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Fish freshness decay measurement with a colorimetric artificial olfactory system

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Abstract

This paper reports about the application of an artificial olfactory system based on optical imaging technology. This arrangement is formed by a distributed layer of chemical indicators illuminated by a computer screen and imaged by a digital camera. The system has been applied to monitor the freshness decay in fish. The set of indicators is formed by porphyrinoids and acid-base indicators, this combination provides an optimal capture of the process with some of the indicators sensitive to first stage, when the product is still fresh, and others more sensitive to the last part of the freshness decay

Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

In the last decades the development of artificial olfaction systems was mostly oriented to improve the application target but the similarities between natural and artificial systems have been subject of little progresses. In natural olfaction about 100,000 olfactory receptor neurons are found with only few hundreds kinds of receptors and for many sensors technologies this situation is hardly reproducible. On the other hand, it was shown that this structure can be easily imitated using optical indicators probed by image sensors [1]. Indeed, an image sensor can at the same time measure the optical properties of a large sensitive area, and the area corresponding to a single image pixel may correspond to an individual sensor. This concept has been recently utilized to define, considering the optical properties of pixels, the second processing layer found in natural olfaction: the glomerular layer [2]. Furthermore, the distributed sensing layer provides also the separation properties of the olfactory mucosa [3].

In this paper we present an application of such a system to the characterization of fish freshness decay. The artificial olfactory system is composed by an almost continuous layer of porphyrinoids and acid-base indicators that

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forms a sort of artificial epithelium. The layer is illuminated by a computer screen and imaged by a digital camera that decomposes the sensing layer into the number of pixels defined by the image resolution.

The platform was tested to monitor the freshness decay of thawed hake fillets held at room temperature and for several hours. During the process fish headspace is known to change both in quality and quantity [5]. Previous investigations evidenced that the headspace composition is a result of the balance between the "fresh fish" odour and the microbial spoilage produced compounds [4]. The most important chemicals involved in the fresh fish odour are long-chain alcohols and carbonyls, bromophenols and N-cyclic compounds. Their concentration and the presence of other compounds are rather typical of each species. On the other side, microbial spoilage produces short-chain alcohols and carbonyls, amines, sulphur compounds, aromatic, N-cyclic, and acid compounds. The concentrations of these chemicals are directly correlated to the degree of spoilage. Among these compounds amines are considered as the typical markers for fish freshness detection. Since the use of a multeplicity of indicators should allow for a proper detection of all the phases leading from a fresh to a stale product, fish freshness classifications has been frequently used as a test for electronic noses since the very beginning [5].

2. Experimental

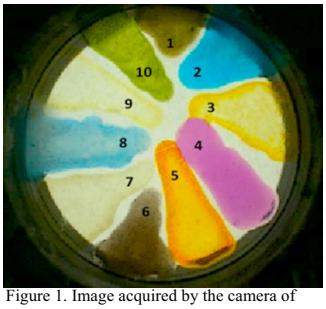

Figure 1. Image acquired by the camera of the artificial epithelium. Sensitive indicators are labelled according to the following list: 1: FeTPP 2: SiPC, 3: Methyl orange, 4: ZnTPP, 5: Bromocresol purple, 6: Biladiene, 7: TPC, 8: Nile, 9: Red Cresol, 10: MnTPP.

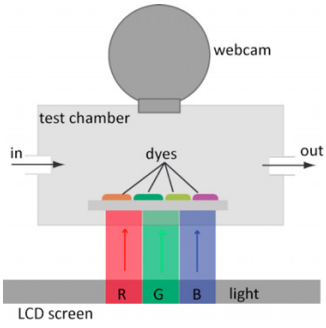

Figure 2. Sketch of the CSPT

The artificial epithelium was formed by an almost continuous layer of chemical indicators. The indicators used in this experiments were three porphyrins, a silicon-phthalocyanine, a corrole, biladiene, and four acid-base inidicators known to cover with different color different pH ranges. Indicators were nile blue, methyl orange, bromocreol purple, and red cresol; porphyrins were tetraphenylporphyrin (TPP) complexed with Mn, Fe, and Zn.

Indicators were spotted in a PVC continuous membrane uniformly coating a 25 mm diameter plastic substrate. The appearance of the substrate is visible in fig. 1.

The artificial epithelium was placed in a cell with gas-tight optical windows and equipped with tube connectors for gas delivery. The epithelium was illuminated through the transparent window with a LCD computer monitor (Philips 1704S) and imaged, in transmission with a digital camera (Philips SPC900NC). A diagram of the experimental arrangement is shown in fig. 2. Changes during gas exposure were probed by a sequence of the three pure colors: red (255 0 0), green (0 255 0), and blue (0 0 255). Such an experimental setup is dubbed as computer screen photoassisted technology (CSPT) [6].

The headspace of a hake fillet was continuously injected for five hours in the sensors cell.

3. Results and discussions

Fig. 3 shows the differential camera signals in the three channels (red, green, and blue) measured under red, green and blue screen illumination. The signals from each spot were subtracted from the background and the first image corresponding to the start of the experiments was subtracted in order to put into evidence only the differences due to the exposure of fish headspace. Signals were further processed eliminating the mean value and scaling all the signals to unitary variance. This procedure, known as

autoscaling, helps in eliminating the dominance of signals of larger magnitude.

From Fig. 3 it is evident that indicators differently behave at the beginning of the process, as the the spoilage progress the headspace becomes so rich that all indicators provide the same value. It is worth to mention the behavior of bromocresol purple that undergoes a sudden change of intensity at a point of evolution where likely the amount of amines exceed a certain threshold.

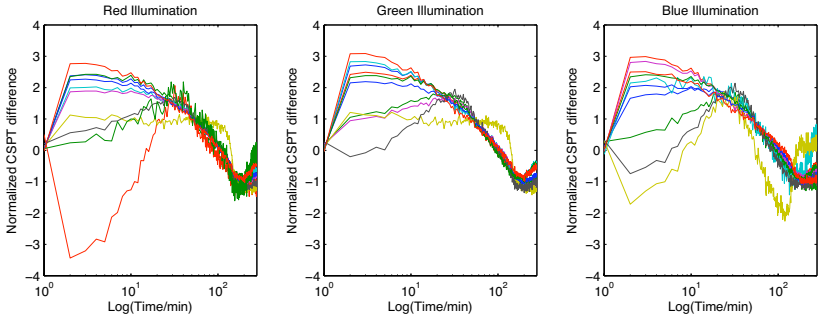

Figure 4. autoscaled indicator signals plotted verus the the logairthm of time. Logarithmic scale has been chosen to put in evidence the change occuring in the first stage of the process.

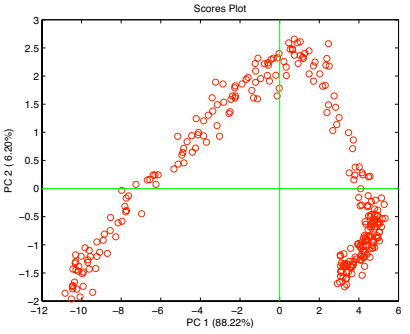

Figure 5. Scores plot of the first two principal components. The abrupt change along the second principal component occurs at about 150 minutes after the experiment start.

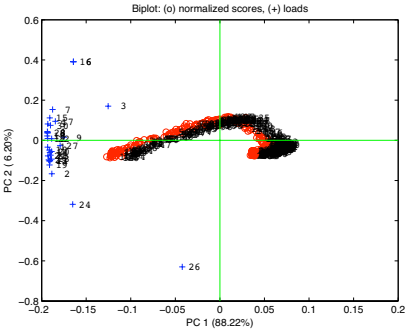

Figure 6. Biplot of the first two principal components. All indicator have little differences excepts four cases.

Fig. 4 shows the scores plot of the principal component analysis of the thirty signals shown in Fig. 3. The behaviour is non linear, changes tend to be smaller as the time increases, and rather surprisingly, at the end of the process the data points in the scores plot tend toward the fresh fish state. Actually a similar behaviour has been observed before with other electronic noses, and this situation has been recently shown to be likely due to the contemporaneous decrease and increase of different classes of chemicals [7]. The contribution of different indicators and light illumination to Fig. 4 can be adequately studied by the biplot. This is a plot where both the scores (data points) and the loadings (direction of the original axis) are simultaneously presented. Fig. 5 shows the biplot of the first two principal components. Most of the indicators lies together along the first principal component, this accounts of the correlation between signals driven by the fact that the process under study is characterized by a constant increase of the total amount of volatile compounds. Nonetheless few indicators can be identified as bearer of

additional information, and they are methyl orange under red illumination (label 3), biladiene under green and blue illuminations (labels 16 and 26), and the Zinc Tetraphenylporphyrin under green illumination (label 14). It is worth to note that these indicators are displaced towards the second principal component where the "curling" effect of the data points takes place.

4. Conclusions

In this paper we demonstrated that an array of different chemical indicators can adequately monitor all the processes occurring in fish during the transition from fresh to stale conditions. Colorimetric detection of fish freshness has been studied in the past by several authors that focused their attention to the detection of amines with a pH sensitive layer [8]. In this case, the detection is limitated to the stale conditions while this results suggest arrays of proper indicator can give a full account of fish state identifying also the changes occurring in the first phase of freshness decay.

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