Direct Determination of the Starch Content in Gravy by Near-Infrared Spectroscopy

Wei Zeng, Hui-Zhen Zhang, and Tung-Ching Lee*

Department of Food Science, Center for Advanced Food Technology, and Institute of Marine and Coastal Sciences, Cook College, Rutgers University, P.O. Box 231, New Brunswick, New Jersey 08903

For the first time, a near-infrared transmission spectroscopic method has been developed to directly determine the starch content in a liquid gravy model system at low starch concentration (less than 5%). The best wavelengths for the model are 605, 623, 919, 1017, and 1031 nm. The regression equation is $C = -3.62 - 10.47a_1 - 14.39a_2 - 29.24a_3 + 25.26a_4 + 50.15a_5$. Using this method to directly determine starch content without any special treatment, we can easily and rapidly estimate the viscosity of liquid gravy and gravy-containing food products to carry out quality control. The time for analysis of one sample is less then 2 min. It is a rapid and nondestructive method and can be applied to on-line analysis at food-processing sites.

Keywords: *Starch; viscosity; gravy; near-infrared spectroscopy*

INTRODUCTION

The viscosity of gravy in gravy-containing food products is an important factor affecting the final quality of the products. It exerts a significant influence on the heat transfer and efficiency of processing. However, it is tedious and time-consuming to continuously measure the viscosity of gravy at food-processing sites. Because achieving on-line analysis is difficult, the food-processing industries are looking for a rapid, easy, and indirect method to estimate the viscosity of gravy and gravy-containing food products.

The viscosity of gravy depends on the type and content of the starch used in preparation. If the starch content in gravy is low, the viscosity of the gravy also becomes low. The gravy therefore looks like water and could not be used for producing canned products. If the starch content in gravy is too high, the viscosity of the gravy becomes too high to flow. It also could not be used for canned products. In addition, the chemical structures of the starch in gravy affect the viscosity of the gravy. The more branched the starch prepared for the gravy is, the higher viscosity the gravy has. It is obvious that the viscosity of gravy is directly related to its starch content and the type of starch. Therefore, direct determination of the starch content in gravy is important for estimating the viscosity of gravy and further monitoring the quality of canned products. The analysis of starch content by conventional wet chemistry methods (AOAC, 1990) is labor-intensive, time-consuming, and destructive. It can not be used for on-line analysis as the method to determine viscosity can be. Therefore, finding a rapid and easy method to determine the starch content in gravy to estimate the viscosity of gravy is very desirable and important.

Near-infrared spectroscopy analysis is an instrumental method for rapidly and reproducibly measuring the chemical compositions of samples with little or no sample preparations. Since the near-IR spectroscopic analysis offers four principal advantages: speed, simplicity of sample preparation, multiplicity of analyses from a single spectrum, and intrinsic nonconsumption of the sample (McClure, 1994), it has been widely used to measure constituents of many agricultural commodities and food products as well as on-line analysis at food-processing sites (Robert, 1987). It made the analyses of protein, oil, moisture, and starch in agricultural commodities and food products an easy, rapid, and nondestructive routine analysis (Burns, 1992; Osborne, 1984; Suzuki, 1986).

Several researchers have reported the use of near-IR spectroscopy for estimating starch content in different food products. Brumm et al. (1991) suggested that the near-IR technique had potential for measuring the wet-milling characteristics of corn, including the yield of starch. Using near-IR spectroscopy, Wehling et al. (1993) predicted the potential yield of starch from different varieties of corn grown in different environments. Kim (1990) determined the starch and energy in feed grains using near-IR reflectance spectroscopy. Davies (1985) derived equations for predicting the starch and lipid contents of dry pea flour, and Finney et al. (1988) predicted the damaged starch in straight-grade flour by near-IR reflectance analysis of whole ground wheat. However, most of the papers concerning the determination of starch content using the near-IR method focused on solid samples, such as corn, wheat, and dry pea flour. The starch contents in these solid samples also were usually higher than 10%. The lower starch content (less than 5%) in liquid food samples, such as gravy-containing food products (canned food), was not investigated by using the near-IR technique.

The objective of our present work was to study the feasibility of using the near-IR technique as a rapid and nondestructive method for determining the starch content in gravy and the possibility of using this technique as an on-line control tool for food processors with direct information about the viscosity of gravy. In this paper, modified food starch (THERMTEX), pure corn starch (ARGO), and beef flavoring were used as gravy models.

MATERIALS AND METHODS

Materials. Modified food starch (THERMTEX) was obtained from National Starch and Chemical Co. (Bridgewater, NJ). Pure corn starch (ARGO) was obtained from CPC

* Author to whom correspondence should be addressed [telephone (908) 932-9611, ext 236; fax (908) 932-6776; e-mail Lee@AESOP.Rutgers.Edu].

S0021-8561(95)00320-7 CCC: $12.00

International, Inc. (Englewood Cliffs, NJ). Beef tip gravy-seasoning mix was obtained from Presco Food Products, Inc. (Flemington, NJ).

Preparation of Calibration Set and Prediction Set. We used two different starches to prepare two calibration sets and two prediction sets. The first calibration set was prepared by mixing 2.7−3.5 g of beef tip gravy-seasoning mix and 2.0−5.5 g of modified food starch (THERMTEX) in 100 mL of distilled water, boiling for 5 min, and then cooling to room temperature. The gravy-seasoning mix and starch were weighed by analytical balance. The standard errors for the weighing were less than 0.5%. This calibration set included 51 samples. The second calibration set was prepared using pure corn starch (ARGO) to substitute the modified food starch by mixing 2.7−3.5 g of beef tip gravy-seasoning mix and 1.5−5.0 g of pure corn starch in 100 mL of distilled water, boiling for 5 min, and then cooling to room temperature. The second calibration set included 54 samples.

The preparations of the prediction sets for each starch were the same as the preparation of the calibration sets. The two prediction sets for modified food starch (THERMTEX) and pure corn starch (ARGO) included 20 and 16 samples, respectively.

Determination of the Viscosity of Gravy. The viscosity of the gravy samples was determined at room temperature using a synchro-lectric viscometer (Brookfield, Brookfield Engineering Laboratories, Inc., Stoughton, MA). The samples used for determining viscosity were prepared by mixing 16 g of beef tip gravy-seasoning mix and 0−27.5 g of modified food starch (THERMTEX) in 500 mL of distilled water, boiling for 5 min, and then cooling to room temperature.

Collection of Near-IR Transmission Spectra. All near-IR measurements were made with a Model ZX-8500 near-IR spectrum composition analyzer (Zeltex, Inc., Hagerstown, MD). The ZX-8500 combines a solid state light source and detection system with a powerful internal microcomputer. This combination allows transmission measurement at every wavelength (1.0 nm intervals) between 604 and 1045 nm. The optical system contains the source array optical path, detector, and preamplifier. The source array is a grid of 37 IREDs each with an individual band-pass filter from 604 to 1045 nm. The detector is a single IR-enhanced silicon detector. The near-IR transmission spectra of the gravy samples in 0.5 cm cuvettes were recorded every 1.0 nm in the range of 604−1044 nm on the ZX-8500 using fiber optics that can be mounted to the sample holder. The 0.5 cm cuvette was placed in the sample holder and between the fiber optic cables. The empty cuvette was used as a reference. Near-IR spectral processing was performed on an IBM-386 interactive computer system. Regression computations were performed with 9000 statistical software system (Zeltex).

Mathematical Treatment for Raw Near-IR Spectral Data. Mathematical treatment is a modification of raw spectral data. The treatment can correct the base line, enhance spectral data, or assist in smoothing a spectrum. Application of a mathematical treatment will prepare the raw spectral data for use in a regression and subsequent development of a calibration equation.

Smoothing. Near-IR quantitative information can best be obtained when the data file has been smoothed. This smoothing process is basically a means of averaging out the electro/optical noise of the system so that the results are dependent only upon true optical information, not upon various noise spikes that could occur in the data.

In this paper, the numbers of wavelengths to be smoothed were 11. This means that the optical data of the five wavelengths preceding a given wavelength is added to the optical data at that given wavelength. In addition, the optical information of the five wavelengths following the given wavelength is also added to this sum. Then this additive total is divided by the smoothing divisor of 11. The first and the last five wavelengths in the data file will not be properly averaged since there are no optical values preceding and following this data point.

Derivative. The first derivative was used for the mathematical treatment of the raw near-IR spectra in this paper to correct the base line and enhance spectral data. The gap size for the first derivative was 10.

Table 1. Relationship between Starch (THERMTEX) Content and Viscosity of the Gravy Samples

starch[a] content (g/100 mL)	viscosity (cps)	starch[a] content (g/100 mL)	viscosity (cps)
0.0	5	3.0	50
0.5	10	3.5	90
1.0	15	4.0	180
1.5	21	4.5	800
2.0	27	5.0	4400
2.5	35	5.5	9600

[a] Modified food starch (THERMTEX), National Starch and Chemical Co., Bridgewater, NJ.

Stepwise Regression. In this paper, the stepwise regression technique was used to determine optimum wavelengths and the corresponding calibration constants. In order to perform the stepwise analysis, the computer first picks the individual wavelength that gives the highest statistical *F*-level with the constituent under analysis (provided the value of the *F*-level is higher than a preset quit level). It then adds a second wavelength, again based upon the highest *F*-level. It continues to add additional wavelengths provided the *F*-level is higher than the quit level.

The initial analysis is performed with a quit level equal to 0.1. The computer will continually compare the *F*-levels of each additional term against this quit level. When the computer finds no more terms with an *F*-level higher than 0.1, it then changes the quit level to 0.5. By changing the quit level to 0.5, it is doing a step down procedure thereby eliminating some of the previously determined wavelengths.

RESULTS AND DISCUSSION

Relationship between the Viscosity and the Starch Content in Gravy. Viscosity is an important index to evaluate the quality of gravy and canned food products. Both a relatively high and low viscosity of gravy can not be used for producing canned products. The starch content plays an important role in determining the viscosity of gravy. The effect of cooking on gravy samples results in starch gelatinization and viscosity build up. The relationship between the viscosity and the starch content of the gravy samples is presented in Table 1 for modified food starch (THERMTEX). The results show that the higher the starch content of the sample, the higher the viscosity. When the starch content is lower than 3.5 g/100 mL, the viscosity of the sample becomes very low. It looks like water. When the starch content is higher than 5.5 g/100 mL, the viscosity of the sample becomes too high to flow.

Selection of the Best Regression Model for Modified Food Starch (THERMTEX). By using the stepwise regression method, we can obtain a series of regression models which include 1, 2, ..., 34 wavelengths. The three regression models selected from all models are illustrated in Table 2.

From Table 2, we can see that each standard error of calibration (SEC) for models 1 and 2 is smaller than the SEC of model 3, and each of the correlation coefficients of calibration (R_c) for models 1 and 2 is larger than the R_c of model 3. However, when the three regression models are used to predict the prediction set, each standard error of prediction (SEP) for models 1 and 2 is larger than the SEP of model 3, and their correlation coefficients of prediction (R_p) are smaller than the R_p of model 3. The results show that using model 3 to predict the starch content in gravy will be better and more stable than using models 1 and 2.

Table 2. Results of Three Regression Models for the Gravy Samples of Modified Food Starch (THERMTEX)

	calibration			prediction		
model[a]	N[b]	SEC[c]	R_c[d]	N	SEP[c]	R_p[d]
1	51	0.177	0.999	20	0.390	0.963
2	51	0.171	0.994	20	0.426	0.979
3	51	0.188	0.989	20	0.178	0.988

[a] Models 1−3 include 34, 16, and 5 wavelengths, respectively. [b] Sample numbers. [c] SEC and SEP are standard errors of calibration and prediction, respectively. [d] R_c and R_p are correlation coefficients of calibration and prediction, respectively.

The results in Table 3 come from repeatedly measuring the same sample under the same condition and are calculated by the three regression models. The results further show that the models 1 and 2 are less stable. The small changes in near-IR data cause very large changes in the calculated results. For example, the precision of the results calculated using model 1 is larger than 10%, and some are even larger than 20%. Therefore, models 1 and 2 are not suitable for prediction of unknown samples. Conversely, the results of model 3 are very stable, and the precision of all results from model 3 is smaller than 5%. This means that model 3 is suitable for the prediction of unknown samples.

Moreover, according to the rule of near-IR spectroscopy (Windham et al., 1989), there should be at least 5−10 samples in the calibration set for each wavelength selected. Therefore, for the 51 members in the calibration set used here, no more than 10 wavelengths should be used in a calibration model. The instability of calibration models 1 and 2 in Table 2 compared with model 3 is probably due to the fact that the calibrations have been overfit. Table 4 shows the regression results of the calibration models using two to eight wavelengths. From Table 4, we can see that when we selected the regression models with four to eight wavelengths, their SEP and R_p are more stable than that of models 1 and 2 in Table 2.

In addition, 900−1000 nm is known to be a wavelength range where starch mainly absorbs. Thus selection of the wavelengths within 900−1035 nm to obtain a calibration model for the determination of starch content is probably more robust. However, from Table 4, we can see that the calibration model only including the calibration model within 900−1035 nm wavelength range is not good. It is probably due to the effect of the beef flavoring within the gravy. We can see that the best regression model for determining the starch content in gravy is still model 3. This model includes five wavelengths of 605, 623, 919, 1017, and 1031 nm. The regression equation is $C = -3.62 - 10.47a_1 - 14.39a_2 - 29.24a_3 + 25.26a_4 + 50.15a_5$.

Prediction of the Starch Content in Gravy by Near-IR Method. In this paper, a modified food starch (THERMTEX) mixed with beef tip gravy-seasoning mix is selected as a gravy model to verify that the near-IR method can determine a low starch content in gravy samples. The relative errors of the predicted results shown in Table 3 are smaller than 5% for most samples. The time for determining one sample is less than 2 min. In food industries, there are many different starches used in food systems with varied chemical structures. Near-IR spectroscopy can detect the different chemical structures of the starches although the differences are minor. Therefore, if we want to determine different kinds of starches in gravy, we only have to build a relative calibration set for that specific starch to compare with the modified starch. Once we establish the calibration set, all the data can be saved in the computer as a file and can be used anytime. In this paper, we selected pure corn starch (ARGO) whose properties are different from modified food starch (THERMTEX). For pure corn starch, the best wavelengths for the calibration model are 610, 910, 931, and 1029 nm. The calibration equation is $C = -9.73 - 37.09a_1 - 13.28a_2 + 53.65a_3 + 57.90a_4$.

From Table 5, we can see that the relative errors of the predicted results from the model selected for pure corn starch (ARGO) are less than 7%. It is reasonable and reliable.

Temperature is another important parameter that affects the near-IR spectrum and viscosity of the gravy sample. In this paper, the temperature used for the gravy model system is room temperature. If we built the calibration set at boiling temperature, it could be

Table 3. Prediction Results of Repeat Measurements of Starch Content by Near-IR Method for the Gravy Samples of Modified Food Starch (THERMTEX)

		starch content (g/100 mL)								
		near-IR measurement								
		model 1			model 2			model 3		
samples	C_{add}[a]	M[b]	A[c] (%)	P[d] (%)	M	A (%)	P (%)	M	A (%)	P (%)
1	3.07	2.71[e]	−0.3	23	3.18	1	5	3.20	5	0.9
		3.41[f]			3.03			3.23		
2	3.26	3.59	−2	24	3.06	4	5	3.02	−5	5
		2.83			3.23			3.17		
3	3.33	3.45	−3	14	3.34	0.2	0.3	3.22	0.6	5
		3.01			3.33			3.40		
4	4.09	3.88	2	6	3.70	−2	15	3.93	−1	5
		4.13			4.30			4.14		
5	3.85	2.93	−0.9	46	3.69	5	16	3.92	2	0.3
		4.70			4.35			3.93		
6	4.14	7.29	0.1	152	5.29	1	52	4.23	4	3
		1.00			3.10			4.35		
7	4.35	4.13	−3	5	4.17	2	5	4.10	4	3
		4.34			4.40			4.21		
8	2.84	3.02	3	7	3.09	4	10	3.04	5	5
		2.82			2.80			2.90		

[a] Modified food starch (THERMTEX) content in samples. [b] Results (M_1 and M_2) of repeat measurements by near-IR method. [c] Accuracy of results of measurements: $A = ((M - C_{add})/C_{add})100$; $M = (M_1 + M_2)/2$. [d] Precision of results of repeat measurements: $P = (|M_1 - M_2|/M)100$. [e] M_1. [f] M_2.

Table 4. Results of Several Regression Models between Two and Eight Wavelengths for the Gravy Samples of Modified Food Starch (THERMTEX)

	calibration			prediction		
wavelengths in models (nm)	N^a	SEC[b]	R_c[c]	N	SEP[b]	R_p[c]
605, 935	51	0.351	0.861	20	0.537	0.891
605, 919, 995	51	0.263	0.927	20	0.428	0.921
604, 669, 920, 990	51	0.188	0.989	20	0.178	0.988
605, 623, 919, 1017, 1031	51	0.190	0.985	20	0.165	0.990
604, 625, 919, 990, 1015, 1033	51	0.192	0.981	20	0.214	0.976
604, 623, 665, 919, 953, 992, 1020, 1033	51	0.185	0.991	20	0.417	0.924
920, 952, 990	51	0.265	0.917	20	0.417	0.924
920, 952, 970, 990, 1017	51	0.227	0.935	20	0.385	0.942
920, 952, 970, 990, 1017, 1031	51	0.271	0.928	20	0.406	0.938

[a] Sample numbers. [b] SEC and SEP are standard errors of calibration and prediction, respectively. [c] R_c and R_p are correlation coefficients of calibration and prediction, respectively.

Table 5. Prediction Results of Near-IR Measurements of Starch Content in the Gravy of Pure Corn Starch (ARGO)

	starch content (g/100 mL)		
samples	C_{add}[a]	$C_{near\text{-}IR\ measurement}$[b]	RE[c] (%)
1	1.38	1.30	−6
2	1.85	1.75	−5
3	2.36	2.33	−1
4	2.85	2.95	4
5	2.03	1.97	−3
6	2.59	2.72	5
7	3.21	3.16	−2
8	3.36	3.51	5
9	3.56	3.48	−2
10	3.71	3.85	4
11	3.83	3.94	3
12	4.05	3.96	−2
13	4.21	4.26	1
14	4.51	4.72	5
15	4.86	4.73	−3
16	4.93	5.11	4

[a] Pure corn starch (ARGO) content in gravy samples. [b] Prediction results of measurements by near-IR method. [c] Relative errors between C_{add} and $C_{near\text{-}IR\ measurement}$.

used for direct determination of the starch content of the boiling sample and simultaneous estimating of the viscosity of this gravy sample at room temperature according to the established relationship between the starch content and the viscosity. Therefore, applying this technique in the on-line analysis of starch content during gravy-containing food processing is feasible for us.

In this work, a model ZX-8500 near-IR spectrum composition analyzer was used for the experiment. The ZX-8500 near-IR spectrum composition analyzer compared with other models has the unique characteristics of only requiring a small volume of sample for determination and low price, and it contains a built-in computer that integrates with the instrument and can independently carry out the analysis after the calibration constants impute. Consequently, this type of near-IR composition analyzer has the potential to be used at food-processing sites for on-line analysis.

The present paper demonstrated the feasibility of using near-IR spectroscopy to determine the starch content in gravy and then to estimate the viscosity of the gravy to evaluate the quality of the gravy and gravy-containing food products. In addition, this method can be used at a varied range of temperatures, and we can measure food samples directly without any special treatment. Furthermore, applying the near-IR technique as a rapid on-line method for the measurement of starch content and the prediction of viscosity of gravy-containing food products is possible.

LITERATURE CITED

AOAC. *Official Methods of Analysis of the Association of Official Analytical Chemists*, 15th ed.; Helrich, K., Ed.; AOAC International: Arlington, VA, 1990; 979.10, pp 789.

Brumm, T. J.; Johnson, L. A.; Hurburgh, C. R. The potential of near infrared spectroscopy for determining maize wet milling characteristics. *Cereal Foods World* **1991**, *36*, 706.

Burns, D. A.; Ciurczak, E. W. *Handbook of Near-Infrared Analysis*; Dekker: New York, 1992.

Davies, A. M. C.; Coxon, D. T.; Cavrel, G. M.; Wright, D. J. Determination of starch and lipid in pea flour by near-infrared reflectance analysis. The effect of pea genotype on starch and lipid content. *J. Sci. Food Agric.* **1985**, *36*, 49−54.

Finney, P. L.; Kinney, J. E.; Donelson, J. R. Prediction of damaged starch in straight-grade flour by near-infrared reflectance analysis of whole ground wheat. *Cereal Chem.* **1988**, *65*, 449−452.

Kim, J.; Williams, P. C. Determination of starch and energy in feed grains by near-infrared reflectance spectroscopy. *J. Agric. Food Chem.* **1990**, *38*, 682−688.

McClure, W. F. Near-infrared spectroscopy: the giant is running strong. *Anal. Chem.* **1994**, *66*, 43A−53A.

Osborne, B. G.; Barrett, G. M.; Cauvain, S. P.; Fearn, T. The determination of protein, fat and moisture in bread by near infrared reflectance spectroscopy. *J. Sci. Food Agric.* **1984**, *35*, 940−945.

Robert, P.; Bertrand, D.; Devaux, M. F.; Grappin, R. M. Multivariate analysis applied to near-infrared spectra of milk. *Anal. Chem.* **1987**, *59*, 2187−2191.

Suzuki, K.; McDonald, C. E.; D'appolonia, B. L. Near-infrared reflectance analysis of bread. *Cereal Chem.* **1986**, *63*, 320−325.

Wehling, R. L.; Jackson, D. S.; Hooper, D. G.; Ghaedian, A. R. Prediction of wet-milling starch yield from corn by Near-infrared spectroscopy. *Cereal Chem.* **1993**, *70*, 720−723.

Windham, W. R.; Coleman, S. W. Animal response prediction. *Near Infrared Reflectance Spectroscopy (NIRS): Analysis of Forage Quality*; Marten, G. C., Shenk, J. S., Barton, F. E., Eds.; Agriculture Handbook No. 643; Agricultural Research Service: Washington, DC, 1989; pp 32−35, 96−103.

Received for review May 16, 1995. Accepted April 21, 1996.[⊗] This is Publication D-10114-7-96 of the New Jersey Agricultural Experiment Station and Contribution 96-15 of the Institute of Marine and Coastal Sciences, Rutgers University, supported partially by State Funds and Hatch project and partially by Rutgers/NOAA Cooperative Marine Education and Research Program.

JF950320F

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.