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Diffuse reflectance mid-infrared Fourier transform spectroscopy (DRIFTS) for rapid identification of dried sea cucumber products from different geographical areas

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ABSTRACT

In this study, diffuse reflectance mid-infrared Fourier transform spectroscopy (DRIFTS), principal components analysis (PCA) and soft independent modeling of class analogy (SIMCA) were performed on the classification of dried sea cucumber samples of the same species from various geographical areas using fingerprint region (1700–600 cm^{-1}). A set of 96 individual dried sea cucumbers (*Apostichopus japonicus* Selenka) grown up in four different geographical regions (Rongcheng, 16 individuals; Weihai, 20 individuals; Yantai, 40 individuals; Dalian, 20 individuals) in East China Sea were analyzed and successfully differentiated into four classes according to the distribution of geographical areas in spite of small differences in IR fingerprints. The result shows that the environmental influencing factor is the key factor contributing to the classification of sea cucumbers. And, this study also demonstrates that DRIFTS is a convenient tool for fast differentiation of seafoods from various geographical areas, such as dried sea cucumber products.

1. Introduction

As traditional Chinese medicinal materials (TCMs) and favorite seafoods, sea cucumbers have been cultivated for centuries in many Asian countries. In China, 134 species have been found, among which only about 20 species are edible and of medicinal functions [1]. As one of the famous aquaculture species, the sea cucumber *Apostichopus japonicus* Selenka is widely distributed in East China Sea. As known, chemical constituents in medicinal materials are the substantial foundations of curative effect which are influenced greatly by various regions [2]. For example, sea cucumbers of the same species but in different geological regions provide discriminative functions in medical applications [3,4], and thus require special treatments in commercial trade and safety management. However, it is impossible for ordinary consumers to distinguish sea cucumber products of the same species but from various habitats using sensory methods (e.g., by eyes, smell, taste), particularly when the products are pulverized as powders or cut into slices. So, the rapid identification of dried sea cucumber products from different habitats requires special treatments for safety.

As a fast, nondestructive and low cost experimental technique, Fourier transform infrared (FT-IR) spectroscopy is playing an important role in analysis of complex samples on molecular compounds and quantitative data with minimal sample pretreatments and good repeatability. In the past few years, FT-IR/NIR methods have been successfully used to classify the plant samples of different geographical areas based on subtle differences in chemical compositions of different cultivation conditions such as TCM [5–8], honey [9], maple syrup [10]. These results demonstrated that FT-IR is a rapid and robust tool for sample identification. However, very few studies have been carried out on the classification of sea cucumber products by diffuse reflectance mid-infrared Fourier transform spectroscopy (DRIFTS) which is one of the most important spectral sampling techniques for a wide variety of solid sample analysis based on reflectance measurements. Thus it is of particular interest to analyze dried sea cucumber samples for rapid differentiation.

In this report, a method based on DRIFTS was built to rapidly differentiate various sea cucumber products of different geographical regions by PCA and SIMCA. The IR fingerprint data were directly recorded from the powder of dried sea cucumber samples without

Abbreviations: DRIFTS, diffuse reflectance mid-infrared Fourier transform spectroscopy; PCA, principal components analysis; SIMCA, soft independent modeling of class analogy; TCM, traditional Chinese medicinal material; FT-IR, Fourier transform infrared; PCs, principal components.

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any further sample pretreatments. Our data showed that DRIFTS provided to be a convenient and fast method for rapid classification of seafood products.

2. Experimental

2.1. Apparatus and software

The measurement of DRIFTS was performed with Vertex 70 FT-IR spectrometer (Bruker Optic, Ettlingen, Germany), equipped with a KBr beamsplitter and a DLaTGS detector. The diffuse reflectance sampling accessory including of a macro sample cup (10 mm diameter, 2.3 mm deep) was made by PIKE® technologies (Madison, USA). The system was operated under OPUS® version 6.5. Only one spectrum was recorded for each sample. All the reflection spectra were recorded in a randomized order from an accumulation of 64 scans in 4000–600 cm^{-1} range with a resolution of 4 cm^{-1} at a room temperature (25 °C).

2.2. Sample and sample preparation

For convenient storage and transportation, dried sea cucumbers are the most popular final products on markets. As dehydrated samples, dried sea cucumbers keep main nutritional constituents unchanged [11]. As known, many factors (such as boiling and drying in the air) may influence the quality of products during the preparation process. However, nowadays dried sea cucumber products are made with regular work flows in northern China [12], the unified processing criterions may have the same degree of influences on the products [13]. Dried sea cucumber samples in total of 96 individuals were randomly picked up from a local sea cucumber outlet. All the samples were cultured in four habitats (Rongcheng: habitat 01, 16 individuals; Weihai: habitat 02, 20 individuals; Yantai: habitat 03, 40 individuals; Dalian: habitat 04, 20 individuals) in East China Sea. All those individuals were identified as one species (Holothuroidea, Stichopodidae, *A. japonicus*) by Prof. Yu-lin LIAO (Marine Biological Museum, Chinese Academy of Sciences, Qingdao, China) according to the morphological characteristics of dorsal ossicles [14].

Every individual was uniformly cut into two equal halves. Consequently, only a half of the individual samples were ground into powder with over 180 mesh by analytical grinding mill (IKA®, Germany) which took about 3 min for one sample making. The homogenization of the samples is essential to get better representational spectral data. It has the same effect as the averaging of spectral data. So, all samples were homogenized for 2 min in a shaker mixer for better homogeneity of samples. Finally, the sample particles were small and evenly dispersed. The samples (powders) were used for direct FT-IR spectrometric analysis without any further sample treatments as soon as the powders were made. The samples were loosely but leveled with the end of cup, and fingerprint spectra of samples were randomly recorded without any dilution in KBr.

2.3. Recording of DRIFTS spectra and spectral pretreatment

Both sample and blank spectra were scanned in the reflection mode. The reference standard was used for the background spectrum against the neat KBr powder (spectrum pure, Sinopharm Chemical Reagent Co., Ltd, China). KBr has no spectral structures in IR range (Fig. S1 in the supporting information) which is always used as optical window in this band. So, no interferences were caused by KBr for further analysis. The nonhomogeneity of samples was overcome by pulverizing the sample into powder and sieving. The software OPUS® 6.5 was used for data acquisition, and the raw data were exported as DPT files (readable file by Excel®). In order to reduce signal interferences of water vapor and CO_2 in the ambient conditions, all the acquired spectra were corrected using the "Atmospheric Compensation" function by OPUS® software. On the other hand, spectral variations caused by physical or chemical differences also need to be eliminated prior to any chemometric analysis. For example, the differential compaction degree and particle size may lead to baseline variations and artefacts because of physical light scattering. Therefore, multiplicative scatter correction (MSC) [15] was employed to reduce this scattering effect. What's more, in order to homogenize the data of peak intensities, another data-pretreatment method, autoscaling [13], was performed using "auto" function by using "PLS_Toolbox 2.1" (for use with Matlab®, Eigenvector Research, Inc., Manson, WA).

2.4. Development of classification model

Two different kinds of pattern recognition techniques, PCA and SIMCA, were employed to test the validity of the classification of sea cucumber samples in this experiment. PCA is a popular unsupervised pattern recognition technique for data compression and information extraction. In principle, PCA finds combinations of variables or factors to describe major trends in the analysis data by eigenvector decomposition. Unlike PCA, SIMCA is an important supervised pattern recognition technique that consists of collections of PCA models [16,17]. When PCA models are created for each class (using calibration set) and the new objects (validation set) can be projected into each class. Then, the distance to all defined classes can be calculated which provides an estimate for the classification of the new object. This is to say, if the distance of an object lies within limits defined for a class then it is considered to belong to the class.

3. Results and discussion

3.1. Representative IR fingerprint analysis of samples

The original reflection spectra (averaged spectrum of samples from the same habitat) of sea cucumbers from various habitats are shown in Fig. 1. The absorption band of atmospheric CO_2 (2400–2280 cm^{-1}) also appeared in some fingerprints. This was because the concentration fluctuations of CO_2 in surroundings. But, typical absorption bands for water vapor were effectively removed by "Atmospheric Compensation" function. As a kind of dehydrated sample, dried sea cucumber can effectively avoid problems found in various high absorptions of water which will be helpful for next analysis coupled with chemometric methods.

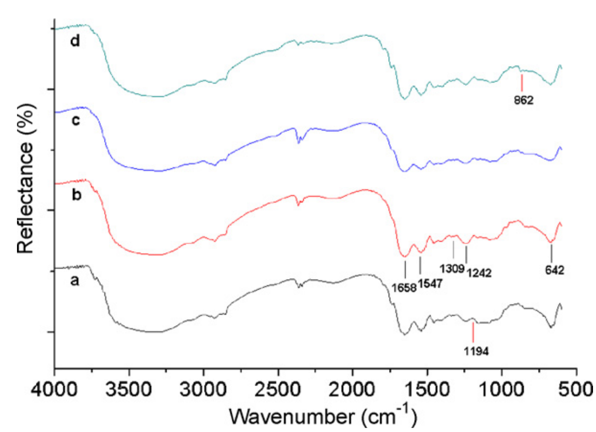

Fig. 1. Representative DRIFT spectra of dried sea cucumbers of various regions: (a) habitat 01 (Rongcheng); (b) habitat 02 (Weihai); (c) habitat 03 (Yantai) and (d) habitat 04 (Dalian).