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RESEARCH PAPER

Rapid Characterization of Triacylglycerols in Edible Oils by Matrix-assisted Laser Desorption/Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Abstract: Composition and types of triacylglycerols (TAGs) in edible oils are closely related to our health. It is of vital significance to develop fast and high-efficiency methods for determination of TAGs. In this manuscript, qualitative analysis of TAGs was demonstrated using matrix-assisted laser desorption/ionization Fourier transform ion cyclotron resonance mass spectrometry (MALDI-FTICR-MS). 2,5-Dihydroxybenzoic acid (DHB) was employed as matrix and dichloromethane was used as solvent for dissolving the edible oils. With laser power of 15%, laser frequency of 100 Hz, and 100 laser shots, relative standard deviation (RSD) less than 9% was obtained. Different kinds of edible oils could be directly distinguished from each other using MS and tandem MS (MS/MS) results. With confidence level of 95%, principal component analysis (PCA) results showed that 34 different kinds of edible oils were clearly classified. Moreover, down to 5% of doped canola in olive was identified directly, indicating that MALDI-FTICR-MS has the potential for rapid analysis and screening of edible oils.

Key Words: Matrix-assisted laser desorption/ionization; Fourier transform ion cyclotron resonance mass spectrometry; Triacylglycerols; Principal component analysis

1 Introduction

As an important source of fat in foodstuffs, edible oils are indispensable contents of nutrition in human beings and more than 170 million tons are consumed every year[1]. Although they offer necessary trophic function, inappropriate intake may cause some diseases, including obesity, cardiovascular disease[2], and liver dysfunction[3]. As the major component of edible oils, TAGs are comprised of three fatty acids esterified with a glycerol molecule. In consideration of the different carbon numbers and unsaturation degree of fatty acids, plenty of TAGs are formed, which is the reason why all the edible oils have similar appearance but differ in nutrition, giving rise to a series of adulterated oils problem. Therefore, it is of paramount importance to develop rapid, direct methods for determination of TAGs in edible oils to ensure food safety and public health.

Nowadays, lots of techniques for analysis of edible oils have been developed, including chromatography[4,5], nuclear magnetic resonance spectroscopy (NMR)[6], infrared spectroscopy (IR)[7], and mass spectrometry (MS) based methods[8]. Among them, MS-based methods have been widely applied due to the fast detection speed, high sensitivity and excellent limits of detection. Gas chromatography-mass spectrometry (GC-MS)[9,10], liquid chromatography-mass spectrometry (LC-MS)[11–13], and direct infusion mass spectrometry (DIMS) are the three popular methods. Compared to those well-established hyphenated techniques, reduced sample separation and derivatization processes facilitate DIMS to be a much faster, higher throughput, and

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easy-to-operate method, which has become a hot research spot in current analytical field[14]. Variety of direct infusion ionization techniques have been developed to detect TAGs in edible oils. Electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and matrix-assistant laser desorption/ionization (MALDI)[14–16] are three prevailing ion sources. Normally, ESI is used in the determination of polar components such as fatty acids and phenols in edible oils, and additional salt is needed to achieve a desired signal-to-noise ratio (SNR). APCI source is suitable for the identification of medium and weak polarity contents. Meanwhile, the TAGs contents and acyl position in fatty acids could be predicted by three characteristic fragmental ions[17]. Compared with these solution-based approach, MALDI source is utilized for direct solid analysis with advantages of simple sample pretreatment, easy operation and high salinity tolerance, promoting its wide application in rapid identification of edible oils[18–20].

In this study, MALDI-FTICR-MS was employed as a rapid and simple method for analysis of TAGs in edible oils and its analytical performance was demonstrated. Different types of oils were preliminarily discriminated from each other via the primary mass spectra. Principal component analysis (PCA) results showed that 34 different kinds of edible oils were clearly classified. The capability for discerning adulterated olive oil via MALDI-FTICR-MS was verified.

2 Experimental

2.1 Instruments and reagents

All the experiments were performed on a 7T FTICR-MS equipped with ESI, APCI, and MALDI source (SolariX XR 7T, Bruker Daltonic GmbH, Germany). A smartbeam laser at wavelength of 355 nm was employed with energy of 0–300 μJ, repetition rate of 0–1 kHz. A miniature whirlpool hybrid instrument (Shanghai Lu Xi Analysis Instrument Co. Ltd, China) was used to sufficiently dissolve the edible oils.

Acetone and dichloromethane were purchased from Guangzhou chemical reagent factory (AR, Guangzhou, China). Sodium trifluoroacetate (NaTFA) and DHB (99%) were from Sigma-Aldrich (St Louis, USA). Apart from the home-made lard, 33 different brands of peanut oils, canola oils, olive oils, corn oils, soybean oils, and sunflower oils were purchased from the local supermarket.

2.2 Experimental methods

2.2.1 Sample preparation

Preparation of edible oils: 4 μL of each edible oil was dissolved in 1 mL dichloromethane and blended before analysis.

Preparation of doped edible oils: a series of mixed edible oils were prepared using canola oils and olive oils (0%, 5%, 10%, 20%, 40% and 60%, *V/V*), and then 4 μL of mixed edible oils was dissolved in 1 mL dichloromethane and blended before analysis.

Load sample: 1 mg DHB was dissolved in 500 μL acetone. 1 μL of DHB solution was first loaded onto spots of the MALDI steel plate and air-dried. Then 1 μL of prepared edible oil was spotted onto the matrix layer. Finally, MALDI steel plate was loaded into the FTICR-MS chamber for the subsequent analysis.

2.2.2 Instrument parameters

All the MS data were acquired in positive ion mode. Medium laser spot size was employed at a repetition rate of 100 Hz, and 100 laser shots. The laser power was attenuated to about 15% of its maximum and "random" walk mode was employed. Each spectrum was acquired by eight scans using 1M data with range of *m/z* 150–1500. The ion accumulation time was set at 2 ms for each scan. For MS/MS analysis, the isolation window was set at 10 and collision energy was optimized to 25 eV. All data were obtained and processed using DataAnalysis 4.4 software and ProfileAnalysis 2.2 software (Bruker Daltonic GmbH, Germany).

3 Results and discussion

3.1 Optimization of MS conditions

For MALDI analysis, the MS signal stability greatly depends on the morphology of matrix crystallization. As we know, the relatively stable MS signal and desired SNR could be achieved when DHB was dissolved in acetone with two-step sample preparation[21]. Hence, this sample preparation method was employed in this study. Normally, low toxic reagents, such as chloroform or cyclohexane, were used for dissolving edible oils. As a less toxic solvent, dichloromethane was employed for sample pretreatment in this work. Apart from sample treatment, the parameters of laser, such as laser frequency, laser power, and laser spot size, also influence the quality of mass spectra. With a suitable laser spot size, abundant ions could be achieved with the increase of laser power and laser frequency, facilitating a higher SNR. However, space charge repulsions could not be avoided in ion cyclotron resonance cell if too much ions were gathered, leading to the detriment of the mass accuracy. To guarantee a desirable mass accuracy, 15% laser power and "medium" spot size were used with laser frequency of 100 Hz, and with 100 laser shots in the following experiments. The repeatability of MALDI-FTICR-MS for TAGs analysis was evaluated from five replicates using four different brands of olive oils. After calculating the intensity ratios between