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Multispecies Trace Gas Sensor for Real-time Quality Control of Stored Fruits

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Summary:
We present the principles and development of a transportable trace gas sensor based on a broadband mid-infrared spectrometer utilizing a supercontinuum laser source. The sensor is able to simultaneously detect multiple gas species, including various hydrocarbons, aldehydes and alcohols in real-time with sub-ppmv sensitivities. We demonstrate the application of our sensor in real-time measurement of the volatile compounds produced due to the respiration of the fruits in the storage facilities, providing a tool for monitoring the status of the stored fruits and minimizing the fruits wastage.

Keywords: mid-infrared, absorption spectroscopy, trace gas sensing, multi-species, fruit storage.

Introduction

After harvesting, the fruits are usually stored in a cold controlled atmosphere with high carbon dioxide and low oxygen concentrations to maximize the storage time. However, it is estimated that around 10% of fruits are wasted in this storage period, prior to delivering to the market. Various studies have shown that different volatile species released from the fruits are related to fruit wastage via different undesirable processes such as ripening (ethylene), fermentation (ethanol, acetaldehyde and ethyl-acetate), rotting (methanol and acetone) and chilling injury (ethane). Therefore, continuous monitoring of these trace volatile species provides a comprehensive information of the storage status and can be used to fine tune the storage condition, preventing degradation processes at the early stage. Recently, we have developed broadband absorption spectroscopy systems based on mid-infrared supercontinuum sources, capable of multispecies detection with high sensitivity [1,2]. Here we present a fully-operational and transportable prototype sensor, based on one of these systems, which is able to simultaneously measure these volatile species in real-time.

Experimental Setup and Methods

An overview of the fully integrated sensor prototype is depicted in Fig. 1. Three functional parts are integrated, including the optical setup for continuous gas sensing, the gas handling system for automatic gas sampling, and the (opto)electronic compartment containing the associated power supplies and hardware drivers. The optical setup is based on broadband absorption spectroscopy utilizing a mid-infrared supercontinuum light source [2].

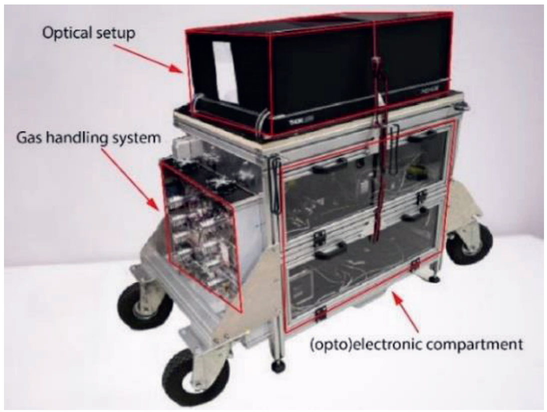

Fig. 1. Graph of variable vs analyte concentration (style “SMSI_Conferences_Caption”) for two different temperatures.

To enhance the interaction length between the sample and the laser beam and achieve higher detection sensitivity, the supercontinuum beam was transmitted through a multipass cell (76 m optical path length). The output beam from the cell is diffracted from a grating mounted on a galvo scanner, scanning at 20 Hz. The diffracted beam is recorded by a single photodetector, constructing the absorption spectrum of the gas sample inside the multipass cell. A data acquisition card in combination with a developed LabVIEW program was used to correlate the amplified photodetector signal and the position signal of the galvo scanner, achieving a spectral coverage of 500 cm^{-1} (2725 - 3225 cm^{-1}) and a spectral resolution of 2.5 cm^{-1}. The gas handling system was developed to deliver the gas sample from the storage room to the multipass cell with the possibility of sending the sample back to the storage room to close the loop. Since water vapor is a common interfering species in our sensor, a water trap based on thermoelectric cooling was integrated into the gas handling system. It reduces the humidity level of the gas sample before sending it to the measurement cell. For automated operation as well as signal processing and concentration retrieval, an integrated LabVIEW program was developed for the sensor. A multi-variant curve-fitting algorithm was implemented to the LabVIEW program to performs a global fitting for different species instead of focusing on a specific narrow spectral feature, enhancing the overall precision for multi-species gas sensing. A more detailed description of the setup and signal processing can be found in [2].

Results

A series of laboratory-scale measurements of apples were performed in different atmospheric conditions. First, Off-the-shelf apples (~750 g, royal gala) were stored inside three interconnected glass containers (6 L total volume) filled with nitrogen gas at 21 °C. The subsequent fermentation process was monitored by continuously measuring the emitted gas volatiles for 150 minutes. A closed loop configuration was adopted to recycle the gas, mimicking the accumulation process in practical storage rooms. Afterwards, the nitrogen atmosphere was replaced by ambient air, while the measurement of the targeted volatiles continued for 250 minutes. A number of volatile species were detected, including ethanol, methanol, ethane, ethyl acetate, ethylene and acetaldehyde, as shown in Fig. 2A. In particular, a pronounced concentration increase by an order of magnitude was observed for ethanol, confirming the expected fermentation process. The concentration values of other fermentation markers, i.e. ethyl acetate and acetaldehyde, evolved on a similar time scale, reaching a more stable plateau of ca. 8 ppmv after two hours. After changing the storage atmosphere from nitrogen gas to normal air, the concentrations of these volatiles recovered, as the gaseous volatiles were depleted, indicating an ongoing emission from the apples. Note that ethylene production was gradually restored, as ethylene was unlikely to be produced in the previous condition of zero oxygen. Following the fermentation experiment, two rotted apples were added into the containers, leading to a significant concentration increase of methanol, which is a typical volatile marker for rotting. The concentration of ethylene also increased steadily within five hours, whereas the concentrations of other volatiles stabilized after one hour, as shown in Fig. 2B. Each data point corresponds to a measurement time of 5 minutes, and the associated errors are derived from the standard deviation of 10 measurements, each averaged for 30 seconds.

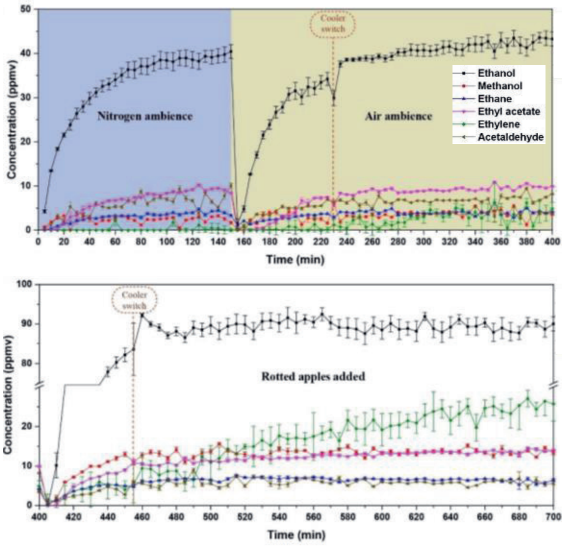

Fig. 2. Concentration evolution of various gas volatiles emitted from apples stored in nitrogen and air atmospheres (A), followed by adding two rotted apples (B).

Conclusions

The developed prototype sensor can automatically and continuously monitor multiple volatiles emitted from fruits, showing application potentials for sampling in commercial fruit storage rooms. In addition, other applications requiring multi-species and real-time trace gas sensing will be targeted, such as environmental monitoring, biomedical research and oil/gas industry. Future work includes a systematic comparison of the developed prototype with standard instrumentation such as GC-MS, while improving the sensitivity to tens of part-per-billion level.

References

[1] K. E. Jahromi, Q. Pan, L. Hogstedt, S. M. M. Friis, A. Khodabakhsh, P. M. Moselund, F. J. M. Harren, Mid-infrared Supercontinuum-based Upconversion Detection for Trace Gas Sensing, *Opt. Express*, 27, 24469-24480 (2019); doi: 10.1364/OE.27.024469

[2] K. E. Jahromi, Q. Pan, A. Khodabakhsh, C. Sikkens, P. Assman, S. M. Cristescu, P. M. Moselund, M. Janssens, B. E. Verlinden, F. J. M. Harren, A Broadband Mid-Infrared Trace Gas Sensor Using Supercontinuum Light Source: Applications for Real-Time Quality Control for Fruit Storage, *Sensors*, 19, 2334 (2019); doi: 10.3390/s19102334