Studies of Oxygen and Oxygen Exchange in Fruits Using Gas in Scattering Media Absorption Spectroscopy

Jing Huang[1], **Hao Zhang**[1], **Tianqi Li**[1], **Guangyu Zhao**[1], **Sune Svanberg**[1,2], **and Katarina Svanberg**[1,2]

[1]Center for Optics and Electromagnetic Research
South China Normal University, University City Campus, Guangzhou 51006, China
[2]Lund Laser Center, Lund University, Lund SE-221 00, Sweden

Abstract— The concentration of the biologically active molecular oxygen gas is of crucial importance for fruits, not only in the maturation and ripening processes, but also in the metabolic respiration. We have studied oxygen content and oxygen exchange in fruits non-invasively by using Gas in Scattering Media Absorption Spectroscopy (GASMAS). By studying how the GASMAS oxygen signal changes during the ripening process of different kinds of tropical fruits-nectarine (NE), mango (MG), papaya (PA), and guava (GU), the state of ripeness of fruits can be assessed. Oxygen diffusion measurements on peeled and unpeeled apples are also performed, and the results show that the skin strongly influences the gas exchange with the environment.

1. INTRODUCTION

From a marketing point of view, it is very important to discriminate between mature and immature fruits. Generally, fruits undergo three main maturity stages, maturation, ripening and senescence. After the fruit reaches maturation, a series of dramatic physiological and biochemical changes occur in the fruits influencing color, flavor, texture and hardness. The concentration of the biologically active molecular oxygen gas is of crucial importance for fruits in the maturation and ripening processes. In metabolic respiration, oxygen is consumed to break down organic compounds of the fruits to release the energy necessary to maintain the life activity. Carbon dioxide is produced in the process. By increasing the carbon dioxide and decreasing the oxygen concentrations in the surrounding,a prolonged fruit shelf-life will result. However, anaerobic respiration happens when the oxygen is below a limit. Thus, the fruits need an optimal surrounding gas concentration in storage. The skin of the fruits is of critical importance in regulating the gas diffusion in fruits.

We have studied oxygen and oxygen exchange in fruits non-invasively by using Gas in Scattering Media Absorption Spectroscopy (GASMAS) [1]. This technique employs a narrow-band tunable diode laser to measure gases in pores and cavities in solid-state matrices. GASMAS relies on the fact that free gases typically have 10,000 times narrower absorption features than the surrounding tissue. The GASMAS imprint is quite small — thus wavelength modulation spectroscopy (WMS) is used for high sensitivity detection. We have studied how the GASMAS oxygen signal changes during the ripening process of different kinds of tropical fruits-nectarine (NE), mango (MG), papaya (PA), and guava (GU). Combining with measurements of reflectance and fluorescence, we show that optical techniques are very powerful in evaluating the state of ripeness of fruits [2]. To study the role of the skin in regulating gas transport in fruits, oxygen diffusion measurements on peeled and unpeeled apples are performed. As illustrated in the present paper, the skin strongly influences the gas exchange with the environment.

2. MATERIALS AND SET-UP

For ripening experiment, four kinds of tropical and climacteric fruits; nectarine (NE), mango (MG), papaya (PA) and guava (GU) are selected for the measurements. The fruits were bought in a local market in South China, and visually immature samples were chosen. Each type of fruit is represented by a group of six fruits from the same batch. Each fruit is marked with a prefix and a number (e.g., NE1, NE2 etc.) written on a small piece of paper which is attached to the fruit far away from the measurement site, in order to avoid interaction with the skin surface to be investigated. The six fruits of the same kind are divided into two groups, among which one group (such as, NE1, NE2 and NE3) is placed in an ambient temperature of 20°C, and another group (such as, NE4, NE5 and NE6) is placed in a temperature of 30°C. The injection of light and the detection are made at positions on the equator of the fruits eparated by 5 cm.

For the oxygen exchange case, five climacteric Fuji apples were acquired from the same batch at the same local fruit shop and one was bought in a different place. Each apple is studied regarding

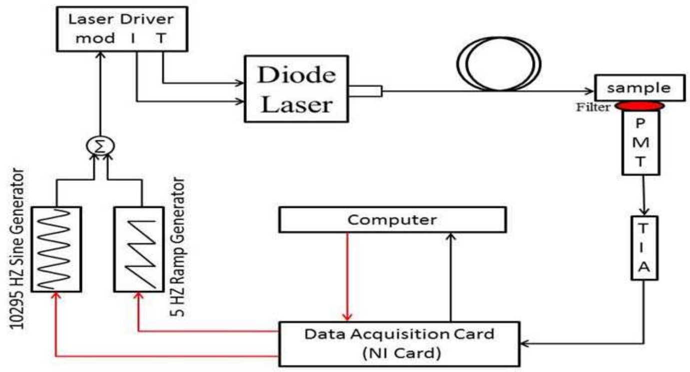


Figure 1: Schematic layout of the GASMAS set-up used for the $2f$ WMS signal recording for oxygen.

gas exchange, first unpeeled, and the following day in a peeled state. Thus, each apple experiences two different experiments in two consecutive days. Before the measurements, the samples are placed in a sealed plastic bag filled with pure oxygen gas overnight. Each peeled and non-peeled apple is placed in the same transparent and sealed plastic bag in the two consecutive days, and the bag is marked with different prefixes and numbers (e.g., Apple_1, Apple_2 etc.) matched to the samples for identification.

A distributed feed-back diode laser (LD-0760-0100, Toptica) with a nominal output power of 1.5 mW, is used as the light source to generate the probing light. A laser temperature controller (TED200C, Thorlabs) and a laser current controller (LCD201C, Thorlabs) are used to control the drive temperature and current of the DFB diode laser. The diode laser is scanned across an O_2 absorption line at 760.445 nm (vacuum wavelength) by sweeping the operating current of the laser by using a 5 Hz saw tooth ramp. In order to achieve sensitive wavelength modulation spectroscopy (WMS) by using lock-in amplification techniques, the diode laser injection current is also modulated by a sinusoidal wave at 10295 Hz. An optical fiber with 600 µm core diameter (727-733-2447, Ocean Optics) is used to guide the light to the sample under our study. A photomultiplier tube with 10 cm cathode diameter (H10722-01, Hamamatsu) is used to detect the diffusely emerging light which contains a weak absorption signal due to the oxygen inside the sample. Ambient light is suppressed not only by the combination of a coloured glass long-pass filter (RG715, Edmund), and the photomultiplier tube quantum efficiency falloff in the near IR region, but also with several black shields to suppress the ambient light even further. For the fruit ripening case, the coloured glass filter was not used. The signal from the photomultiplier tube is amplified by a trans-impedance amplifier (DLPCA-200, Femto) to yield a voltage signal. Then the voltage signal is fed to the same DAQ card (PCI-6120, NI) which is also used to generate the modulation signal for the DFB diode laser. The data from the DAQ card are stored in a computer. The lock-in detection and signal processing procedure of the $2f$ WMS signal are digitally performed with MATLAB. A detailed description of the signal processing is given in [3].

3. RESULTS AND DISCUSSION

Since the optical path length that light travels through the fruits is unknown due to strong scattering, the Beer-Lambert law is not applicable in determining the exact oxygen concentration. Instead, L_{eq}, the equivalent mean path length in normal 21% oxygen air, resulting in the same fractional imprint on the received light intensity, is used to express the gas content. L_{eq} is proportional to the normalized WMS signal (i.e., the $2f$ WMS signal amplitude divided by the light intensity received by the detector). Thus, it is convenient to use L_{eq} to estimate the changes of oxygen contents in fruits maturing and the oxygen content in the process of gas exchange.

3.1. Fruit Ripening

From Fig. 2, it can be seen that the value of L_{eq} decreases gradually to a minimum value from a high value, and then rises to a secondary peak. Finally, it decreases to a quite low value. During this period, the fruits experience a series of physiological and biochemical changes. Changes in L_{eq} are the results of changes in oxygen concentration or in the path length through the gas, or

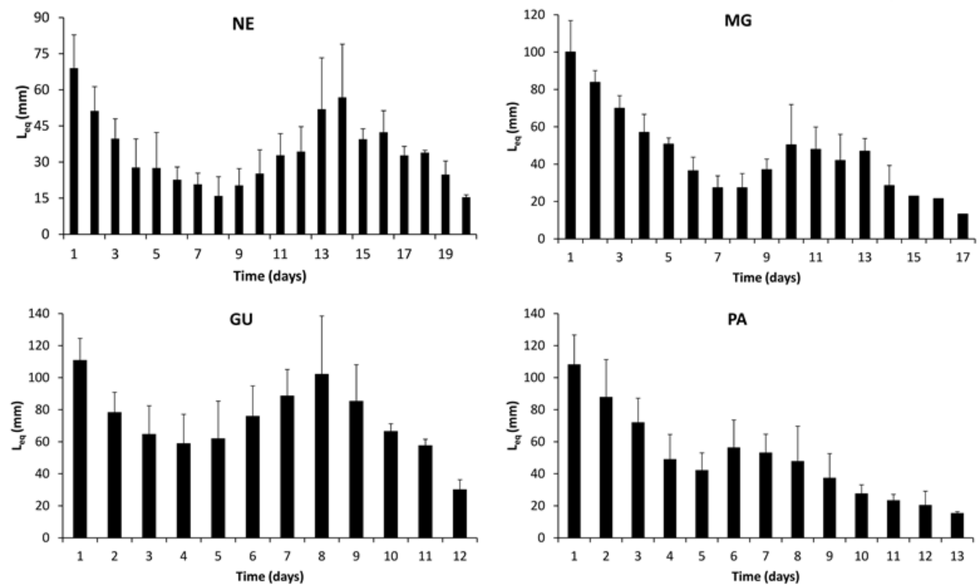


Figure 2: The measured time evolution of the oxygen signal for nectarine, mango, guava and papaya [2].

both. For climacteric fruits, the respiratory rate increases to a peak value with fruit maturation, and then returns to or even goes below the point before the event [4, 5]. The initial reduction of L_{eq} could be attributed to the changes of respiratory rate during fruit ripening. After reaching the climacteric point, the climactic fruits are more susceptible to fungal invasion and begin to degrade, ultimately leading to cell death. So, in Fig. 2 the L_{eq} rises to a secondary peak and then decreases to a very low value after the climacteric point. The characteristic temporal variation of L_{eq} is useful for assessment of maturity, and the likely day of ripeness can be inferred, as coupled to the occurrence of the initial minimum in the GASMAS signal. The days of estimated ripeness are shown in Table 1, with errors bars considering the standard deviations.

Table 1: The indicated days of ripening for four kinds of fruits as assessed from the minimum of the GASMAS signal.

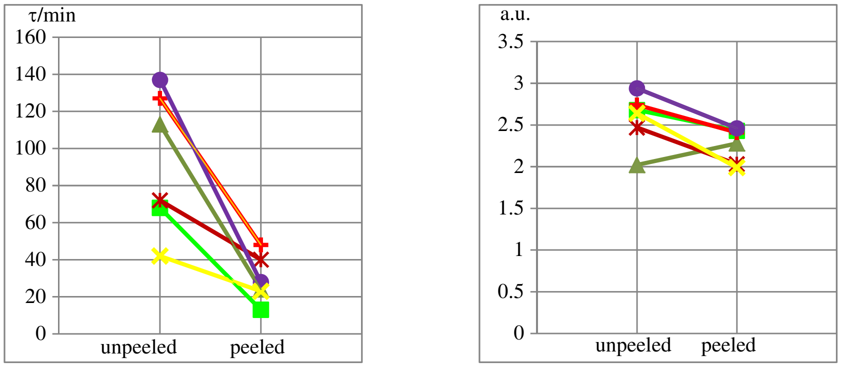
Type	Nectarine (NE)	Mango (MG)	Guava (GU)	Papaya (PA)
Day of ripening	8 ± 1	8 ± 1	4 ± 1	5 ± 1

4. GAS EXCHANGE

After taking the apple out from a pure oxygen environment and putting it into the GASMAS system, by fitting an exponential function to the experimental data with a Matlab program, the initial L_{eq} for apple out of the oxygen filled bag, the final equilibrium L_{eq} and the time-constant (τ) are all evaluated. τ is the time the signal takes to change its initial value by a factor of $1/e$ in relation to the final equilibrium value.

By analyzing τ for unpeeled and peeled apples (i.e., Fig. 3(a)), it can be seen that the time-constant τ for unpeeled ones are larger than for the peeled ones, which means that the unpeeled ones exchange gas slower than the peeled ones. It agrees with the assumption that the major site of resistance to gas exchange in fruits is probably the skin [6] and agrees with the results of [7]. As can be seen in Fig. 3(b), the ratios of the initial L_{eq} and the final equilibrium L_{eq} for the six apples are just slightly different, it seems that either with skin or without skin, the fruits experience gas exchange of the same magnitude, although of different rates.

As shown in Fig. 4, after the apples exchange gas and get to the equilibrium state, the final equilibrium L_{eq} values for unpeeled apples are smaller than the peeled ones. The apple skin seems to keep apples in a lower oxygen condition with than without the peel, while the apples experience gas exchange slower with than without the skin. An active role by the skin in regulating oxygen content was earlier suggested in a test on a single apple [7]. More efforts should be put into these



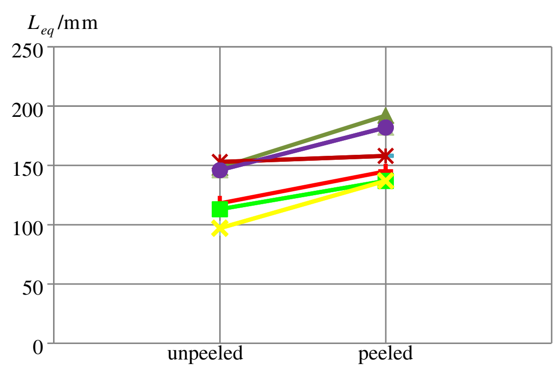
(a) (b)

Left: unpeeled and right: peeled.

Six apples were measured, Apple_1, Apple_2, Apple_3, Apple_4, Apple_5, Apple_6.

Figure 3: (a) Time-constant τ for gas exchange for the same apple with different treatment. (b) Ratio of initial L_{eq} for apple out of the oxygen filled bag and the final equilibrium L_{eq}.

aspects, where eliminating the large data spread due to interference fringe problems in the present study, would be a priority.



Six apples were measured, Apple_1, Apple_2, Apple_3, Apple_4, Apple_5, Apple_6.

Figure 4: The final equilibrium L_{eq} for apples after experiencing gas exchange.

5. CONCLUSION

As illustrated in this paper, optical techniques are very powerful in evaluating the state of ripeness of fruits. Further, the skin was found to strongly influence the gas exchange with the environment. In contrast to other techniques, our technique has the advantages of measuring the gas content inside the sample non-intrusively, in situ and in real-time. It suggests the prospect of developing the GASMAS technique into a valuable and portable tool for gas studies in fruits and foods.

ACKNOWLEDGMENT

The authors are grateful for the support from Prof. Sailing He. This work was financially supported by the Guangdong Innovative Research Team Program (Grant 201001D0104799318).

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