



Analytical Methods

Solid-phase extraction of flavonoids in honey samples using carbamate-embedded triacontyl-modified silica sorbent

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ABSTRACT

In this study, carbamate-embedded triacontyl-modified silica (Sil-CBM-C30) is successfully prepared and used as an efficient sorbent for solid-phase extraction. The extraction performance of the resultant sorbent is evaluated with five flavonoids including myricetin, quercetin, luteolin, kaempferol and isorhamnetin. Main parameters, which affect extraction efficiencies, are carefully investigated and optimized. Comparative experiments between Sil-CBM-C30 and commercial C18 sorbents indicate that the extraction efficiencies of the former one surpass the latter one. The modification of carbamate-embedded triacontyl group on surface of silica causes analytes extracted by hydrophobic, hydrogen bonding and π - π interactions. Under optimal conditions, good linearities and satisfied LODs and LOQs are achieved. The SPE-HPLC-DAD method is successfully developed and applied for the honey sample analysis.

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1. Introduction

In honey samples, flavonoids represent the most important active constituents, which have anti-aging, anti-tumor, antioxidant, anti-inflammatory, antibacterial and antiviral effects (Alvarez-Suarez, Giampieri, & Battino, 2013; Alvarez-Suarez, Gonzalez-Paramas, Santos-Buelga, & Battino, 2010; Alvarez-Suarez, Tulipani, Romandini, Bertoli, & Battino, 2010; Alvarez-Suarez et al., 2012; Prasain, Wang, & Barnes, 2004). Types and contents of flavonoids in honey are important indices, reflecting its inherent quality. A good method is essential for determination of types and concentrations of flavonoids in honey sample to evaluate the quality of targeted honey (Jasicka-Misiak, Poliwoda, Deren, & Kafarski, 2012; Sergiel, Pohl, & Biesaga, 2014). However, the concentrations of flavonoids in real honey samples are extremely low, and the interferences of matrix are complex, which hinders direct analysis of flavonoids in honey. So, it is very important and necessary to develop a reliable method for the analysis of flavonoid contents in real honey samples.

Due to the low solubility of flavonoids in aqueous medium, various organic solvents such as methanol, ethanol, acetone, and ethyl

acetate have been commonly used as the extraction solvents. Many extraction methods are used, including heat reflux extraction (HRE), microwave-assisted extraction (MAE), pressurized liquid extraction (PLE), and ultrasound-assisted extraction (UAE), etc (Chen et al., 2007; Stalikas, 2007; Xiao, Han, & Shi, 2008; Xu et al., 2013). However, these methods usually require large amounts of solvent and long extraction time (Nam, Zhao, Lee, Jeong, & Lee, 2015). Solid-phase extraction (SPE) plays an important role in sample pretreatment, which has some advantages, such as high enrichment factor, rapid separation, low consumption of reagents, and easy operation. Furthermore, the sorbent can be recycled (Behbahani et al., 2013; Chen et al., 2007; Guo et al., 2013; Liu, Liang, Wang, Guo, & Liu, 2015; Liu et al., 2015; Tahmasebi & Yamini, 2012; Vidal, Parshintsev, Hartonen, Canals, & Riekkola, 2012). Therefore, SPE has been developed rapidly for the trace analysis of complex sample matrices (Liu, Guo, Wang, Liang, & Liu, 2015; Nam et al., 2015; Pardo et al., 2014; Tian, Qiao, & Row, 2013; Xiao et al., 2014). The type of sorbent material is the soul of SPE determining the selectivity, sensitivity, enrichment factor, and recovery of the method (Wang, Gao, Zang, Li, & Ma, 2012). So far, various SPE sorbents have been developed and widely used in many fields successfully solving lots of practical problems (Jak, Patel, & Mishra, 2004; Lemos et al., 2007; Rao, Praven, & Daniel, 2004). Among them, silica C18 is the most widely used sorbent, which has excellent performance in the extraction of hydrophobic compounds. Through our experiments, we

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disappointedly found commercial silica C18 sorbent cannot achieve efficient extraction of flavonoids. Consequently, to develop a new SPE sorbent is meaningful and necessary focusing on the efficient extraction of flavonoids from honey samples.

The disadvantage of silica C18 may be ascribed to its total reliance on hydrophobicity. The absence of polar groups in commercial silica C18 sorbents, however, hampers the hydrophobic interaction between sorbent and flavonoids with multiple polar groups. To that end, we put forward a novel absorbing material of carbamate-embedded triacontyl modified silica sorbent (Sil-CBM-C30). The ultra-long triacontyl (C30) renders sorbent higher lipophilicity compared to C18. The carbamate polar group is expected to not only improve the wettability of silica material, but also endow polarity-related interactions, such as hydrogen bonding and π - π interactions. Consequently, the purpose of this study is to verify the extraction behavior of the novel Sil-CBM-C30 sorbent. Myricetin, quercetin, luteolin, kaempferol and isorhamnetin are selected as the model analytes to evaluate its adsorption capacities. Meanwhile, the comparisons between Sil-CBM-C30 and commercial silica C18 are to be conducted to reveal their differences of extraction performances.

2. Experimental

2.1. Reagents and materials

The parameters of porous silica particles were 15 μm (average diameter), 16 nm (pore size), 150 $\text{m}^2 \text{g}^{-1}$ (specific surface area) and they were synthesized using polymerization-induced colloid aggregation method in our laboratory. The volume of SPE cartridges was 3 mL and pore size of polyethylene sieve plate was 5 μm , which were all purchased from Shenzhen Biocomma Biotech Corp. (Shenzhen, China). The model of Welch[®]C18 SPE cartridge was 200 mg sorbent in 3 mL cartridge and they were purchased from Welch Materials, Inc. (Tianjin, China). Triacontanol (99%) was purchased from Nitritopper Biotechnology Co. Ltd. (Changsha, China). Isocyanatopropyltriethoxysilane (ICPTES) (98%) and triethylenediamine (DABCO) (99%) were purchased from Sun Chemical Technology Co., Ltd. (Shanghai, China). Ultrapure water (18.3 $\text{M}\Omega \text{cm}$ at 25 $^{\circ}\text{C}$) was produced by a Millipore Direct-Q 3 UV water purification unit. Myricetin, quercetin, luteolin, kaempferol and isorhamnetin were all purchased from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). The structures of the five flavonoids were shown in Fig. 1. In the analysis of real

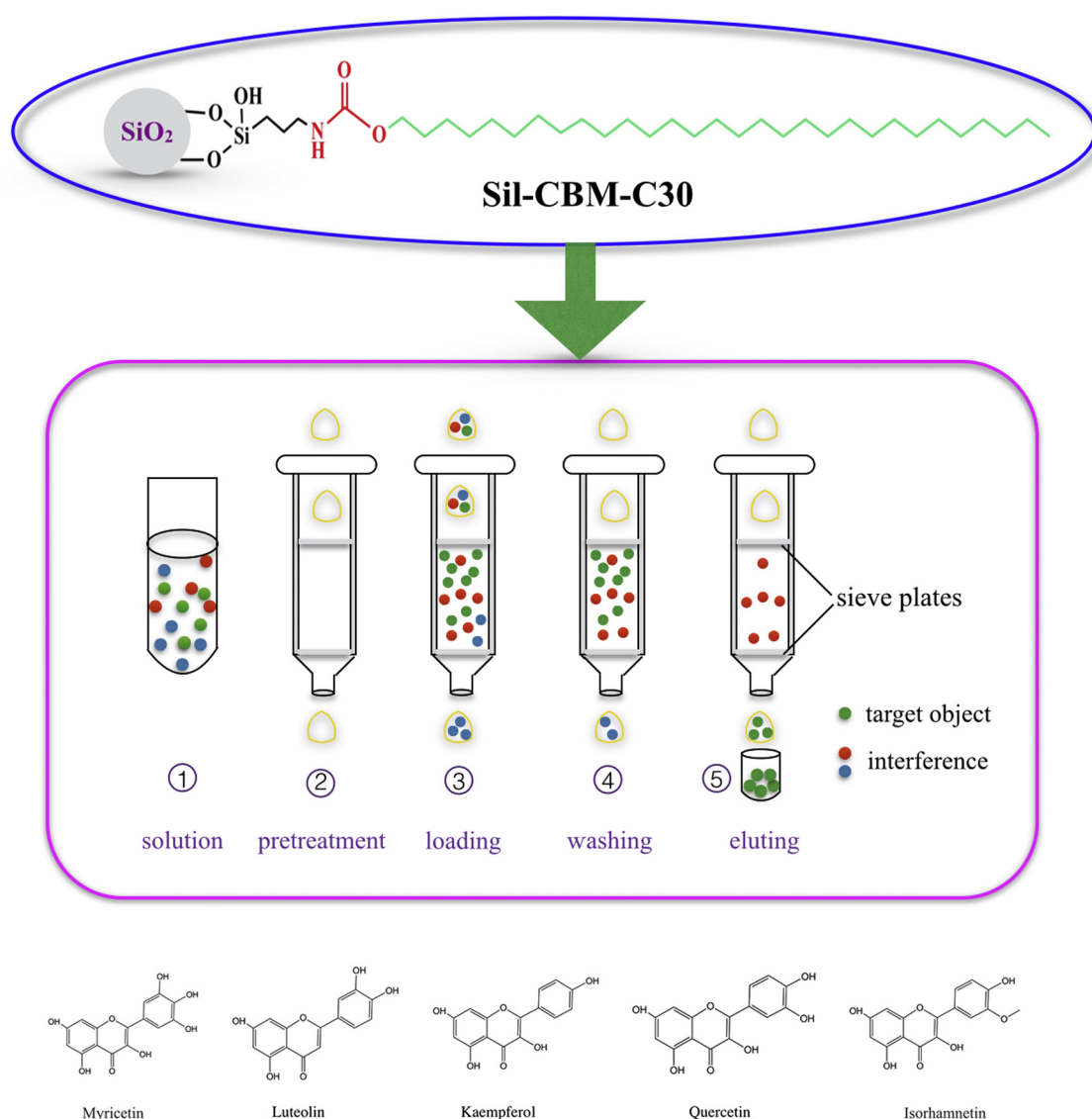


Fig. 1. Schematic diagrams of SPE extraction process and the structures of the five flavonoids.

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