifrais™ package, manufactured by SARL Codimer (Paris, France), has been used to extend the shelf life of fresh meats. This innovative package consists of a standard MAP tray but has a perforated false bottom under which, a porous sachet containing sodium bicarbonate/ascorbate is positioned. When juice exudates from the packaged meat drips onto the sachet, carbon dioxide is emitted, thus replacing any carbon dioxide absorbed by the meat and preventing package collapse.

The inhibition of spoilage bacteria utilizing active packaging technology may reduce bacterial competition and thus permit growth of toxin producing, non-proteolytic *C. botulinum* or other pathogenic bacteria (Sivertsvik, 2003). Lövenklev *et al.* (2004) reported that while a high concentration of carbon dioxide decreased the growth rate of non-proteolytic *C. botulinum* type B, the expression and production of toxin was greatly increased. As such, the risk of botulism may be increased, rather than reduced, in high carbon dioxide MAP systems. It would appear that further research into the safety risks associated with the use of carbon dioxide in such packaging systems is necessary.

Carbon dioxide absorbers, (sachets) consisting of either calcium hydroxide and sodium hydroxide, or potassium hydroxide, calcium oxide and silica gel, may be used to remove carbon dioxide during storage in order to prevent bursting of packages. Possible applications include use in packs of dehydrated poultry products and beef jerky (Ahvenainen, 2003).

3.4 Moisture Control

The main purpose of liquid water control is to lower the water activity of the product, thereby suppressing microbial growth (Vermeiren *et al.*, 1999). However, as the growth sector in fresh chilled muscle-based foods has evolved, another very good reason to control residual levels of predominantly product-released water in packs is to enhance the visual impact of product at retail level during product–consumer interaction. Temperature cycling

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Figure 3.3 Dri-Loc® Absorbent pads, Cryovac®, Sealed Air Corporation. Reproduced with permission from Cryovac Food Packaging, Sealed Air Corporation, USA.

of high water activity foods, like meat and poultry products, has led to the use of plastics with an antifog additive that lowers the interfacial tension between the condensate and the film. This promotes film transparency and enables the customer to see clearly the packaged food (Rooney, 1995), although it does not affect the amount of liquid water present inside the package. Several companies manufacture drip absorbent sheets or pads such as Cryovac® Dri-Loc® (Sealed Air Corporation, USA), Thermarite® or Peaksorb® (Australia), Toppan™ (Japan) and Fresh-R-Pax™ (Maxwell Chase Technologies, LLC, USA) for liquid control in high water activity foods such as meat and poultry. Typically, these systems consist of a super-absorbent polymer located between two layers of a microporous or non-woven polymer (Figure 3.3). Such sheets are used as drip-absorbing pads placed under whole chickens or chicken cuts (Suppakul *et al.*, 2003).

3.5 Antimicrobial Packaging

Microbial contamination and subsequent growth reduces the shelf-life of foods and increases the risk of food borne illness. Traditional methods of preserving foods from the effects of microbial growth include thermal processing, drying, freezing, refrigeration, irradiation, MAP and addition of antimicrobial agents or salts. However some of these techniques cannot be applied to certain products such as fresh meats (Quintavalla

and Vicini, 2002). Antimicrobial packaging is a promising form of active packaging especially for meat and poultry products. Since microbial contamination of muscle-based food products occurs primarily at the surface, attempts have been made to improve safety and to delay spoilage by the use of antibacterial sprays or dips. Limitations of such an approach include neutralisation of antibacterial compounds on contact with the meat surface or diffusion of compounds from the surface into the meat mass. Incorporation of bactericidal agents into meat formulations may result in partial inactivation of the active compounds by meat constituents and therefore exert a limited effect on surface microflora (Quintavalla and Vicini, 2002). Antimicrobial food packaging materials must extend the lag phase and reduce the growth phase of microorganisms in order to extend shelf life and to maintain product quality and safety (Han, 2000). Comprehensive reviews on antimicrobial food packaging have been published by Appendini and Hotchkiss (2002), Suppakul *et al.* (2003), and Coma (2008). To confer antimicrobial activity, antimicrobial agents may be coated, incorporated, immobilised, or surface modified onto package materials (Suppakul *et al.*, 2003). The classes of antimicrobial compound used include acid anhydrides, alcohols, bacteriocins, chelators, enzymes, organic acids and polysaccharides. Examples of commercial antimicrobial materials include concentrates (e.g. AgION™, AgION Technologies LLC, USA), extracts (Nisaplin® (Nisin), Integrated Ingredients, USA) and films (Microgard™ Rhone-Poulenc, USA). Antimicrobial packages have not been commercially successful, with the exception in Japan, of Ag-substituted zeolite, which is the most common antimicrobial agent incorporated into plastics. Ag-ions inhibit a range of metabolic enzymes and have strong antimicrobial activity (Vermeiren *et al.*, 1999). Antimicrobial films can be classified into two types: those that contain an antimicrobial agent that migrates to the surface of the food and, those which are effective against surface growth of microorganisms without migration. Research conducted on the use, application and operation of antimicrobial agents contained within or on meat packaging materials has been reviewed by Kerry *et al.* (2006) and Coma (2008).

3.6 Sensors

The most important (non-inert) gases in MAP products are oxygen and carbon dioxide and their headspace partial pressures serve as useful indicators of the quality status of a meat product. Headspace profiles of oxygen and carbon dioxide can change over time and are influenced by product type, respiration, packaging material, pack size, volume ratios, storage conditions, package integrity, etc. A number of analytical techniques are available to monitor gas phases in MAP products. Instrumental techniques such as GC and GC/MS are not suitable for rapid measurements and are time consuming and expensive. Portable headspace oxygen and/or carbon dioxide gas analysers use ‘minimally destructive’ techniques (packages can be resealed) but tend not to be applicable to real-time, on-line, control of packaging processes or large scale usage. An optical sensor approach is thought to offer a realistic alternative to such conventional methods.

Many intelligent packaging concepts involve the use of sensors and indicators. For the purposes of clarity the two areas will be discussed separately, although such a distinction is somewhat arbitrary and some overlap is unavoidable. In general, the use of these systems

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is envisaged in terms of incorporation into established meat and poultry packaging formats such as MAP and vacuum packaging.

A sensor is defined as a device used to detect, locate or quantify energy or matter, giving a signal for the detection or measurement of a physical or chemical property to which the device responds (Kress-Rogers, 1998a). To qualify as a sensor, a device must provide continuous output of a signal. Most sensors contain two basic functional units : a receptor and a transducer. In the receptor physical or chemical information is transformed into a form of energy that may be measured by the transducer. The transducer is a device capable of transforming the energy carrying the physical or chemical information about the sample into a useful analytical signal.

Research and development of sensor technology has been largely concentrated in biomedical and environmental applications (Demas *et al.*, 1999). The specifications of such sensors are, however, quite different from those required for food packaging applications. The development of improved methods to determine food quality such as freshness, microbial spoilage, oxidative rancidity or oxygen and/or heat induced deterioration is extremely important to food manufacturers. In order to maximise the quality and safety of foodstuffs, a prediction of shelf-life based on standard quality control procedures is normally undertaken. Replacement of such time-consuming and expensive quality measurements with rapid, reliable and inexpensive alternatives has lead to greater efforts being made to identify and measure chemical or physical indicators of food quality. Development of a potential sensor for rapid quantification of such an indicator is known as the marker approach (Kress-Rogers, 2001). Determination of indicator headspace gases provides a means by which the quality of a meat product and the integrity of the packaging in which it is held can be established rapidly and inexpensively. One means of doing so is through the production of intelligent packaging incorporating gas sensor technology.

Chemical sensor and biosensor technology has developed rapidly in recent years. The main types of transducers with potential use in meat packaging systems include electrical, optical, thermal or chemical signal domains. Sensors can be applied as the determinant of a primary measurable variable or, using the marker concept, as the determinant of another physical, chemical or biological variable (Kress-Rogers, 1998a). In the case of headspace gas sensing, accurate measurements are desirable as indicators of meat product quality. Developments in sensor technology has narrowed the gap between the theoretical and the commercially viable, and although practical uses of sensors in the meat industry remain very limited, significant practical steps towards more widespread use have been made (Kerry and Papkovsky, 2002). High development and production costs, strict industry specifications, safety considerations and relatively limited demand (in comparison with the biomedical sector) from industry and consumer alike, have proved the main obstacles to commercial use. Very few systems to date have been able to match exacting industry standards required for successful application. However, developments in materials science, continuous automation processes, signal processing and process control, along with transfer of technology from the biomedical, environmental and chemical sectors all lead toward the likelihood of more universal adoption of sensor technology in food packaging. Greater pressure on food manufacturers to guarantee safety, quality and traceability is also likely to promote the establishment of commercial sensor technology in food packaging.

3.6.1 Gas Sensors

Gas sensors are devices that respond reversibly and quantitatively to the presence of a gaseous analyte by changing the physical parameters of the sensor and are monitored by an external device. Systems presently available for gas detection include amperometric oxygen sensors, potentiometric carbon dioxide sensors, metal oxide semiconductor field effect transistors, organic conducting polymers and piezoelectric crystal sensors (Kress-Rogers, 1998b). Conventional systems for oxygen sensors based on electrochemical methods have a number of limitations (Trettnak *et al.*, 1995) including consumption of analyte (oxygen), cross-sensitivity to carbon dioxide and hydrogen sulfide and fouling of sensor membranes. They also involve destructive analysis of packages.

In recent years, a number of instruments and materials for optical oxygen sensing have been described (Papkovsky *et al.*, 1995; Trettnak *et al.*, 1995). These sensors are usually comprise a solid-state material and operate on the principle of luminescence quenching or absorbance changes caused by direct contact with the analyte. They are chemically inert, do not consume analytes and provide a non-invasive technique for gas analysis through translucent materials.

Approaches to optochemical sensing have included (a) a fluorescence-based system using a pH sensitive indicator (Wolfbeis *et al.*, 1988), (b) absorption-based colourimetric sensing realised through a visual indicator (Mills *et al.*, 1992), and (c) an energy transfer approach using phase fluorimetric detection (Neurater *et al.*, 1999). The latter allows for the possibility of combining oxygen and carbon dioxide measurements in a single sensor through compatibility with previously developed oxygen sensing technology. Most carbon dioxide sensors, however, have been developed for biomedical applications and the use of existing carbon dioxide sensors in food packaging applications is still not feasible (Kerry and Papkovsky, 2002).

3.6.2 Fluorescence-based Oxygen Sensors

Fluorescence-based oxygen sensors represent the most promising systems to date for remote measurement of headspace gases in packaged meat products. Reiniger *et al.* (1996) first introduced the concept of using luminescent dyes quenched by oxygen as non-destructive indicators in food packaging applications. A number of disposable oxygen sensing prototypes has been developed that can be produced at low cost and provide rapid determination of oxygen concentration (Kerry and Papkovsky, 2002).

The active component of a fluorescence-based oxygen sensor normally consists of a long-delay fluorescent or phosphorescent dye encapsulated in a solid polymer matrix. The dye-polymer coating is applied as a thin film coating on a suitable solid support. Molecular oxygen, present in the packaging headspace, penetrates the sensitive coating through simple diffusion and quenches luminescence by a dynamic, i.e. collisional, mechanism. Oxygen is quantified by measuring changes in luminescence parameters against a predetermined calibration. The process is reversible and clean: neither the dye nor oxygen is consumed in the photochemical reactions involved, no by-products are generated and the whole cycle can be repeated.

Materials for oxygen sensors must meet strict sensitivity and working performance requirements if they are to prove suitable for commercial intelligent packaging applications.

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They must also have fluorescence characteristics suited to the construction of simple measuring devices. Fluorescence and phosphorescence dyes with lifetimes in the microsecond range are best suited to oxygen sensing in food packaging. Other necessary features include suitable intensity, well resolved excitation and emission longwave bands and good photostability characteristics of the indicator dye. Such features allow sensor compatibility with simple optoelectronic measuring devices (LEDs, photodiodes, etc.), minimise interference by scattering and sample fluorescence, and allow long-term operation without recalibration (Papkovsky *et al.*, 1995). Materials using fluorescent complexes of ruthenium, phosphorescent palladium(II)- and platinum(II)-porphyrin complexes and related structures have shown considerable promise as oxygen sensors (Papkovsky *et al.*, 1991; 1995).

The combination of indicator dye and encapsulating polymer medium determines the sensitivity and effective working range of such sensors. For the purposes of food packaging applications, dyes with relatively long emission lifetimes ($\sim 40\text{--}500\ \mu\text{s}$) such as Pt-porphyrins combined with polystyrene as polymer matrix appear to offer greatest potential (Papkovsky *et al.*, 2000). Other polymers with good gas-barrier properties such as polyamide, polyethylene terephthalate and PVC are not suitable for oxygen sensing as oxygen quenching is slow in such media. The use of plasticised polymers is also unsuitable due to toxicity concerns associated with potential plasticiser migration.

Details relating to sensor fabrication and the criteria that must be considered in order that commercialisation of such technology becomes a reality is described in more detail by Kerry and Papkovsky (2002) and Kerry *et al.* (2006).

Publications on the suitability of fluorescence-based oxygen sensors have provided useful data on their effectiveness in meat packaging applications. Fitzgerald *et al.* (2001) examined the potential of platinum-based disposable oxygen sensors as a quality control instrument for vacuum-packed raw and cooked meat and MA packed sliced ham (Figure 3.4). Direct contact of sensors on the foods provided accurate oxygen profiles over time and correlated well with conventional headspace analysis. Smiddy *et al.* (2002a) used oxygen sensors to examine the effects of residual oxygen concentration on lipid oxidation in both anaerobically packaged MA and vacuum-packed cooked chicken. Similarly, this approach was repeated for raw and cooked beef (Smiddy *et al.*, 2002b). These studies further demonstrated the suitability of such sensors for measuring oxygen levels in commercially used meat packaging and their potential as predictors of quality. Papkovsky *et al.* (2002) used oxygen sensors to measure oxygen content in the headspace of four commercial sliced ham products. Accurate measurements were made under ambient light conditions, in direct contact with the product and under conditions of significant temperature variation. Although the sensor demonstrated minor changes in calibration as a result of direct physical contact with the meat surface over a prolonged period, these effects were minimised through optimisation of the sensor material. It is unlikely in any event, that sensors placed in direct contact with a meat product would be acceptable to producer or consumer alike. O'Mahony *et al.* (2004) used sensors printed directly onto the packaging material of *sous vide* beef lasagne. Although oxygen profiles, microbial growth and lipid oxidation were clearly correlated, further studies appear necessary to investigate issues relating to sensor/packaging material compatibility. Fluorescent oxygen sensors were also useful in detecting a substantial fraction of commercial anaerobic MA or vacuum packed meat products that contained elevated levels of oxygen (Papkovsky *et al.*, 2002; Smiddy *et al.*, 2002c).



Figure 3.4 Use of platinum fluorescent-based disposable oxygen sensors in MAP packed sliced ham (number 4 in figure indicating as part of this mail).

The development of oxygen sensors is indicative of a move towards commercialisation of indicator-based, intelligent, meat packaging systems. Full commercial realisation might ultimately mean the production of huge numbers of sensors for use throughout the meat distribution chain. It has been estimated that in today's terms, each sensor should cost less than €0.01 to produce (Kerry and Papkovsky, 2002) and impact minimally on packaged meat production costs.

3.6.3 Biosensors

Recently developed biosensor technologies represent another area with considerable potential for application in intelligent meat packaging systems. Biosensors are compact analytical devices that detect, record and transmit information pertaining to biological reactions (Yam *et al.*, 2005). They consist of a bioreceptor specific to a target analyte and a transducer to convert biological signals to a quantifiable electrical response. Bioreceptors are organic

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materials such as enzymes, antigens, microbes, hormones and nucleic acids. Transducers may be electrochemical, optical, calorimetric, etc., and are system dependent. Intelligent packaging systems incorporating biosensors have the potential for extreme specificity and reliability. Market analysis of pathogen detection and safety systems for the food packaging industry suggests that biosensors offer considerable promise for future growth (Alocilja and Radke, 2003).

The majority of available biosensor technology is not yet capable of commercial realisation in the food sector. ToxinGuard™ developed by Toxin Alert (Ontario, Canada) is a visual diagnostic system incorporating antibodies printed on polyethylene-based plastic packaging capable of detecting target pathogens such as *Salmonella* sp., *Campylobacter* sp., *Escherichia coli* 0517 and *Listeria* sp. (Bodenhammer, 2002; Bodenhammer *et al.*, 2004). When the food packaging comes into contact with targeted bacteria, a visual signal alerts the consumer or retailer. Toxinguard™ can be targeted to detect freshness degradation, as well as the presence of specific food hazards such as pesticides, or indicators of genetic modification.

Bioett has developed a system based on a biosensor for temperature monitoring. The Bioett System monitors the accumulated effect of temperature on products over time. The system consists of a chipless RF circuit with a built-in biosensor that can be read with a handheld scanner at various points in the supply chain. The information is stored in a database and can be used to analyse the cold chain and validate that the agreed temperature has been maintained. A Time Temperature Biosensor (TTB), attached to 5-kg cases of frozen meat balls, is activated at source. The biosensor registers the accumulated temperatures that the product has been exposed to and this information can be used to optimise and monitor the cold-chain distribution system. A scanner can read the biosensor via radio waves (radio frequency) and also uniquely identifies the goods using a barcode system. The scanner also incorporates a software defined radio subsystem that can also be used for reading of RFID tags. Such systems give some insight into products likely to become more mainstream in the years to come.

3.7 Indicators

Indicators may be defined as a substances that indicate the presence, absence or concentration of another substance, or the degree of reaction between two or more substances by means of a characteristic change, especially in colour. In contrast with sensors, indicators do not comprise receptor and transducer components and communicate information through direct visual change. Numerous forms of indicator exist.

3.7.1 Integrity Indicators

Another alternative approach to established package-destructive techniques for measuring meat quality is the use of non-invasive indicator systems. Such systems usually provide qualitative or semi-quantitative information through visual colorimetric changes or through comparison with standard references. The majority of indicators have been developed to test package integrity. The most common cause of integrity damage in flexible plastic packages is associated with leaking seals (Hurme, 2003). Permanent attachment of a leak

indicator or sensor (i.e. visual or optochemical) to a package holds promise as a means of ensuring package integrity through the distribution chain. A number of studies on package integrity in MAP meat products (Eilamo *et al.*, 1995; Randell *et al.*, 1995; Ahvenainen *et al.*, 1997; Smolander *et al.*, 1997) have established critical leak sizes and associated quality deterioration. Standard (destructive) manual methods for package integrity and leak testing are both laborious and can test only limited numbers of packs (Hurme, 2003). Currently available non-destructive detection systems have other disadvantages such as requirements for specialised equipment, slow sampling time and an inability to detect leakages that are penetrable by pathogens (Stauffer, 1988; Hurme and Ahvenainen, 1998).

Much of the research into integrity detection has focused on visual oxygen indicators for MA packaged products (the oxygen sensors discussed previously are also applicable to integrity testing). With the exception of high oxygen content MA packaging of fresh meat (primarily to enhance colour) many foods are packaged in low (0–2 %) atmospheres. In such cases, leaks normally result in a significant increase in oxygen concentration. Many visual oxygen indicators have been patented and are based mainly on the use of redox dyes (Yoshikawa *et al.*, 1987; Krumhar and Karel, 1992; Mattila-Sandholm *et al.*, 1995; Davies and Gardner, 1996). Such devices have been tested as leak indicators in MA packaged minced steaks and minced meat pizzas and reported as reliable (Eilamo *et al.*, 1995; Ahvenainen *et al.*, 1997). Disadvantages of such devices include high sensitivity (colour change resulting from oxygen concentrations as low as 0.1 % means that many indicators are susceptible to residual oxygen in MA packs) and reversibility (undesirable where leak-induced increases in oxygen are consumed through subsequent microbial growth). Few of these devices have been taken up commercially. One indicator system, specifically designed for MAP foods contains, in addition to an oxygen sensitive dye, an oxygen absorbing component and exemplifies active and intelligent packaging in a single system (Mattila-Sandholm *et al.*, 1998). In-line, non-destructive package leak detection systems are not yet commercially viable due to high costs and a lack of reliability.

A number of companies have produced oxygen indicators, the main application of which has been for the confirmation of proper functioning of oxygen absorbers. Trade names of such devices include Ageless Eye[®] (Figure 3.5), Vitalon[®], and Samso-Checker[®].

A visual carbon dioxide indicator system consisting of calcium hydroxide (carbon dioxide absorber) and a redox indicator dye incorporated in polypropylene resin was described by Hong and Park (2000) and may be applicable to certain meat packaging applications.

3.7.2 Freshness Indicators

The information provided by intelligent packaging systems on the quality of meat products may be either indirect (e.g. changes in oxygen concentration within packs may imply quality deterioration through established correlation) or direct. Freshness indicators provide direct product quality information resulting from microbial growth or chemical changes within a food product. Microbiological quality may be determined through reactions between indicators included within the package and microbial growth metabolites (Smolander, 2003). As yet the number of practical concepts of intelligent package indicators for freshness detection is very limited. Despite this, potential exists for the development of freshness indicators based on established knowledge of quality indicating metabolites. The improved detection of biochemical changes during storage and spoilage of foods (Dainty, 1996; Nychas *et al.*,

AGELESS-EYE® Oxygen Indicator

The AGELESS-EYE is an in-package monitor which indicates the presence of oxygen at a glance.

Magnified

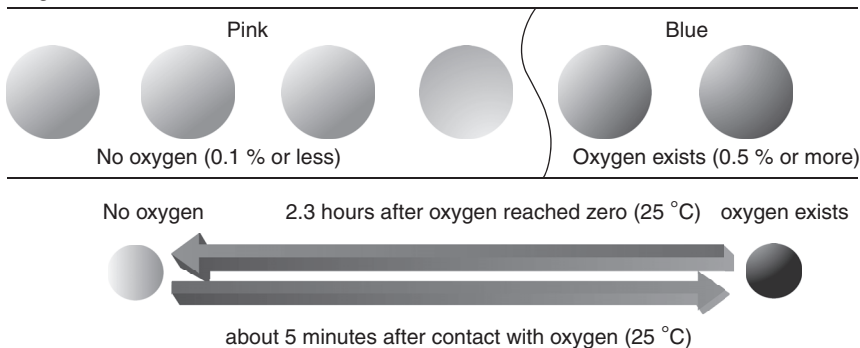


Figure 3.5 Ageless-Eye® by Mitsubishi Gas Chemical Co. used for oxygen detection. Reproduced with permission from Ageless sales, Mitsubishi Gas Chemical Co. Japan.

1998) provide the basis on which freshness indicators may be developed based on target metabolites associated with microbiologically induced deterioration.

The formation of different potential indicator metabolites in meat products is dependent on the interaction between product type, associated spoilage flora, storage conditions and packaging system. A number of marker metabolites associated with muscle food products exist upon which indicator development may be based.

Changes in the concentration of organic acids such as n-butyrate, L-lactic acid, D-lactate and acetic acid during storage offer potential as indicator metabolites for a number of meat products (Shu *et al.*, 1993). Colour based pH indicators offer potential for use as indicators of these microbial metabolites.

Ethanol, like lactic acid and acetic acid, is an important indicator of fermentative metabolism of lactic acid bacteria. Randell *et al.* (1995) reported an increase in the ethanol concentration of anaerobically MA packaged marinated chicken as a function of storage time.

Biogenic amines such as histamine, putrescine, tyramine and cadaverine have been implicated as indicators of meat product decomposition (Okuma *et al.*, 2000; Kaniou *et al.*, 2001; Rokka *et al.*, 2004). Given toxicological concerns associated with these compounds and their lack of impact on sensory quality, the development of effective amine indicators would be of benefit. Detection systems described by Miller *et al.* (1999) and Loughran and Diamond (2000) provide potential for commercial development. In 1999, COX Technologies, USA, launched FreshTag® colourimetric indicator labels that react to volatile amines produced during storage of fish and seafood products.

Carbon dioxide produced during microbial growth can in many instances be indicative of quality deterioration. In MA packaged meat products containing high carbon dioxide concentration (typically 20–80 %), indication of microbial growth by changes in carbon dioxide content is problematical, although application of pH dye indicators may hold promise in other meat packaging systems.

Hydrogen sulfide, a breakdown product of cysteine with intense off-flavours and low threshold levels, is produced during the spoilage of meat and poultry by a number of bacterial species. It forms a green pigment (sulphmyocin) when bound to myoglobin and this pigment formed the basis for the development of an agarose-immobilised, myoglobin-based freshness indicator in unmarinated broiler pieces (Smolander *et al.*, 2002). The indicator was not affected by the presence of nitrogen or carbon dioxide and offers potential.

Freshness indicators based on broad spectrum colour changes have a number of disadvantages that need to be resolved before widespread commercial uptake is likely. A lack of specificity means that colour changes indicating contamination can occur in products free from any significant sensory or quality deterioration. The presence of certain target metabolites is not necessarily an indication of poor quality. More exact correlations need to be established between target metabolite, product type and organoleptic quality and safety. The possibilities of false negatives are likely to dissuade producers from adopting indicators unless specific indication of actual spoilage can be guaranteed.

3.7.3 Time–Temperature Indicators

Among the intelligent packaging solutions available, time–temperature indicators or integrators (TTIs) are expected to witness the sharpest growth in sales in the next 5 years. A time–temperature indicator or integrator (TTI) is defined as a device used to show a measurable, time–temperature dependent change that reflects the full or partial temperature history of the food product to which it is attached (Taoukis and Labuza, 1989). Operation of TTIs is based on mechanical, chemical, electrochemical, enzymatic or microbiological change, usually expressed as a visible response in the form of a mechanical deformation, colour development or colour movement (Taoukis and Labuza, 2003). The visible response thus gives a cumulative indication of the storage temperature to which the TTI has been exposed. TTIs are classified as either partial history or full history indicators, depending on their response mechanism. Partial history indicators do not respond unless a temperature threshold has been exceeded and indicate that a product has been exposed to a temperature sufficient to cause a change in product quality or safety. Full history TTIs give a continuous temperature-dependent response throughout a product's history and constitute the main focus of interest for research and commercial exploitation.

Essentially TTIs are small tags or labels that keep track of time–temperature histories to which a perishable product is exposed from the point of manufacture to the retail outlet or end-consumer. Their use in meat and poultry products, where monitoring of the cold distribution chain, microbial safety and quality are of paramount importance, offers enormous potential.

The basic requirement of an effective TTI is to indicate clear, continuous, irreversible reaction to changes in temperature. Ideally, TTIs should also be low cost, small, reliable, easily integrated into food packaging, have a long pre- and post-activation shelf-life and be unaffected by ambient conditions other than temperature. TTIs should also be flexible to a range of temperatures, robust, pose no toxicological or safety hazard and convey information in a clear manner.

A large number of TTI types have been developed and patented, the principles and applications of which have been reviewed previously (Taoukis and Labuza, 2003). TTIs currently commercially available include a number of diffusion, enzymatic and polymer-based systems, all of which offer potential in meat and poultry products.

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Diffusion-based TTIs. The 3M Monitor Mark[®] (3M Company, St Paul, Minnesota, USA) is a non-reversible indicator dependent on the diffusion of a coloured fatty acid ester along a porous wick made of high quality blotting paper. The measurable response is the distance of the advancing diffusion front from the origin. The useful range of temperatures and the response life of the TTI are determined by the type and concentration of ester.

Another diffusion-based TTI, Freshness Check[®], produced by the same company incorporates a viscoelastic material that migrates into a diffusively light-reflective porous matrix at a temperature dependent rate. This causes a progressive change in the light transmissivity of the porous matrix and provides a visual response.

Enzymatic TTIs. The VITSAB[®] TTI (VITSAB A.B., Malmö, Sweden) is based on a colour change induced by a drop in pH resulting from the controlled enzymatic hydrolysis of a lipid substrate. The indicator consists of two separate compartments containing an aqueous solution of lipolytic enzymes and another containing the lipid substrate suspended in an aqueous medium and a pH indicator mix. Different enzyme–substrate combinations are available to give a variety of response lives and temperature dependencies. Activation of the TTI is brought about by mechanical breakage of a seal separating the two compartments and may be done manually or by online automation. Hydrolysis of the substrate causes a drop in pH and a subsequent colour change in the pH indicator from dark green to bright yellow. Visual evaluation of the colour change is made by reference to a five-point colour scale. CheckPoint[®] labels are the latest TTIs developed by VITSAB, which comprise a label type designed to create a better subjective reading response for users and offer direct application to poultry and ground beef products (Figure 3.6).

Cryolog (Gentilly, France) has developed two TTI systems relevant to the food industry. (eO)[®] is an adhesive label TTI in the form of a small gel pad shaped like the petals of a flower that changes from green (good) to red (not good) as shown in Figure 3.7. The colour change represents a pH change due to microbial growth of food microorganisms within the gel itself and its abrupt nature removes any possibility for confusion over whether



Figure 3.6 The TTI CheckPoint[®] system by Vitsab International, Sweden.



Figure 3.7 The TTI Cryolog system from Gentilly, France. Reproduced with permission from Cryolog S.A., Gentilly, France.

the end point has been reached. TRACEO[®] is a transparent adhesive label, designed for use on refrigerated products, placed over the barcode. It uses colouring and opacifying reactions (colourless to red) to indicate when a product is no longer fit for consumption, either because the product has reached its 'use-by date', or because it has been subject to a critical accumulation of ruptures in the cold chain. Once the label is red the barcode is rejected by the scanner at check-out.

Polymer-based TTIs. Lifelines Freshness Monitor[®] and Fresh-Check TTIs (Lifelines Technology, Inc., Morris Plains, New Jersey, USA) are based on temperature dependent polymerisation reactions in which diacetylene crystals polymerise via 1,4-addition polymerisation to a highly coloured polymer. Resulting changes in reflectance can be measured by scanning with a laser optic wand. The Fresh-Check[®] consumer version uses a circular label in which the colour of the inner circle is compared to that of an outer circle in order to establish use-by status.

OnVu[™] (Ciba Specialty Chemicals, Inc., Switzerland) produce TTI labels based on organic pigments that change colour with time at rates determined by temperature. The TTI labels consist of a heart shaped 'apple' motif containing an inner heart shape. The image is stable until activated by UV light from an LED lamp, when the inner heart changes to a deep blue colour. A filter is then added over the label to prevent it being recharged. The blue inner heart changes to white as a function of time and temperature (Figure 3.8). The system can be applied as a label or printed directly onto the package. Universal Product Codes (UPC) or barcodes, are quintessential to food packaging. Data acquired from barcode readers provides an enormous wealth of information. The Food Sentinel System[™] from SIRA Technologies in the USA uses a modified barcode containing a proprietary thermochromic printing ink which is printed in non-scannable colour. On encountering product abuse, the thermochromic ink changes to an irreversible deep magenta colour which is visible and will

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Figure 3.8 The TTI system OnVu™ from Ciba Specialty Chemicals, Inc., Switzerland. Reproduced with permission from Ciba Specialty Chemicals Inc., Switzerland.

be detected during scanning (Figure 3.9). It is therefore capable of adding a temperature and shelf-life monitor to any product barcode, thus preventing the sale of contaminated food and archiving the incident.

A number of TTI systems have their histories read by RFID readers (see next section) rather than by direct visual means. These include Bioett®, Timestrip®, KSW Microtec® and TempTime®. The use of electronic readers allows storage of information and subsequent downloading to local networks and databases.

A number of validation studies has been undertaken in order establish the usefulness of TTIs to food products (Riva *et al.*, 2001; Shimoni *et al.*, 2001; Welt *et al.*, 2003). Yoon *et al.* (1994) showed a positive correlation between oxidative stability and TTI colour change using a phospholipid/phospholipase-based TTI in frozen pork. Smolander *et al.* (2004)

SIRA Food Sentinel System™

Activated Label

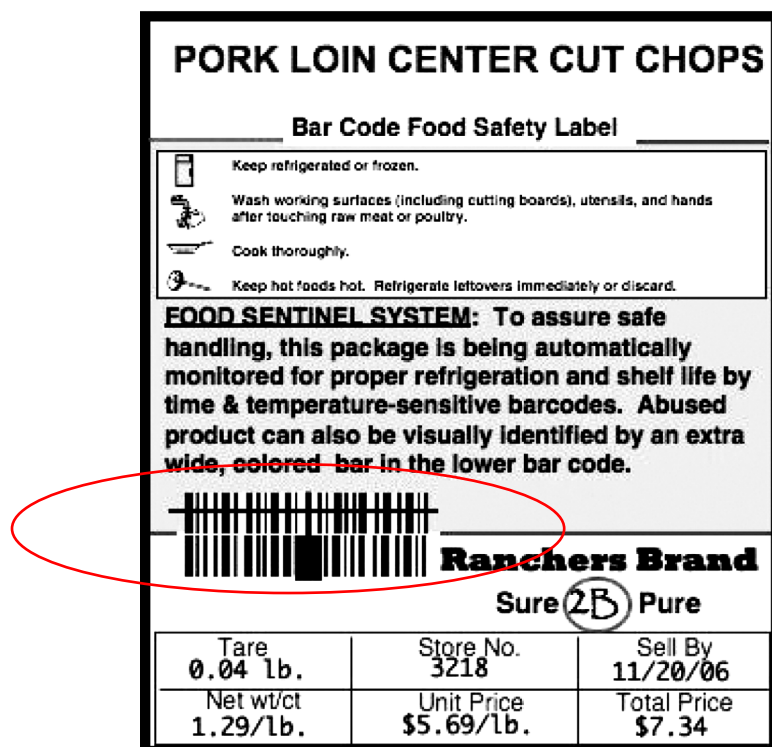


Figure 3.9 The Food Sentinel System™ from SIRA Technologies in the USA. Reproduced with permission from SIRA Technologies Inc., USA.

and Vainionpää *et al.* (2004) determined the applicability of VITSAB®, Fresh-Check® and 3M Monitor® TTIs for monitoring the quality of MA packed broiler cuts at different temperatures and in comparison with several standard analytical methods respectively. In both studies, TTIs were closely correlated with microbiological analyses of spoilage bacteria and were shown to be more effective than certain metabolic quality indices such as spoilage-associated volatiles, biogenic amines and organic acids.

Initial expectations for the potential of TTIs to contribute to improved standards in food distribution, quality and safety have not been realised to date. Factors such as cost, reliability and applicability have all been influential in this regard. The cost of TTIs has been estimated to range from \$0.02 to \$0.20 per unit (Taoukis and Labuza, 2003). Given normal economies of scale, cost-benefit analysis should favour more widespread use of TTIs in due course. The use of thermochromic inks (inks that change colour with temperature) is likely to become more widespread particularly in the light of views that only printing can deliver sophisticated electronic capabilities to packaging at a price that makes next generation TTIs

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economically viable. Recent developments in the area of printed electronics make such a scenario a real possibility.

In recent years, TTI systems have achieved high standards of production and quality assurance and can provide reproducible responses according to BSI specifications (BS 7908: 1999). A substantial hurdle to more extensive commercialisation of TTIs has been the question of applicability. Generalisations on the relationship between temperature and quality of food classes have proved insufficient, as even foods of similar type differ markedly in terms of response. For successful application of TTIs to meat and poultry products, and food products in general, there is a requirement that the TTI response matches the behaviour of the food. Whilst the expectation for a TTI to strictly match the behaviour of a foodstuff over a wide temperature range is unfeasible, a thorough knowledge of the shelf-life loss behaviour of a food system based on accurate kinetic models is essential (Taoukis and Labuza, 2003). Advances in food modelling are now making this possible (Taoukis, 2001).

In 1991 a UK survey (Anonymous, 1991) indicated that 95 % of respondents ($n = 511$) considered TTIs to be a good idea but indicated that substantial publicity or an educational campaign would be required for general use. It is likely that such attitudes still apply today. Despite predictions for the full commercial realisation of TTIs, adoption has been limited. However, given technological development and greater consumer appreciation for the need for food safety monitoring (particularly in meat products), analysts believe that TTIs will find widespread commercial application in the food industry. The critical importance of maintaining proper storage temperatures for meat and poultry products throughout the distribution chain means that this sector of the food industry could be a major beneficiary from such a development.

3.8 Radio Frequency Identification

Radio Frequency Identification (RFID) is an electronic, information-based form of intelligent packaging. RFID uses tags affixed to assets (cattle, containers, pallets, etc.) to transmit accurate, real time, information to a user's information system. RFID is one of the many automatic-identification technologies (a group which includes barcodes) and offers a number of potential benefits to the meat production, distribution and retail chain. These include traceability, inventory management, labour saving costs, security and promotion of quality and safety (Mousavi and Sarhadi, 2002). Prevention of product recalls is also considered to be an important role of RFID technology (Kumar and Budin, 2005). RFID technology has been available for approximately 40 years although its broad application in packaging is a relatively recent development.

At its most basic level, an RFID tag contains a tiny transponder and antenna that have a unique number or alphanumerical sequence; the tag responds to signals received from a reader's antenna and transmits its number back to the reader. While the tags are relatively simple, much better inventory information than barcode or human entry systems can be gained through tracking software. RFID tags have the advantage over barcoding in that tags can be embedded within a container or package without adversely affecting the data. RFID tags also provide a non-contact, non-line-of-sight ability to gather real-time data and can penetrate non-metallic materials including bio-matter (Mennecke and Townsend, 2005). Tags can hold simple information (such as identification numbers) for tracking or can carry

more complex information (with storage capacity at present up to about 1 MB) such as temperature and relative humidity data, nutritional information, cooking instructions, etc. Read-only and read/write tags are also available depending on the requirements of the application in question.

Tags are classified according to two types: active tags function with battery power, broadcast a signal to the RFID reader and operate at a distance of up to 50 metres. Passive tags have a shorter reading range (up to about 5 metres) and are powered by the energy supplied by the reader (giving them essentially unlimited life).

Common RFID frequencies range from low (~ 125 KHz) to UHF (850–900 MHz) and microwave frequencies (~ 2.45 GHz). Low frequency tags are cheaper, use less power and are better able to penetrate non-metallic objects. These tags are most appropriate for use with meat products, particularly where the tags might be obscured by the product itself and are suitable for close-range scanning of objects with high water content.

The costs of RFID are decreasing as major companies such as Wal-Mart, 7-Eleven and Marks & Spencer adopt the technology. At present, the cost of passive RFID tags ranges from approximately \$0.50 to \$1.00. For the technology to be truly competitive it is estimated that tags must cost less than \$0.05 (others believe tags must be available at less than \$0.01) (Want, 2004). Opinion on possible cost developments differs. Mennecke and Townsend (2005) reported that tags are expected to fall to the \$0.01 per tag level after 2007, although concern remains that tags will be prove too expensive for individual food product monitoring. Initiatives to establish formal standards should serve to reduce further the cost of RFID. The use of organic semiconductor materials, capable of being coated on flexible substrates such as plastics, to create electronic circuits is apparently close to commercial realisation. It is forecast that such printable electronics will be widely available within two or three years. Such a development would see the price of RFID tags drop to that of bar-codes and catalyse the spread of RFID technology.

At present, a number of countries are using RFID to trace individual animals (mainly cattle) from birth to the processing plant. The key to individual animal traceability lies in the ability to transfer animal information sequentially and accurately to sub-parts of the animal during production. RFID-based tracking systems provide an automated method of contributing significantly to that information exchange (Mennecke and Townsend, 2005). At present, individually RFID tagged meat products are not available to the consumer, although the use of RFID tagging of meat cuts has extended to the pig processing industry (Dalehead Foods, Cambridge, UK), where tracking occurs from the individual pig to its subsequent primal pieces, i.e. hams. Although the purpose of this tracking scheme is for quality control, employee accountability and precision cutting, and does not extend beyond the cutting room floor or provide information about the individual animal with the final product, it does exemplify the developing use of RFID technology within the meat industry. In another instance, RFID has been used to track boxed imported beef into the UK from Africa.

The effective use of RFID is extremely specific to the immediate environment in which the technology is applied. Customised system design and trials to minimise localised interferences are necessary to establish properly functioning systems. Such requirements, along with a poorly understood cost efficiencies, are contributing to a slow uptake of this technology in the meat industry. The implementation of RFID technology as an intelligent packaging strategy for meat products is still largely hypothetical. Should the forecasts for an exponential, multi-sector increase in RFID use come to be realised, it is

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likely that such an expansion will also be reflected in applications for meat packaging and distribution.

3.9 Potential Future Applications for Smart Packaging with Meat Products

In addition to those packaging techniques already discussed, other packaging technologies more commonly associated with other foodstuffs (Ahvenainen, 2003) may have potential application for meat and meat products. For example, self-heating aluminium or steel cans and containers, currently used by coffee manufacturers (Nescafe, 'hot when you want it'), may find use in the production of ready meals containing various meats. Microwave susceptors typically consist of aluminium or stainless steel metallised polyester films and are used to provide even heating, surface browning and crisping in microwave-oven-heated foods (Ahvenainen, 2003). Incorporation of such susceptors or modifiers into meat product packages may represent a future development for meat and meat-based convenience-style products. Flavour/odour adsorbers also have potential in active packaging technology. Adsorber systems employ mechanisms such as cellulose triacetate, acetylated paper, citric acid, ferrous salt/ascorbate and activated carbon/clays/zeolites. A Swedish company, EKA Noble, in cooperation with a Dutch company Akzo, has developed a range of synthetic aluminosilicate zeolites, which they claim absorbs odorous gases within their highly porous structure. Their BHMTM powder can be incorporated into packaging materials, especially those that are paper based and odorous aldehydes are adsorbed in the pore interstices of the powder. Such technology may prove useful in removing off-odours and flavours generated, for example, as a result of the oxidation of lipids in packaged muscle foods. Similar applications may exist for various flavour emitting polymers (Ahvenainen, 2003).

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4

Application of Time–Temperature Integrators for Monitoring and Management of Perishable Product Quality in the Cold Chain

Petros S. Taoukis

4.1 Introduction

Research and industrial data show that chilled or frozen distribution, handling and storage of food and other perishable products frequently deviate from specified temperature conditions. Since temperature is the main determining post-processing parameter for shelf-life under Good Manufacturing Practices, following and managing it to the point of final use of the product is of central importance. This task is very challenging, especially if one considers the potential variation in temperature exposure of single products within batches or transportation subunits. A cost-efficient way would be required to monitor the temperature conditions of the products, individually, and to indicate their real safety and quality throughout the cold chain. Smart, active packaging tags, Time Temperature Integrators (TTI), can be employed (Taoukis and Labuza, 2003). Based on reliable models of product shelf-life and the kinetics of TTI response, the effect of temperature can be monitored, recorded and translated, from production to the final use. A TTI-based system could lead to realistic control of the chill chain, optimization of stock rotation, reduction of waste, and efficient shelf life management. Most of the studies, developed methodology and applications refer to chilled and frozen food products but the same principles would apply for all other perishable consumer goods, provided that the mechanisms of quality degradation of these products are approached thoroughly as in the case of foods.

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A novel chill chain management system, coded SMAS, was developed (Koutsoumanis *et al.*, 2005) in order to use the information from the TTI response at designated points of the chill chain, ensuring that the temperature-burdened products reach consumption at an acceptable quality level. The effectiveness of the TTI based SMAS system was evaluated by simulations and field test experiments in order to demonstrate and quantify the improvement in food product quality at the time of consumption in comparison with the conventional First In First Out (FIFO) rule.

4.2 Time–Temperature Integrators

TTI are inexpensive, active ‘smart labels’ that can show an easily measurable, time–temperature dependent change that reflects the full or partial temperature history of a product to which it is attached (Taoukis and Labuza, 1989). The principle of TTI operation is a mechanical, chemical, enzymatic or microbiological irreversible change, usually expressed as a visible response in the form of a mechanical deformation, colour development or colour movement. The rate of change is temperature dependent, increasing at higher temperatures similarly to the deteriorative reactions responsible for product quality deterioration. The visible response of the TTI thus cumulatively reflects the time–temperature history of the product it accompanies.

A number of TTI systems have been proposed in the past, of which few reached the industrial prototype and fewer achieved commercial application. TTI technologies that are currently available and aim to satisfy most of the above requirements are based on different operational principles.

The CheckPoint® TTI, (VITSAB A.B., Malmö, Sweden) is an enzymatic system. The TTI is based on a colour change caused by a pH decrease that is the result of a controlled enzymatic hydrolysis of a lipid substrate. Hydrolysis of the substrate causes acid release and the pH drop is translated into a colour change of a pH indicator from deep green to bright yellow to orange red (Figure 4.1). Different combinations of enzyme-substrate types and concentrations can be used to give a variety of response lives and temperature dependencies.

The Fresh-Check® TTI (Temptime Corp., Morris Plains, NJ, USA) is based on a solid state polymerization reaction, resulting in a highly coloured polymer. The response of the TTI is the colour change measurable as a decrease in reflectance (Figure 4.2). The colour of the ‘active’ centre of the TTI is compared to the reference colour of a surrounding ring.

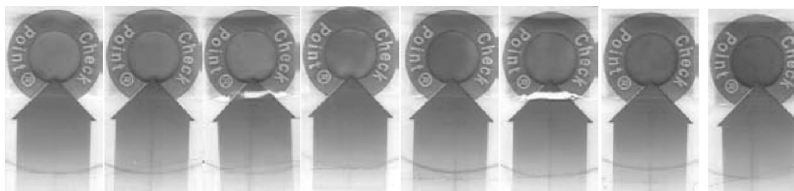


Figure 4.1 Response scale of enzymatic CheckPoint® TTI (Vitsab, Sweden).

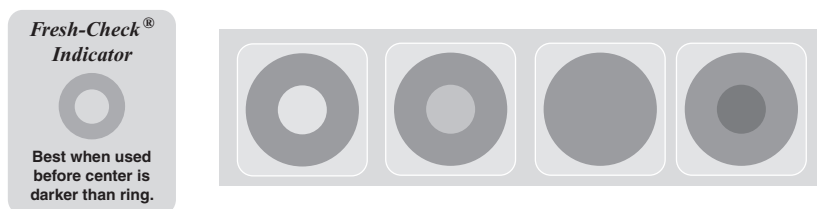


Figure 4.2 Polymer based Fresh-Check® TTI (Temptime Corp.).

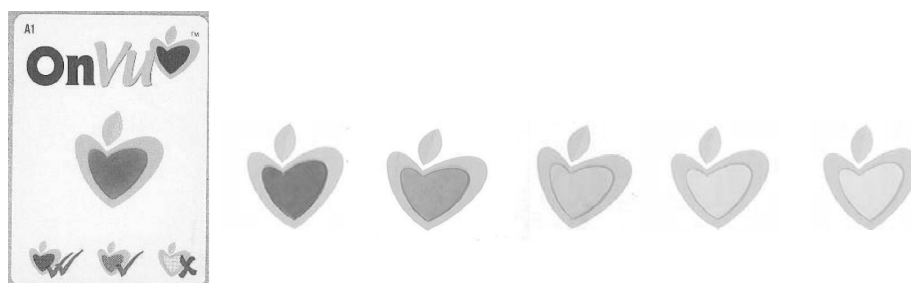


Figure 4.3 Solid state photochromic OnVu™ TTI (Ciba Specialty Chemicals).

Before use the indicators, active from the time of production, have to be stored deep frozen where change is very slow.

The OnVu™ TTI (Ciba Specialty Chemicals & Freshpoint, SW) is a newly introduced solid state reaction TTI (Figure 4.3). It is based on the inherent reproducibility of reactions in crystal phase. Photosensitive compounds are excited and coloured by exposure to low wavelength light. This coloured state reverses to the initial colourless at a temperature depended rate. This TTI can take the form and be applied as a photosensitive ink.

The (eO)® TTI (CRYOLOG, Gentilly, France) is based on a time-temperature depended pH change caused by controlled microbial growth that is expressed to colour change through suitable pH indicators (Figure 4.4).

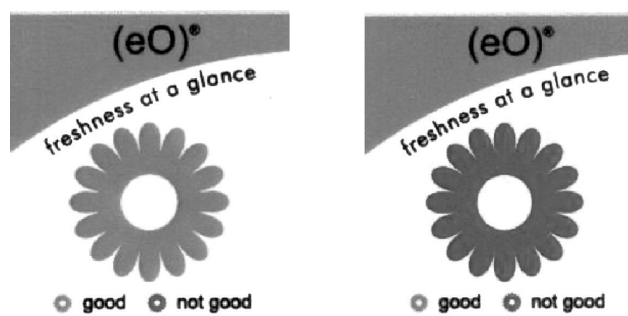


Figure 4.4 Microbial TTI (eO)® (Cryolog, France).

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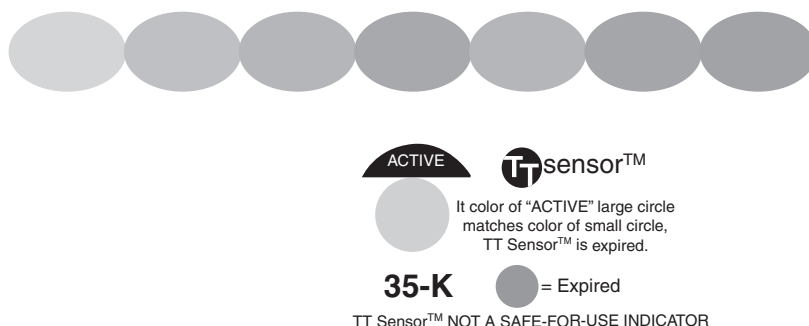


Figure 4.5 TT Sensor™ TTI (Avery Dennison Corp.).

The TT Sensor™ TTI (Avery Dennison Corp., USA) is based on a diffusion–reaction concept. A polar compound diffuses between two polymer layers and the change of its concentration causes the colour change of a fluorescent indicator from yellow to bright pink (Figure 4.5).

The 3M Monitor Mark® (3M Co., St Paul, Minnesota) is based on diffusion of proprietary polymer materials (Figure 4.6). A viscoelastic material migrates into a diffusely light-reflective porous matrix at a temperature dependent rate. The response rate and temperature dependence is controlled by the tag configuration, the diffusing polymer's concentration and its glass transition temperature and can be set at the desirable range.

Use of TTI can help optimize product distribution, improve shelf life monitoring and management and thus reduce product waste and benefit the consumer by improving shelf life monitoring and management. Cost, reliability, and effective application are criteria for practical success of TTI. The cost is volume dependent, ranging from 2 to 20 cents per unit. Current TTI systems provide reliable and reproducible responses according to their specifications. With regards to effective application of the suitable TTI for the intended perishable product, it has been widely assumed that the response of the TTI should exactly mimic quality deterioration behaviour of the product to be monitored at all temperatures.

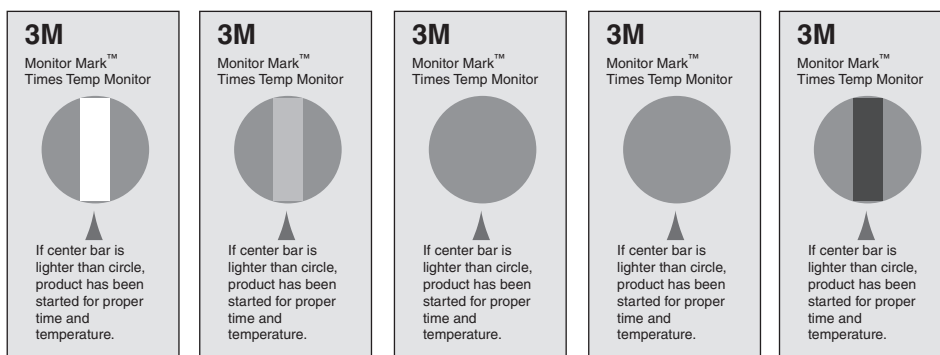


Figure 4.6 Diffusion based 3M Monitor Mark® TTI.

This approach would require an unlimited number of TTI models. Instead, a methodology of translating TTI response to product quality status based on systematic modelling of both the TTI and the food could be used as a tool for product quality monitoring and shelf life management.

Determination and modelling of the shelf life or keeping quality of perishable consumer products is the most important prerequisite for the application of a TTI-based monitoring and management system, usually evaluated by the measurement of the change of one or more characteristic quality indices, A , with time t . The selected indices can be chemical (like development of off flavours or off colours from oxidations or other chemical reactions, loss of an active component like a nutrient, a cosmetic or a therapeutic ingredient), biological (microbial growth, enzymatic deterioration) or physical (texture loss, phase separation). The change of indice A can be expressed as

$$f(A) = k(T)t \quad (1)$$

where $f(A)$ is the *quality function* of the product and k the reaction rate constant.

The rate constant is an exponential function of inverse absolute temperature, T , given by the Arrhenius expression,

$$k = k_{\text{ref}} \exp \left[\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (2)$$

where k_{ref} is the reaction rate constant at a reference temperature T_{ref} , E_A is the activation energy of the reaction that controls quality loss and R the universal gas constant. The form of the quality function of the product depends on the reaction order of the phenomenon controlling the deterioration of the product, e.g. $f(A) = \ln(A_0/A_t)$ for $n = 1$ order and $f(A) = [A_t^{1-n} - A_0^{1-n}]/n - 1$ for $n \neq 1$. The activation energy of food related chemical reactions and spoilage or pathogenic microbial growth usually falls within 30–140 kJ/mol (Taoukis *et al.*, 1997).

The value of the quality function, $f(A)_t$, at time t , after exposure of the product at a known variable temperature exposure, $T(t)$, can be found based on Equation (1) by calculating the integral of $k[T(t)] dt$, from 0 to time t . We can define the effective temperature, T_{eff} , as the constant temperature exposure to which for the same time results in the same quality value, $f(A)_t$, as the variable temperature distribution, $T(t)$. The same kinetic approach can be used to model the measurable change X of the TTI. If a *response function* $F(X)$ can be defined such that $F(X) = kt$, with k an Arrhenius function of T , then the effective temperature concept as described above can also be used for the TTI. For an indicator exposed to the same temperature distribution, $T(t)$, as the food product, and corresponding to an effective temperature T_{eff} , the response function can be expressed as

$$F(X)_t = k_{I_{\text{ref}}} \exp \left[\frac{-E_{A_I}}{R} \left(\frac{1}{T_{\text{eff(TTI)}}} - \frac{1}{T_{\text{ref}}} \right) \right] t \quad (3)$$

where $k_{I_{\text{ref}}}$ and E_{A_I} are the Arrhenius parameters of the indicator.

Thus for applying a TTI based product quality monitoring scheme we need to define experimentally the quality function of the product, the response function of the TTI and the respective kinetic parameters. From the measured response X of the TTI at time t the value of the response function is calculated, from which by solving Equation (3), the T_{eff} of the exposure is derived. With the T_{eff} and the kinetic parameters of the product known,

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the quality function value is calculated from Equations (2) and (1), and the value of index A is found. This gives the extent of the quality deterioration of the product and allows the calculation of the remaining shelf-life at any reference conditions.

The developed principles give a potential user the ability to select and apply the most appropriate TTI without the need for extensive side-by-side testing of the product and the TTI. A TTI with an activation energy E_{A_i} that differs from the product's E_A by less than 20 kJ/mol would result in a T_{eff} estimation of the product within ± 1 °C.

Based on TTI testing and the described principles, the response function and the response rate of different TTIs has been reported (Taoukis *et al.*, 1999; Taoukis, 2001; Mendoza *et al.*, 2004; Giannakourou and Taoukis, 2002; Giannakourou *et al.*, 2005). More recent testing has been conducted by the author's research group (Taoukis, 2007, unpublished data). The Arrhenius parameters that describe the temperature dependence of the response were obtained by plotting the logarithm of the response rate constant versus temperature ($1/T$) and calculating the best statistical fit.

All tested TTIs can be tuned with regards their total response time from few hours to several weeks and thus cover the required monitoring time for the different perishable products. Most TTIs have to be manufactured with different specifications to achieve this (e.g. use different enzyme or chemical concentration). The OnVu TTI has the flexibility to set the response length by selection of activation time.

The second requirement is that the temperature dependence of the quality of the products expressed by the E_A value should be similar to the E_A of the TTI response. The TTIs fall in the useful range with the Checkpoint and the OnVu showing the widest range and flexibility of setting the E_A value. The Fresh Check and TT Sensor basically have fixed E_A value in the middle of the range, where most but not all products fall.

The response signal is the parameter that determines the ease of reading of the TTI. The Checkpoint and eO TTIs change from green to red, a change that is understandable and discernible by the consumer. The TTsensor changes from yellow to bright pink. The Fresh-Check change is from transparent to dark blue and the OnVu from dark blue to white. All configurations are easy to read visually and translated if the correct message follows the TTI and if the appropriate training is provided to the chill chain personnel.

Other aspects that can be considered when evaluating a TTI have to do with their applicability. All tested TTIs come as shelf adhesive labels suitable for high speed application on the food product packages. Additionally the OnVu TTI can be pre-applied on the packaging material as a temperature sensitive ink.

Another issue concerns the TTI stability before application. The Fresh-Check and eO TTIs are active from the time of production and have to be stored and transported frozen. At these temperatures the rate of change is practically zero. The other three types are activated at application. The Checkpoint has two separate compartments with the enzyme and substrate. The separating seal is broken by pressure at the time of application, and enzyme and substrate are mixed to start the reaction, which translates into the colour response of the TTI. The Checkpoint before use is cold stored to assure stability and full activity of the enzyme. However this TTI can be also stored in ambient temperature for short times, e.g. during transportation. The TT Sensor and OnVu TTI can be stored at ambient conditions before activation for long times. TT sensor is activated by attaching the top polymer layer so that diffusion starts. The OnVu is activated by exposure to a UV source for a preset time (5–30 s) that will also determine the total response time.

Another practical index is of course cost. Cost per TTI unit depends on the TTI technology but also very much on the production volume. At this moment no TTI is produced in high enough volumes so only estimates can be obtained. Based on these estimates and indicative quotes from the TTI developers cost could range from 1 to 15 Euro cents.

The characteristics of all the tested TTIs are summarized in Table 4.1.

4.3 Cold Chain Management

The information provided by the TTI smart labels, translated to remaining shelf life at any point of the cold chain, can be used to manage shelf-life by improving distribution control and stock rotation practices. The approach currently used is the First-In/First-Out (FIFO) system according to which, products received first and/or with the closest expiration date on the label are shipped, displayed and sold first. This approach aims at establishing a 'steady state' with all products being sold at the same quality level. The assumption is that all products have gone through uniform handling, thus quality is basically a function of time. The use of the indicators can help to establish a system that does not depend on this unrealistic assumption. The objective is again a 'steady state' situation with the least remaining shelf life products being sold first. This approach was coded LSFO (Least Shelf-life First Out). The LSFO reduces the number of rejected products and largely eliminates consumer dissatisfaction since the fraction of product with unacceptable quality at the time of use or consumption is minimized. LSFO aims at reducing the rejected products at the consumer end, by promoting, at selected decision making points of the product life cycle, those product units with the shorter shelf-life, according to the response of the attached TTI (Taoukis *et al.*, 1998; Giannakourou and Taoukis, 2002). LSFO allows the calculation of the actual remaining shelf life of individual product units at strategic control points of the chill chain. Based on the distribution of the remaining shelf life, decisions can be made for improved handling, shipping destination and stock rotation. A further improvement of the LSFO approach, is a chill chain management system coded SLDS (Shelf-Life Decision System) (Giannakourou and Taoukis, 2003). Compared with LSFO, SLDS policy additionally takes into account the realistic variability of the initial quality state A_0 of the product.

The state of the TTI technology and of the scientific approach with regard to the quantitative safety risk assessment in foods allows the undertaking of the next important step, i.e. the study and development of a TTI-based management system that will assure both safety and quality in the food chill chain (Koutsoumanis *et al.*, 2005). The development and application of such a system, coded with the acronym SMAS, was the target of the multinational European research project 'Development and Modeling of a TTI based Safety Monitoring and Assurance System (SMAS) for chilled Meat Products' (project QLK1-CT2002-02545, 2003-2006; <http://smas.chemeng.ntua.gr>). SMAS uses the information from the TTI response at designated points of the chill chain, ensuring that the temperature-burdened products reach consumption at acceptable quality level. Although SMAS is developed for meat products the same principles can be effectively applied to the management of the chill chain of all chilled food or non-food perishable products.

The effectiveness of the TTI based SMAS system was evaluated by running a large number of chill chain scenarios using a Monte Carlo simulation approach. Field test experiments

Table 4.1 *TTI properties*

Type of TTI	Operation principle	Response type	Response range	E_A range (kJ/mol)	Activatable	Cost ^a
CheckPoint® Types M, L	Enzymatic	Tricolour Green to yellow to red	Hours to weeks at 4 °C	70–170	Y	B
Fresh-Check®	PolymERIC	Colourless to blue	Hours to weeks at 4 °C	80–90	N	A
OnVu™	Photochemical	Dark blue to colourless	Hours to weeks at 4 °C	90–150	Y	A
TT Sensor™	Diffusion-reaction	Yellow to pink	Hours to weeks at 4 °C	115–125	Y	B
eO	Microbiological	Green to red	Hours to weeks at 4 °C	100–110	N	B

^aA: 1–5 cents, B:5–15 cents

to demonstrate and quantify the improvement at the time of consumption in comparison to the conventional First-In/First-Out (FIFO) rule, were also conducted.

The SMAS decision making routine at a specified control point of the chill chain is based on the microbial growth that has potentially occurred within the period between production and arrival of the product at the control point. The growth is estimated based on the product's characteristics and the time-temperature history of the product using the appropriate predictive model. The above elements form the programme core of an integrated software that allows the calculation of growth in individual product units (e.g. small pallets, 5–10 kg boxes or single packs) at strategic control points of the chill chain. Based on the relative growth, it is possible to make decisions for optimal handling, shipping destination and stock rotation, aiming to obtain a narrow distribution of quality at the point of consumption. At a certain point of the chill chain, e.g. at a distribution centre, product from the same initial shipment is split in half and forwarded to two different retail markets, one close and a distant one that requires long transportation. The split could be random according to conventional, currently used FIFO practice or it can be based on the actual microbial growth of the product units and the developed decision system. For all units, the time-temperature history of the product, monitored by TTI, is input. This information directly fed into a portable unit with the SMAS software, is translated to microbial status, N_t , based on the growth models of the pathogen of concern. Having calculated N_t for all the n product units, a microbial load distribution for the products at the decision point is constructed. Based on the load of each product unit relative to this distribution, decisions about its further handling are made (Figure 4.7).

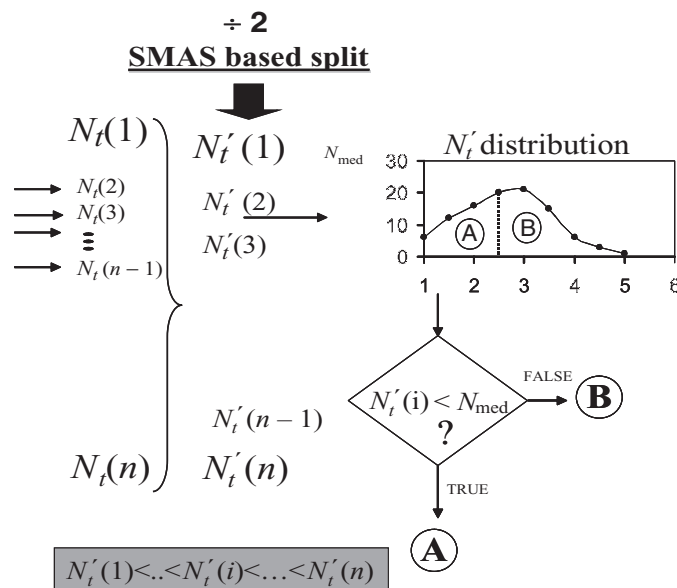


Figure 4.7 Classification of products based on their microbial load and rationale of SMAS based split at the decision point (where A and B are the two possible destinations, the distant and the local market).

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In order to simulate the results of the application of the developed SMAS system and quantitatively prove its effectiveness the Monte Carlo method can be applied (Koutsoumanis *et al.*, 2005). By taking into account the status of the product after production and various temperature distributions at different steps and alternative storage conditions, the distribution of the quality of the studied set of products at the final stage of consumption can be estimated.

To confirm the SMAS effectiveness appropriate experiments were also designed and conducted. One such experiment is described below to demonstrate the SMAS approach and the kind of information required for its application.

Modified-atmosphere-packed fresh pork cuts, were used in the experimental chill chain simulation. Two sets of experiments were conducted. The first was used to model the growth of the natural spoilage microflora of the products and the second for the 'field test' experiment. Fifty 600-g MA packaged pork cuts (60 % CO₂, 40 % air) were stored under controlled isothermal conditions (0, 5 and 10 °C) in high-precision (± 0.2 °C) low-temperature incubators. Samples were taken at appropriate time intervals to allow for efficient kinetic analysis of microbial growth. Total plate count and lactic acid bacteria, the dominant spoilage flora at these conditions were measured. Sensory evaluation was also conducted at each sampling time.

Lactic acid bacteria were the dominant organisms at all temperatures in MAP samples. The growth data of spoilage bacteria of pork cuts stored at different isothermal conditions (0, 5, 10 °C) were modelled as a function of time using the Baranyi model, and the kinetic parameters (exponential growth rate constant k , lag phase) were estimated. The temperature dependence of the kinetic parameters was modelled using the Arrhenius equation. The Arrhenius model sufficiently described the temperature dependence of the growth of spoilage lactic acid bacteria. At all temperatures, growth of lactic acid bacteria, which is a well established spoilage index for MAP chilled meat, followed closely the decrease of sensory quality. End of shelf-life coincided with an average level of log 7.2 of lactic acid bacteria within the studied range of temperatures.

For the field test the same major meat packer supplied 72 MAP units of packed pork cuts. The transportation of the products from production site in the island of Crete to Athens (NTUA) took 18 hours. They were distributed in different trucks and at different locations within the trucks. Electronic data loggers recorded the temperature for all 72 products during the transportation. On half of the products, TTIs were attached to be handled with the SMAS approach, the rest were handled according to the FIFO approach. Two different enzymatic TTI tags were used for each package at time of production; M4-10 and L5-8 (CheckPoint[®] TTI). The M4-10 was designed to expire within 10 days at 4 °C, thus serving as a shelf life indicator at the end of the storage ($E_A = 88$ kJ/mol). L5-8 having a higher activation energy ($E_A = 200$ kJ/mol), and being more temperature sensitive, expire within 2 days at 10 °C, serving as indicator at the time of split (decision point).

Simulated testing of distribution and storage of MAP packed pork cuts was conducted. All products were stored in programmable cabinets simulating the conditions of the real chill chain to the point of consumption. The simulated chill chain conditions consisted of six different time-temperature scenarios (including the 18 hours' storage during the transfer from the meat producer and packer to the laboratory) that were conducted in programmable controlled temperature cabinets (Figure 4.8).

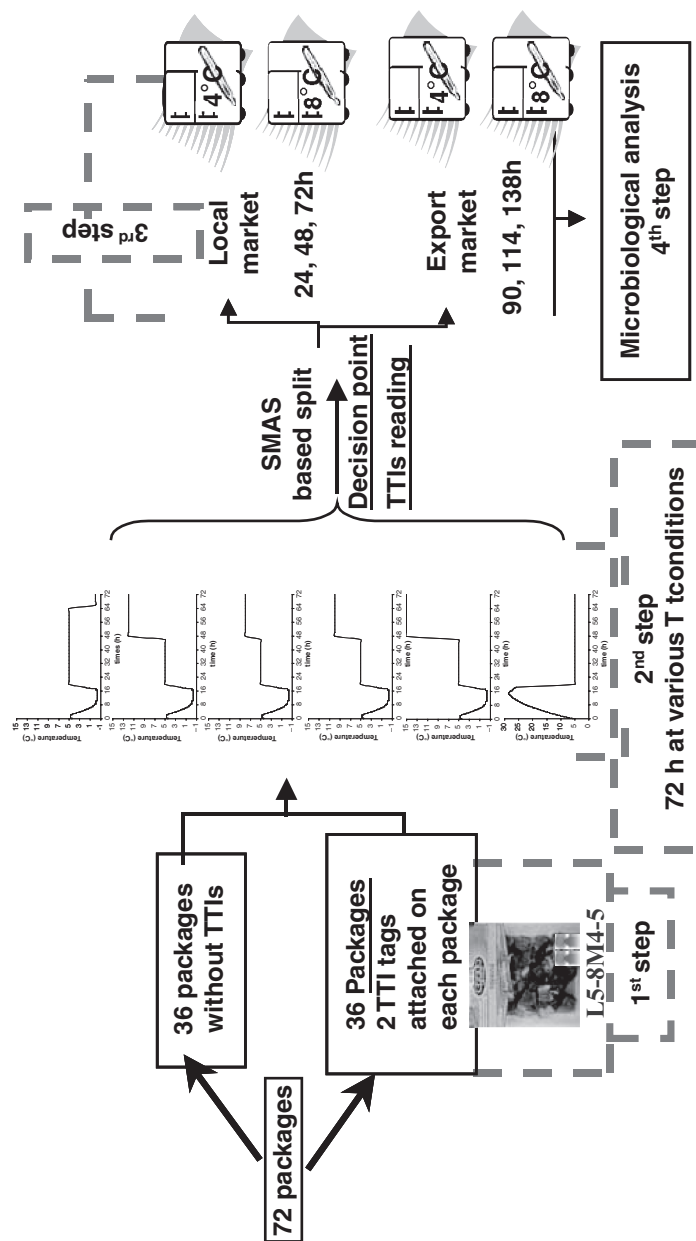


Figure 4.8 Design of the field test for pork cuts products.

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Colour change readings of the attached TTIs were taken throughout the field test at appropriate times corresponding to critical stages of the actual transportation process at a designated decision time simulated to be the distribution centre, 72 hours after meat production and packaging TTI visual reading was conducted with an eight-stage TTI colour reference scale (Figure 4.1).

According to TTI colour scores and using the SMAS Decision Maker Software all SMAS products (36) were sorted according to their actual temperature history as obtained by the TTIs. After sorting, the products were split into two groups, products for 'local' market and products for 'distant' market, for further handling. The 36 samples that had no TTI attached were split randomly. After split at the decision point, samples were split and stored at 4 °C and 8 °C.

Microbiological analyses of the meat products were conducted at six different stages. Products that belonged to the local market group were microbiologically analysed at three stages; 24, 48 and 72 hours after the split. Products coded as products for the distant market were microbiologically analysed 90, 114 and 138 hours after the split.

For the field test microbiological results after storage (at 4 and 8 °C) at different times following the split are shown in Figure 4.9.

According to the field test results as illustrated in Figure 4.8, 33 % of samples reach the spoilage level of log7.2 with the FIFO approach and 16 % when the SMAS split is applied. Similar results are obtained by Monte Carlo calculations using the above microbial growth model.

The overall results from this and other field tests with a variety of meat products and the Monte Carlo simulation showed that the SMAS sorting at a decision point worked satisfactorily thus demonstrating the usefulness of TTI monitoring and the applicability of SMAS.

In summary, SMAS uses the information from the TTI, at appropriate points of the cold chain (e.g at a central distribution centre), to make decisions for the further management of products based on their temperature history and hence quality and safety status. The

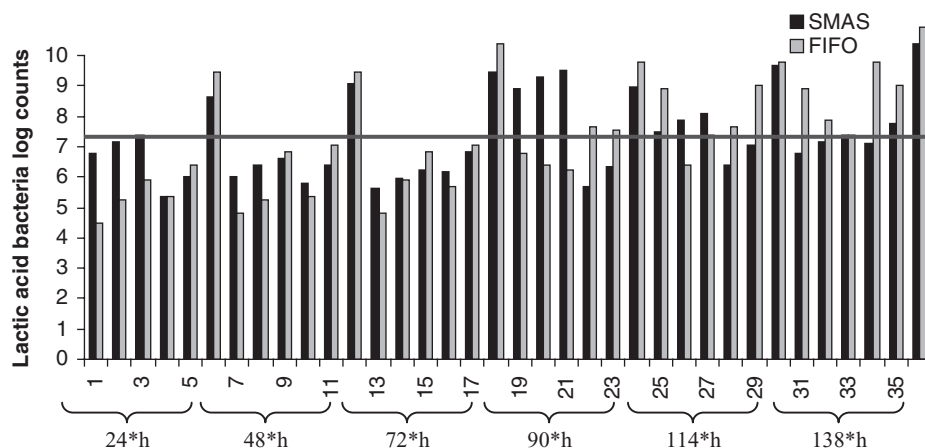


Figure 4.9 Measured lactic acid bacteria log counts for each date of microbiological analysis for all 72 samples (* hours after the split).

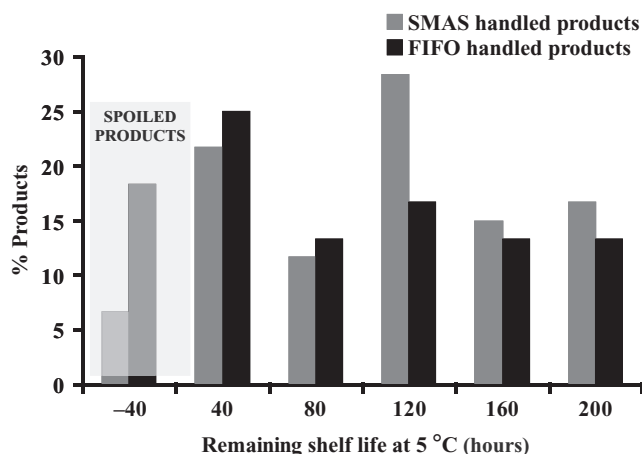


Figure 4.10 Distribution of the remaining shelf-life of meat products at the time of 'consumption' with FIFO and SMAS approach.

conducted work established the applicability of the TTI based SMAS approach in improving the meat chill chain. The overall work showed that the SMAS based sorting at a decision point resulted in substantially reducing the spoiled products at the time of consumption in comparison with the conventional FIFO approach (Figure 4.10). Similarly the risk factor (i.e. the probability that the pathogen might exceed a specified level) was significantly reduced (Koutsoumanis *et al.*, 2005).

Cold chain optimization and effective management will be a central issue in striving for food and other perishable consumer products of higher quality, in the coming years, both in research, industrial practice and regulatory efforts. Integrated systems, like the proposed SMAS based on the availability of quality data and temperature history of individual product units will be applied and validated in practice. TTIs will be combined with RFID technology and all will supplement and benefit from the traceability requirements that are being currently put in place by regulation and by industry initiative.

Acknowledgements

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