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Monitoring of VOC Emissions in Berries During the Spoiling Process

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Summary:
Commercially available metal oxide semiconductor gas sensors have been used to investigate the substances emitted by raspberries. A calibration on the gas sensors was performed trough random gas mixtures made up with wide concentration ranges of 11 substances which compose air and are emitted by food. After, the sensors and different amounts of raspberries have been placed in different food boxes for several days. Estimates based on data were able to track the emissions' change of some volatile organic compounds, e.g. ethanol and acetaldehyde, during the spoiling process.

Keywords: MOS sensors, calibration, spoilage process, food, VOC

Introduction

About one-third of the world's food production is wasted. The first step towards implementing effective strategies to prevent and reduce food waste is to fully understand the amount and the quality of wasted food that is generated. This awareness is crucial to reveal the opportunities for reusing wasted food in a circular economy context, where waste can be transformed into valuable resources [1].
For the assessment of food' state, metal oxide semiconductor (MOS) gas sensors emerge as promising candidates due to their cost-effectiveness and ability to provide real-time measurements on site. Moreover, the employment of temperature cycled operations on these sensors leads into a greater selectivity in detecting various types of gases and expanding the quantitative ranges of detectable substances [2]. In previous works, the sensitivity of commercially available MOS sensors to gas emitted by food has been shown [3]. In this work, the sensors are employed to define chemical states, expressed as volatile organic compounds (VOC) emissions' changes, of raspberries over the spoiling process.

Materials and Methods

Different amounts of raspberries along with MOS sensors have been placed inside several closed food boxes for five days in a room temperature-controlled set at 23 °C, allowing the sampling of the headspace of the VOC of each box individually.
To assess the type of gases involved and their respective ranges' quantities, a calibration of the sensors was performed before the study of the raspberries: the sensors were calibrated with a custom-built gas mixing apparatus (GMA), described in detail in [4]; it was performed with unique random gas mixtures made up with different quantities of eleven different substances which compose air and are emitted by food (selected based on literature studies of the typical gases emitted by raspberries [5]), cf. Tab. 1 for the comprehensive list. The gas mixtures were created with random values of each gas belonging to pre-selected ranges given in table 1. Over 150 unique mixtures, each of which was 25 minutes long, were considered.

Tab. 1: Table of the considered substances and respective ranges for the random gas mixtures.

Gas / Range	Minimum	Maximum
CO	100 ppb	2000 ppb
H_2	500 ppb	2000 ppb
R.h. at 23 °C	25%	70%
1-Propanol	25 ppb	2500 ppb
Acetone	10 ppb	1000 ppb
Acetaldehyde	10 ppb	2500 ppb
Ethyl acetate	10 ppb	1000 ppb
Ethanol	25 ppb	2500 ppb
Ethylene	10 ppb	1000 ppb
Limonene	10 ppb	500 ppb
Methanol	25 ppb	2500 ppb

The selected sensors are commercially available metal oxide semiconductors, e.g., SGP40 (Sensirion AG, Stäfa, Switzerland). The MOS sensors were run in a temperature cycled operation (TCO) which comprises 12 temperature jumps from high to low temperature in the range 100 °C to 400 °C. The total length of each cycle was of 144 s.
A feature extraction was performed: the cycles were divided into 144 equidistant segments of 1 s. For each segment, mean and slope are calculated resulting in 288 features for each gas-sensitive layer of the considered sensors. A partial least square regression (PLSR) model was calculated based on the feature extraction followed by a dimensionality reduction performed trough a principal component analysis. The root mean squared error (RMSE) of 10-fold group based cross-validation, equal to 235 ppb, was considered to build up the regression model. 20% was withheld for testing the trained model.

Results and discussion

Fig. 1 shows the regression plot for ethanol of the lab calibration of one of the SGP40. A hold out test was performed resulting in an RMSE value of 223.9 ppb. Fig 2 shows the models' estimates from the sensors over the five days acquisition of the boxes containing 0, 24 and 101 grams of raspberries. A variation of the ethanol concentration can be observed over each cycle that run on the sensor. Even though the absolute concentration has to be verified, the trend provided by the model reflects the observed behavior of the raspberries during the spoiling process: by the end of the first day of monitoring, the sensor had adapted to the air of the environment and recorded a gradual increase of ethanol, emitted by the raspberries during the final ripening stage; by the second day, there was evidence of mold development on some samples, evidenced by a decrease of the concentration; between the third and the final day, all samples showed signs of mold, with those that developed mold first gradually changing the color of their mold from white to green, which explains the change in trend observed in the concentration curve.
Current analysis of other models of MOS sensors and other gases included in the lab calibration is being carried out to define a more comprehensive and complete chemical profiling over the different states of the spoiling process.

Acknowledgements

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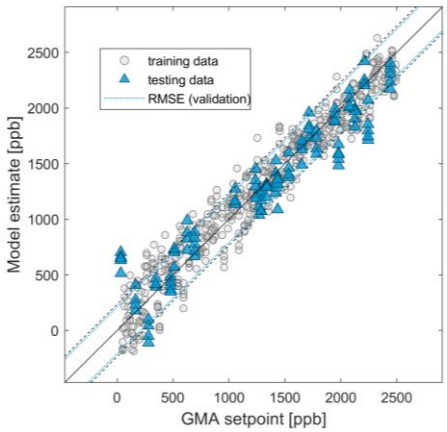

Fig. 1. Regression for sensor's calibration over the different random gas mixtures.

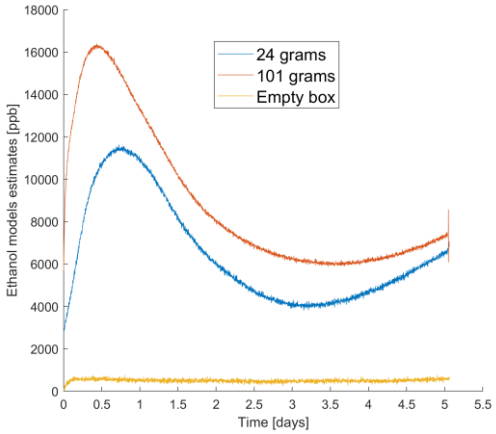

Fig. 2. Model estimates over 3 boxes of 0, 24 and 101 grams of raspberries.

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