Application of time-of-flight near infrared spectroscopy to Satsuma mandarin

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Introduction

The detection of near infrared (NIR) light from the sample is through either transmittance or reflectance.¹ The transmittance NIR method is very desirable for detecting internal information, whereas the optical information from diffuse reflectance spectra is confined to the subsurface layer of samples. Therefore, it is especially important that progress be made in developing an NIR transmission device for detection of internal characteristics of high-moisture fruit. For example, the nondestructive detection of sugar content in Satsuma mandarin would be of considerable value to the fresh fruit industry. Some techniques and devices for the transmittance method, which could detect inner information of Satsuma mandarin have been proposed previously.^{2,3} However, the behaviour of transmitted light from an agricultural product is directly affected by physical and chemical properties of tissues, so that it is preferable to examine the optical characteristics of the tissue and its origin in detail from a new concept.

In this study, an optical measurement system, which was mainly composed of a parametric tunable laser and a near infrared photoelectric multiplier, was introduced to accomplish this purpose from the viewpoint of time-of-flight near infrared spectroscopy (ToF-NIR).^{4,5} This system combines the best features of the spectrophotometer and the laser beam, and more advantageously, the time-resolved profile of transmitted output power can be measured sensitively in nanoseconds. The combined effects on the time-resolved profiles of sample diameter, sugar content, the wavelength of laser beam and the detection position of transmitted light were investigated in detail.

Material and methods

The samples used were Satsuma mandarin (*Citrus unshu* M_{ARC}) (location: Wakayama, Japan) having the diameters of 50–84 mm. The sugar content measured by a refractometer varied from 9.9 to 16.3 Brix %.

The wavelength of the pulsed laser λ was tuned from 600 nm to 1100 nm by the optical parametric oscillation of a BBO (β -BaB₂O₄) crystal.^{6,7} The transmitted output power was measured by an NIR photoelectric multiplier with a spectral response ranging between 300 nm and 1700 nm through an optical fibre cable having a diameter of 7 mm. The equator of the sample was irradiated vertically with the pulsed laser and the detection position was varied at the equator of the sample. The sampling time and the number of averaging of the transmitted output power were 100 ns and 300 times, respectively.

The time-resolved profile refers to the variation of the intensity of the detected light beam with

time. In this study, the time-resolved profile of the cuticle was employed as the reference. The measure of attenuance A_i is defined as follows:

$$A_{t} = \log\left(\frac{Pw_{0}}{Pw}\right) \tag{1}$$

where Pw_0 and Pw indicate the peak maxima of the reference and the object, respectively. The measure of time delay of peak maxima Δt is expressed as follows:

$$\Delta t = t - t_0 \tag{2}$$

where t_0 and t indicate the time at peak maxima of the reference and the object, respectively. The variation of the full width at half maximum value of the profile Δw is also expressed as follows:

$$\Delta w = w - w_0 \tag{3}$$

At3 2 3 (us) 影 Ar 2 1. (us) 1.2 Wavelength: 800 nm Sugar content(Brix)11 \pm 0.5% 1.0 A 0.8 Number of sample: 19 oœ Detection position 0.6 • **Opposite** face Side face 0 0.4 80 50 60 70 Distance between irradiation position

and detection positon l(mm)

Figure 1. Variation of attenuance A_{t} , time delay of peak maxima Δt and variation of full width at half maximum Δw with detection position.

where w_0 and w indicate the full width at half maximum value of the profile for the reference and the object, respectively.

Results and discussion

Figure 1 indicates the variation of A_i , Δt and Δw with the distance between irradiation position and detection position l, respectively. The detection position is either opposite face or sider face (see Figure 1). The diameter of the sample varied from 50 mm to 84 mm. The sugar content in the population is nearly constant at $11 \pm 0.5\%$. These optical parameters increased gradually as l increased to be greatly absorbed and vigorously scattered. In particular, Δt is positively correlated with l.

Figure 2 indicates the variation of A_t , Δt and Δw with the sugar content, respectively. The diameter in the population is nearly constant at 60 ± 1 mm. Each optical parameter had a tendency to increase as the sugar content increased. Such behaviour was remarkable when the transmitted light was detected at the side face of a sample. However, there is little correlation of sugar content with Δt and Δw when the transmitted light is detected at the opposite face.



Figure 2. Variation of attenuance A_t , time delay of peak maxima Δt and variation of full width at half maximum Δw with sugar content.

Next, we examined the relationship between each optical parameter and sugar content of the Satsuma mandarin having various sizes. To compensate the effect of sample size on the time- resolved profile, each parameter was normalised by *l*. Figure 3 shows the correlation coefficient between sugar content and each normalised parameter. The correlation coefficient at the side face shows a larger value than that at the opposite face, independent of wavelength. Furthermore, it is known that the relationship between sugar content and A, is not necessarily coupled with the relationship between sugar content and Δt . To correctly interpret these results, however, we may consider that the characteristics of the transmitted light differ with the detection position. The output detected at directly opposite the irradiation position may include the straight-through or near-straight beams. The output at other detection positions could be defined as diffusely scattered light. The difference in the optical characteristics of transmitted beams directly reflects the substantial optical path length.

When we apply ToF-NIR to detection of the information for the inside of fruit with high moisture content such as Satsuma mandarin, it is very important to give attention to the difference in the scattered light within tissues and the semi-straight propagated light. Furthermore, we tried to express the resulting phenomena by using model samples composed of water, sucrose and milk. The variation of the time-resolved profile is strongly governed by the combination of the light absorption component, scattering medium and refractive index.



Figure 3. Correlation coefficient between sugar content and each normalised parameter.

Conclusions

In this study, a newly constructed optical measurement system, whose main components were a parametric tunable laser and a near infrared photoelectric multiplier, was applied to detection of the sugar content of Satsuma mandarin using ToF-NIR spectroscopy. The combined effects on the time-resolved profile of sample diameter, sugar content, the wavelength of the laser beam and the detection position of transmitted light were investigated in detail.

The variation of the attenuance of peak maxima At, the time delay of peak maxima Δt and the variation of full width at half maximum Δw were strongly dependent on the detection position and the wavelength of the laser beam. At, Δt and Dw increased gradually as the sample diameter increased to be greatly absorbed and vigorously scattered. On the other hand, each optical parameter had a tendency to increase as the sugar content increased. Such behaviour was remarkable when the transmitted light

0.8

0.6

was detected at the side face of a sample. To find the resulting phenomena of the time-resolved profile, it is very important to give attention to the difference in the scattered light within tissues and the semi-straightly propagated light.

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