Introduction

Potatoes are used in the food industry to produce food products such as potato flakes, potato chips, and French fries. In each instance, potatoes are presorted before being introduced to the processing line. Consequently, the composition of the potato must be measured for variables such as dry matter, carbohydrate, and reducing sugar content (fructose and glucose) prior to determining its correct use, handling, and processing [1-3]. In the fried products industry, the determination of the reducing sugars content is particularly important because the presence of high levels of reducing sugars not only causes browning, but also generates acrylic amide by the Maillard reaction with asparagines during the high temperature heating process. Acrylic amide is believed to be carcinogenic and poisonous to the nervous system and is therefore a highly undesirable attribute for consumers.

Potato tubers are normally stored at low temperatures to prevent sprouting and weight loss; however, during storage sugar content increases. Freshly harvested tubers normally have sugars in trace amounts. Very high sugar levels may be reached when stored at low temperatures. Removal of these potatoes with high reducing sugar content is necessary in the fried food industry.

The reducing sugar content of potatoes is generally determined by very accurate chemical methods, such as high performance liquid chromatography (HPLC). These methods are performed off-line, are time consuming and usually require trained personnel for their execution. Additionally, these methods destroy the material that is being analyzed. Due to these reasons, chemical methods are generally not feasible for on-line measurement applications in the food industry. Therefore, a rapid method for determining the amounts of sugars in intact tubers would be useful for monitoring sugar levels during extended storage or for testing of shipments prior to processing.

Near infrared (NIR) spectroscopy offers a rapid and nondestructive alternative to chemical measurement techniques to evaluate compounds in food. NIR spectroscopy has been used to nondestructively estimate the specific gravity of potato tubers [4] and dry matter in potatoes [5], as well as the main ingredients including the carbohydrate content in potatoes [6-9]. In contrast, there are no reports describing nondestructive measurement of the sugar content in intact potatoes; however, a destructive NIR analysis of the sugar content of potato slices was reported [10,11]. The objective of this study was to ascertain whether NIR spectroscopy could be used to determine the reducing sugar content of intact potato tubers.

2. Materials and methods

2.1 Experimental sample preparation

Potatoes of one cultivar (May–Queen) were purchased...
on the 7th of September, 2008 from the Akita fruits and vegetables distribution market and were used as the experimental samples. The potato samples were grown at locations around Hokkaido, Japan. A total of 100 potato samples were used. Potato samples were individually separated into two groups. To provide a wide range of sugar concentrations in the sample groups, one group was stored at 5°C for 4 months, and the other group was stored at 25°C for 4 months. At biweekly intervals, five tubers were removed from each storage room for testing.

2.2 Spectra acquisition

NIR spectra were measured on all intact potato samples using a spectrophotometer (NIRSystems Model 6500) equipped with a fiber optics interactance probe as shown in Fig. 1. The fiber optic probe consisted of a central bundle (diameter: 7.6 mm) of Schott glass fibers and a concentric ring of the fibers (outside diameter: 19 mm, width: 0.64 mm). The ring was separated from the central bundle by a 5 mm thick metal barrier. To obtain the optical spectrum, an intact potato is placed on the optical probe and the cover of the sample-housing is closed. Monochromatic light is emitted by the ring, and “interacts” with the tissue. Some of the non-absorbed light is internally reflected to the central bundle. NIR spectra in the wavelength range of 400–1100 nm at 2 nm intervals were collected as absorbance measurements. A 2.5-mm thick white ceramic plate was used as a standard optical reference. Each spectrum was an average of 32 scans and one spectrum was obtained per potato sample. Prior to spectral measurements, each sample was placed in the measurement room (25°C) for 5 hours.

Raw spectra obtained from three differently sized potatoes are shown in Fig. 2. The spectra clearly shift according to the sample size. To reduce the sample-size effect, we used the second derivative spectra. In addition, the second derivative spectra in the 600–1100 nm wavelength range showed higher resolution than the spectra in the 400–600 nm wavelength range. Thus, second derivative spectra were used to estimate sugar content of stored potatoes in this study.

2.3 Chemical analysis

After NIR spectra were measured, flesh of the potato tuber samples was cut and mashed by a mixer, the material was wrapped in gauze, and then the juice was extracted by squeezing. This juice was used for sugar analysis. The sugar compositions (fructose, glucose, sorbitol, sucrose) of the potato juices were analyzed using an HPLC (Shimadzu, SCL-10A VP) method with a refractive index detector (Shimadzu, RID-10A). Sample mixtures were separated on a Shodex Asahipak NH2P-50 4A column using an acetonitrile/water (3:1 v/v) solution as the eluate. The operating conditions were as follows: flow rate of 1 mL/min; column temperature of 40°C; injection sample volume was 10 μL. The raw potato juice samples were centrifuged at 3000 rpm for 30 min, diluted 1:5 by adding distilled water and subsequently passed through a 0.45-μm pore-size filter.

2.4 Statistical Analysis

Data analyses were carried out using "Unscrambler" (CAMO, Oslo, Norway) and Excel software (Microsoft Office 2003). Second derivative spectra (Savitzky–Golay algorithm, left and right averaging of 20 nm and 2nd order polynomial) were used. The partial least square (PLS) regression was used to develop calibrations for analyzing the sugar compositions of intact potato tuber samples. Calibrations were performed on glucose and fructose. PLS regression was performed in the wave-
length range of 600 to 1100 nm where the absorption bands were assigned to the fourth, third, and second overtones of O–H and C–H fundamental bands or their combinations. Validation was performed by leave-one-out full cross validation.

3. Results and discussion

3.1 Variations in the sugar content of potato tubers during storage

Figure 3 shows the variations in the contents of glucose and fructose of potato tubers stored at either 5 or 25°C, as measured by chemical methods. The sugar content values shown are averages of five potato tubers. In tubers stored at 5°C, the glucose contents of the potato tuber samples gradually increased after 1 week of storage and continued to increase until 8 weeks of storage. The sugar contents of the potato tuber samples decreased after the 8th week of storage, suggesting that the potato tubers had begun to germinate. Fructose levels in the potato tuber samples also increased until the 8th week of storage. For potato tubers stored at 25°C, there were no clear variations in the glucose and fructose contents at the beginning of storage, but clear decreases were observed after storage for 6 weeks.

3.2 Variations of the NIR spectra during the storage process

The average NIR second derivative spectra of 15 potato tuber samples stored at 25°C for 0, 2, 4, 6, 8, 10, 12, 14, and 16 weeks are shown in Fig. 4(a). The variations in the second derivative spectra that result from the changing composition of the stored tubers may be very subtle, and therefore, can be difficult to observe. To clearly observe and confirm the variations in spectral intensity, the variance of these average spectra was calculated and plotted as shown in Fig. 4(b). In the variance plot of the second derivative spectra, the peaks around 970 nm and 760 nm were attributable to water. The differences in the sizes of these peaks indicated that the potato tuber samples lost weight during the storage process. Other peaks were observed around 670, 710, 798, 830, and 926 nm. The peak at 670 nm is attributable to chlorophyll, which is present in greater quantities in immature fruit than in mature fruit [12]. However, we also observed an absorption peak of glucose and fructose around 670 nm in the second derivative spectra of glucose and fructose (Fig. 5). Moreover, the NIR second derivative spectra of potato tuber samples stored at 5°C showed relatively large variations around 670 and 710 nm (Fig. 6(b)). Based on these facts, the considerable variations around 670 and 710 nm may be associated, either directly or indirectly, with the sugar content of potato tubers (see Fig. 4(b) for compari-
The spectra values at 710 nm and 934 nm are the fourth and third overtones of C–H stretching [13]. The values at 798 nm and 826 nm also may be related to fructose and glucose (Fig. 5).

3.3 PLS regression

PLS regression analysis was performed based on the sugar (glucose and fructose) contents and NIR second derivative spectra (600–1100 nm) of all potato tuber samples (total of 80: 40 stored at 5°C and 40 stored at 25°C). Figure 7 shows the calibration and validation results of the fructose (a) and glucose (b) contents of the potato tubers. The correlation coefficients of the calibration were 0.71 and 0.65, respectively, with a standard error of validation (SECV) equal to 0.26 mg/g and 0.46 mg/g, respectively. As an index for determining the validity of the calibration models, the RPD (ratio of standard deviation of reference data in prediction sample set to SECV) is usually employed [14]. A RPD value of 1.4–1.7 is regarded as adequate for rough screening and a value above 1.7 is regarded as satisfactory for screening. In this study, the RPD values of 1.42 for fructose content and 1.32 for glucose (close to the value proposed by Williams) were obtained. As such, the NIR calibration models are suitable for rough screening of the sugar contents of the potato tubers. Here, this nondestructive sorting approach can roughly partition the potato tubers into two groups; those with high values, and those with low values.

3.4 Discussion of the NIR Calibration Models

Regression coefficients can be used to discuss the contributions of individual wavelengths to a PLS calibration model, because a regression coefficient spectrum shows characteristic peaks and troughs that can indicate which wavelength range is important for the calibration model [15,16]. Figure 8 shows the regression coefficients of the PLS calibration models of the fructose (a) and glucose (b) components, respectively. These regression coefficient spectra showed several marked peaks, such as those observed at 670, 710, 798, and 830 nm. Variations in the size of these peaks of the NIR second derivative spectra were observed in potato tuber samples during storage. We confirmed that these peaks were the absorption bands of glucose or fructose by comparison to the second derivative spectra of glucose and fructose standards (Fig. 5). In particular, the peak around 798 nm is consistent with the findings of Miyamoto and Kitano [17], who reported a sugar absorbance band around 794 nm. The results presented here are also consistent with those reported by McGlone [18] and Abebe [19], who reported a calibration model to estimate soluble solids content of mandarin fruit. In addition, there is a small peak around 830 nm in the regression coefficient of the PLS calibration model that can only be accounted for by glucose, as shown in Fig. 8. We confirmed that this peak represented the absorption band of glucose by comparison to the second derivative spectra of glucose and fructose standards (Fig. 5). In other words, it is possible to differentiate glucose from fructose on the basis of these small differences in the calibration models. Furthermore, we confirmed that the peak at 888 nm in the regression coefficient
spectra represented the absorption band of fructose, as shown in Fig. 5. Consequently, the PLS calibration models for estimating the sugar components of potatoes were established based on the specific absorption characteristics of the various sugar components.

3.5 NIR Prediction Results

The PLS calibration models for estimating the sugar components were applied to other independent potato tuber samples. The potato samples were separated into two groups; one was stored at 5°C for 3 months, the other was stored at 25°C for 3 months. As in the calibration analysis, five tubers were removed from each storage room every 2 weeks, and their NIR spectra were evaluated. Fructose and glucose contents of the potato tubers were predicted based on the calibration models. The changes in the glucose and fructose levels of the potato tuber samples during storage are shown in Fig. 9. These results were consistent with pattern of glucose and fructose values determined in the potato tuber samples using chemical methods.

4. CONCLUSION

In this study, we roughly estimated reducing sugar contents in potato tubers during storage using a simple non-destructive approach that involved the acquisition of NIR spectra (400–1100 nm) with fiber optics in the interactance mode. The marked variations around 670, 798, 830, and 888 nm were associated with sugar content in the potato tubers. Comparisons between variance plots of the second derivative NIR spectra of potato samples stored at 25 and 5°C showed clear differences that were attributable to sugar and water content. Based on the variations around these major wavelength bands, calibration models to accurately estimate fructose and glucose contents were developed by a partial least squares statistical analysis method. This preliminary study demonstrates that near infrared spectroscopy can be used for
nondestructive sorting of potatoes according to their sugar content. However, the accuracy of this method could still be improved, and further research is required to develop the method to a level that is suitable for practical use.

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和文要約

可視および近赤外分光法によるじゃがいもの糖成分の非破壊測定

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じゃがいものの糖成分の非破壊測定法の開発のため、可視および近赤外分光法の利用を検討した。光ファイバを利用したラクラクタンス法でじゃがいものの可視および近赤外スペクトル（400-1100 nm）を非破壊的に測定できた。測定されたスペクトルと糖成分の関係を検討した上で、PLS 回帰分析法を用いて糖含量の予測モデルを開発したところ、2次微分スペクトルとフルクトースおよびグルコース含量の間に有意の相関関係が認められ、標準誤差がそれぞれ 0.26 mg/g と 0.46 mg/g の予測モデルが得られた。本研究では、ラクラクタンス測定法を用いた近赤外分光法がじゃがいものの糖含量の非破壊的測定法として利用の可能性があることを示唆した。