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How Ripe is the Fruit?

Assessing Fruit Condition in the Store with Electrochemical Sensors

Assessing the quality of fruit in closed stores is economically important, because the easily perishable products undergo fast changes. Various complicated technologies can currently be used to randomly sample the fruit ripening process. It is impossible to determine the ongoing changes in the products during horticultural produce storage. Investigations on gas composition during storage and transport will supply answers on fruit ripening stages and health status in the future.

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Storage, transport, food safety, gas analysis

Quality decrease during storage and transportation frequently leads to economical losses. Decay and microbe propagation are severe and sometimes dangerous processes, which cause at least the rejection of the product by the consumer. Such processes appear quite rapidly in perishable produce due to over-ripeness of fruit and resulting physiological changes as well as microbe contamination in certain storage or transportation facilities. Food safety issues and food quality can be improved by appropriate monitoring of products, leading to reduced economical drawbacks.

The report presented will introduce a method for non-destructive product monitoring based on gas analysis. Gas samples out of the produce headspace are analysed by means of a multi-gas sensor. In recent laboratory experiments, samples are manually injected into a sensor cuvette (*Fig. 1*). In praxis sampling will be carried out with a sensor system, which possesses features for conditioning gas samples as well as conducting samples from the storage room into a separate sensor cuvette.

The multi-gas sensor is equipped with three specific, different in gas sensitivity layers. Characteristic redox processes of gas molecules sampled take place at such sensitive sides, resulting in changes of electrical sensor resistance due to changes in the fermi level.

Multigas-SENSORiCCARD®

The sensor consists of an aluminium oxide substrate, which carries three tin oxide semiconductors. Each of these layers (S1, S2, S3) is specifically doped. Platinum heaters enable us to perform a cyclically adjustment of the sensor temperature in the range from ambient temperature to 400 °C. Flooding the sensor cuvette with synthetic air cleans the layers and subsequently the target gas sample is injected into the cuvette and subjected to the sensor. Sensor signals are taken after time interval specific for the volatile compounds, which are develop from the horticultural produce (e.g. apple fruit: 15 minutes). Within such time period the specific equilibrium between present volatile compounds and sensitive layers has been adjusted. Sensor data are recorded during the entire heating cycle and transferred to the PC for further data processing.

Determining ethylene in gas mixtures

Processing of multi-gas sensor's data ("electronic nose") is frequently described in the literature using pattern recognition methods, based on sensor resistance data at characteristic temperature or difference between start signal and signal after reaching specific equilibrium. With respect to such approaches, sensor data were processed. Simple algorithm helps to calculate the sensor data on the basis of fruit mass targeted, while the difference of product cuvette volume (e.g. storage room) and fruit volume (VK-VA) provides the apparent volume of headspace.

$$\text{Messdaten}\left[\frac{\text{r.u.}}{\text{g}}\right] = \frac{\text{Messsignal}\ [\text{r.u.}] \bullet (V_K - V_A)[\text{ml}]}{V_K[\text{ml}] \bullet \text{Apfelmasse}\ [\text{g}]} \quad (1)$$

A severe drawback of this method is the necessity of knowing the product volume and at minimum the mass, which is mostly unknown in praxis. Therefore comparing the start level and actual level in relative units seems to be more capable for monitoring changes in the composition of volatile compounds during storage and transportation.

In initial experiments different ethylene concentrations were measured, since fruit ethylene production increases exponentially during decay processes. Pure substances as well as headspace samples of fruit at different ripeness stages as well as after microbial infection were used. Reference data were obtained by means of gas chromatographic determination of ethylene.

Ethylene concentrations as pure substances in the range from 20 to 100 ppm were determined at sufficient signal to noise ratio. Ripe apple fruit produces such concentrations. However, data processing using pattern recognition method as described

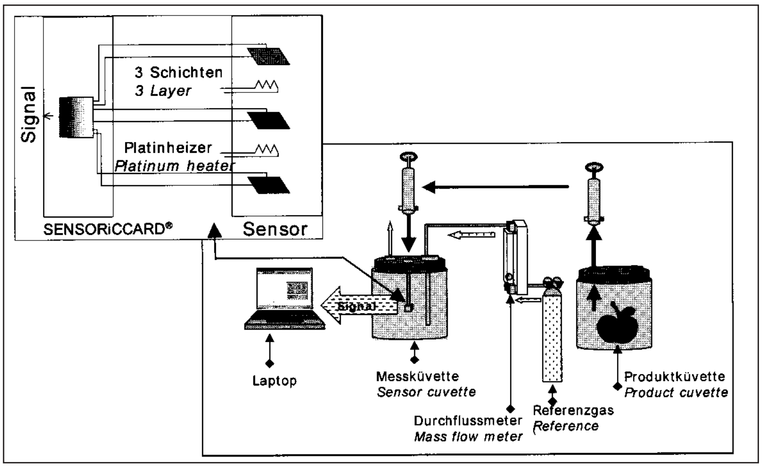

Fig. 1: Experimental set-up for analysing pure substances as well as headspace gas samples of fruits with the multi-gas sensor

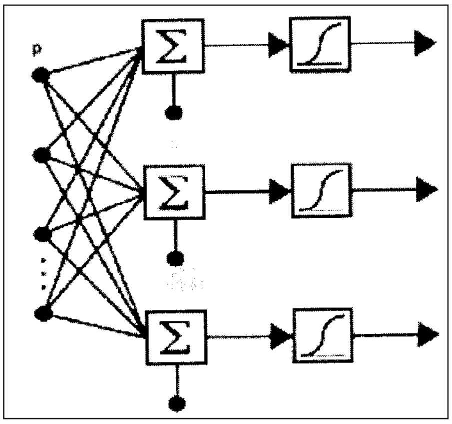

Fig. 3: Neural network architecture using 3 sigmoid neurones (p = 150/layer)

above was not capable to discriminate ethylene merged with aroma compounds (*Fig. 2*) produced by fruit at different ripeness stages as well as sound and contaminated fruits. Therefore changes in ethylene concentrations in gas mixtures of different compositions, causing influence on sensor response, were calculated with non-linear multidimensional statistical analysis [1]. Classification levels were defined with respect to ripeness stages as well as to product safety issues to classify sound, contaminated, infected and decayed product. The recognition of ripeness stage of fruit and vegetable as well as of decay appearance has been materialised with neural network. Furthermore, the prediction of ethylene concentration referenced by gas chromatography was aimed in the development of an appropriate network. A SQL database enables structured data acquisition and data read for calibration and validation purposes. Using the sensor data, such development of a database and neural network is the first step for valuing the produce quality and safety during storage and transportation.

First results were obtained by presenting different ethylene concentrations in synthetic air or merged with fruit aroma compounds to the sensor. Data processing was carried out using sensor data in the temperature range from 250 to 400 °C, since only marginal influence of varying relative humidity on the sensor signal appears at such high temperatures. Data were temperature corrected and analysed by a neural network (*Fig. 3*). Accuracy obtained with such data processing method strongly depended on the data pre-treatment. Data normalisation led to improved correlation coefficients. Furthermore, sensor offset was reduced with a method used by JENASENSORIC: Enhanced correlation coefficients resulted from value correction (Q) of each of the three layers. A specific instrument calibration factor (k) was calculated and used for recalculation of specific layer's values (S_i, i=1,2,3) according to equation 2.

$$Q_i = S_i - k_i \cdot S_{i-1} \qquad (2)$$

Laboratory results pointed out the feasibility of sensor and method of data processing combination to calibrate on different ethylene concentrations in gas mixtures.

Fruit ethylene production increased after microbe infection could be recognised in the future by means of the multi-gas sensor. First results gave evidence of sensor sensitivity for botrytis and penicillium infection in strawberry and orange, respectively. Such feasibility would capture the early detection of product decay and reduce economical losses.

Outlook

A portable sensor system based on a multi-gas sensor is under development by the ATB and JENASENSORIC. Such system would enable us to monitor changes in volatile compounds for determining the stage of fruit ripeness as well as microbe propagation during storage or transportation.

The new method would be a valuable tool for responding to such changes in due time, while reducing losses. Economic advantage is expected for companies with storage facilities, fruit distributors and retailers.

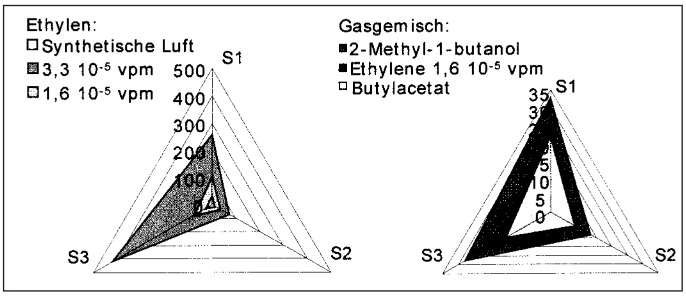

Fig. 2: Recognition of ethylene concentrations, measured as pure volatiles and as gas mixture with aroma compounds. Data represent the sensor signals (S1, S2, S3) at 350°C , because here the highest variance with differently concentrations of ethylene and aroma compound was assessed.

Table 1: Coefficient of determination for ethylene in gas mixtures using different methods of data pre-processing

Data pre-processing	R^2 for sensor data (S)	R^2 for calibrated sensor data (Q)
none	0,36	0,34
autoscale[1]	0,88	0,98
derivative[2]	0,01	0,45
sav-gol smoothing[3]	0,41	0,69

1 autoscale = (data-mean)/SD
2 derivative = f'(x)
3 sav-gol = 70 % smoothing using Savitzky-Golay algorithm

Literature

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