Comparison of Near-Infrared Reflectance Spectroscopy and Texture Analyzer for Measuring Wheat Bread Changes in Storage

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ABSTRACT

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Bread staling affects bread texture properties and is one of the most common problems in bread storage. Bread firmness, as measured in compression mode by a texture analyzer (TA) has been commonly used to measure bread staling. This study investigated the potential of visible and near-infrared reflectance spectroscopy (NIRS) to detect bread changes during storage by comparing NIRS results with those obtained by TA. Twenty-five loaves of commercial wheat white pan bread from one batch were studied over five days. NIRS and TA measurements were made on the same slice at approximately the same time. The experiment was repeated five times using the same kind of commercial samples from five different batches. NIRS measurements of slices, loaf averages, and daily averages were compared with TA measurements. NIRS spectra had a high correlation to TA firmness. NIRS measurements correlated better with the actual storage time and had smaller standard deviations than the TA measurements. The batch differences had less effect on NIRS measurements than on the TA measurements. The results indicate that NIRS could follow bread changes during storage more accurately than the TA. NIRS is probably based on both physical and chemical changes during bread staling, unlike the TA method that only measures bread firmness, which is only one aspect of the staling phenomenon.

Bread staling is one of the most common problems in bread storage. Bread firmness correlates negatively with the organoleptic assessment of staleness (Bice and Geddes 1949). As a result, firmness becomes an important attribute in assessing bread staling. Current standard methods of testing firmness include the universal testing machine (UTM) (Approved Method 74-09, AACC 2000) and the baker compressimeter (BC) (Approved Method 74-10). The BC method was recommended by the AACC in 1947. Use of the BC is a valid method for measuring firmness but can only detect limited physical properties. This drawback limits the applications of BC (Kamel et al 1984). Researchers began to use the UTM and texture analyzer (TA) methods in the 1980's. Even though the TA has not been adopted as the Approved AACC Method of testing, the TA is commonly used and Approved Method 74-09 is applicable to the TA (Hebeda and Zobel 1996). The American Institute of Baking (AIB) standard procedure for white pan bread is designed specifically for testing white pan bread firmness with the TA-XT2 texture analyzer. Because white pan bread is chosen in this study, firmness is measured using the TA.

Visible and near-infrared spectroscopy (NIRS) is widely used in the wheat milling industry for measuring protein and moisture content. NIRS has also been used to detect wheat and corn attributes such as class, color, damage, aflatoxin, and fumonisin (Dowell et al 2002). Suzuki et al (1986) applied NIRS to study bread constituents and quality parameters such as moisture, protein, total sugar, and crude fat. NIRS applications have typically been directed at rapid analysis for quality control.

NIRS was first used by Wilson et al (1991) to study bread staling. Osborne (1998) studied starch crystallinity in stored bread crumbs using NIRS. The wavelength range used in both studies was 1,100–2,500 nm. Osborne (1996) investigated starch and water in bread using the NIRS wavelength range of 400–2,498 nm.

Generally, results from these studies showed that three changes could be followed by NIRS. These include crumb scattering, moisture loss, and starch structure changes due to inter- and intramolecule hydrogen bonding. Crumb scattering refers to the light-scattering properties of the crumb. It was reported that the bread staling rate constant calculated from NIRS absorbance (log (1/*R*)) at wavelength 1,934 nm was in close agreement with that obtained by differential scanning calorimetry (DSC). After scattering correction, absorbance at 1,934 nm had no correlation with storage time but a high correlation with moisture content (Wilson et al 1991; Osborne 1998). This demonstrated that NIRS could provide information about scattering change and moisture loss during storage. Absorbance generally decreased over the whole range as crystallinity developed during bread staling. This may be due to starch crystallinity development in bread (Wilson et al 1991; Osborne 1998). NIRS detects kernel texture (hardness) by virtue of its effect on scattering. It is reasonable for NIRS to follow bread staling in an analogous manner because starch crystallinity changes crumb physical properties such as scattering of NIR radiation.

In addition, it was observed that the rate constants calculated from the second derivatives of log (1/*R*) at wavelengths 1,414 (or 1,412) and 1,465 (or 1,466) nm were similar to those obtained from DSC measurements (Wilson et al 1991; Osborne 1998). Iwamoto et al (1986) had previously assigned these two wavelengths to different hydrogen-bond states of water in food such as intra- and intermolecular hydrogen bonds. Osborne (1996) stated that spectra over the range 1,350–1,650 nm provide information about changes in starch structure during bread staling. Absorption at wavelengths 1,412, 1,466, and 1,510 nm has been assigned to OH in water with no hydrogen bond (W_0), with one hydrogen bond (W_1), and with two hydrogen bonds (W_2), respectively. Absorptions at wavelengths 1,430 and 1,520 nm are associated with OH in starch with no hydrogen bond (S_0) or with one hydrogen bond (S_1), which could be intra- or intermolecular to adjacent water molecules (Osborne and Douglas 1981; Davies and Miller 1988; Osborne 1996). Osborne (1996) reported that W_0 decreased, while W_1 and W_2/S_1 increased during storage due to starch crystallinity development. Starch crystallinity is extensively hydrogen bonded, both intramolecularly and intermolecularly to solvent water. These results demonstrated that NIRS could measure bread staling by following the changes of hydrogen bonding in the starch crystallinity network (Wilson et al 1991; Osborne 1996, 1998).

Previous research showed that NIRS has the potential to measure bread staling. However, no information has been available about how well NIRS can measure bread staling. The objective of this study was to investigate that how well NIRS measures bread changes in storage and compare the NIRS method with the TA method.

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MATERIALS AND METHODS

Bread Samples

Bread samples (Dillon signature homelike white bread of brand name: "Dillons") were purchased from a local grocery store. Bread was baked from frozen dough in the store. The baker was instructed to cut each loaf into 12.5-mm slices after cooling down, and wrap the loaf in a single plastic bag. Twenty-five loaves (16 oz per loaf) were obtained from each batch. Five fresh loaves were tested on the day of purchasing, which was considered day 1. The others were stored in a chamber at temperature (27 ± 1°C) and humidity (50 ± 1%) for days 1–4. Five loaves were taken out each day ≈30 min before measurement. The two or three heel slices of each loaf were excluded. The experiment was repeated five times using bread from five different batches (batches *a–e*).

NIR Spectra Collection

A diode-array NIR spectrometer (DA7000 Perten Instruments, Springfield, IL) was used to collect spectra. The wavelength range was 400–1,700 nm. Data were recorded as log (1/*R*), where *R* is the relative reflectance. A reference standard (Spectralon) was used to collect the baseline. Each spectrum was recorded as an average of 15 scans taken in ≈1 sec.

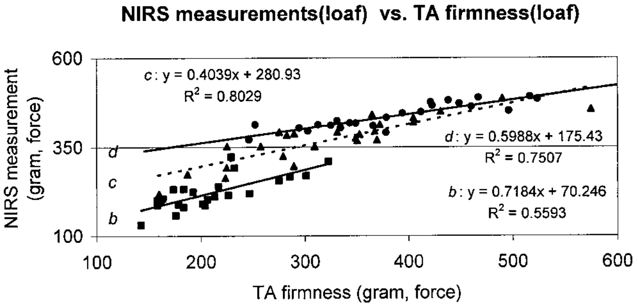

Fig. 1. Near-infrared reflectance spectroscopy (NIRS) and texture analyzer (TA) measurements of firmness using a calibration (partial least squares factor = 8).

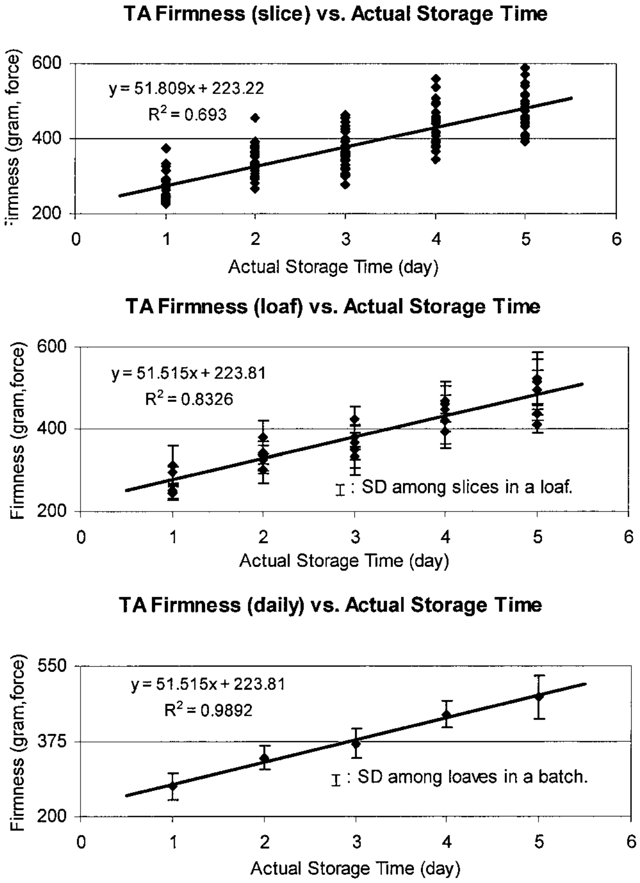

Fig. 2. Correlation of texture analyzer (TA) firmness with actual storage time in batch *c*.

In each loaf, measurement was taken on each of five or six sets of two continuous slices at room temperature and humidity. The bag was reclosed after every two continuous slices were taken out. During scanning, the two continuous slices were placed on top of each other on a horizontal flat glass window (diameter 12.7 cm); and the orientation was kept constant for all tests. The light source illuminated the sample through the window. Then the reflected light went back though the window and to the detector. After NIRS scanning, the slices were immediately measured using the TA test.

Texture Analyzer Data Collection

A texture analyzer (TA-XT2, Texture Technology, Scarsdale, NY) was used to measure bread firmness by following the AIB standard procedure for white pan bread. A TA-3 1" acrylic cylinder probe was used according to the procedure. The probe compressed the sample by 6.2 mm at a pretest, test, and posttest speed of 2.0, 1.7, and 10.0 mm/sec, respectively. The compression force was 10 g. The maximum peak force in compression was recorded as the firmness value in gram units. The TA and NIRS measurements were taken from the same side of each two continuous slices at approximately the same time. The sample orientation was kept constant in all TA tests. Only one measurement was taken from the center of each of the two continuous slices. About five or six measurements were taken from each loaf. The samples were discarded after the TA test.

Data Analysis

Grams/32 software (Galactic, Salem, NH) and a partial least squares (PLS) regression (Martens and Næs 1989) were used to analyze NIR spectra data. Due to a high noise level at <550 nm,

TABLE I
Summary of Near-Infrared Reflectance Spectroscopy (NIRS) and Texture Analyzer (TA) Measurements

			NIRS			
	TA		Cross-Validation		Validation[a]	
Batches	R^2[b]	SEE[c]	R^2	SEE[d]	R^2	SEE[d]
a						
Slice	0.27	64.89	0.84	0.53	0.56	0.81
Loaf	0.37	53.67	0.91	0.41	0.62	0.74
Daily	0.85	21.44	0.97	0.30	0.88	0.43
b						
Slice	0.07	63.85	0.95	0.32	. . .	. . .
Loaf	0.14	45.64	0.98	0.19	. . .	. . .
Daily	0.90	7.57	1.00	0.11	. . .	. . .
c						
Slice	0.69	49.06	0.97	0.23	. . .	. . .
Loaf	0.83	34.06	0.99	0.16	. . .	. . .
Daily	0.99	9.64	1.00	0.09	. . .	. . .
d						
Slice	0.43	74.21	0.91	0.42	0.68	0.76
Loaf	0.48	69.57	0.96	0.28	0.83	0.65
Daily	0.88	31.12	0.98	0.22	0.83	0.63
e						
Slice	0.24	70.84	0.95	0.31	0.79	0.38
Loaf	0.33	59.40	0.97	0.21	0.92	0.22
Daily	0.56	45.32	0.99	0.14	0.99	0.10
Average						
Slice	0.34	64.57	0.92	0.36	0.68	0.65
Loaf	0.43	52.47	0.96	0.25	0.79	0.54
Daily	0.84	23.02	0.99	0.17	0.90	0.39

[a] Calibration developed from batches *b* and *c* and used to predict samples of batches *a*, *d*, and *e*.

[b] All R^2 values are with actual storage time.

[c] Standard error of estimation in gram (force) unit.

[d] Standard error of estimation in day unit.

the wavelength range 550–1,700 nm was used in data analysis. Beta coefficients were used to determine the important wavelength regions for calibration models. Experimental data from the NIRS and TA measurements were calculated separately. For the TA data, the original data obtained from one loaf were averaged and recorded as the loaf average. The loaf daily averages in the same test were averaged and recorded as the daily average. For the NIRS data, the loaf and daily averages were calculated from values obtained from the cross-validation and from independent samples that were not included in the calibration.

Cross-validation was applied to optimize calibration models and detect outliers. These results were the NIRS cross-validations. There are two main advantages of using the cross-validation method. First, there is no need to measure an entirely new set of data. Cross-validation attempts to emulate measuring unknown samples by using the training set data. The second advantage is better outlier detection. During cross-validation, one sample was removed from the data set, and then a calibration was made using the rest of the samples. The removed sample was measured by the calibration. All samples in the data set would be left out and measured once in turn. The value of residual error sum of squares (PRESS) showed the effect of adding a PLS factor to the calibration model. A calibration was selected based on PRESS value. The other method of developing a calibration was just to combine samples from different batches. The rest of the batches were considered as unknown samples and measured by the calibration model. The results were called NIRS measurements in this study.

According to the AIB procedure, the bread staling trend was investigated by studying the relationship between the TA measurements and sample's actual storage time. To compare the NIRS and TA methods, NIRS spectra were correlated with actual storage time. The bread staling trend was studied by plotting NIRS measured storage time against the actual storage time for the NIRS method. For certain bread samples stored under certain conditions, storage time can be used to indicate the sample's staling level.

RESULTS AND DISCUSSION

The relationship between NIRS spectra and TA firmness was studied. A calibration was made from batch *a* and *e* because they had the highest and lowest R^2, respectively, on cross-validation samples. Samples in batches *b*, *c*, and *d* were measured by using this calibration. The results are shown in Fig. 1. NIRS measured firmness had the highest R^2 in both of batch *c* and *d*. Standard error of estimation for *b*, *c*, and *d* batch was 16.66, 33.22, and 31.38, respectively. The results indicate that NIRS could follow firmness changes occurring during bread staling.

When studying bread staling trend, the results of NIRS and TA measurements were compared among different batches and within each batch. Summarized results are shown in Table I. The average R^2 of five batches obtained by the TA was 0.34, 0.43, and 0.84 for slices, loaf averages, and daily averages, respectively. The average R^2 obtained by the NIRS cross-validation for slices, loaf averages, and daily averages was 0.92, 0.96, and 0.99, respectively. The higher R^2 obtained by the NIRS indicates that the NIRS cross-validations correlated better to actual storage time than the TA. Comparisons

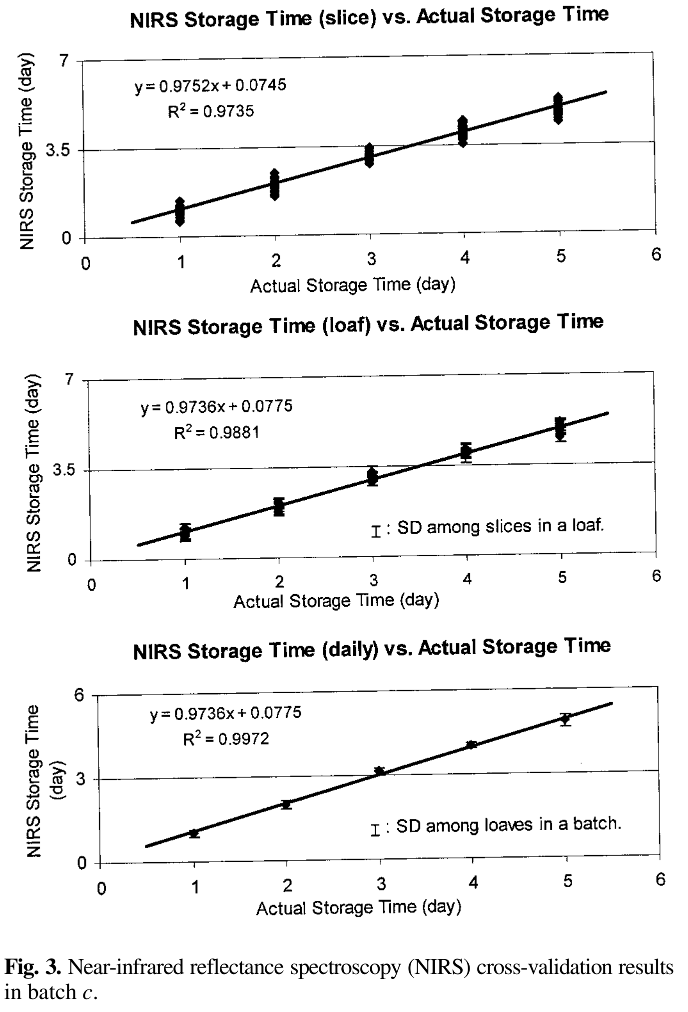

Fig. 3. Near-infrared reflectance spectroscopy (NIRS) cross-validation results in batch *c*.

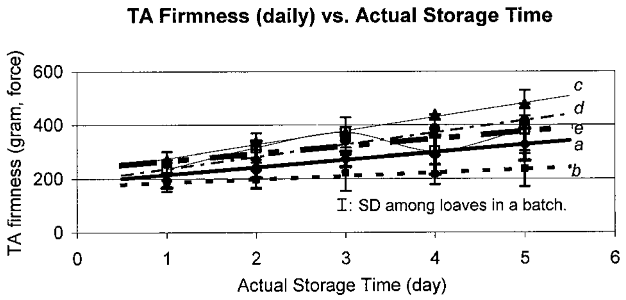

Fig. 4. Actual storage time vs. texture analyzer (TA) firmness for five batches.

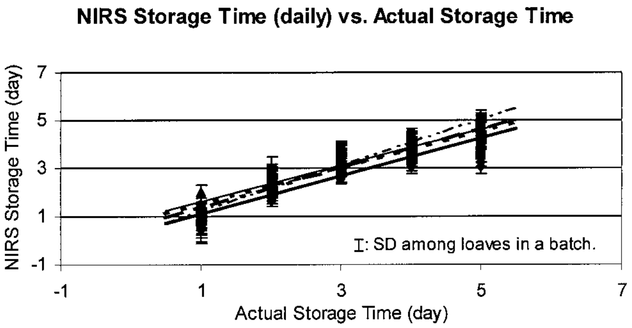

Fig. 5. Near-infrared reflectance spectroscopy (NIRS) results in five batches using cross-validation method (legends as in Fig. 4).

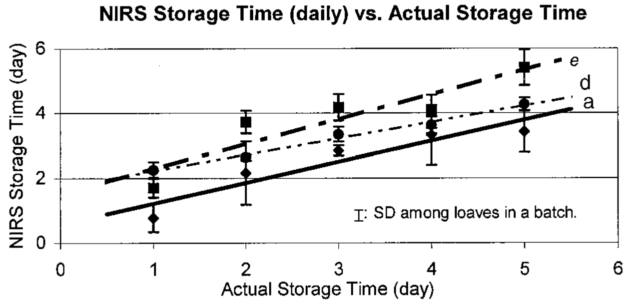

Fig. 6. Near-infrared reflectance spectroscopy (NIRS) measurements of storage time using a calibration (partial least squares factor = 8).

within each batch (Table I) also show that the NIRS cross-validation had higher correlation with the actual storage time.

Figures 2 and 3 show the results of TA measurements and the NIRS cross-validations obtained from batch *c*. For each method, the bread staling trend was shown by plotting slices, loaf averages, and daily averages against actual storage time. For all slices, loaf averages, or daily averages, the NIRS cross-validation correlated better with actual storage time than TA measurements. The range of R^2 obtained by the NIRS from batch *c* was 0.97–1.00. The range of R^2 obtained by the TA was 0.69–0.98. Also, the NIRS cross-validation had smaller standard deviation (SD) than TA measurements for both loaf averages and daily averages. According to the AIB procedure, the daily average and SD were recorded as the final bread firmness and SD. For daily averages, the NIRS had larger R^2 and smaller SD than the TA. This indicates that the NIRS cross-validation correlated better with actual storage time in batch *c* than TA measurements. The smaller SD shows that the NIRS was more precise in indicating staling level. In addition, TA measurements had more overlapping among samples of different actual storage times than NIRS cross-validations (Figs. 2 and 3). The results indicate that the TA had more difficulties when classifying bread staling levels than the NIRS.

TA measurement (daily averages) versus storage time in different batches is shown in Fig. 4. The relationship of daily averages for NIRS cross-validation versus actual storage time in different batches is shown in Fig. 5. Apart from higher R^2, NIRS cross-validation had smaller SD and less overlapping among samples of different storage times than TA measurements. This shows that the accuracy of the TA for measuring bread staling levels is lower than the NIRS. In addition, the NIRS cross-validation regression lines were more parallel and closer to each other than were the TA lines. This demonstrates that batch differences have less effect on the NIRS cross-validation than on TA measurements. Therefore, NIRS measures the actual staling level more accurately than TA.

For the TA firmness measurements, Fig. 4 shows that batch differences have larger effect on batches *b* and *c* than that on batches *a*, *d*, and *e*. A calibration model was developed for the NIRS method by combining samples from batches *b* and *c*. The model was used to measure the samples from batches *a*, *d*, and *e*. The results are given in Table I. For all slices and loaf averages in each batch, NIRS measurements had slightly lower R^2 value when compared with the NIRS cross-validation results. For NIRS daily averages, the R^2 was 0.88, 0.83, and 0.99 for batches *a*, *d*, and *e*, respectively. For TA daily averages, the corresponding R^2 was 0.85, 0.88, and 0.56, separately. The average R^2 of the NIRS for slices, loaf averages, and daily averages was higher than that of the TA. Daily averages of NIRS measured values in *a*, *d,* and *e* batches were plotted against actual storage time in Fig. 6. NIRS regression lines were parallel and close to each other. The results show that this calibration model could precisely measure actual bread staling levels among samples made from different batches.

Bread firmness is a partial indicator of bread texture. This gives a useful means for routine assessment of bread, but does not give a fundamental measure of staleness (Fearn and Russell 1982). NIRS not only follows physical changes in bread staling but also provides chemical information without any damage to the integrity of bread. Physical changes refer to scattering property changes, which are modified by developed crystallinity during bread aging. NIRS can also reflect chemical information such as moisture loss and starch structure changes during staling (Wilson 1991; Osborne 1996, 1998). This is likely the reason that the NIRS method showed superior testing accuracy when measuring bread staling level. Moisture loss and starch crystallinity change could cause firmness development during bread storage time. This can also explain that why NIRS could follow bread firmness changes during storage.

Batch *d* and *e* had a smaller bread volume than the other batches. The volume differences among batches may have affected TA measurements and decreased the accuracy of this method. However, the volume differences had less effect on NIRS measurements. Fern and Russel (1982) reported that high specific volume loaves would have a lower initial crumb modulus that indicated softer texture and showed a smaller change in modulus with time on staling than those of low specific volume. Another observation was that no trend existed in NIRS measurements throughout a loaf. Many researchers have found that the center slices of the loaf tended to be firmer than the outer slices (Short and Roberts 1971; Redlinger et al 1985). The original TA measurement did vary throughout the loaf, with the firmest crumbs at the center of the loaf. The reason why this firmness pattern exists is not clear and may due to lower specific volume, moisture migration, less gelatinized starch, and larger starch crystals in the center (Short and Roberts 1971; Piazza and Masi 1995). Based on these two observations, future work should study specific volume effects on NIRS measurements. Even though NIRS could measure bread changes in storage well, the theoretical basis of the technique is not clear yet. Further investigation of this NIRS method will be helpful for developing this technique. Research is needed to interpret beta coefficients for NIRS spectra to assign a wavelength to specific chemical changes that influence bread staling.

CONCLUSIONS

NIRS spectra had a high correlation to TA firmness. NIRS measurements had a higher correlation to bread storage time than the TA measurements. This indicates that the NIRS measures bread changes more accurately than the TA. Batch differences had less effect on NIRS measurements. This shows that the NIRS model could measure changes in bread samples made from different batches more precisely than the TA method. The NIRS method is based on both physical and chemical changes during bread staling, unlike the TA method that only measures bread firmness, which is only one aspect of the staling phenomenon. Future work should investigate specific volume effects on NIRS measurements and interpret beta coefficients for NIRS spectra.

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