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Short communication

Rapid, accurate, and simultaneous measurement of water and oil contents in the fried starchy system using low-field NMR

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Waxy starch (PubChem CID: 86278134)
Water (PubChem CID: 962)
Amylose (PubChem CID: 53477771)
Amylopectin (PubChem CID: 439207)
$MnCl_2 \cdot 4H_2O$ (PubChem CID: 643989) (*Please note* that oil is not a specific chemical, it is the mixture of triglyceride and fatty acid, therefore, it will not have a specific record in PubChem.)

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ABSTRACT

Fried starchy food is rich in oil that may pose a risk to health. For controlling of the oil uptake, a rapid and accurate method for the determination of oil content in the fried starchy food is important. In this study, low-field nuclear magnetic resonance (LF-NMR) was applied to simultaneously determine water and oil contents in the model fried starchy system. The proton signals from oil and water were verified and distinguished by desiccation at 105 °C. There was no superposition between oil and water signals in the fried starch, making it possible for quantitative analysis of water and oil in a single test. Compared with Soxhlet extraction, the LF-NMR analysis provided a more accurate result of oil content in the fried starchy system, confirming the practicability of the application of LF-NMR technology as a fast and accurate method for the quantification of water and oil in the fried starchy system.

1. Introduction

Frying is a popular processing method, and is widely applied to prepare a wide spectrum of products in food industry throughout the word (Dobarganes, Marquez-Ruiz, & Velasco, 2000; Saguy & Dana, 2003). Raw-food material is immersed within edible oil and heated at high temperature during frying. The evaporation of water and the uptake of oil inevitably occur in connection with acute heat and mass transfer, which endues fried foods with unique texture, flavor, and appearance (Mellema, 2003; Troncoso & Pedreschi, 2009).

However, the consumption of fried foods that absorbed excess oil may have undesirable health benefits to the normal population, including the induction of cardiovascular and cerebrovascular diseases and the exacerbation of obesity (Varela & Fiszman, 2011). The increasing concerns for reducing the oil contents of fried foods have evoked a wide range of research and gained considerable consumer awareness in the last few years (Bajaj & Singhal, 2007; Varela & Fiszman, 2011). Also, these potential risks of fried foods urgently underline the need to establish acceptable methods for the determination of oil content in a principle of independence, rapidity and convenience. However, the traditional method for oil determination, i.e. the Soxhlet extraction requires large amounts of organic solvents and is time-consuming and susceptible to interference. Therefore, a new method for accurate and rapid measurements of oil and water contents in fried starchy foods is needed.

Low field nuclear magnetic resonance (LF-NMR) is a reliable, non-invasive technology to probe the proton of small molecules in the complex food system, and LF-NMR has been used for the

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characterization of water distribution and mobility in starchy gel during cold storage in our previous work (Chen, Tian, Tong, Zhang, & Jin, 2017). LF-NMR also has been successfully applied in the oil measurement of botanical seed (Niu, Li, Chen, & Xu, 2014) and the real-time determination of lipid in the cells during microalgal fermentation processes (Wang et al., 2016). However, the application of LF-NMR in the oil determination of fried starchy food has not been frequently reported.

Therefore, the primary mission of the present work was to verify the validity of LF-NMR in the simultaneous determination of water and oil contents in fried starchy samples. Traditional methods including oven method (for water measurement) and Soxhlet extraction method (for oil measurement) were also used for comparison purpose.

2. Materials and methods

2.1. Materials

Waxy maize starch (WMS) with 12.52% moisture, normal maize starch (NMS) with 13.12% moisture and high amylose maize starch (HAMS) with 14.37% moisture were obtained from Gaofeng Starch Technologies Co., Ltd. (Suzhou, China). The amylose contents of WMS, NMS, and HAMS were 2.48%, 27.34%, and 50.63%, respectively, which were determined using the AACC Method (2000). Soybean oil was purchased form the local supermarket. $MnCl_2\cdot 4H_2O$ was chromatographically pure and produced by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Preparation of fried starchy samples

In this study, a starch-water-oil model system was used by reason that the organoleptic characteristics, nutritive value, and the oil absorption behavior of fried food made from cereal were mainly dependent on the properties of the major component, i.e. starch. WMS, NMS, and HAMS were firstly hydrated to 40% moisture as reported by Bosmans, Pareyt, and Delcour (2016). WMS with 20% and 50% moisture was also prepared to verify the hydrogen proton signals in water and oil. Then the hydrated starches (5 g in dry basis) were dispersed into 100 mL of soybean oil at room temperature by magnetic stirring for 10 min. Subsequently, samples were heated at 180 °C in an oil bath for 20 min to mimic the frying procedure. After heating, samples were filtered using vacuum filtration to remove uncombined oil. The resultant solid samples were preserved in a brown vacuum bag for further analysis.

2.3. Measurement of water and oil contents by LF-NMR and conventional methods

2.3.1. LF-NMR

The LF-NMR measurements of reference substance (water and soybean oil) and samples were performed using a 23 MHz NMR analyzer (NMI20-015V-I, Niumag Co., Ltd., Suzhou, China) with a sample tube of 25 mm in diameter. The temperature of the LF-NMR instrument was maintained at 32 °C during the spin-spin relaxation time (T_2) measurements, which were performed using a sequence based on the Carr-Purcell-Meiboom-Gill (CPMG) sequence.

For the accurate determination of water contents in the fried starch system, 3% $MnCl_2\cdot 4H_2O$ aqueous solution was substituted for pure water in the preparation of calibration curve. Specific amount of reference substance ($MnCl_2$ aqueous solution and soybean oil) and samples were transferred to a 10 mm diameter NMR glass tube and sealed with three layers of preservative film to prevent evaporation of water or the oxidation of oil during the experiments.

The peak areas under the curves of the populations with a certain range of T_2 were proportional to the number of protons in the population and expressed in arbitrary units (a. u.). All samples for T_2 analysis were the same weight, and were measured under the same condition to ensure that the signals were comparable in terms of intensities. Calculation curves were obtained by linear regression between the peak area and the mass associated with water and oil, respectively.

2.3.2. Conventional methods

For the purpose of comparison, oven drying and Soxhlet extraction (AOAC, 1990) were also used to measure moisture and oil contents in samples.

2.4. Statistical analysis

Data were presented as the mean ± SD. Statistical significance was assessed by one-way ANOVA with Tukey's test using SPSS 20.0 (SPSS Inc., Chicago, USA). $p < 0.05$ was considered to be statistically significant throughout the study.

3. Results and discussion

3.1. Identification of proton from water and oil in model fried starchy system

The corresponding transverse relaxation time (T_2) spectra of free water and oil were distinct, and the proton signals could be easily distinguished between each other. Usually, the hydrogen proton of triglyceride molecules in oil relaxed faster ($T_2 < 1000$ ms) than the hydrogen proton of water ($T_2 > 2000$ ms), because triglyceride had more complex structure and larger chain length than the simple and small water molecule, i.e. the proton in oil located in a more restricted environment than the proton in water did.

However, T_2 values of proton in water rapidly decreased due to the occurrence of interactions between water and other components, especially the macromolecules (Chen et al., 2017). Additionally, the mobility of proton in water might be further restricted during the processing treatment or transition process, such as the thermal gelatin and coagulation process.

The T_2 relaxation time spectra of fried starches with or without desiccation were shown in Fig. 1. Three water fractions, with the lowest T_2 range of 0.01–1 ms, medium T_2 range of 1.15–8.11 ms and highest T_2 range of 18.74–533.67 ms, were distinguished in the fried WMS with 20% moisture (Fig. 1**A**); while two water fractions, one fraction with the lower T_2 range of 0.87–6.14 ms and another fraction with higher T_2 range of 21.54–613.59 ms, were distinguished in the fried WMS with 50% moisture (Fig. 1B).

In order to distinguish the proton signal between water and oil, aforementioned two samples were heated at 105 °C to constant weight. As shown in Fig. 1, the peaks for the proton with T_2 values >10 ms almost had no changes after desiccation, which could be assigned to the higher mobility proton in the oil molecules. As for the peaks with T_2 ranged between 1–10 ms, signals were disappeared in both Fig. 1A and B after desiccation, indicating that this peak was representative of the signal of weakly bound water. A small peak with T_2 values < 1 ms remained even after the sample was suffered from heating at high temperature in Fig. 1A, the intensity of this peak slightly decreased. It is reasonable to assign this peak as the signal of proton in tightly bound water. Compared with bound water, the signal ranges for oil were wider, which indicating the heterogeneity of proton mobility in the oil phase.