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Development of an Electronic Nose for Determining the Freshness of Fish by the Desorption Constants of Sensors

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An electronic nose (EN) reduced in size, based on commercial sensors array with a particular thermally stabilized chamber and an advanced processing algorithm was developed. In this work using a heater system that controls the temperature of the sensors chamber, it was possible to study the desorption process on SnO_2 sensor array. Data signal of sensors applying a two exponential decay functions were analyzed in order to determine the desorption constants. These constants were used to measure the fish freshness using the PCA algorithm. This is a first approach using this method that shows the ability of the EN to detect interruptions during the cold storage.

Keywords: Electronic Nose, Fish Freshness, Pattern Recognition.

RESEARCH ARTICLE

1. INTRODUCTION

The control and monitoring of fish freshness is very important in the food industry. Indeed, freshness is the most important quality of fish, according to consumers, possibly because of its strong relationship to taste. The deterioration of fish depends mainly on the temperature, which largely controls the bacterial decomposition.

Different electronic noses have been applied to the detection of fish freshness with good results.[1–3] In this work the capabilities of a simple electronic nose to investigate fish freshness was explored. A low cost portable electronic nose with commercial sensors designed to be operated easily, with the particularity of a heater system that controls the temperature of the chamber was developed. It is well known that the use of chambers with the sensors in the e-nose improves the measurements, due to a constant gas flow and the controlled temperature sensors.[4,5] However, the chamber takes a long time to reach an unstable equilibrium temperature which depends on environmental conditions. As demonstrated previously by increasing the temperature of the chamber, the humidity content was reduced and the time desorption of the SnO_2 sensors was decreased.[6] These factors reset the baseline faster, reduce measurement and drift times and enhance the repeatability. Due to these improvements it was possible to calculate the first desorption constants as a function of concentration. The method developed in this work to measure the freshness of fish could be used for on-site analysis by mid-level technicians.

2. EXPERIMENTAL DETAILS

An electronic nose with a teflon chamber of 12 cm^3 rectangular shape with a gas inlet and outlet of 0.5 cm diameter was developed. The samples were introduced into the chamber through a micro pump of 600 cm^3/min and the variation of electrical resistances of eight SnO_2 sensors was measured. Also, it was placed a temperature and humidity sensor for determining these quantities change during the measurement. It was performed the experiments to determine the time delay of the chamber in establishing the thermal equilibrium when the sensor heaters were turned off. A scheme is shown in Figure 1.

Samples of fresh hake kept inside a refrigerator at a temperature of 2 °C in closed recipients were taken off

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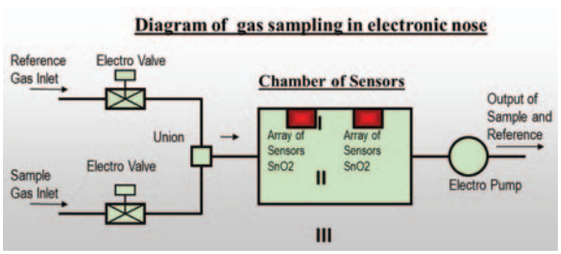

Fig. 1. Scheme of experimental set-up: Region (I) temperature sensors: 300 °C to 500 °C, Region (II) chamber temperature: 10 °C to 45 °C, Region (III) room temperature: 10 °C to 35 °C.

the refrigerator and kept at 38 °C during three different periods of time between 0 and 24 hours and then turned back to the refrigerator. After that process each sample were analyzed as follows:
(1) a reference gas (air) purges the chamber during 115 seconds,
(2) sample vapour from the headspace is injected during 5 seconds and
(3) the reference gas purges the chamber during 155 seconds.

Five repetitions for sample were done. The chamber temperature was stabilized at 43 °C and humidity maintained at about 20%.

3. RESULTS AND DISCUSSION

Measurement with the e-nose: in Figure 2 a set of measurements of 1 sensor of fresh hake for different times outside of the refrigerator is shown. In order to determine the freshness of hake, the desorption process of trimethylamine (TMA) on the surface sensors was analyzed. The desorption zone of the signals was modeled with an exponential equation of 2nd order:

$$R_s(t) = A - B \cdot e^{-(t-t_0)\cdot D\cdot k_1} - C \cdot e^{-(t-t_0)\cdot D\cdot k_2}$$

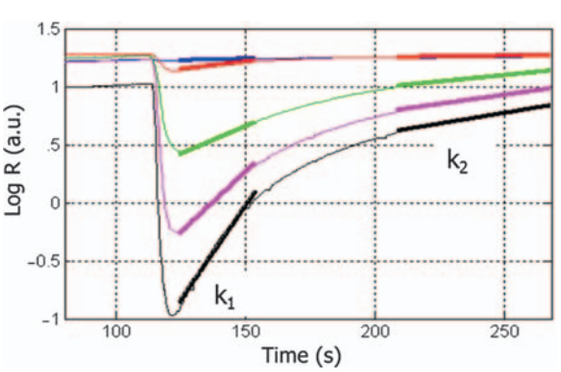

Fig. 2. Fresh hake fillet measurements: loss time cold chain, 0 hs (▬), 4 hs (▬) 8 hs (▬), 24 hs (▬) and air (▬). The thick lines correspond to the desorption lines with slopes k_1 (desorption onset) and k_2 (end of desorption).

Table I.

	Time (Hs)	Average value k_1 [1/s]	$\Delta k_1/k_1$:
Air		0.0065	0.554
Hake: period of cold chain loss	0	0.0988	0.435
	4	0.3172	0.192
	8	0.5386	0.098
	24	0.6949	0.111

Where: $R_s(t)$: Sensor resistance time-dependent

k_1: First desorption constant
k_2: Second desorption constant
t_0: Temporal Displacement Constant
$A - D$: Scaling Constants

According with the desorption processes, the following reactions of the TMA on the surface sensor are proposed:

$$(CH_3)_2\text{–N–}CH_3 + 2O^- \rightarrow (CH_3)_2NCHO + H_2O + 2e^- \quad (1)$$

$$(CH_3)_2NCHO_{(s)} \xrightarrow{k_1} (CH_3)_2NCHO_{(g)} \quad (2)$$

$$(H_2O)_{(s)} \xrightarrow{k_2} (H_2O)_{(g)} \quad (3)$$

Where (s) means that the compound is retained on the surface sensor and (g) indicates that the compound is released as a gas.

The SnO_2 sensors are n-type semiconductors, that in presence of a reducing gas and temperatures between 200 °C and 500 °C increase the free-electron and consequently their conductivity. According with reaction (1) the adsorption of TMA generates two electrons that also increase the conductivity of the sensor. Later the desorption reactions (2) and (3) proceed with constants k_1 and k_2 respectively. Then the values k_1 and k_2 can be obtained as the slope of the logarithm of the signal shown in Figure 2. As can be observed from the figure, the values of k_2 are

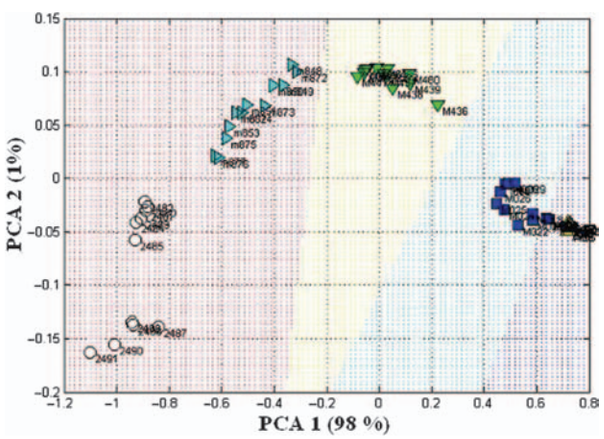

Fig. 3. Principal component analysis of fish samples with different storages times outside the refrigerator with the use of covariance matrix and linear classifier. (■) perfect storage, (▼) 4 hours, (►) 8 hours, (○) 24 hours and (▲) air.

similar, however the constants k_1 show considerable differences (see Table I).

For each sample and for each of the eight sensors the constants k_1 were obtained, and these matrixes of data constitute a characteristic fingerprint. Using the PCA algorithm a successfully assignation of each class was obtained by a linear classifier as can be seen in Figure 3.

4. CONCLUSIONS

This is a first approach that shows the ability of the EN to detect interruptions during the cold storage using this method. The information needs to be complemented with other biochemical studies and also with panel evaluation to analyze the importance of the obtained results, starting from reference fish samples. Similar studies for different storage days are in progress. Moreover, complementary spectroscopic studies are needed to clarify the reactions of the TMA on SnO_2 films.

The calculation of the desorption constant in conjunction with PCA analysis give a very good discrimination of the different state of freshness.

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