Sensor for real-time monitoring of food degradation

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ABSTRACT

We have developed a simple and cheap optical thin film sensor chip able to detect the decay of food through a specific colour change providing reasonable sensitivity and selectivity to indicate "best use before" period. The design of the sensor relates to the phenomenon of "anomalous absorption", which can best be described as a thin film enhanced absorption. A metal cluster film positioned at a well defined distance to a smooth metal surface shows that the minimum of spectral reflectivity strongly depends on the thickness of the interlayer: This setup represents a special kind of reflection interference filter. In such a sensor setup we have integrated a biodegradable polymer which is degraded by the same enzymes and at the same rate as food decay will happen. The degradation of the polymer results in reduction of the film thickness and thus in a specific change of the color.

Keywords: optical thin film sensor, anomalous absorption, interference, food degradation, biodegradable polymer

1. INTRODUCTION

For centuries human senses were the only instruments available, until scientific advances in physics, chemistry, biology as well as the growing demands of the food processing industry, led to the development of the analytical techniques aiming at understanding and controlling of all aspects of food quality.

The need for healthier, safer, more convenient, competitively superior and seasonally invariant foods along with the need of more efficient processing plants with reduced waste drive the development and improvement of food processes. While level, flow, pressure and temperature sensors for on - line implementation are widespread; instruments for chemical analysis are scarce and often limited to pH and conductivity and pO2 and pCO2 for gases. On - line optical instruments such as refractometers, spectrophotometers, turbidity meters and color meters that may be used to assess food composition have been developed. However, their applicability is often limited by the presence of compounds that interfere with the measurement and that are present in different amounts due to variability of raw materials. Unfortunately, often the quality of raw materials cannot be assessed and maintained.

In recent years, the combination of knowledge in electrochemistry, biochemistry, physics and integrated circuit silicon technology made it possible to provide highly specific, sensitive, selective, accurate and reliable micro-biosensors [1,2,3]. The biosensor field is growing so rapidly and has become so diverse that it is impossible to comprehensively cover the entire field in this introduction.

If a biosensor is defined as a device with a biological recognition element built in (physically attached or confined) and this is the primary selectivity element, the freshness sensor for food we want to represent herein is a typical biosensor. This freshness sensor for food is irreversible and therefore suitable for single use only. It is not activated until it gets in contact with the meat. Fast and easy real time tests for direct optical visualization of the degradation of food are still desirable as tests currently in use for monitoring freshness of food do not meet the demands of consumers because of several reasons:

Conventional tests for the detection and identification of food borne pathogens and the detection of microbial food deterioration give very reliable results. But they need conventional culturing techniques and thus are time consuming, need sophisticated lab equipment and well trained staff. Thus only testing of random samples is possible and contaminated probes might be detected too late.

Thus for monitoring meat freshness during the interval between packaging and selling other methods are needed. The methods currently in use rely on detecting a change in environmental conditions like increase of the temperature or change in pH.

These parameters do not reflect the real quality of the meat to be tested.

- Monitoring the pH gives only indirect information and most tests are reversible, and therefore generally unapt to contribute to the safety of the meat supply chain against willful or neglectful corruption of the sensor function.
- Monitoring the cold chain through chemical or electronic sensors is expensive and yields indirect information as well, strongly raising the risk of creating a lot of additional wasted food.

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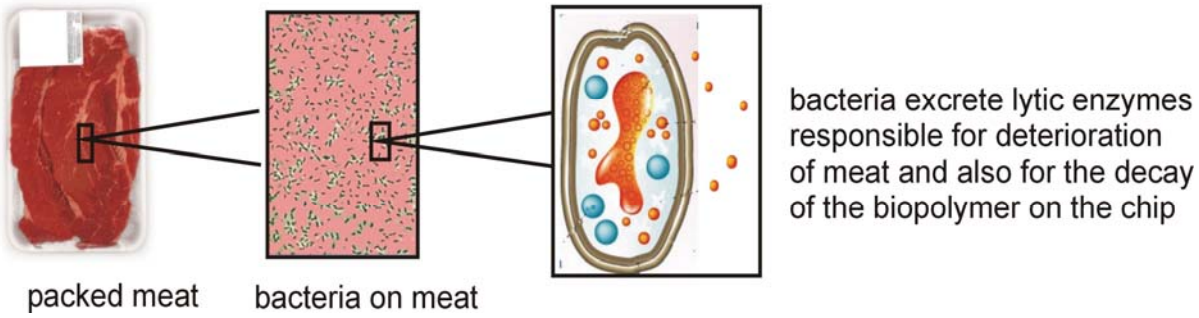

Fig. 1: sensor principle

- The laboratory tests as used and especially if combined with each other yield very reliable results but are very expensive and time consuming.
The aim of our novel approach has been to create a sensor that provides reasonable sensitivity and selectivity to indicate the "best use before" period combined with a memory effect that cannot easily be corrupted.

Another big advantage of this new sensor system is the cost efficiency for its production. Every step of the sensor production has been carried out on industrial testing equipment and with coating procedures like PVD and gravure printing. These production methods guarantee very good economies of scale and thus low cost per unit.

The freshness sensor for food is an optical thin film sensor with an integrated biopolymer, which is degraded by the same enzymes at the same rate like food, as e.g. meat (Fig.1). Due to the special optical behaviour of a metal island film and due to the thin film set up, this system shows characteristic spectral reflection behaviour, strongly dependent on the thickness of the transparent interlayer [4].
The optical property of metal island films, necessary for our application, is the so called "Plasmon absorption", a strong, broad-band absorption in the visible, which is due to the confinement of the conduction electron plasma in nanometric particles.

This is in contrast to the unconfined electron movement in an extended metal, responsible for strong, unspecific reflectivity, well known as metallic glance. An absorbing thin film positioned at a defined distance to a metal mirror represents a special kind of reflection interference filter. At an appropriate distance of the absorbing layer to the mirror, fields reflected by the mirror have the same phase at the position of the absorbing layer as the incident fields and, thus, by this feedback mechanism the effective absorption coefficient of the absorbing layer is strongly enhanced.
This combination of the two phenomena plasmon absorption and optical interference is generally called *anomalous absorption.*

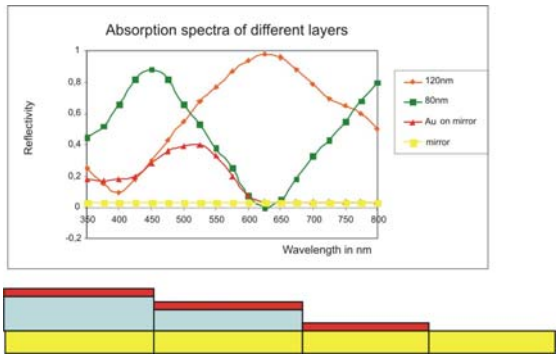

Fig 2: distance depended colour of the sensor

Fig. 2 shows the visual impression obtained by observation of the reflected light upon diffuse white-light illumination of the layer system used in our sensor set up in the interlayer optical thickness range 0 – 490 nm (optical thickness = geometrical thickness x effective refractive index) and some corresponding, measured reflection spectra.

The authors and other research groups have developed a number of sensor applications based on the principle of anomalous absorption targeting amongst other parameters pH, humidity and salt concentration [5]. In a number of these publications the reversible thickness change of the sensor layer has been transduced into an optical signal. In the so-called MICSPOMs sensors a polymer with shrinking and swelling properties is integrated as the distance layer. The response of MICSPOMS on ionic strength is fully reversible and due to the direct exposure of the very thin swelling polymer layer to the analyte is so fast that no delay of response can be observed visually [6].

In this paper we report the setup of the sensor and our first results we made with the detection with different meat juices. Unlike MICSPOMS our sensor response is not reversible. The irreversible degradation of the polymer results in a decrease of sensor layer thickness and this creates a permanent colour change.

2. MATERIALS AND METHODS

2.1 Materials

For our experiments we bought packaged fresh meat from pork from local retailers in Vienna (Billa). We then aliquoted the meat juice in 500 µl Eppendorf tubes in 100 µl aliquots and froze them at -20 °C. Every experiment was carried out with 0.1M Tris-HCl buffer and ddH_20 as a negative control. Our substrate for the thin film setup was PET foil from Ineos Films (UK). For all necessary washing steps we used ddH_2O. Our degradable interlayer polymer is PLA (Polylactic acid) from Biomer (Germany) in 2, 2, 2-Trifluorethanol as a solvent for printing applications. As a crosslinker for the sensoric polymer we used industrial grade Desmodur 2460 (Diphenylmethan-diisocyanat) from Bayer (Germany). We have used as a mirror layer Inconnel (Ni-Cr composition).

2.2 Methods

2.2.1. Coating

Gravure Printing, also known as Intaglio printing, is accomplished by cutting or engraving and etching various sizes or depths of minute cells (or wells) below the surface of a plate or cylinder to form the ink film. The cells are flooded and loaded with ink, the excess ink is scraped off the surface of the plate by a doctor blade, and the ink left in the cells is transferred to the substrate. The depth and size of each cell determines the amount of ink that is transferred to the printed surface. The nature of the process permits a heavy lay down of ink, which accounts for the rich, saturated colours typical of the gravure process. We used a semi automatic gravure printer for laboratory use from Erichson (Germany). We prepared a PLA (Polylactic acid) solution in the concentration range of 8%- 12% in tFEtOH with linking agent in concentration range of 10^{-3} – 10^{-10} % w/ v and printed these solutions on top of mirror layer.

Sputter Coating: we applied nanoparticles by sputter coating, generating the anomalous absorption and visualizing the homogeneity of the printed layers. The nanoparticles were sputter coated with an Agar sputter coating system for electron microscopy. We sputtered Au with an Argon Plasma at 0.08 mbar for 120 sec.

2.2.2 Sensor-Setup

The here presented thin film sensor has a sensor layer with a maximum thickness from 50 to 500 nm and, thus, shows very fast response. The decomposition of only a few links between the polymer chains causes instability to the degree that the sensor layer is destroyed upon immersion in aqueous solutions. As the metal island film is highly permeable for the analyte the sensor layer is directly exposed to the analyte. For a tuning of interlayer thickness there is one important consideration: Like all interference colours the visual perception of the sensor surface is strongly dependent on the distance layer thickness. Thus the visually observed colour can be used to determine the actual thickness of the polymer layer.
In order to provide sensors for food sensing, the sensor setups have to be stable over prolonged incubation with meat juice. The typical incubation conditions along the meat supply chain range from -20 °C up to 40 °C.

2.2.3. Test Procedure

For a functional assay different solutions were prepared as described in the scheme:

	fresh meat juice	spoiled meat juice
1	undiluted	undiluted
2	1:2 with buffer	1:2 with buffer
3	1:4 with buffer	1:4 with buffer
4	buffer	buffer
5	ddH_2O	ddH_2O

Tab. 1

On top of the sensor surface 1 µL .of every solution was pipetted and then the sensors incubated in a humidity chamber for 4 hours and over night at 4°C and room temperature. After the incubation time the sensor surface was washed with ddH_2O and dried under an airstream.

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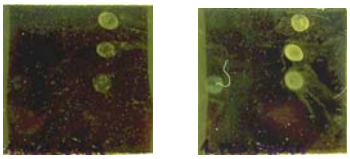
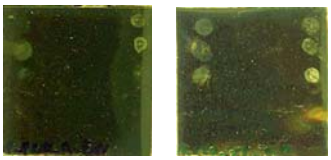
3. RESULTS

For the results documentation was used a flat bed scanner HP Scanjet 4890.
The colour changes shown in Fig. 3 and Fig. 4 are a result of enzymatic degradation of the sensor. This degradation is highly selective and very sensitive; no degradation through negative controls took a place. As can be seen with the naked eye, undiluted spoiled meat juice at 4°C and shows the strongest signal after 4 hours. Negative controls showed no signals.



at 4°C **at RT**

Fig. 3: Incubation for 4 hours



at 4°C **at RT**

Fig. 4: Incubation overnight

4. CONCLUSIONS

In this work we could present a freshness sensor for food for the first time, which is able to show the deterioration of fresh meat with a color change visible for the naked eye in real time.
The freshness sensor for food is able to adapt for different potential commercial applications: to enforce in store quality control, or to give the consumer a transparency of meat freshness and the possibility for self-control of the fresh meat at home.

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