Estimation Method of Moisture Content at the Meat Surface During Drying Process by NIR Spectroscopy and Its Application for Monitoring of Water Activity

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Monitoring of water activity at meat surface is important on controlling the quality of aging beef, because the fermentation microorganisms are grow on the meat surface. Although in previous study water activity of beef under drying process was investigated by near infrared (NIR) spectra, spectra data have been obtained from the whole beef cut. Therefore, this study aimed to estimate water activity of the surface of the sample using NIR spectra in the 700–1050 nm. Different thick samples in the 2–10 mm were prepared and the optimization of the measurement conditions was carried out for surface monitoring. Consequently, the optimal measurement condition were determined for monitoring the spectra from the surface of a beef cut. The change in moisture content and water activity about lump sample of beef were investigated for drying at 4°C. A linear decrease in water activity estimated by NIR spectra was observed, and the estimated water activity reached 0.8 after around 22–25 days. These results showed the evaluation potential of dry state at surface of beef by using NIR spectroscopy.

Keywords: aging beef, near infrared spectroscopy, water activity

1. Introduction

The drying of foods is generally used to control food production and storage stability. In the production of aged beef, it is well known that drying contributes to the improvement in tenderness, palatability, and flavor as has been reported extensively [1–5]. In many fermentation foods containing aging beef microorganisms grow at surface. The aging of foods is accompanied by structural changes, chemical reactions, and microorganism reactions at the surface. Hence, in these foods, the drying process is defined as the pre-treatment to produce the aging foods.

Therefore, in the production of aging foods, the design and optimization of the drying process is essential and important aspects of hydration/dehydration such as mass transfer, loss of water, and water activity ($a_w$) should be considered [6,7]. Numerous studies have demonstrated that the monitoring of moisture content of meat samples is an attractive indicator of an optimized drying process and hence effective water diffusivity in meat has been modeled mathematically [8–10]. However, the method for monitoring of $a_w$ is not fully developed and optimized for production processes [8]. Moreover, to understand the equilibrium dynamics at the interface between the food surface and other materials, gases, or liquids, the activity coefficient has especially been considered [11–13]. Although the activity coefficient model that has been developed consists of temperature and concentration components, the estimation accuracy of activity coefficient was not always high enough for real configurations. Therefore, it is necessary that activity at the phase interface is directly monitored with a non-destructive method to control food quality during the drying process to mitigate the limitations of theoretical models.

For use in food process monitoring systems, spectroscopic techniques have distinct advantages such as fast, non-destructive, accurate, and on-line/at-line availability [14]. Thus, infrared (IR) and near infrared (NIR) spectroscopy have been widely employed as process monitoring tools for various food products [15–17]. Rohman et al. have reported effective chemical assignment of components in beef cuts and quantitation using IR spectra [18]. Moreover, the heterogeneity of major food components was demonstrated by Elsmasy et al. [19]. However, the strong absorption in IR region of water is one of the constraint factors for the monitoring of water molecules. The major characteristics of NIR spectroscopy are useful.
spectra allow the convenient monitoring of food products, so that this technique has received significant attention from researchers. Specifically, the behavior of water molecules in meat samples as observed by NIR spectroscopy is of interest [19, 20]. However, surprisingly few studies have been performed to monitor \( a_w \) of food such as meat by using the spectroscopic technologies described above [20, 21].

Our research group has previously proposed an estimation model for \( a_w \) using intensity in the NIR region [22]. Although band intensity obtained by a spectrometer reflects the concentration of component according to Lambert Beers law, \( a_w \) cannot directly evaluate by the intensity of the NIR spectra. Thus, the proposed model was based on the relationship between water content and \( a_w \). The results in the previous study demonstrated the basic efficiency of the estimation by NIR spectra to evaluate the \( a_w \) of beef. However, there are still some issues that we must consider to expand this model to lump beef with various thicknesses.

Particularly, when using diffuse reflectance for analysis such as this study, it is important to take into account the penetration depth of the incident to develop the optimum estimation model. Ongoing studies are making use of NIR techniques to examine the penetration depth [23]. However, in foods the results especially depend on the analyte states such as particle size, density, and composition of contents [24, 25]. In other words, estimation method developed using whole of sample must be adjusted for the surface before applying to lump beef.

The aim of the present study is therefore to propose the estimation method for \( a_w \) at the surface during dry process using NIR spectroscopy. At first, the estimation model for \( a_w \) of thin sample during drying process was constructed through quantitative analysis of moisture content by NIR spectra. While, to expand the model for thick sample, optimization of NIR measurement condition was attempted. Finally, the model was applied for lump samples, and the time-series profile of estimated moisture content and \( a_w \) was investigated.

### 2. Materials and methods

#### 2.1 Sample preparation

##### 2.1.1 Slice samples for development of estimation model

To develop the estimation model for \( a_w \) during the drying process, the shoulder cloud provided from a meat dealer was trimmed to 64 pieces that were of area 80×60 mm² and thickness approximately 2~4 mm (slice sample). The branch of shoulder cloud containing 22% protein, 4% lipid, 0.52% sodium, and 72% water was prepared and stored in a low temperature chamber set at 2°C. The moisture contents were graduated between 64 pieces by control the drying time.

#### 2.1.2 Lump samples for application of estimation model

The moisture state of the meat surface in practical situations was investigated by measuring NIR spectra from the surface of the lump sample. The shoulder cloud was trimmed at 4 samples that were area of 100×100 mm² and thickness of 80 mm (lump samples). The lump samples were stored under 4°C and 80% humidity in the chamber (SSB-70C2, HOSHIZAKI Co., 700×550×1410 mm³) for 27 days as shown in Fig. 1. To accelerate the drying of the beef samples, the mass transfer resistance of the surface of the samples was constrained by a continuous air cycle. To avoid excessive surface evaporation, the chamber was maintained at a low temperature and relatively high humidity.

#### 2.2 Water activity and moisture content of slice sample

Approximately 2 g of each slice sample was trimmed and weighed. The \( a_w \) was measured by Aqua lab (Decagon Devices Inc.). Then the samples were dried absolutely at 135°C for 2 h, and re-weighed to calculate moisture contents.
2.3 Spectral collection
Diffuse reflectance NIR spectra in the 700–1050 nm region of samples were obtained by FAT–Analyzer (S–7040, Soma Optics Co., Tokyo, Japan). This instrument has an arm equipped with an optical fiber with which incident light is irradiated from the edge of the arm to a sample and diffused reflected energy from the sample is collected by contact with the edge of this arm. All spectral measurements were carried out in the chamber.

The obtained spectra were subjected to second-derivative procedures (9 points, 2 orders), including Savitzky–Golay smoothing [26]. Second derivative spectra corresponding to the moisture contents of all samples were also used in the estimation model.

2.4 Experimentally optimization of measurement method for surface monitoring
Figure 2 shows schematic diagram of the measurement set up using the NIR spectrometer. NIR spectra of sample are collected by contact with the sensor of this instrument as shown in Fig. 2 (a). When samples with different thicknesses were measured, incident radiation penetrates not only the surface but also inside the sample (shown in upper of Fig. 2(b)). Namely, diffuse reflectance collected from the thick sample is detected redundantly. To obtain the profile of diffuse reflected energy from only the surface, thus as shown in middle and bottom of Fig. 2 (b), adjusting measurement set ups were attempted by alternating the distance between the sample and the sensor, spot size, and integration time using different sample thicknesses.

In this study, we determined approximately 2~4 mm thickness as the surface, and to optimize spectral measurements for surface, samples with different thicknesses of approximately 2, 4, 6, 8 and 10 mm were prepared from the shoulder cloud. The arm of NIR spectrometer equipped with a detector was varied gradually from the sample by using 10~40 mm spacers. Spot size was defined as 5 mm in this study. Integration times of 50, 100, and 150 ms were also tested for optimization of the measurement.

2.5 Application of estimation model to lump beef
NIR spectra of the lump sample were measured during 27 days of drying at arbitrary interval. The measurement carried out by the optimization method determined section 2.4 in a chamber as shown in Fig. 1.

The estimation model was applied to the spectral data obtained from the lump samples and the time series of moisture contents and $a_w$ at the surface of the beef were calculated.

3. Results and discussion
3.1 Development of estimation model for moisture content and water activity
3.1.1 NIR spectra of slice sample of beef vs moisture content
NIR spectra in the 700–1050 nm region corresponding to the absorbance from the moisture content of the slice samples are shown in Fig. 3. Strong absorption from the water molecules was observed in the 920–1000 nm region [22]. The decrease of absorbance in the 920–1000 nm region was observed according to the decrease of moisture content.

3.1.2 Estimation model of moisture content and water activity
The estimation of moisture content of slice sample was performed using spectra in the 920–970 nm region due to
water. Results obtained by PLS regression (in the case of PLS factor=1) and the second derivative spectra of this band had a similar prediction accuracy with $R^2=0.81$ and RMSE=0.34 $g/g$-d.s in this study. As we have described in previous studies [22], addition of the PLS factor may contribute to the improvement of the suggested model. In this study, since the spectra mainly reflected changes in moisture content, the estimation method using the second derivative spectra was more attractive.

The adsorption isotherm for slice sample is shown in Fig. 4. Moisture contents changed only slightly in the 0.84–0.95 $a_w$ range, and then rapidly increased when $a_w$ was higher than 0.96. Overall, the major trend of the isotherms used in this study agreed well with similar studies by other groups and with our previous results [27, 28]. Consequently, the relationship between moisture content and $a_w$ was accurately estimated by using the Guggenheim Anderson de Boer (GAB) equation (Eq.1) with the following parameters: $q_m=0.036$, $c=97.21$, and $K=0.99$ (RMSE=0.35 $g/g$-d.s). Recently Trujillo et al. reported that no significant changes of $a_w$ were found for lean beef in the temperature range 5–40°C [10]. Thus the

Fig. 3 NIR spectra of beef cut in the 700–1050 nm region during drying period reproduced from Ishikawa et al. 2016. [ref.22]

Fig. 4 Moisture sorption isotherm at room temperature for slice sample.
$a_w$ of room temperature was used in this study.

$$q = \frac{q_m c K_a}{(1-K_a)(1-K_a+c K_a)}$$

(1)

where $a_w$ is the water activity of material, $q_m$ is the partition function of molecule in multilayer, $c$ is the Guggenheim constant in the GAB sorption equation, and $K$ is the constant in the GAB sorption equation factor corresponding to properties of the multilayer molecules relative to the bulk liquid.

### 3.3 Application of estimation model for surface monitoring

#### 3.3.1 Optimization of monitoring method for the beef surface

The second derivative spectra in the 900–1050 nm region obtained from 2–4, 6, 8 and 10 mm thick samples were shown in Fig. 5 (a). A linear increase in intensity according to sample thickness was observed in that region. Intensity obtained from samples with thickness between 2–4 and 10 mm was nearly constant under the distance of 10 mm with as shown in Fig. 5 (b). When the distance between sample and detector of the spectrometer was more than 10 mm, the spectra of each sample varied obviously (not shown).

The spectra obtained under integration times of 50, 100, and 150 ms are shown in Fig. 6. Note that the spectrometer was equipped with a 10 mm spacer and the FOV was at 5 mmϕ for these trials. A significant difference in absorbance at 50, 100, and 150 ms was observed. During the 150 ms measurement, absorbance saturation occurred so that the accurate absorbance could not be obtained. The absorbance at the 50 and 100 ms integration times was similar and a high linear correlation between absorbance and moisture contents was confirmed. Consequently, in this study, we determined several parameters experimentally for optimal spectral measurement. In particular, the distance between sample and sensor of the spectrometer was 10 mm (with 5 mmϕ of

![Fig. 5 Second derivative spectra in the 900–1050 nm region of different thick sample measured by (a) original and (b) optimization method.](image-url)
collecting area), and an integration time of less than 100 ms gave the best results.

3.3.2 Change in estimated moisture contents and $a_w$ of the beef sample surface

The course of the surface moisture contents and $a_w$ of the lump samples estimated from the second derivative of the 950–980 nm region is shown in Figs. 7 and 8, respectively. Note that the NIR spectra were obtained under the optimization condition.

The estimated moisture content decreased linearly, and after 20 days it was nearly constant (Fig. 7). The moisture content approached the value of 0.20 g/g-d.s, that was estimated from the $a_w$ value of 0.8 by the moisture sorption isotherm shown in Fig. 4. As shown in Fig. 8, a linear decrease in $a_w$ was estimated during the total drying period. From the experimental results, the $a_w$ value was observed to approach 0.8 at around 22–25 days.

The drying rate curves of the samples presented in the literature contain a constant rate period prior to falling rate period in whole sample [29]. Namely, the moisture of the surface in this period is maintained because the free water migrates to the surface and evaporates at a constant rate.

However, in the case of food samples, the two periods are often not clearly present [30]. For whole of the beef

![Graph](image_url)

**Fig. 6** Change in second derivative with moisture content by integration time.

![Graph](image_url)

**Fig. 7** Courses of moisture content of beef surface estimated from second derivative spectra in the 950–980 nm condition.
sample, some authors studied, wherein some have identified the constant drying rate period and others did not observe this period [30, 31].

In our study, estimated moisture contents obtained from surface of beef also decreased from early drying period. The $a_w$ at the beef surface was also not constant despite sufficient moisture, and the value decreased with consistent rate during the drying period.

Wahlby and Skjoldebrand reported a similar behavior of moisture at the surface in pork [32]. Their results were obtained under a high temperature condition of 145°C, and the whole drying period (3000 s) was much shorter than in our experiment. Since the constant rate period was short, moisture supply from inside of beef already decelerated after 5 days. This is also reason why the change in the $a_w$ of the surface is linear for 5–22 days.

Moreover, not only mass transfer but also heat transfer of cause affects progress of drying. Since constant rate decrease of estimation $a_w$ was observed in our study, the dry of beef surface is progress by heat transfer rate limit. Therefore, these results successfully demonstrated that the thermal treatment is an effective method to accelerate the surface dry of beef.

The linearity of the estimated $a_w$ deteriorated after 22–25 days. At the end of the drying period, the intensity of the NIR spectra in the 950–980 nm range using the prediction model reduced due to low moisture contents, and the increase of surface roughness constrained to obtain the correct data from the beef surface. Hence, estimation of $a_w$ at the end of the drying period had a lower accuracy than that in the first 5–20 days. Therefore, in future phase of this study, modification of spectral measurement method should be considered separately for the low $a_w$ period in order to improve the accuracy of the estimation model. Moreover, adjust of the GAB parameters may contribute the estimation accuracy of $a_w$, so that GAB parameters should be evaluated in whole $a_w$ range.

### 4. Conclusion

In this study, estimation methods for $a_w$ at the surface of beef during the drying process were proposed experimentally by NIR spectroscopy. The moisture content of slice sample was estimated by the 2nd derivative spectra with $R^2=0.81$ and RMSE=0.34 g/g-d.s. And relationship between moisture content and $a_w$ was described well by GAB equation with the following parameters: $q_m=0.036$, $c=97.21$, and $K=0.99$. The different thick samples of 2–10 mm were measured by the NIR spectrometer in the 700–1050 nm region. The optimal measurement condition was determined to be as follows: 10 mm spacer with 5 mmØ hole, and integration time of 50 and 100 ms.

The lump samples with dimensions of $80 \times 100 \times 100$ cm$^3$ under drying were measured in the 750–1050 nm region using NIR spectroscopy with the optimized measurement parameters described above. In estimated moisture content at the surface, constant rate period of drying did not present clearly. The estimated $a_w$ at the surface reached 0.8 at approximately 22–25 days, and a
linear decrease of $a_w$ was observed during the drying process up until that time. The results obtained in this study successfully demonstrated only profile of $a_w$ at the surface during dry process. It revealed that estimation of $a_w$ by NIR spectroscopy has great potential to evaluate drying state of beef with non-destructive.

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近赤外分光法を用いた乾燥過程における牛肉表面の含水率推定手法と水分活性モニタリングへの応用

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熟成肉は、表面で発酵微生物が増殖することから、牛肉表面の水分活性制御が可能となれば品質管理の有効な手段となる。本研究では、乾燥過程での牛肉表面の水分活性の非破壊推定手法の提案をめざし、近赤外分光法によるモニタリングを実施した。まず、約2〜4mm厚のスライスサンプルの含水率、水分活性と近赤外スペクトルの測定を実施した。920〜970nm付近の近赤外スペクトルの二次微分を用いることで含水率がR2 = 0.81, RMSE = 0.34 g/g-d.s.の精度で予測可能となった。また水分活性と含水率の関係はGAB式でよくフィットされ、水分活性が近赤外スペクトルを用いて間接的に推定可能となった。サンプル表面部分のデータ取得を行うため厚みが2〜10mm程度まで異なるサンプルの測定から、最適な測定距離:サンプルから10mm、積算時間:100msを実験的に決定した。最終的に室温4℃、湿度0.8の庫内で乾燥させた牛肉ブロックの乾燥過程における近赤外スペクトルを最適条件下で取得し、スライスサンプルから作成したモデルを適用することで、表面水分活性の予測値を算出した。その結果水分活性の予測値は直線的に減少し约22〜25日の後に0.8に達すると推定された。本研究によって牛肉表面の非破壊的な水分活性モニタリング手法確立の可能性が示唆された。