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Detection and Monitoring of VOC Emission in Raspberries during the Spoiling Process

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Introduction

Approximately one-third of the world's food production is lost or wasted each year, which represents a significant challenge both environmentally and economically [1]. A considerable amount of food is often discarded while still being edible, especially towards the end of the supply chain, such as in households [2]. This waste comes largely from consumer uncertainty about the real condition of food; when in doubt, individuals tend to be more cautious and dispose of it. Also, the "best-before" and "use-by" dates label on food package lead the consumers to premature disposal of the food [2].Therefore, a strategy to reduce food waste lies in providing measures of food freshness, helping consumers make informed decisions and avoid unnecessary waste; by assessing these aspects, it is possible to reduce wasted food within a circular economy framework [1].

Metal oxide semiconductor (MOS) gas sensors are particularly promising tools in this regard due to their cost-effectiveness, integrability and ability to provide real-time and on-site measurements [3]. To improve their performance, MOS sensors can be operated with temperature cycled operations (TCO), which involve changing of the temperature of the sensitive layer, to reach a greater selectivity in detecting various types of gases and expanding the quantitative ranges of detectable substances [4].

In previous research, commercially available MOS sensors have been employed to detect gases emitted by various foods during the spoiling process [5, 6]. In this study, MOS sensors have been used to monitor raspberries: by tracking changes in volatile organic compounds (VOC) emissions over time, the sensors can help identify different phases of edibility throughout the spoilage process.

Materials and Methods

To determine the concentration variations of the involved gases, a calibration of the sensors was conducted prior to starting the experiment on the fruits.

The purpose of this calibration process is to calibrate the sensors on specific target gases in a predefined and controlled environment before using the sensors in a real-world scenario, i.e. estimate the concentration of the gases emitted by the raspberries during the spoiling process. Moreover, this procedure takes into account potential interference from other environmental factors, such as humidity fluctuations, which could otherwise affect the readings.

The calibration is performed with a custom-built gas mixing apparatus (GMA), described in detail in [7], where the sensors are exposed to known concentrations of various gases: based on literature studies of the typical gases emitted by raspberries [8] and typical gases that can be found in the air [9], a list of gases and concentration ranges has been selected for the calibration.

For the calibration, over 150 unique gas mixtures, each 25 minutes long, were randomly created by using Latin Hyper Cube Sampling based on the chosen gases and their defined concentration ranges, given in Table 1.

Tab. 1: Overview of substances with respective concentration ranges considered for the random gas mixtures of the calibration procedure.

Gas/range	Minimum	Maximum
r.h. at 23 °C	25 %	70 %
carbon monoxide	100 ppb	2000 ppb
hydrogen	500 ppb	2000 ppb
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 MOS sensors in this study are the commercially available SGP40 (Sensirion AG, Stäfa, Switzerland) which were used with a sample rate of 10 Hz.

The MOS sensors were run in temperature cycled operation [10] which comprises twelve temperature jumps from high to low temperature, in the range 100 °C to 400 °C, as represented in Fig. 1: in the high temperature phase, the sensor is heated at the maximum temperature of 400 °C for 5 seconds; after the high temperature phase, the sensor works at the low temperature phase, for 7 seconds. The temperature of the low temperature phase increases by 25 °C (starting from 100 °C) after each high temperature phase. The total length of each cycle is 144 seconds.

After the calibration procedure, a processing of the data is performed, as represented in Fig 2. After a preprocessing of the raw data, a feature extraction was performed: the cycles were divided into 144 equidistant segments of 1 second and then, for each segment, the mean and the slope have been calculated, resulting in 288 features for each gas-sensitive layer of the considered sensors. Since the SGP40 has 4 sensitive layers, a total of 1152 features per sensor have been computed.

After a dimensionality reduction performed via principal component analysis (PCA), in which 20 components have been considered, a partial least square regression (PLSR) model of 20 components was calculated for each gas and for each sensor. To build this model, the root mean square error (RMSE) of 10-fold group based cross-validation was considered. 20 % was withheld for testing the trained model.

In all the phases (training, validation and testing) the samples were divided based on the unique gas mixture, i.e. group based, they referred to, as explained in [11], to achieve more reliable and robust results.

An example model for methanol is presented in Fig. 3: on the x-axis there is the ground truth represented by the concentration of, in this example, methanol set by the GMA while on the y-axis there is the estimate provided by the regression model. In this case, an RMSE of 192 ppb for the training set and 217 ppb for the test set have been achieved for a concentration range of 25 ppb to 2500 ppb methanol, corresponding to an uncertainty of 7.7% and 8.6%, respectively, over the concentration range.

After completing the calibration phase, different amounts of raspberries along with the calibrated MOS sensors have been placed inside several closed food boxes for five days in a temperature-controlled room at 23 °C, allowing the sampling of the headspace of the VOC of each box individually. Figure 4 shows one of the food boxes on the first day of measurement (top) and the same box on the last day of measurement (bottom).

The considered boxes are commercially available food boxes made of food contact certified polypropylene (PP), that allows a quasi-hermetic closure, to not interfere with spoiling process. The boxes have a volume of 0.8 liters.

A total of four boxes containing varying amounts of raspberries were examined: one empty box (to serve as a background reference) and boxes with 24, 50 and 102 grams, respectively, of raspberries. The last one was opened multiple times during the measurement to evaluate the models' response to rapid change of the environment.

After the five days of measurements, the regression models developed during the calibration have been applied to the field data.

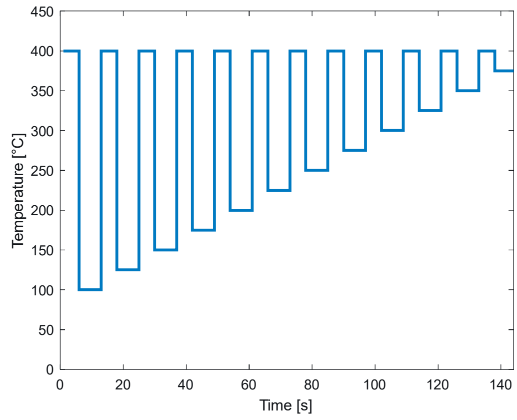

Figure 1: Representation of the used temperature cycle.

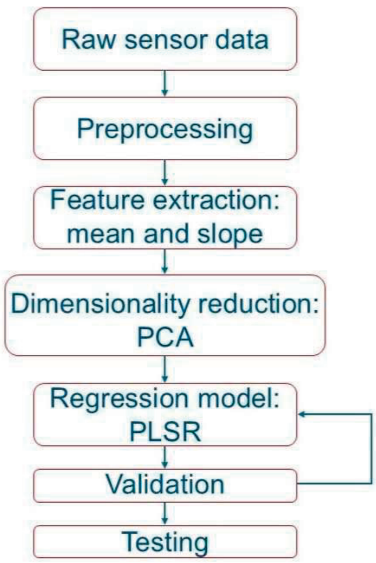

Figure 2: Representation of processing of the data.

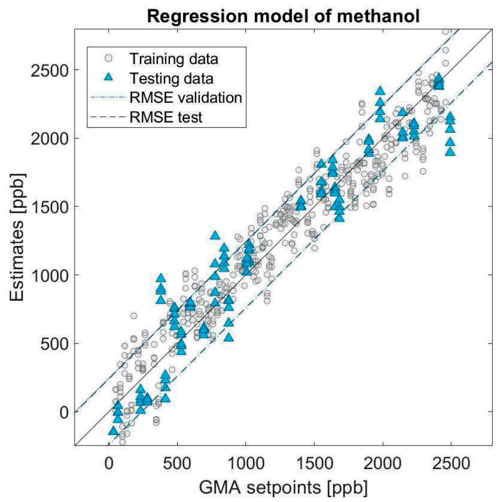

Figure 3: Regression plot for methanol using one SGP40 sensor.

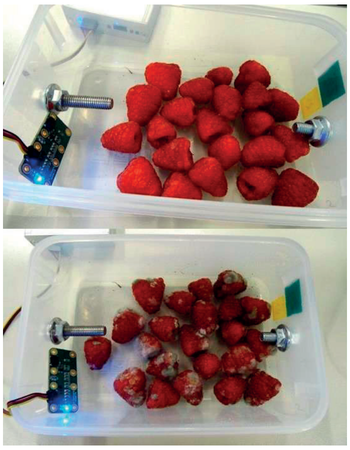

Figure 4: Food box with 102 grams of raspberries on the first day of measurements (top) and on the last day of measurements (bottom).

Results and discussion

After the application of the regression model to the field data, several gases concentration estimates have been obtained. Figure 5 shows the model estimates of methanol of the boxes containing raspberries plus the estimate of an empty box that was used as reference.

A variation of the methanol concentration can be observed over each cycle that runs on the sensor. Even though the absolute concentration has to be verified, the trends provided by the models reflect the observed behavior of the raspberries during the spoiling process: after the end of the first day of monitoring, the sensor had adapted to the environment and they started to record a gradual increase of methanol emitted by the raspberries during the final ripening stage; by the second day, there was already evidence of mold development on some samples, which reflects as a continuous increase of the concentration; between the third and the final day, all samples started to show signs of mold, with those that developed mold first gradually changing the color of their mold from white to green, which can be related to the change of the trend observed in the concentration curve.

The negative concentration estimated at the beginning of the measurement, during the sensor's adaptation to the environment, is likely due to the presence of oxidizing gases that were not accounted for during calibration or high humidity in the enclosed box.

The box with 102 grams of raspberries (in Fig. 5, the purple trend) was opened multiple times during the measurement process, and this behavior was detected by the sensor and processed by the corresponding model. Each time the container was opened, the sensor registered a sharp increase followed by relaxation to the previous trend. These temporary changes indicate a disruption in the environmental conditions within the container, likely due to the influx of fresh air. Once the container was sealed again, the system gradually stabilized, and the sensor's readings realigned with the expected trend, reflecting the food's ongoing spoilage process.

Even though the height of the concentration estimates does not correlate with the weight of the berries in the boxes, the shape of all curves is the same independently of the weight.

For the estimates of other substances, such as limonene and acetaldehyde (shown in Figures 6 and 7, respectively), similar patterns can be observed, within the same graph, across the boxes with varying amounts of raspberries. However, the trend shifts previously noted in the methanol estimate are not present, suggesting that maybe different biological processes are influencing the rise and fall of these substances.

In the case of the opened box (purple trends), both the curves exhibited similar drops following the opening of the container, however the recovery of the curves to their original trajectory is notably slower, cf. Fig. 6 and 7

Conclusions

The results of this study highlight the effectiveness of MOS sensors in monitoring of the spoilage process of raspberries. The sensors demonstrated their sensitivity to environmental changes, such as the repeated opening of the container, which was reflected in temporary drops in the gas concentration curves. These drops were followed by a gradual return to the original trend, underscoring the sensor system's ability to recover and keep accurate monitoring after disturbances.

In the case of methanol, although the concentration estimates do not correlate with the weight of the raspberries in the boxes, the shape of all curves remains consistent regardless of the weight. For a further estimate of freshness, ratios between different VOC needs to be studied rather than absolute values to achieve predictions that are independent of the amount of food being monitored or the distance between sensors and food.

The comparison between different groups of substances revealed distinct behaviors, suggesting that different biological processes govern the production and release of various gases during the food spoilage. While methanol exhibited trend changes relatable with the observed dynamic at specific points in time, these shifts were not observed for other substances like acetaldehyde and limonene, pointing to a more complex interplay of factors influencing their concentration levels. Moreover, the recovery of the trajectory in the opened box proved slower for these substances, pointing out that the environmental disturbances had probably a greater impact on the measurements of these gases.

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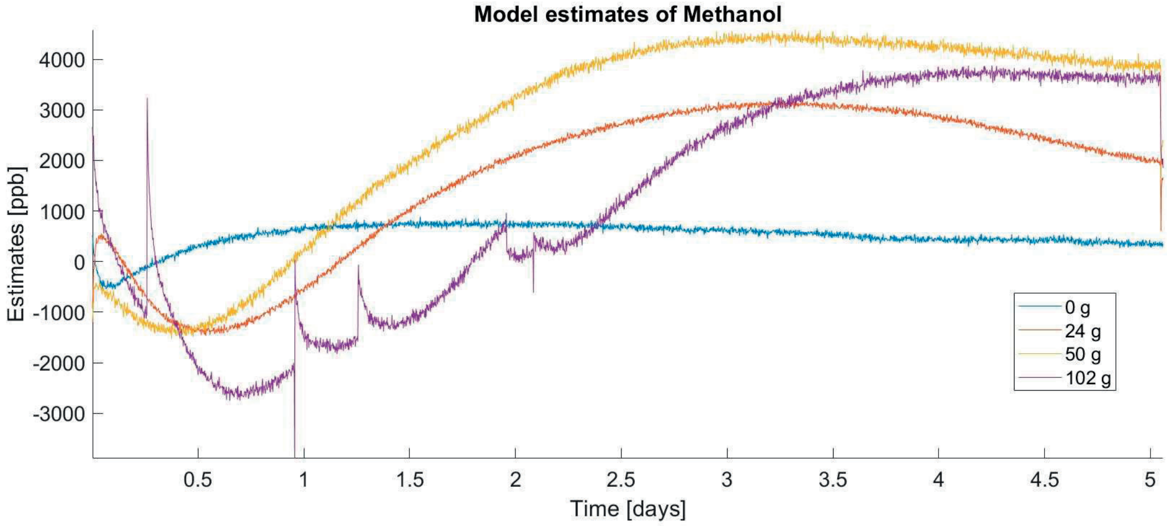

Figure 5: Model estimates of methanol over the empty box and the boxes of 24, 50 and 102 grams of raspberries.

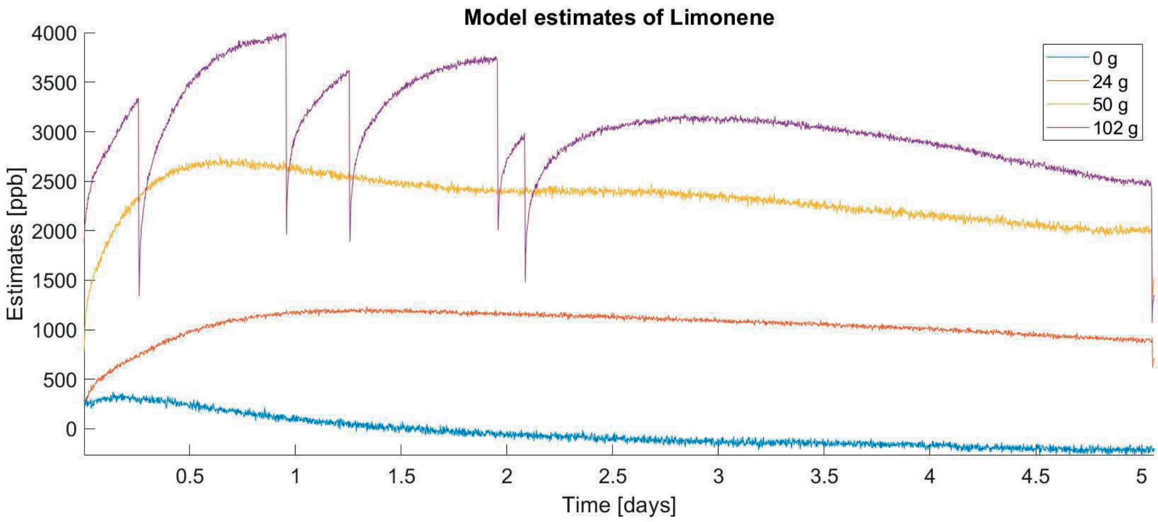

Figure 6: Model estimates of limonene over the empty box and the boxes of 24, 50 and 102 grams of raspberries.

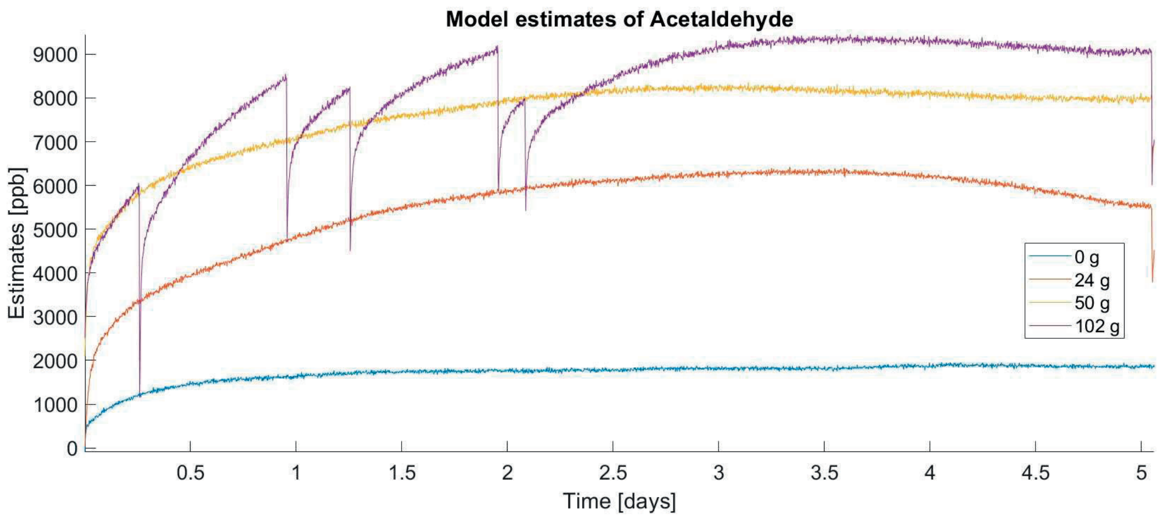

Figure 7: Model estimates of acetaldehyde over the empty box and the boxes of 24, 50 and 102 grams of raspberries.

Overall, this study reinforces the potential of MOS sensors for real-time monitoring of food spoilage and provides valuable insights into the chemical processes that occur during decay. These findings open pathways for further research and development of smart technologies aimed at reducing food waste by providing a warning of food spoilage and so optimizing the repurposing of food within a circular economy.

In the future, simultaneous biological analysis will be conducted alongside gas emission studies to provide a more comprehensive and detailed understanding of the various stages of the spoiling process.

Another goal is to develop predictive models capable of classify the different stages of food edibility. By training models on the changes during the spoiling grade, it may be possible to anticipate when food transitions from fresh to spoiled, offering valuable tools for better food management and reducing waste.

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