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Analytical Methods

# Simultaneous determination of phenolic compounds in sesame oil using LC–MS/MS combined with magnetic carboxylated multi-walled carbon nanotubes

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ABSTRACT

A novel magnetic carboxylated multi-walled carbon nanotubes (c-MWCNT-MNPs) was proposed for magnetic solid-phase extraction coupled with liquid chromatography–tandem mass spectrometry to determine phenolic compounds in sesame oil. In this study, c-MWCNT-MNPs were acquired by simply dispersing $Fe_3O_4$ magnetic nanoparticles into carboxylated multi-walled carbon nanotubes. The major parameters affecting extraction efficiency were optimized, including the type and volume of desorption solvents, extraction and desorption time, washing solution, and sorbent amount. The limit of quantifications and limit of detections were from 0.03 μg/kg to 43.00 μg/kg and from 0.01 μg/kg to 13.60 μg/kg, respectively. The recoveries of phenolic compounds in vegetable oils were in the range of 83.8–125.9% with inter-day and intra-day precisions of less than 13.2%. It was confirmed that this method was simple, rapid and reliable with an excellent potential for routine analysis of phenolic compounds in oil samples.


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## 1. Introduction

Sesame oil possesses a pleasant odor and good taste, as well as resistant to oxidative rancidity significantly, although it contains nearly 85% unsaturated fatty acids (Abou-Gharbia, Shehata, & Shahidi, 2000), which is widely used in China, Korea, Middle East, and Southeast Asian countries. A group of phenolic compounds are found in sesame oil, which are correlated with the nutritional and organoleptic properties, as well as the oxidative stability. High concentrations of phenolic compounds have been reported to have health-promoting effect due to various biological activities, e.g. antioxidant (Idowu et al., 2010), antimicrobial (Alves et al., 2013), anti-inflammatory (Miles, Zoubouli, & Calder, 2005), anticarcinogenic (Morton, Caccetta, Puddey, & Croft, 2000), and antiproliferative effects (Siess et al., 1996). Besides sesame lignans, the phenolic compounds also play an important role in protecting sesame oil from oxidation process (Konsoula & Liakopoulou-Kyriakides, 2010).

A wide range of phenolic compounds have been found in olive oil, including phenolic acids, phenolic alcohols, flavonoids and lignans (Artajo, Romero, Suárez, & Motilva, 2007). Most previous studies mainly focused on the total phenolic content (TPC) but few focused on phenolic compositions in sesame oil. Traditionally, phenolic compounds were determined by high-performance liquid chromatography (HPLC) coupled with ultraviolet spectrophotometer (UV), diode-array detection (DAD) (Cilliers, & Singleton, 1991; Ossipov, Nurmi, Loponen, Haukioja, & Pihlaja, 1996; Zheng, & Wang, 2001) or mass spectrometry (MS) (Ballus et al., 2015; Tatsis et al., 2007), and nuclear magnetic resonance (NMR) (Albert, 1999). Liquid chromatography tandem mass spectrometry (LC–MS/MS) serves as a high-throughput screening and confirmatory tool, which is generally a crucial technique for analyzing phenolic components in plant samples. The extraction and purification technologies for edible oils are key to quantitative analysis of phenolic compounds since their contents were relatively low. The extraction methods involve liquid-liquid extraction (LLE) (Bakhouche et al., 2013, 2014; Taamalli, Román, Zarrouk, Segura-Carretero, & Fernández-Gutiérrez, 2012), gel permeation chromatography (GPC) (Sun, Yang, Li, Zhang, & Sun, 2012), solid-phase extraction (SPE) (Lozano-Sánchez, Cerretani, Bendini, Segura-Carretero, & Fernández-Gutiérrez, 2010a), and dispersive solid-phase extraction (DSPE) (Deme et al., 2014). Most of those conventional sample preparation methods are time-consuming, laborious, complicated, and also require using organic solvents and large sample volumes.

Recently, a novel extraction and preparation method magnetic solid-phase extraction (MSPE) attracts increasing attention due to its rapid and simple procedure (Ding, Gao, Luo, Shi, & Feng, 2010; Gao, Luo, Bai, Chen, & Feng, 2011; Gao, Luo, Ding, & Feng, 2010; Guo, Li, Zhang, Li, & Wang, 2009; Li et al., 2008). MSPE does not need to be packed into the cartridge such as traditional SPE (Liu, Li, & Lin, 2009). Through vortex and ultrasonic agitation based on an "aggregation wrap" mechanism (Ding et al., 2011), the sorbents can be completely dispersed into the sample solution, which makes the contact area between the sorbents and the analytes large enough to ensure fast mass transfer. The sorbents could be quickly separated from the complicated matrix with an external magnet, and therefore achieves highly efficient extraction in a short time, which is desirable for high-throughput sample preprocessing (Zhao et al., 2012).

MWCNTs were a type of powerful sorbent used for extracting organic compounds (Ding et al., 2011) after modified with various agents such as nitric acid, hydrogen peroxide, sulfuric acid, and mixed acid of potassium permanganate and sulfuric acid. The modification might alter the surface chemical properties and absorption abilities. Up to now, the strategy was expanded to fabricate various MWCNTs, for example, multi-walled carbon nanotubes modified with carboxyl (c-MWCNTs), which could be applied to various analytes (Abe et al., 2005; Asensio-Ramos, Hernández-Borges, Ravelo-Pérez, & Rodríguez-Delgado, 2010; Guo, & Lee, 2011; Moazzen, Ahmadkhaniha, Gorji, Yunesian, & Rastkari, 2013). Furthermore, magnetic $Fe_3O_4$ particles were selected as the magnetic core because of its rapid, cheap and high-yield synthesis technique, especially its highly magnetic property to satisfy the magnetic separation requirement (Liu et al., 2009).

The aim of this study was to develop a rapid, simple and sensitive method based on c-MWCNT-MNPs and LC–MS/MS for the determination of phenolic compounds in sesame oil. The phenolic compounds were extracted from sesame oil by using c-MWCNT-MNPs and were subsequently separated and analyzed by LC–MS/MS. Under the optimal conditions, 23 phenolic compounds in sesame oil were analyzed.

## 2. Experimental

### 2.1. Chemicals

Methanol, *n*-hexane, formic acid and acetic acid of HPLC grade were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethylene glycol (EG), ferric trichloride hexahydrate ($FeCl_3{\cdot}6H_2O$), and sodium acetate (NaAc) were of analytical grade and purchased from Shanghai Chemical Co., Ltd. (Shanghai, China). The long c-MWCNTs (length: ~30 μm, diameter: <8 nm, –COOH content: 3.86%) used in this study were obtained from XF Nano (Shanghai, China). Unless otherwise stated, all other inorganic chemicals and organic solvents were of analytical reagent grade or better. Ultra-pure water (18 mΩ) was obtained from a Milli-Q water purification system (Millipore Co., Ltd., Milford, MA, USA).

### 2.2. Standards

2-(4-Hydroxyphenyl) ethanol, cinnamic acid, 3,4-dihydroxybenzoic acid, *p*-coumaric acid, 2-hydroxycinnamic acid, vanillic acid, gallic acid, caffeic acid, ferulic acid, syringic acid, sinapic alcohol, sinapic acid, apigenin, luteolin, catechin, epicatechin, quercetin, daidzein, genistein, daidzin, and sesamin were gained from Sigma–Aldrich Co., Ltd. (Shanghai, China). *trans*-Resveratrol with purity of >98% was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan).

Stock solutions were freshly prepared for all standards by accurately weighing out 10 ± 0.1 mg of standard substances and separately dissolving it in 10.0 mL methanol. A series of standard