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REVIEW ARTICLE

Temperature monitoring for quality management in Cold Chain

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ABSTRACT

Time temperature indicators are devices which integrate the exposure to temperature over time by accumulating the effect of such exposures and exhibiting a change of colour (or other physical characteristic). TTI's are commonly used in food, pharmaceutical and medical products to indicate exposure to excessive temperature abuse. TTI's help in assure the cool chain of food products, they are expected to reduce the amount of food waste, as well as reducing the number of food borne illnesses. The mandatory regulations on pharmaceutical cold chain logistics by international and national associations like WHO are influencing the demand for TTI labels. Global time temperature indicator labels market is expected to witness rapid growth during the forecast period. This growth is expected to be primarily driven by growing concern about food wastage and its impacts on economy.

Keywords: Temperature indicators, time temperature indicators (TTI), enzymatic , polymerization, diffusion

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INTRODUCTION

Temperature monitoring is an integral part of quality management and product safety management throughout the cold chain (Deen, 2014). Improvements in microelectronics have produced monitoring devices that can both store large amounts of data and integrate this into computerised management systems. Woolfe (2000) lists the specifications of commonly used temperature data loggers, which may also sound an alarm if the temperature exceeds a preset limit. These are connected to temperature sensors, which measure either air temperature or product temperature. There are three main types of sensor that are used commercially: thermocouples, semiconductors and platinum resistance thermometers (thermistors). The most widely used thermocouples are type K (nickel-chromium and nickelaluminium) or type T (copper and copper-nickel). The advantages over other sensors are lower cost, rapid response time and very wide range of temperature measurement (-184^{0}C to 1600^{0}C). Thermistors have a higher accuracy than thermocouples, but they have a much narrower range (-40^{0}C to 140^{0}C). Platinum resistance thermometers are accurate and have a temperature range from -270^{0}C to 850^{0}C, but their response time is slower and they are more expensive than other sensors.

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Monitoring air temperatures is more straightforward than product temperature monitoring and does not involve damage to the product or package. It is widely used to monitor chill stores, refrigerated vehicles and display cabinets, and Woolfe (2000) describes in detail the positioning of temperature sensors in these types of equipment. However, it is necessary to establish the relationship between air temperature and product temperature in a particular installation. Air in a cold store is warmed by incoming products, by lights in a store, and vehicles or operators entering the store. The temperature of the returning air is therefore slightly higher than the product temperature. The performance of the refrigeration system can be found by comparing the return air temperature to the temperature of air leaving the evaporator in the refrigeration unit. 'Load tests' are conducted to relate air temperature to product temperature over a length of time under normal working conditions. The operation of open retail display cabinets is sensitive to variations in room temperature or humidity, the actions of customers and staff handling foods, and lighting to display products. The temperature distribution in the cabinet can therefore change and load testing becomes more difficult. In such situations there is likely to be substantial variations in air temperature, but the mass of the food remains at a more constant temperature, and air temperature measurement has little meaning. To overcome this problem the food temperature can be measured using thermocouples, or the air temperature sensor can be electronically 'damped' to respond more slowly and eliminate short-term fluctuations.

Water Holding Capacity

Weight loss in fish is directly related to the water holding capacity of each fillet. Depending upon distribution and handling post mortem, water-holding capacity within fish can change overtime (Offer *et al*., 1988). Weight loss during distribution and storage can be attributed to evaporation from freezing storage, as well as drip loss from thawed meat preparation. Drip loss within meat contains water, but also water-soluble proteins, sarcoplasmic proteins (myoglobin), depleting the weight and therefore value of the meat (Offer *et al*.,1988). Drip loss increases when additional processing is preformed on fish, such as filleting or mincing. To maintain water-holding capacity and deplete the opportunity for dehydration of meat, acid and salt treatments to adjust the pH and ionic strength between filament lattices within fish muscle. As a result of acid and salt treatments, there is more room for water molecules to bind within muscle filament (Offer *et al*.,1988).

Time-temperature indicators

In addition to temperature sensors, the temperature history of chilled or frozen foods can be monitored by time-temperature indicators (TTIs), which indicate whether a product has been held at the correct storage temperature to give the required shelflife,or if temperature abuse has occurred. TTIs may be grouped into three categories:

- Critical temperature indicators (CTIs) show when a product has been exposed to temperatures above a reference temperature for sufficient time to cause a change in the quality or safety of the product. However, CTIs do not show how long the temperature abuse has lasted or by how much the critical temperature was exceeded. They are useful for foods that undergo irreversible damage above or below a certain temperature (e.g., freezing of fresh or chilled foods or thawing of frozen foods), or for foods that are susceptible to growth of a pathogen above a certain temperature.
- Critical temperature_time integrators integrate the temperature and the time that a food has been exposed to a particular temperature. They are used to indicate failures in the distribution chain and for products in which reactions that are important for quality or safety are initiated above a critical temperature (e.g., microbial growth or enzymatic activity that is inhibited below the critical temperature).

- Time_temperature integrators (TTIgs) continually monitor temperature exposure (known as 'full history' TTIgs) throughout the life of a product. In full history indicators, the kinetics of a colour change reaction are designed to closely match the spoilage kinetics of the food for which the indicator is intended.

A TTIg must show a reproducible time_temperature-dependent change that is easily measured. This is an irreversible physical, chemical, enzymatic or microbiological change, usually expressed as visible change in colour or development of a colour (Pavelkova´, 2013; Taoukis, 2008). For physical or chemical responses, the change is based on a chemical reaction or a physical change with time and temperature, such as an acid_base reaction, melting of wax that releases a coloured dye when an unacceptable increase in temperature occurs, polymerisation, electrochemical corrosion or liquid crystal coatings that change colour with storage temperature (Woolfe, 2000). A biological response is based on the change in biological activity of a microorganism or enzyme, which causes a reaction that changes the colour of a pH indicator (Kuswandi *et al*., 2011). In each case, the rate of change increases at higher temperatures in a similar way to the deteriorative reactions responsible for product quality deterioration. Topping and Patel (2010) describe the mechanism of action and the use of each type of indicator and a detailed description of TTIgs is given by Evans and Woolfe (2008) and Taoukis and Labuza (2003).

Three uses of TTIgs are:

1. Continuous temperature monitoring of a chill chain to identify problematic stages in distribution when temperature abuse occurs. TTIgs allow the location and the improvement of the critical points of the chill chain;
2. Correlation with food quality deterioration kinetics to predict the remaining shelf-life at any point in the distribution chain or to signal the end of the usable shelf-life;
3. Improvements to management and stock rotation systems (e.g., first-in-first-out, least shelf-life out or shelf-life decision system).

To give an indication of the end of shelf-life, the TTIg characteristics should be matched to the quality deterioration of the product, so that when a food is kept at the correct storage temperature the indicator reaches its end-point at the same time as the end of the product shelf-life. At other temperatures, the change in shelf-life with temperature should be known for both the product and the TTIg, using the Arrhenius relationship. A TTIg may supplement, or in some cases replace, the expiration date-code because it gives the actual temperature conditions to which the product has been exposed and thus provides a greater level of confidence that a perishable product is within its shelf-life.

In minimally processed refrigerated foods, rapid growth of pathogenic bacteria at elevated temperatures may pose a serious health hazard before deterioration in quality becomes evident. In this case, an expiration date may be used for storage at the correct temperature, and a threshold-temperature TTIg is used to indicate exposure to temperatures at which growth takes place. Alternatively, a dual-function TTIg may be used, with a standard TTIg indicating the shelf-life at the correct storage temperature and the threshold temperature component indicating exposure to higher temperatures (ASTM, 2014). Lu *et al*. (2013) describe a mathematical model of the relationships between changes in the colour of an enzyme-based TTIg with time and temperature, using fresh milk as an example.

Types of TTIgs

TTIgs are used in ‘smart’ or ‘intelligent’ packaging, and are of various types.

Enzymatic TTIgs: Enzyme and substrate are mixed by mechanically breaking a separating barrier inside the TTIg. The CheckPoint TTI is an adhesive label that uses an enzymatic system that reacts to time and temperature in the same way as the food product reacts, to indicate the freshness and remaining shelf-life. A colour change from deep green to bright yellow to orange-red is caused by a fall in pH, due to acid release from the controlled enzymatic hydrolysis of a lipid substrate. Different combinations of enzyme and substrate types and concentrations give a range of response times and temperature dependencies (Taoukis, 2008). It has two configurations: CheckPoint I has a single dot and CheckPoint III a triple dot. Single-dot tags are used for temperature monitoring of cartons of product and consumer packages, whereas triple-dot tags have three graded responses for sequential development of colour in a single label and are used in wholesale distribution chains (Kuswandi *et al*., 2011). Rani and Abraham (2006) report an enzyme-based TTIg and Yan *et al*. (2008) developed a TTIg based on the reaction between amylase and starch.

Polymer-based TTIgs: The Fresh-Check TTIg (Temptime, 2018) is based on a solid-state polymerisation reaction that produces a highly coloured polymer. The indicator has a polymer circle surrounded by a printed reference ring. The polymer circle darkens irreversibly from cumulative time and temperature exposure, and the intensity of the polymer circle colour is compared to the reference colour. This indicator is fixed to packs of perishable products at the time of processing (e.g., lettuce, milk, prepared chilled foods, seafood and meats) as a complement to date codes to enable consumers to know if the product is still fresh at the time of purchase and at home (Taoukis, 2008; Han *et al*., 2005). Another design contains diacetylene in the centre of a ‘bull’s eye’, which changes with temperature to produce an irreversible colour change, and when it matches the reference ring the product has no remaining shelf-life.

Diffusion-based TTIgs: 3M MonitorMark (3M, 2020) is a diffusion-based indicator label that has a colour change controlled by temperature-dependent permeation of a blue-dyed fatty acid ester through a film and along a wick into a porous matrix. The response rate and temperature dependence are controlled by the concentration of diffusing polymer and its glass transition temperature, and can be set at the required range (Taoukis, 2008). These indicators are an inexpensive and effective way to monitor product temperature exposure through the entire supply chain. They provide a non reversible record of exposure above the specified temperature threshold that is accurate and easy to interpret. The 3M™ MonitorMark™ Time Temperature Indicator works best when placed inside insulated shipping boxes near the temperature sensitive product, where it monitors the temperature and indicates not only if a product is exposed but also for how long. The large indicator window displays exposure, the smaller windows to the right indicate for how long temperature exposure took place, up to 48 hours. When all packaging requirements have been followed and precautions observed, 3M MonitorMark Time Temperature Indicators add a critical layer of content security by providing a noticeable indication that the package and contents were exposed to damaging temperatures (3M, 2020). MonitorMark has two versions: a threshold indicator for monitoring distribution and a smart label for consumer information (Kuswandi *et al*., 2011). The response is measured by the progression of the blue dye along the wick, and is complete when all five windows are blue. Response times of 7 and 14 days are available, with response temperatures from -17^{0}C to +48^{0}C. In the TT Sensor TTIg (from Avery Dennison Corp., California), a polar compound diffuses between two polymer layers and the change in concentration causes a fluorescent indicator to change colour from yellow to bright pink (Taoukis, 2008).

Microbial TTIgs: The (eO) TTIg (Cryolog, 2020) is based on a time-temperature depended pH change caused by controlled microbial growth selected strains of lactic acid bacteria that is expressed to colour change through suitable pH indicators. Prior to utilization, these TTIs are stored in a frozen state (−18 °C) to prevent the bacterial growth in the TTI medium. As they are very thin, their activation is obtained simply by defrosting them for a few minutes at room temperature. Once they are put on the food, and in case of temperature abuse, or when the product reaches its use by date, the temperature dependent growth of the TTI microorganisms causes a pH drop in the tags leading to an irreversible color change of the medium chromatic indicator which becomes red (Ellouze *et al*., 2008; Taoukis, 2008).

Photochemical TTIgs: OnVu is a solid-state reaction TTIg, based on photosensitive organic pigments (e.g., benzylpyridines) that are stable until activated by UV light from an LED lamp. It is based on photosensitive compounds; organic pigments e.g. benzylpyridines, 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. The system can be applied as a label or printed directly onto the package (Taoukis, 2008; Tsironi *et al*., 2008). TimestripPLUS is a TTIg label that monitors how long a perishable product has been open or in use, to enable consumers to record the time elapsed since activation of the label, from 10 min to 12 months. The label is either automatically activated when the consumer opens the packaging or the consumer can manually activate the label when they first use a product (Timestrip, 2016; Kuswandi *et al*., 2011). A material mixture changes from solid to liquid when a threshold temperature is exceeded and then moves through a porous membrane, visible through a viewing window. A blue colour appears in the viewing window if a breach of the threshold temperature has occurred. Each movement is irreversible so the cumulative time of any temperature breaches is shown by how far the blue colour has moved along the time markers. Different TTIgs are available for frozen foods (0^0C or -20^0C, 8 or 12 h run-out windows) or chilled foods (8^0C or 10^0C, 8 h run-out window).

RFID and other TTIgs: Radio frequency identification (RFID) is used in food logistics and RFID temperature loggers have found applications as TTIgs (Wessel, 2007). Wessel (2007) describes a TTIg that can be attached directly to a RFID transponder to enable companies to remotely monitor the shelf-life of refrigerated foods based on temperature exposure during shipment. It uses both colour changes and an electrical signal to express the temperature history and it can transfer the electrical signal and temperature information to an active RFID tag (a microchip plus antenna). The tag contains a unique identification number and may have other information, such as the account number for a customer. This type of 'smart label' can have a barcode printed on it, or the tag can be mounted inside a carton or embedded in plastic. A tag reader interrogates the tag to enable cold-chain operators to calculate the remaining shelf-life of specific goods, based on the temperature information.

CoolVu labels are TTIgs based on a temperature-dependent dissolution (etching) of a fine aluminium layer. The indicators have two parts: a printed aluminium label and a transparent label that contains the etchant in an adhesive layer. The label is activated by pressing the adhesive label onto the aluminium label. After activation, the aluminium layer becomes thinner as a function of the time and temperature, still preserving its mirror-like appearance. The 'active spot' then becomes black, and at the end of its life the background colour is revealed (Deen, 2014). At more advanced stages of the process the active spot turns from being a metallic mirror into black. Towards the end of its life, the active spot slowly adopts the color that was printed at its backside and at the end of its life the full color of the background is revealed.

A barcode system has been developed that is applied to a pack as the product is dispatched. The barcode contains three sections: a code giving information on the product identity, date of manufacture, batch number, etc., to uniquely identify each container. A second code identifies the reactivity of a TTIg and the third section contains the indicator material. When the barcode is scanned, a hand-held microcomputer display indicates the status and quality of the product with a variety of preprogrammed messages (e.g., 'Good', 'Don't use' or 'Call QC'). A number of microcomputers can be linked via modems to a central control computer to produce a portable monitoring system that can track individual containers throughout a distribution chain.

Nanotechnology is also being applied to develop new TTIgs and Zhang *et al*. (2013) describe a kinetically programmable and cost-efficient TTIg protocol constructed from plasmonic nanocrystals.

TT Sensor Plus records the temperatures an item is exposed to throughout its supply chain journey. Based on the temperatures the product is exposed to, TT Sensor Plus can indicate if the item is suitable for its intended use. The data is stored in a chip and can be uploaded to a smartphone at anytime, anywhere throughout the supply chain. The technology incorporates sensor functionality and temperature data logging capabilities in a cost effective, disposable temperature data label solution. When affixed to a product or container, the thin, flexible label can be programmed, by the user, to record the temperature history of goods at defined intervals during shipment (Manjunath, 2018).

CONCLUSION

Use of time temperature indicators can help optimize product distribution, improve shelf life, monitoring and management of food produce and thus reduce product waste from foodstuffs. Cost, reliability, and effective application are criteria for practical success of time temperature indicators. Current time temperature indicators systems provide reliable and reproducible responses according to their specifications. Time–temperature indicators provide a visual summary about temperatures of product accumulated in time history, recording the effects of time and temperature. A modern quality and safety assurance system should prevent contamination through the monitoring, recording, and controlling of critical parameters such as temperature during a food product's entire life cycle. It includes the postprocessing phase and extends to the time of use by the consumer. Hence, monitoring and recording the temperature conditions during distribution and storage are of importance.

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