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Analytical Methods

Vortex assisted deep eutectic solvent (DES)-emulsification liquid-liquid microextraction of trace curcumin in food and herbal tea samples

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ABSTRACT

We developed a new microextraction method for separation and preconcentration of curcumin using deep eutectic solvent known as green solvent. Deep eutectic solvent (DES) formed by mixing of choline chloride and phenol was used as an extraction solvent in microextraction study to extract the curcumin at pH 4.0. The curcumin concentration in enriched DES phase was analyzed by UV–Visible spectrophotometer. The effect of parameters such as pH, mol ratio of DES composition, volume of DES, volume of tetrahydrofuran (THF) and sample volume were examined. Interference effects of matrix components were investigated. The preconcentration factor was 12.5. The detection limit of method (n = 10) was 2.86 μg L^{-1} and the relative standard deviation (RSD, n = 8) was 1.8%. The method was successfully applied to determination of curcumin in food and herbal tea samples. The mean recoveries were between 96% and 102% and standard deviations were found in the range of 1–6%.

1. Introduction

Curcumin (E100) is isolated from the rhizomes of turmeric, which belongs to the ginger family, Zingiberaceae. Turmeric comes from polyphenolic pigments known as curcuminoids. Curcuminoids comprise mainly of mixtures of curcumin (~77%), demethoxycurcumin-DEMC (~17%) and bisdemethoxycurcumin-BDMC (~3%). Curcumin found in turmeric is considered to be the most active (Gupta, Kismali, & Aggarwal, 2013). Curcumin is the most important fraction of turmeric (Curcuma longa) used for the prevention and treatment of various malignant diseases such as cancer, diabetes, allergies and other chronic illnesses, due to its anti-oxidant, anti-inflammatory, anti-microbial, anti-parasitic and anti-cancer activities. Phenolic compounds are generally used in food industry to increase the quality and the nutritional values of foods. Even curcumin has low water-solubility, it has been used as a nutritional supplement like capsules or syrups (Asai, Nakagawa, & Miyazawa, 1999), cosmetic product like face creams (Miquel, Bernd, Sempere, Diaz-Alperi, & Ramirez, 2002), food coloring in cheese, butter and other foods (Lee & Choung, 2011; Jayaprakasha, Rao, & Sakariah, 2005), spice and used for curative purposes (Modasiya & Patel, 2012) and used for as herbal tea. It is widely used as a spice in South Asian and Middle Eastern countries. Many South Asian countries also use it as antiseptic and antibacterial agents for cuts and burns (Prasad & Aggarwal, 2011). A large number of investigation published on the beneficial effects of curcumin exposed that this natural product can be used for prevention and treatment of some important diseases such as antibacterial, antifungal, anti-inflammatory, anti-tumor, antioxidant, anti HIV and anticancer (Negi, Jayaprakash, Jagan, & Sakariah, 1999; Apisariyakul, Vanittanakomm, & Buddhasukh, 1995; Wu, 2004; Ruby, Kuttan, Dinesh, Rajasekharan, & Kuttan, 1995; Mazumder et al., 1997; Wilken, Veena, Wang, & Srivatsan, 2011; Chang et al., 2014; Bahrani, Ghaedi, Mansoorkhani, & Ostovan 2017). Some studies on curcumin reveals that curcumin will also be an important treatment for Alzheimer's disease (Progressive Neurodegenerative Disorder) (Mishra & Palanivelu, 2008).

Some analytical applications have been described using thin layer chromatography (TLC) densitometry (Pothitirat & Gritsanapan, 2005), high-performance liquid chromatography (HPLC) (Li et al., 2009; Wichitnithad, Jongaroonngamsang, Pummangura, & Rojsitthisak, 2009), high-performance thin-layer chromatographic (HPTLC) (Paramasivam, Poi, Banerjee, & Bandyopadhyay, 2009; Pathania, Gupta, & Singh, 2006), liquid phase mass spectrometry (Herebian, Cho, Abd El-Aty, Shim, & Spiteller, 2009; Yang, Lin, Tseng, Wang, & Tsai, 2007), matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI– TOFMS) (May, Tourkina, Hoffman, & Dix, 2005) and spectrofluorimetry (Navas Diaz and Ramos Peinado, 1992) for identify of curcumin and/or determination of curcumin content in some matrixes. But, most of these instruments are generally expensive and

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can't be found in many laboratories. Therefore, more simple, rapid and economic methods are needed to determine the curcumin. Spectrophotometry is the most used simple and cheap technique. Spectrophotometry is distinguished by its low cost and the simplicity of its apparatus (Soylak, Divrikli, Elci, & Dogan, 2001; Turkoglu, Soylak, & Colak, 2002).

In analytical process, separation/preconcentration methods are used as sample preparation methods for determination of trace level analyte in complex matrix. The sample preparation steps consist of isolation and enrichment of target analyte from sample matrix. Therefore, more sensitive determinations can be carried out applying of separation and preconcentration methods. Solid phase-microextraction (SP-ME) and liquid phase-microextraction (LP-ME) methods have recently been used as a new separation/ preconcentration procedures in extraction studies.

Microextraction methods are more miniaturized, easy and economic than classical solid and liquid phase extraction methods. Only a few micro liters of organic solvent and very little adsorbent are needed to extract analyte from the aqueous samples in these techniques. In dispersive liquid liquid-microextraction (DLL-ME) studies, extraction phase with high or low density and a disperser solvent such as methanol, acetone, acetonitrile and tetrahydrofuran in only micro liter volumes are added to the sample solutions to extract the target analyte to the extraction phase from aqueous phase. A cloudy solution is formed and so, the formation of small droplets in the medium is achieved. After centrifugation procedure of the cloudy solution, the amount of analyte extracted to the extraction phase is determined using an appropriate technique (Rezaee, Yamini, & Faraji, 2010).

There is a growing demand for the development of more environmentally friendly procedures in analytical studies. Recently, deep eutectic solvents (DESs) have begun to attract interest as a novel green solvent types in some applications. DESs are superior in terms of the availability of materials, the ease of synthesis and the low toxicity. Eutectic mixtures are obtained by mixing of two or three safe component that are capable of associating with each other through mostly hydrogen bonding, occasional electrostatic forces, and van der Waals interactions (Zhao et al., 2015; Zhang, Vigier, Royer, & Jerome, 2012). DESs are prepared using a quaternary ammonium salt (QAS) and hydrogen-bond donor (HBD) such as aminoacids, organic acids, sugars, polyalcohols, etc. in different rate. The melting point of deep solvents is lower than that of each individual component. Choline chloride is widely used as nontoxic QAS in DES. Choline defined as B vitamin (water-soluble) is also widely used as an animal feed supplement. The studies have shown that the type of QAS and HBD and the mole ratio of compounds has a significant effect on the properties of the studies (Smith, Abbott, & Ryder, 2014). DES have been used for many applications in several fields of science and technology. Some of them are organocatalysis (Brenna et al., 2016), electrochemistry (Abbott, Ttaib, Frisch, McKenzie, & Ryder, 2009), synthesis of nanomaterials (Oseguera-Galindo, Machorro-Mejia, Bogdanchikova, & Mota-Morales, 2016), biotransformations (Domínguez de María & Hollmann, 2015), molecular biology and separation and purification of some natural products in biotechnological applications (Li et al., 2016).

Herein, a novel VA-DES-ELLME (vortex assisted-DES-emulsification liquid–liquid microextraction) procedure has been applied for the first time to separate and preconcentrate the trace level of curcumin before UV–vis spectrophotometric determination.

2. Experimental

2.1. Apparatus

A Hitachi UH 5300 Double Beam Spectrophotometer (Hitachi, USA) has micro-sampling cuvette system) was used to measure curcumin concentration. To check the accuracy of the developed VA-DES-ELLME method, real samples were also analyzed by high performance liquid chromatogragpy (HPLC) (Agilent 1260) equipped with a 1260 DAD detector and a 1210 Quat solvent delivery system at Technology Research & Application Center (TAUM), Erciyes University, Kayseri, Turkey. Chromatographic separation was accomplished using a 250 × 4.6 mm (Particle size: 5 μm) C_{18} column (ACE, Scotland). Curcumin in last phase quantified by isocratic HPLC method using ultra violet (UV) detection at a wavelength of 428 nm. A 25 μL of last phase was injected onto a reversed-phase column and eluted with a mobile phase containing a mixture of methanol:acetonitrile:acetic acid :water (23:41:1:36, v/v/v/v).

Vortex mixer (VWR international model, Germany) was used as auxiliary apparatus for extraction of curcumin from aqueous phase to deep eutectic phase. A Sartorius PT-10 model pH meter with glass-electrode was used for pH adjustments of sample solutions (Sartorius Co., Goettingen, Germany). An ALC PK 120 model centrifuge (Buckinghamshire, England) was used to form the separated extraction phase.

2.2. Reagents

Ultra pure water purified through reverse osmosis (0.055 μS cm^{-1}, Millipore) was used as the working medium. All reagents used were of at least analytical grade and no need to additional purification THF was purchased from Merck (Darmstadt, Germany).

Choline chloride, ChCl (Alfa Aesar, Karlsruhe, Germany) as a quaternary ammonium salts and phenol (Sigma St. Louis, MO, USA) as a hydrogen bond donor were used for formation of deep eutectic solvent (DES). The components of DES were mixed in a beaker and then stirred at room temperature until a clear liquid was formed about 5 min.

2.3. VA-DES-ELLME procedure

The schematic diagram of the presented VA-DES-ELLME procedure given in Fig. 1. The curcumin standard solution aliquot volumes were pipetted into 50 mL centrifuge tubes and mixed with 2 mL of phosphate buffer solution at pH 4. 400 μL of DES (1 ChCl: 4 Phenol) used as a water-miscible extraction solvent was injected rapidly into a sample solution to the sample solution to form a homogeneous solution. Then, 400 μL of THF as an emulsifier agent was injected into the solution and at this stage a cloudy solution, which prove the formation of insoluble self-aggregation in nano and molecular dimensions was formed. The cloudy solution was subjected to ultrasonication for 2 min to guarantee well distribution of DES droplets in aqueous phase, which cause the extraction of curcumin. The separation of DES phase from aqueous phase was accomplished by centrifugation at 4500 rpm for 5 min. The water phase was discarded with a syringe and the last volume of DES rich phase containing curcumin was completed to 1 mL with ethanol. The curcumin concentration in the last volume was analyzed by UV–Vis spectrometer at 425 nm (λ_{max}). The same steps were used for the blank solutions.

2.4. Analysis of real samples

Different real samples that contain curcumin were analyzed to examine the accuracy of the curcumin microextraction method. Turmeric liquid extract was purchased from a local pharmacy. Sample was diluted with pure water appropriately and then; the addition/recovery test was performed using 4 mL of the diluted sample.

Herbal tea samples were purchased from a local market. It is necessary that to determine water soluble levels of curcumin due to people are consumed it as herbal tea extract on boiled water. 1 packet of teas (2 g) was extracted with 100 mL boiling demineralized water. After 15 min, the extract was filtered and then, 1 mL concentrated HNO_3 was added to the solutions for stabilizing the solutions. After centrifugation, addition /recovery test was applied to the 5 mL of tea samples according to the VA-DES-ELPME procedure developed and