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Analytical Methods

Development of hyperspectral imaging coupled with chemometric analysis to monitor *K* value for evaluation of chemical spoilage in fish fillets

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ABSTRACT

K value is an important freshness index widely used for indication of nucleotide degradation and assessment of chemical spoilage. The feasibility of hyperspectral imaging (400–1000 nm) for determination of *K* value in grass carp and silver carp fillets was investigated. Partial least square (PLS) regression and least square support vector machines (LS-SVM) models established using full wavelengths showed excellent performances and the PLS model was better with higher determination coefficients of prediction (R_P^2 = 0.936) and lower root mean square errors of prediction (RMSEP = 5.21%). The simplified PLS and LS-SVM models using the seven optimal wavelengths selected by successive projections algorithm (SPA) also presented good performances. The spatial distribution map of *K* value was generated by transferring the SPA-PLS model to each pixel of the images. The current study showed the suitability of using hyperspectral imaging to determine *K* value for evaluation of chemical spoilage and freshness of fish fillets.

1. Introduction

The quality and safety of food is a fundamental and legal requirement. It means that all food products provided for circulation and sale must be safe and acceptable for consumers. Therefore techniques such as drying (Delgado & Sun, 2002a, 2002b; Sun and Byrne, 1998; Sun and Woods, 1997), refrigeration (Kiani & Sun, 2011; McDonald & Sun, 2001; McDonald, Sun, & Kenny, 2001; Sun, 1997a, 1997b; Sun, Eames, & Aphornratana, 1996) and edible coating (Xu et al., 2001) should be investigated for the industry for possible quality maintenance. Fish is one of the most highly perishable aquatic products. During different handling processes and storage conditions, quality deterioration of fresh fish occurs quickly and significantly influences the shelf life of the product. The quality degradation of fish muscle is usually associated with the changes of fish physical, chemical, biochemical properties and microbiological activities (Sallam, 2007). In the chemical spoilage process, enzymatic and chemical reactions are generally responsible for the initial loss of freshness whereas microbial activity is responsible for the obvious spoilage (Gram & Huss, 1996; Sallam, 2007). The former is called biochemical or enzymatic freshness and the latter is related to bacterial freshness or spoilage (Pacheco-Aguilar, Lugo-Sánchez, & Robles-Burgueño, 2000). Fish freshness loss affects consumer demand and the shelf life of the products. Therefore, determination and evaluation of fish chemical spoilage and freshness is obviously important. There are some effective methods and techniques for determining the chemical spoilage and freshness quality of fish such as sensory evaluation based on quality index method (QIM), physical properties, and chemical index measurements (Cheng, Sun, Zeng, & Pu, 2013).

K value as an important chemical index has been widely used for fish chemical spoilage and freshness assessment based on nucleotide degradation. The *K* value evolves from the quantification of adenosine-5′-triphosphate (ATP) and its corresponding series of breakdown products, namely adenosine-5′-diphosphate (ADP), adenosine-5′-monophosphate (AMP), inosine-5′-monophosphate (IMP), inosine (HxR) and hypoxhantine (Hx) (Lowe, Ryder, Carragher, & Wells, 1993). Based on ATP-related breakdown compounds, the *K* value is usually calculated as the percentage rate of HxR and Hx to the sum of ATP and degradation products shown as follows:

$$K = \frac{\mathrm{HxR} + \mathrm{Hx}}{\mathrm{ATP} + \mathrm{ADP} + \mathrm{AMP} + \mathrm{IMP} + \mathrm{HxR} + \mathrm{Hx}} \times 100\% \quad (1)$$

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Generally, the nucleotide concentration in the flesh of live fish is strongly associated with the feeding habits and physiological activity (Lowe et al., 1993). After slaughter, ATP is gradually degraded to its relevant breakdown products on the basis of a series of catalyzing enzymes and the degradation process is usually described below: ATP → ADP → AMP → IMP → HxR → Hx. The decomposition patterns and rates of nucleotide degradation usually depend on the fish species, muscle type (dark or white muscle), antemortem condition, stress during capture, season, handling methods and storage conditions (Erikson, Beyer, & Sigholt, 1997). The initial value of *K*, immediately after capture, is usually less than 10% and then gradually increases due to endogenous enzyme actions. Later, usually after an inflection point, *K* value shows another quick increase attributing to bacterial spoilage (Lowe et al., 1993). The *K* value of 20% is considered as the optimal freshness limit, with 60% being the rejection point (Ehira, 1976). Thus, the *K* value shows a predictive function throughout the trial and could provide a useful and objective indicator for monitoring early storage changes and the remaining storage life (Lougovois, Kyranas, & Kyrana, 2003).

High-performance liquid chromatography (HPLC) is one of the most important chromatographic techniques and is a commonly used analytical method to determine ATP breakdown products for the estimation of *K* value and assessment of freshness in muscle foods. For example, Veciana-Nogues, Izquierdo-Pulido, and Vidal-Carou (1997) determined the ATP breakdown products in fresh and canned tuna fish by HPLC and Özogul, Taylor, Quantick, and Özogul (2000) developed a rapid HPLC method based on the determination of ATP related compounds to estimate *K* value for evaluating herring freshness stored under modified atmosphere. Also, Sallam (2007) utilized the *K* value measured by HPLC method for chemical analysis and shelf life evaluation of sliced salmon treated with salts of organic acids. All these findings proved that HPLC is capable of providing effective and accurate measurement of ATP degradation for estimating *K* value. Nevertheless, the applicability of this chromatographic analysis is somehow restricted because it is time-consuming, costly and destructive. It also commonly requires high-skilled operators and needs precise control of the experimental conditions. Obviously, this technique is not suitable for rapidly and non-invasively on-line and real-time monitoring fish freshness. Therefore, development of rapid and non-destructive inspection system for the evaluation of fish freshness and industrial application is urgently needed. Some investigations of *K* value measurement for fish freshness analysis have been developed using sensors and electrodes such as metallic potentiometric with Au and Ag electrodes for cultured gilthead sea bream (Gil et al., 2008), an electrochemical microfluidic device with two sensing sites for jack mackerel, yellow tail, and sea bream (Itoh et al., 2013), an optoelectronic nose for sea bream (Zaragozá et al., 2013) and double multi-enzyme reactor electrodes for yellowfin tuna and scallops adductor muscle (Okuma & Watanabe, 2002). The resulting data suggest that these techniques are convenient and effective for the assessment of fish freshness. However, they show strong specificity and they are not multi-target and non-invasive in nature.

Recently, hyperspectral imaging technique as an emerging and innovative tool has been increasingly put into use for rapid and non-invasive determination and evaluation of food quality and safety (Barbin, ElMasry, Sun, & Allen, 2012; Cheng & Sun, 2014; Costa et al., 2013; Elmasry, Iqbal, Sun, & Allen, 2011; ElMasry, Sun, & Allen, 2011; ElMasry, Sun, & Allen, 2012; Kamruzzaman, ElMasry, Sun, & Allen, 2011, Kamruzzaman, ElMasry, Sun, & Allen, 2012; Wu, Sun, & He, 2012). A typical hyperspectral imaging system combines the digital imaging or computer vision (Jackman, Sun, Du, & Allen, 2008; Jackman, Sun, Du, & Allen, 2009; Sun, 2004; Sun & Brosnan, 2003; Valous, Mendoza, Sun, & Allen, 2009; Wang & Sun, 2002) and spectroscopy technology into one system, generating a spatial map of spectral variation of sample (Liu, Sun, & Zeng, 2014; Lorente, et al., 2012; Sun, 2010). The hyperspectral image contains a three-dimensional (3D) dataset called hypercube $I(x, y, \lambda)$ that has one spectral dimension and two spatial dimensions. In addition, in order to enhance the application of hyperspectral imaging, chemometric methods such as partial least squares (PLS) regression and least squares support vector machines (LS-SVM) are required. PLS regression is a typical spectral calibration technique and has been widely used for spectral analysis due to its better flexibility in some conditions such as variables more than samples and multicollinearity. LS-SVM is a developed version of the standard SVM and has been introduced for the optimal control of nonlinear systems and spectral calibration (Suykens & Vandewalle, 1999). Based on these chemometric techniques, some exploratory studies of application of hyperspectral imaging have developed for quality evaluation of fish and fish fillets related to the color, texture and moisture (He, Wu, & Sun, 2013; Liu, Zeng, & Sun, 2013; Quevedo & Aguilera, 2010). However, to the best of our knowledge, up to now, there is no report on determining *K* value for assessment of freshness of fish fillets and monitoring ATP degradation during cold storage using hyperspectral imaging technique.

Therefore, the aim of this study was to develop the hyperspectral imaging system in the spectral range of 400–1000 nm for rapid and non-invasive measurement of *K* value and chemical spoilage evaluation in farmed grass carp and silver carp fillets. The specific objectives of this study were to (1) acquire the hyperspectral images of tested fish fillets during cold storage, (2) recognize the important region of interests (ROIs) and extract the corresponding spectral data within the acquired hyperspectral images, (3) establish the quantitative analysis model between the acquired spectral data and the reference *K* values measured by the traditional HPLC method based on PLS and LS-SVM algorithms, and (4) visualize the spatial distribution map of *K* value within the fish fillets. This would be the first study in the topic using hyperspectral imaging technique.

2. Materials and methods

2.1. Preparation of fish fillet samples

A total of forty fresh fish samples from two species including twenty grass carp (*Ctenopharyngodon idella*) and twenty silver carp (*Aristichthys nobilis*) from the same batch each weighting approximately 1.5 kg were purchased from a local aquatic products market in Guangzhou, China, and immediately transported to the laboratory alive in water within 15 min. Upon arrival, the fish were stunned by a sharp blow to the head with a wooden stick and then gill cutting. The internal organs were removed at the same time with bloodletting from the fish belly location. Then they were instantly beheaded, filleted, skinned, and washed with cold water. Eighty fish fillets (40 fillets from two fish species) with similar size were obtained. In order to acquire more fish samples, the fresh fillets were directly subsampled into a rectangular shape with similar size of $4.0 \times 3.0 \times 1.0$ cm (length × width × thickness). Accordingly, a total of two hundred and forty subsamples of fish fillets were obtained from different locations of tested fish fillets. In order to collect a practical range of *K* values for further indication of freshness loss and establishment of better prediction models, the whole subsamples were labeled and packaged into the sealed plastic bags and divided into four groups (60 subsamples in each group) that represented a complete process of fish from freshness to chemical spoilage during cold storage within 0, 2, 4, and 6 days at 4 ± 1 °C in a lab refrigerator (Haier Company, Qingdao, China) for