VISIBLE-NIR SPECTROSCOPY: A NON-DESTRUCTIVE RAPID TECHNIQUE TO ASSESS END-POINT TEMPERATURE OF KAMABOKO GEL

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Background

Inadequate cooking of food products and use of improper holding times are common causes of food-borne disease outbreaks (Walton and McCarthy, 1999). Many of these outbreaks result from undercooking at food service and retail outlets where time and temperature of processing do not need to be adequately documented. Because of the high correlation of these outbreaks with consumption of undercooked food products, the elimination of these microorganisms from processed foods has become a prime concern for consumers, the meat industry, and the regulatory agencies. Heat treatment is given to meat to produce a palatable product, to improve the shelflife, and to minimize the risk of food-borne illness. Consequently, optimum cooking is necessary to keep the maximum food qualities but minimize the risk of heat-labile pathogens.

A large number of researches have been conducted to track the previous heat treatment (end-point temperature, EPT) of meat products (Townsend and Blankenship 1989; Miller *et al*, 2003), however, similar studies on marine products are almost negligible. Moreover, seafood are common vehicles of food-borne diseases can be contaminated with pathogens during several stages of processing. Therefore it became more important to achieve optimum heat treatment to seafood. We are conducting a series of study to assess EPT of processed marine products since they have an ever-growing role in human food source (Uddin *et al*, 2000; 2002a). Near infrared (NIR) spectroscopy, a non-destructive rapid technique, which has been widely used in the food industry, is based on the electromagnetic absorption of organic compounds. We successfully applied this NIR technique to investigate the heating adequacy of heated fish and shellfish meats (Uddin *et al*, 2002b).

Objectives

The purpose of this study was to assess EPT of kamaboko gels since surimi-based fish-meat gels have been gaining popularity in recent years for their protein quality, law fat content, and convenience in consumption. Surimi-based most common finished product kamaboko gel was used as a model of fish-meat gels. A potential useful application of NIR reflectance spectroscopy would be the reliable, rapid and non-destructive determination in these regards.

Materials and methods

Preparation of kamaboko gel

Two types of surimi were used to prepared kamaboko gel. Frozen SA grade walleye pollack (*Theragra chalcogramma*) surimi (Maruha Co., Tokyo, Japan) was thawed overnight at 5ºC then chopped in a kitchen-cutter (Yamada FP-1S, Mitsubishi Co., Ltd, Tokyo, Japan). Horse mackerel (*Trachurus japonicus*) surimi was prepared according to the procedure of Konno *et al*. (2000). The final moisture content was adjusted to 80% by adding cold distilled water prior to add NaCl equivalent to 2.5% of the surimi weight. Kamaboko gel was prepared by pressing the salt-ground surimi into a polyvinylidene chloride casing measuring 48 mm in circumference and approximately 150 mm in length. Both ends of each tube casing were tied with cotton thread, and all of the proceeding operations were accomplished at 5ºC. The filled casing samples were incubated at 10ºC intervals between 30 and 90ºC for 30 min in water bath incubators then cooled immediately in ice-cold water and kept at 4ºC overnight before NIR spectroscopic measurement.

Internal temperture of kamaboko gels were monitored using a recorder (Thermodac EF 5020A, Eto Denki Co., Tokyo, Japan) with connected thermocouples. Thermocouples (copper-constantan) were inserted through the side edge of separate samples in to the geometric center. Sixteen individual kamaboko samples

were prepared for each selected temperature therefore 112 samples were made for each walleye pollack and horse mackerel surimi respectively.

NIR spectroscopy

Visible-NIR spectra were recorded at 2 nm intervals using a NIRSystems 6500 scanning monochromator instrument (NIRSystems, Silver Spring, MD). Kamaboko spectra (n = 224) were collected using a surface interactance fibre optic accessory. Within a 4 cm square probe face, 7 quartz windows (1 x 20 mm) are fitted; windows are alternatively light exit (n = 4) and collection (n = 3) ports. Prior to spectral acquisition, the surface of the kamaboko was wiped with a paper tissue to remove excess moisture. Before spectra of the Kamaboko gels were measured, a background spectrum was collected. Spectra were collected between 650 and 1100 nm; above this range, the fibre optic probe becomes a significant absorber of radiation and were stored in optical density units log (1/R), where R represents the percent of energy reflected. Only a single spectrum was taken from an individual sample therefore 56 spectra were use to developed a calibration and remaining 56 spectra were used for validation set in both of walleye pollack and horse mackerel kamaboko gels. Two linear regression methods Partial Lest Squares (PLS) and Multiple Linear Regression (MLR) were used to develop calibration and validation set.

Data analysis was performed by the Vision spectral analysis software package (Version 2.11. NIRSystems, Silver Spring, MD) and The Unscrambler software (version 8.05. CAMO, USA).

Results and discussion

Figure 1 illustrates the spectra collected from kamaboko gel prepared by walleye pollack surimi heated at different temperatures. The higher curve is for the sample heated at lower temperature, whereas the lower curve applies to the higher temperature. Kamaboko made from horse mackerel surimi also showed similar fenomenon (data not shown). In every spectrum, the log (1/R) peaks at any wavelength decreased with increasing EPT. Water absorbs strongly in specific wavelengths which is expected and usually exhibits a broad band because of H-bonding interactions with itself and with other components in the meat. In visible-NIR spectroscopy, the regions from 740–760 nm and 960–980 nm are related to O–H bond of the water in the sample (Osborne *et al*, 1993; Murray and Williams, 1990). Since protein conformations, protein water interactions, or their combination might depend on the variation of water content, the NIR reflectance spectra of a heated sample could be affected separately with a different heating process. The kamaboko gels in this study were heat-treated in a stirred-water bath. The water content was constant before and after heat treatment which allowed us to minimize the differences in water contents between samples heat-treated at different temperatures. Therefore, these changes of NIR reflectance spectra upon heat treatment could be related to the heating temperature.

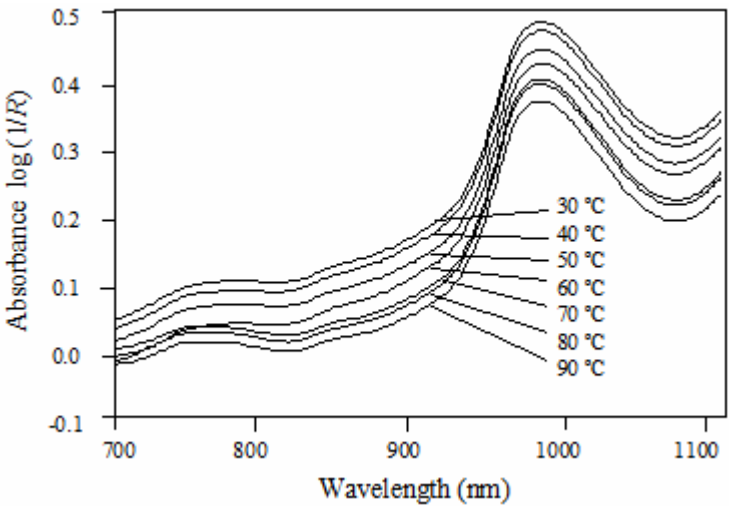

Fig. 1. Average reflectance spectra of kamaboko gels prepared from walleye pollack surimi.

Studies on thermal denaturation of muscle proteins indicate that the changes of meat proteins during cooking take place in a step-wise process (Findlay and Barbut, 1990). Moreover, food and feed substances of plant or animal origin are composed of constituents possessing functional groups such as C-H, O-H, N-H, S-H, and C=O which are selectively absorb NIR radiation. Therefore, if there is any linear relationship between NIR

spectral changes and heating temperature of meats, a calibration equation could be developed to track their previous heat treatment. It has been suggested that standard normal variance and de-trend (SNVD) transformation would remove multiplicative interference of scatter and particle size, baseline shift and curvilinearity. Consequently, derivative treatment reduces scattering effects and also increases resolution of spectrum peaks (Barnes *et al*, 1989; Ding and Xu, 1999). Therefore, to determine EPT of kamaboko gel, the spectra were subsequently scatter corrected using SNVD and 2nd-derivative treatments. Systematic differences in absorbance related to the heat treatment were observed at different wavelengths throughout the derivative treated spectra where the characteristic absorption peaks are more clearly separated. These differences are more visible between 800 and 930 nm region due to the main absorbance band of proteins (data not shown). Spectral changes upon heat treatment were related to the heating temperature which might be the reason for changes in the environment of the secondary structure due to the denaturation of proteins, and to changes in the state of water.

Table 1. Calibration and validation results obtained by MLR for assessing EPT of Kamaboko

Kamaboko sample	Wavelength selected (nm)				R	SEC (%)	SEP (%)	Bias (%)
	λ1	λ2	λ3	λ4				
Walleye pollack	910				0.81	5.07	5.41	-0.35
	910	848			0.94	3.22	3.95	-0.52
	910	848	822		0.97	1.88	1.73	-0.08
	910	848	822	938	0.98	1.76	1.71	-0.31
Horse mackerel	910				0.84	4.95	4.92	-0.26
	910	858			0.95	2.73	2.76	-0.06
	910	858	822		0.98	2.06	2.22	-0.28
	910	858	822	938	0.98	1.78	1.84	-0.07

R : Multiple correlation coefficient.
SEC: Standard error of calibration.
SEP: Bias corrected standard error of prediction.
Bias: The average of difference between actual value and NIR velue.

In order to predict EPT of kamaboko gels, the derivative-treated spectra were calculated. Spectral changes with heating temperatures were recorded by computer and analyzed by MLR and PLS regrassions. MLR analysis allowed us to select appropriate wavelengths related to specific known chemical bonds without interference. On the other hand, PLS regression has been widely applied recently because no selection of wavelengths is needed. However, even in PLS calibration, selection of the wavelength region was needed to make a good calibration equation, which was more complicated and time consuming. In MLR analysis, the wavelengths selected by a stepforward – stepreverse regression in this study to provide the calibration equations with the lowest standard error of calibration (SEC) and highest correlation coefficients of calibration (R) are given in Table 1. The first wavelength selection which most important and one of the major steps for MLR analysis 910 nm due to the absorbance of protein was selected by manually. The standard error of prediction (SEP) using 4 wavelengths were calculated to be less than 1.85%, suggesting that the calibrations developed are appropriate. Selected wavelengths for the prediction of EPT are extensively related to C-H, N-H and C=O groups (Murray and Williams, 1990; Osborne *et al*, 1993). It was suggested that the wavelengths selected by MLR could be used as a good indicator for selection of the wavelength region in PLS calibration (Saranwong *et al*, 2001). Therefore, the wavelength region selected by MLR was applied for PLS calibration which also gave better indication (Table 2).

Table 2. Calibration and validation results of PLS regression using whole spectrum and selected region obtained by MLR for assessing EPT

Kamaboko sample	Wavelength region	F	R	SEC (%)	SEP (%)	Bias (%)	RPD
Walleye pollack	650 - 1100	9	0.98	1.83	1.87	-0.21	2.63
	800 - 950	5	0.97	1.87	1.76	-0.07	3.07
Horse mackerel	650 - 1100	9	0.98	1.95	1.94	-0.13	2.25
	800 - 950	6	0.98	1.91	1.81	-0.11	2.49

F : The number of factor/variable used in the calibration equation.
RPD : The ratio of standard deviation of reference data in validation set to SEP.

Figure 2 depicts scatter plots of NIR predicted EPT against the actual heating temperatures obtained by MLR and PLS calculations of walleye pollack kamaboko gel. Similar results also observed from horse mackerel. A comparison of the NIR predicted EPT with known actual heating temperatures showed extreamely close detections. Both MLR and PLS could be used in making calibration equations with similar predictive eficiency. The R were better than 0.98 indicating a good model structure. Such a non-destructive, simple and reliable technique which is expected to assess EPT of processed products is essential in today's demand. In this study kamaboko was made from walleye pollack and horse mackerel surimi, however, it could be valid as a general technique for other species.

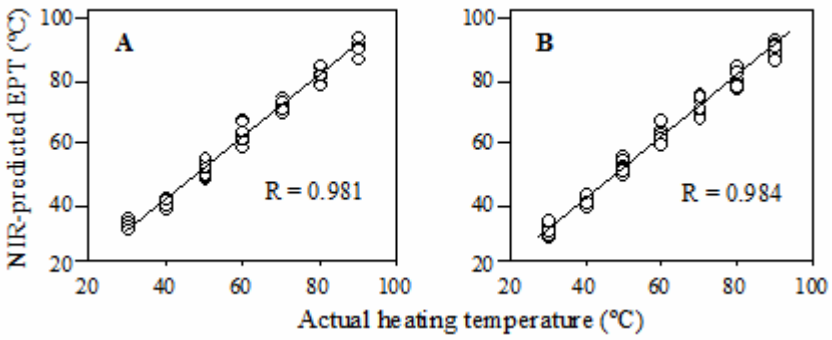

Fig. 2. NIR-predicted endpoint temperatures obtained by MLR (A) and PLS (B) of walleye pollack kamaboko gels plotted against the actual heating temperatures.

Conclusions

The results discussed above demonstrate the potential of visible-NIR reflectance spectroscopy for determining EPT of kamaboko gels in a rapid, reliable and non-destructive manner. Once perfected, this technique will have several advantages over other techniques, in that it will take the least time for analysis and will not require any consumables or supporting equipment.

References

Barnes, R.J., Dhanoa, M.S. and Lister, S.J. 1989. Standard normal variance transformation and de-treading of near-infrared diffuse reflectance spectra. Appl. Spectrosc. 43:772-777.

Ding, H.B. and Xu, R.J. 1999. Differentiation of beef and kangaroo meat by visible/near infrared reflectance spectroscopy. J. Food Sci. 64:814-817.

Findlay, J.C. and Barbut, S. 1990. Thermal analysis of meat. In: Thermal Analysis of Food. Harwalker, V.R. and Ma, C.Y. (ed). London: Elsevier Applied Science.

Konno, K., Yamamoto, T., Takahashi, M. and Kato, S. 2000. Early structural changes in myosin rod upon heating of carp myofibrils. J. Agric. Food. Chem. 48:4905-4909.

Miller, D.R., Keeton, J.T., Acuff, G.R. and Prochaska, J.F. 2003. Verification of cooking endpoint temperatures in beef by immunoassay of lactate dehydrogenase isozyme 5. J. Food Sci. 68:2076-2079.

Osborne, B.G., Fearn, T. and Hindle, P.H. 1993. Practical spectroscopy with application in food and beverage analysis. Harlow, England: Longman Scientific and Technical.

Saranwong, S., Sornsrivichai, J. and Kawano, S. 2001. Improvement of PLS calibration for Brix value and dry matter of Mango using information from MLR calibration. J. Near Infrared Spectrosc. 9:287-295.

Townsend, W.E. and Blankenship, L.C.1989. Methods for detecting processing temperatures of previously cooked meat and poultry products-A review. J. Food Prot. 52:128-135.

Uddin, M., Ishizaki, S. and Tanaka, M. 2000. Coagulation test for determining end-point temperature of heated blue marlin meat. Fisheries Sci. 66:153-160.

Uddin, M., Ishizaki, S., Ishida, M. and Tanaka, M. 2002a. Assessing the end-point temperature of heated fish and shellfish meats. Fisheries Sci. 68:768-775.

Uddin, M., Ishizaki, S., Okazaki, E., Tanaka, M. 2002b. Near-infrared reflectance spectroscopy for determining end-point temperature of heated fish and shellfish meats. J. Sci. Food. Agric. 82:286-292.

Walton, J.H. and McCarthy, J.M. 1999. New method for determining internal temperature of cooking meat via NMR spectroscopy. J. Muscle Foods, 22:319-330.