Measurement of sugar contents in apples by near infrared spectroscopy and development of a compact near infrared sugar-measuring instrument

T. Temma, M. Chiba, K. Hanamatsu and F. Shinoki
Aomori Advanced Industrial Technology Center, 202–4 Ashiya, Yatsuyaku, Aomori-shi, Aomori, Japan.

T. Tsushima
Towa Electric Industrial Corporation, 5–1 Kinzoku-cho, Hirosaki-shi, Aomori, Japan.

Introduction

The internal quality evaluation of apples has mostly been conducted by destructive inspection requiring much labor and time. Thus, a more rapid, simpler and highly accurate method of inspection is needed.

By using near infrared (NIR) spectroscopy,[1] one can analyze a sample non-destructively and rapidly, through the analysis of the protein of flour[2] and water[3] etc. in the food. In sugar content measurements, such as in peaches and pears,[4] the application of NIR was examined for use on-line for practically measuring the sugar content of fruits by near infrared rays on a fruit selecting conveyer. After the development of the on-line system, a compact instrument was developed to measure the sugar content of the fruits on a tree.

In this work, the possibility of using NIR to measure the sugar content quantitatively in apples and apple juices was examined and the compact NIR sugar-measuring instrument, that can be used outdoors, was developed.

Sugar content measurement

Materials and methods

Samples of the apple fruits were cultivated in Aomori Prefecture. 40 samples of the following varieties were prepared "*Malus domestica* Borkh. cv. Fuji", "*Malus domestica* Borkh. cv. Starking Delicious", "*Malus domestica* Borkh. cv. Jonagold" and "*Malus domestica* Borkh. cv. Golden Delicious". Calibration of the sugar content of each apple was made. Samples of the apple juices were the turbid type and lucid type which are sold in markets. The numbers of each sample were 71 turbid apple juices and 38 lucid apple juices. Concentration of the apple juices was controlled by diluting with pure water. Calibration was evaluated by comparing the sugar content presumed by NIR with the sugar content measured by digital-refractometer in unknown samples. Unknown samples were 18 "Fuji", 17 "Starking Delicious", 20 "Jonagold", 20 "Golden Delicious", 31 turbid apple juices and 40 lucid apple juices.

The NIR instrument was the Pacific Scientific Model 6250 system. The measurement was conducted at room temperature and the measurement wavelength region was from 680 nm to 1235 nm. A reflectance was calculated by comparing near infrared energy reflected from the sample with that from the standard reference. Brix, as a reference measurement, was analyzed by an Atago PR-1 digital-refractometer. Moreover, the detection mode was a diffuse-reflectance method (coaxial optical fiber use) in the case of the apples and was a transmission method in the case of the apple juices.

Results and discussions

In the case of the apples, to select the first wavelength of the sugar content in "Fuji", we analyzed it from the simple regression between the value of the second derivative spectra and the value of Brix as a reference. As a result, among six wavelengths that have a large negative correlation coefficient (physical significance), we conducted the multiple regression analysis of two variables by setting the first wavelength candidature for the three wavelengths (912 nm, 984 nm and 1014 nm). Using the absorbance at 912 nm and 888 nm, the correlation of the value between Brix as a reference and the NIR value obtained a large correlation coefficient of 0.94 as shown in Figure 1. Therefore, we drew calibration from these two wavelengths. Here, the NIR value is the value of the presumed sugar content applied by the multiple regression analysis in the NIR method. The 912 nm was selected as the first important wavelength that was thought to be assigned to C–H str. third overtone. In this calibration for sugar content in "Fuji", standard errors of prediction (*SEP*) became 0.339 ^{o}Bx as the result of a conducted check of performance through 18 samples of prediction set for calibration evaluation. The obtained calibration equation showed high accuracy. "Starking Delicious", "Jonagold" and "Golden Delicious" were measured by the same method for the sugar content as that of "Fuji". The first wavelength selected was 912 nm, for the "Fuji". When we selected 866 nm, 875 nm, 877 nm as the second wavelength, the correlation coefficient obtained a large value of 0.95, 0.98, 0.96 respectively. In addition, the *SEP* was calculated as 0.307 °Bx, 0.357 °Bx and 0.546 °Bx and each obtained a calibrative equation showing high accuracy.

In the case of apple juices, we regarded 912 nm as the first wavelength that was assigned to C–H str. third overtone as the effective absorption wavelength for the sugar of the turbid apple

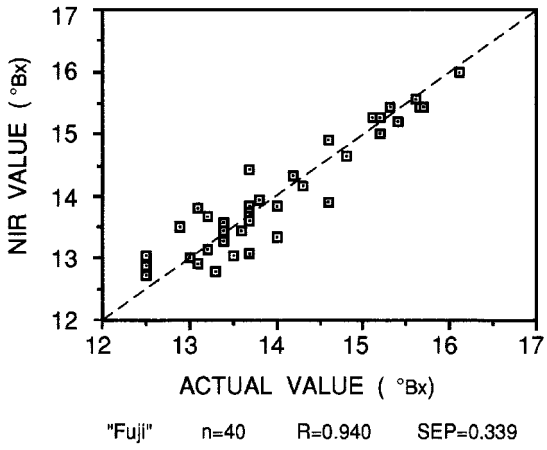

Figure 1. Plot of NIR value vs. actual value.

juices. The second wavelength was selected at 955 nm. At this time, a correlation coefficient of 0.97 was obtained. The *SEP* became 0.439 °Bx and the obtained calibration equation showed high accuracy. Also, we thought of the first wavelength 938 nm that was assigned to C–H str. third overtone as an effective absorption wavelength for the sugar of the lucid apple juices and then the second wavelength was selected at 989 nm. At this time, a correlation coefficient of 0.99 was obtained. The *SEP* became 0.191 °Bx and the obtained calibration equation showed high accuracy. We show in Table 1 the correlation coefficient and standard errors of prediction for the various samples.

As mentioned in the above results, we understand that the NIR method effectively measured the sugar content with very high accuracy for apples and apple juices.

Considering the effective absorption wavelength for the sugar of the apples and apple juices the selected first wavelength was this time found to be approximately 900–940 nm. In our analysis, the first wavelength was determined by the following three points, (i) physical significance (the correlation coefficient of the second derivative value is a negative value), (ii) statistical significance (the correlation coefficient must be large) and (iii) spectroscopic significance (the assignment of near infrared absorption).

Further, in order to confirm spectroscopic significance, we conducted the following measurement. Since it is known that the apples hold mainly three kinds of sugar, namely fructose, glucose and saccharose, three water solutions that include each sugar were analyzed at the NIR absorption wavelength. As a result, the correlation of the wavelength of 912 nm and 938 nm indicated through the high value that these wavelengths were derived from sugar. Therefore, the first wavelength that was selected for both the apples and the apple juices was thought to be the proper spectroscopic wavelength.

It is very important in using NIR to decide the first wavelength that derives from the constituent.

Development of a compact NIR sugar-measuring instrument

Materials and methods

The spectrum system consists of a polychromator and an optical fiber. The polychromator has a multi-channel detector that has 256 devices of 50 μm and a concave diffraction grating that is

Table 1. Correlation coefficient and standard errors.

	Wavelength seleted (nm)			
Varieties	1st	2nd	*R*	*SEP* (°Bx)
Fuji	912	888	0.940	0.339
Starking Delicious	912	866	0.950	0.307
Jonagold	912	875	0.985	0.359
Golden Delicious	912	877	0.964	0.546
Turbid apple juices	912	955	0.976	0.439
Lucid apple juices	938	989	0.997	0.191

R: Multiple correlation coefficient.
SEP: Standard errors of prediction.

–1 Order, 9.5 nm mm^{-1}, with reciprocal linear dispersion and the size is $15 \times 15 \times 5$ mm with 450 grooves mm^{-1}. The optical fiber is a coaxial fiber bundle with a detection area of 12.56 mm^2 and an irradiation area of 103.82 mm^2. The wavelength range is 800–1000 nm. The incidence slit width is 500 μm. The optics system of the light source is composed of a halogen lamp with a low electric power of 30 watts and a filter (intercept less than 750 nm). The power supply is a battery. Moreover, we made a special circuit for the processing and control of the signal from the detector. The special circuit consisted of a Z80 as CPU and a A/D converter (10 msec, 8 Bit). Getting the reflection light strength data required about 0.73 sec/scan and it needed 0.19 sec for the sugar content calculation.

In addition, the compact NIR sugar-measuring instrument was evaluated by measuring the value of the full width at half maximum (FWHM) of the spectrum and the brightness of the output light power according to the changing of incidence slit width and by the concentration measurements of the saccharose solution and the sugar content measurements of the apples.

Results and discussions

The size of our experimental spectroscope is $100 \times 95.6 \times 50$ mm. In the compact NIR sugar-measuring instrument, the light was irradiated to the sample through the optical fiber bundle and was incident in the spectroscopical optics through the optical fiber bundle on the receiving side. Further, the sugar content value was shown on the liquid crystal panel by processing the signal from the detector using the special circuit. The size of the compact NIR sugar-measuring instrument is $231 \times 112 \times 76$ mm (Figure 2).

The FWHM of the spectrum and brightness were measured. The slit widths used were 50 μm, 500 μm, 1 mm and 2 mm. The photospectrum analyzer was made of ANRITSU, Model MS9030A-MS9701B.

When the light source was a halogen lamp, the value of FWHM decreases and the brightness increased in proportion to the incidence slit width as shown in Figure 3. We can get the resolution

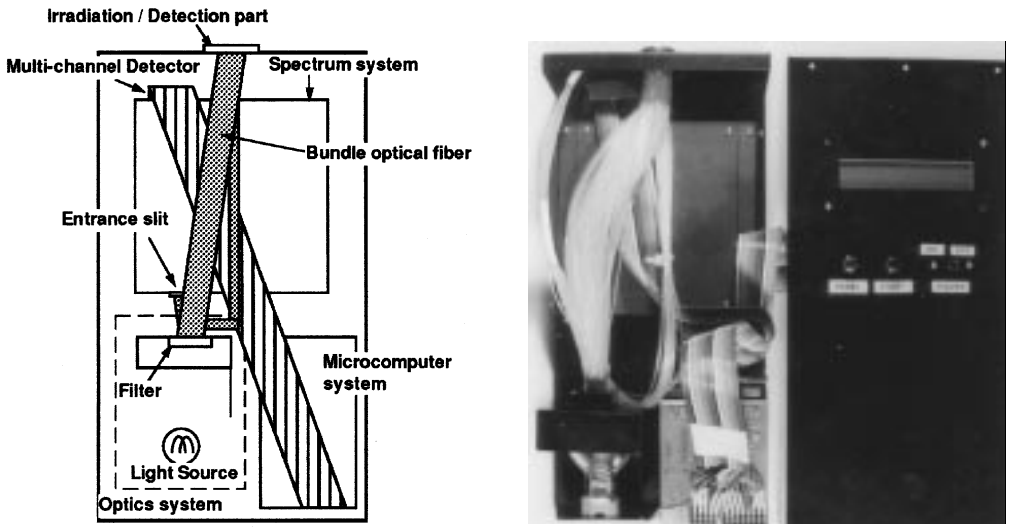

Figure 2. Exterior view of the compact NIR sugar-measuring instrument.

by means of multiplying the equation of the reciprocal linear dispersion by limited slit width. As a result, the actual value of FWHM showed agreement with the calculated value in the case of 500 μm, 1 mm and 2 mm as shown in Figure 3 and the resolution of the experimental spectroscope was about 12 nm.

The change in each concentration of the saccharose solution at 912 nm was measured when the concentration of the saccharose solution was assumed to be 1, 3, 5, 7, and 9 w%. Thus, the concentration of the saccharose solution of l w% or more was able to be measured.

When the sugar content of the apple fruit was measured by the compact NIR sugar-measuring instrument, the correlation coefficient between that instrument and the refractometer showed a satisfactory value, 0.84. Further, we got 0.71 °Bx as the measurement accuracy (Figure 4).

Conclusion

The NIR method was evaluated to develop a non-destructive sugar content analysis method for apples and apple juices.

We obtained a high *SEP* value of 0.546 °Bx and a large correlation coefficient of 0.94 or more, when we measured the sugar content in the four kinds of apple fruits. In the case of the two kinds of apple juices, we obtained a high SEP value of 0.439 °Bx and a large correlation coefficient of 0.97 or more.

It is most important in the NIR method to decide the first wavelength that derives from the adequate constituent. The first wavelength was decided from three points of condition “physical significance”, “statistical significance”, “spectroscopic significance”. For the apples and the apple juices, the 912 nm was an important wavelength derived from the sugar. In addition, the method of measuring sugar content of apples and apple juices by the NIR method was established by showing a high accuracy with an obtained calibration.

In the compact NIR sugar-measuring instrument, the spectroscopic optics were composed of a polychromator and an optical fiber and we made the special circuit for data processing and

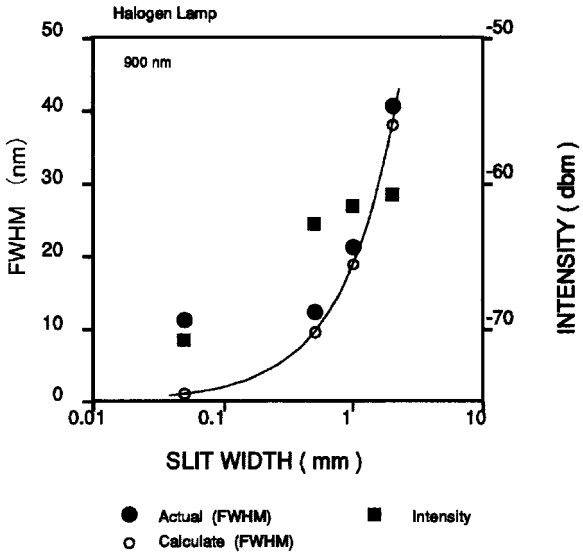

Figure 3. Slit width vs. FWHM/intensity.

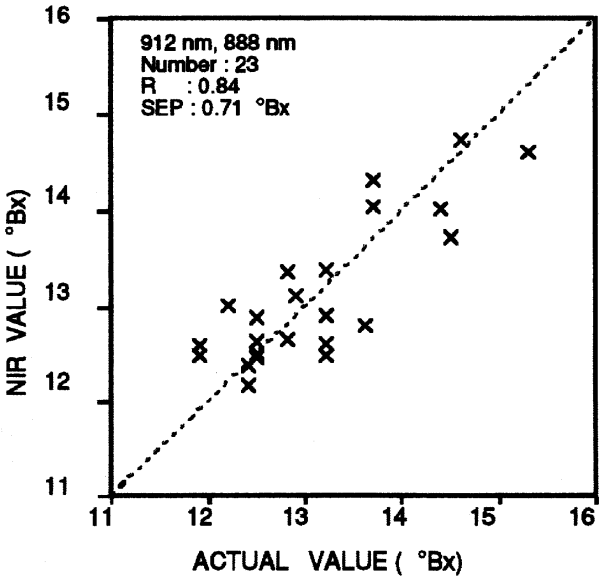

Figure 4. Plot of NIR value vs. actual value.

control. The resolution of a sugar-measuring instrument was about 12 nm with a 500 μm slit width. When the sugar content of apples was measured, there was a correlation coefficient of 0.84 and a SEP of 0.71 °Bx. Therefore, it is understood that the compact NIR sugar-measuring instrument showed us adequate performance for possible practical use.

References

1. K. Norris, *Near Infrared Technology in Agricultural and Food industries*, Ed by P.C. Williams and K.H. Norris. American Association of Cereal Chemists, St Paul, MN (1987).
2. B.G. Osborne *et al., J. Sci. Food Agric.* **32,** 200 (1981).
3. B.D. Bonner *et al., J. Phys. Chem.* **72,** 899 (1968).
4. S. Kawano *et al., 4th International Conference on Diffuse Reflectance Spectroscopy*. Chambersburg, USA, pp. 5A (1988).