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Rapid and non-invasive detection and imaging of the hydrocolloid-injected prawns with low-field NMR and MRI

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ABSTRACT

Method development for monitoring economically motivated food adulteration is pivotal for preventing health problems caused by illegal food additives. In this work, low-field nuclear magnetic resonance (LF-NMR) spectroscopy and magnetic resonance imaging (MRI) was applied for the detection and mapping of adulterated prawns injected with different hydrocolloids including gelatin, carrageenan, agar, amorophophallus konjac and xanthan gum. The characteristic T_2 fitting curves were obtained which can be used to tell apart adulterated prawns from normal ones. Furthermore, the benefit from high quality LF-MRI images showed the major accumulation site of the hydrocolloids injected in prawn. The location of these injections was mainly confined to well resolved accumulation in brain region and three following subtle sites: back, tail and claws. Different hydrocolloids can be successfully distinguished in adulterated prawns with principal component analysis. Therefore, rapid, non-invasive and low-cost LF-NMR technique offers a powerful tool for the identification of hydrocolloids adulteration in real-time.

1. Introduction

Prawns contain high quality protein and other essential nutrients such as vitamins, unsaturated fatty acids and carotenoids, which are an important part of a healthful diet. However, adulteration of prawns and other seafood products is still sometimes reported (Kamruzzaman, 2016). A few seafood producers inject substances such as hydrocolloids into the head and belly of prawns. Compared with normal prawns, adulterated prawns injected with hydrocolloids have similar color appearance and fresh look, but their weight increased by 5–30% (Wu, Shi, He, Yu, & Bao, 2013). The adulterated prawns are rich in hydrocolloids making it easier to breed pathogenic bacteria, which will cause persistent deficiencies in the safety and wholesomeness (Williams, 2011) The situation can be even worse if industrial hydrocolloids are injected which contain toxic heavy metals and carcinogens, such as pentachlorophenol and formaldehyde (Weiner, 1991). At present, visual inspection is often used by cutting the head/belly of prawns; however, it is hard to make good judgements because most hydrocolloids are transparent in particular for the average customers. Therefore from an analytical perspective, there remains a need for innovation that addresses the challenges associated with rapid, non-destructive and accurate discrimination of food adulteration (Karoui & De Baerdemaeker, 2007).

Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) is one of the most attractive non-invasive techniques which are suitable for tracking physicochemical changes in the food materials (Nielsen, 2010). Generally, NMR and MRI instruments require large, immobile, and expensive superconducting magnets, limiting the use of the technology. Therefore, low-cost, low-field NMR (LF-NMR) and MRI technique has gained broad interests which is used to assess food quality, probe food functionality and detect food adulteration (Hills, 2006). In current study, a rapid, non-invasive and low-cost LF-^{1}H NMR and MRI method was developed to identify prawns that were deliberately injected with hydrocolloids. The general workflow of screening prawns injected food hydrocolloid is shown in Fig. 1. Five different hydrocolloids were measured including gelatin, carrageenan, agar, amorophophallus konjac and xanthan gum in order to obtain individual relaxation times of water protons in adulterated prawns.

The small NMR analyzer used in this work is versatile and available to be brought to the spot, and therefore it can be used to detect the adulterated prawns in real-time in aquatic products market. Moreover, the method developed here can be straightforwardly extended to other adulteration in marine products.

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Fig. 1. Schematic illustration of a typical LF-NMR and MRI experimental workflow for the detection of prawns injected with hydrocolloids.

2. Experimental

2.1. Sample preparation

Five batches of the fresh prawns were collected from the local seafood market from January to June 2016. Five different commercial hydrocolloids were purchased from Cooling of Shanghai Biological Technology (Shanghai, China) including gelatin, carrageenan, agar, amorophophallus konjac and xanthan gum. Aqueous solutions of hydrocolloids were prepared at five different concentrations: 0.5%, 2.0%, 3.5%, 5.0% and 6.5% (w/v) by dissolving solid powders in 100 mL distilled water. The ways to prepare different hydrocolloid solutions were slightly different depending on their nature. For gelatin solution, gelatin was swollen in distilled water at room temperature for 2 h, and then dissolved in distilled water by heating in a water bath at 70 °C. Carrageenan and agar were dissolved in hot distilled water (~70 °C) by stirring for 2 h. Amorphophallus konjac was dissolved in distilled water at room temperature, and xanthan gum was soaked with stirring in distilled water for 2 h at 30 °C.

The fresh prawns were stored in the refrigerator (−20 °C) for 2 days before experiment. After thawing in 4 °C for 3 h, 6 mL hydrocolloid solutions were injected throughout the whole body of prawn. Each group for individual food hydrocolloid included 30 samples, 5 replicates for each concentration. Furthermore, 20 samples were collected for the following measurement of moisture content. In total, 200 samples were analyzed in this study.

2.2. Measurement of moisture content (MC) and weight gain

MC of control and adulterated prawns was determined according to the method of determination of moisture in foods (GB50093, 2010). The prawn samples were weighed respectively before and after injection. Cleaned weighing bottle was dried to constant weight at 105 °C. The prawn sample was placed into the weighing bottle, which was then dried to constant weight in an Electrothermal Constant-temperature Drying Box (DHG-9055A, Shanghai YiHeng Scientific Instrument, China) for 4 h at 105 °C. The weighing bottles were taken out and immediately cooled in vacuum desiccators (containing allochroic silica gel) for 30 min. MC was calculated as the percentage ratio of gravimetric difference and the original sample weight. All samples were weighed before and after injection of hydrocolloids to determine percentage weight gain.

2.3. LF-^{1}H NMR measurements

LF-^{1}H NMR measurements were performed at 32 °C on a 21.16 MHz NMR Analyzer (Meso MR23-060H-I, Niumag Electric, Shanghai, China). The surface water on prawn sample was gently wiped off in order to reduce interfering signal from traces of water. The prawn samples were wrapped in commercial plastic food wrap to avoid contamination of NMR bed. The NMR instrument was equipped with a 60 mm diameter radio frequency coil. The control and adulterated prawns were placed on the NMR bed and inserted in the NMR probe. Carr-Purcell-Meiboom-Gill (CPMG) sequences were employed to measure spin-spin relaxation time (T_2) to collect decay signals. Inversion-Recovery (IR) sequences were employed to measure spin-lattice relaxation time (T_1) to confirm the MRI parameters. T_2 measurements were performed with a τ-value of 100 μs (time between 90° pulse and 180° pulse). Data was acquired from 6000 echoes as 4 scan repetitions, and the repetition time between two successive scans was 5 s. The optimized parameters for NMR measurements were shown in Table S1. The optimized CPMG sequence parameters were suitable for measurement of both control and adulterated prawn samples. Each measurement was performed in triplicate.

Post processing of NMR T_2 data distributed exponential fitting of CPMG decay curves were performed by Multi-Exp Inv Analysis software (Niumag Electric, Shanghai, China). From the multi-exponential fitting analysis, time constants for each process were calculated from the peak position, and the area under each peak (corresponding to the proportion of water molecules exhibiting that relaxation time) was determined by cumulative integration, which continuous distribution of exponentials is defined by the following equation:

$$M(t) = \sum_{i=1}^{n} A2i\exp\left(\frac{-t}{T2i}\right) + A0$$

where M (t) is the residual magnetization as a function of acquisition time t, A_{2i} and T_{2i} are the spin-spin relaxation amplitude and time respectively, of the its component, and A_0 is the residual error. Here multi-exponential fitting analysis was performed on the relaxation data according to a previously reported modified inversion method (Li et al., 2015; Mohnke & Yaramanci, 2005; Roy & Lubczynski, 2005). The relaxation time T_{2i} and its corresponding water population (area ratio) M_{2i} were recorded. After the data processing using inversion method, the discrimination in prawns is presented on fitting curve.

2.4. MRI detection

After the measurement of LF-NMR, ^{1}H MRI images of control and adulterated prawns were also acquired on MR23-060H-I NMR Analyzer. The MRI images, including T_1, T_2 and proton density weighted images, were acquired by using the multiple-spin-echo (MSE) sequence. The distribution of hydrocolloids in prawns can be clearly visible in proton density weighted images. Based on the principle of proton density weighted image, MRI parameters are determined by the following inequality:

$$\begin{cases} TE << T_{2min} \\ TR \geqslant 5T_{1max} \end{cases}$$

where T_2 is determined by the CPMG sequence, T_1 is determined by the IR sequence, TE and TR are no exact value, but it can be obtained the certain range to be feasible (Guoxin Xiong, 2007). The optimized parameters for MRI measurements were shown in Table S1. The images obtained from MRI were processed with two software: unified mapping and pseudocolor processing. After unified mapping and pseudocolor processing, the gray level images were changed to color images. At last, the distribution map of food hydrocolloid is presented on the color images.