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Analytical Methods

Liquid-phase microextraction combined with gas chromatography mass spectrometry for rapid determination of nicotine in one-drop of nightshades vegetables and commercial food products

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ABSTRACT

A simple, rapid and sensitive ultrasound-assisted hollow fibre liquid-phase microextraction (UA-HF-LPME) is evaluated for the determination of nicotine in one-drop of nightshade vegetables and some of the commercial food products. The optimum extraction of nicotine was obtained by using 1.5 μL as an extracting solvent in 1.0 cm of hollow fibre for 10 min extraction time with addition of salt. The calculated calibration curves showed a high level of linearity in the range 2–100 ng g^{-1} with correlation coefficients >0.998. The limit of detection (LOD) for the target analyte was found to be in the range of 0.2–0.5 ng g^{-1} and the relative standard deviations (RSD) of 2.3–4.5% were obtained. The results showed that under the optimised experimental conditions, the method showed good sensitivity and relative recoveries, as well as advantages such as linearity, simplicity, low cost and high feasibility. The extraction performance of present method to the target compound was also compared with drop-to-drop solvent microextraction (DDSME) and we found that the present approach showed better extraction efficiency of target molecule from sample solution. Finally, the proposed method was successfully applied for the determination of nicotine in nightshade vegetables (potatoes, tomatoes, peppers and eggplants) and commercial food products (tomato sauce, tomato juice, and pepper sauce).

1. Introduction

Nicotine is a colourless to pale yellow oily base with acrid burning taste. The compound is a very hygroscopic and turns brown on exposure to air or light. Nicotine (3-(1-methyl-2-pyrrolidinyl) pyridine) is a clear, naturally occurring liquid found in several species of plants. Nicotine has been detected in potatoes, tomatoes, eggplants, and sweet peppers, all food plants and members of the large family, Solanaceae. The nicotine levels are extremely low, 10 μg/kg, in fresh potatoes, tomatoes and sweet peppers. In recent years, several different nicotine replacement products, including chewing gum and transdermal patches, have been marketed as a smoking cessation aids in the United States and many other countries (Le Houezec, 2003; Siegmund, Leitner, & Pfannhauser, 1999). The body's response to nicotine is immediate and causing short-term increases in blood pressure, heart rate, and blood flow from the heart. Nicotine also causes arteries to narrow, while carbon monoxide reduces the amount of oxygen in the blood. Smoking can cause chronic lung disease, coronary heart disease, and stroke, as well as cancer of the lungs, larynx, oesophagus, mouth, and bladder (Law & Tang, 1995; Muramatsu, Umemura, Fukui, Arai, & Kira, 1987; National Research Council, 1986; US Department of Health & Human Services, 1988). Thus, the determination of nicotine in vegetable samples has been a subject of growing interest due to the adverse effect of smoking on human health.

The most frequently used analytical techniques, spectrophotometry (Willits, Swain, Connelly, & Brice, 1950). enzyme-linked immunosorbent assay (ELISA) (Bjercke et al., 1986), gas chromatography (GC) (Cai, Liu, Lin, & Su, 2003; Djordjevic, Bush, Gay, & Burton, 1990), gas chromatography coupled to mass spectrometry (GC–MS) (Dimich-Ward, Gee, Brauer, & Leung, 1997; Kintz, Ludes, & Mangin, 1992; Trundle & Skellern, 1983), high-performance liquid chromatography (HPLC) (Dash & Wong, 1996; Sellergren, Zander, Renner, & Swietlow, 1998), capillary electrophoresis (Yang & Smetena, 1995) have been reported for the determination of nicotine and its metabolites in various type of samples. Prior to instrumental analysis, separation and preconcentration of analytes are required in order to remove the interferences and to obtain the high sensitivity of the method applied for determination of targeted compound. Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are traditional methods for separation and preconcentration of analytes from complex sample matrices, where the large amount of organic solvents are used and also time consuming

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steps (EPA Method 8041, 1995; Marczenko, 1986). Liquid-phase microextraction (LPME) is a novel miniaturized sample preparation technique that has gained extensive attention in analytical chemistry (Jeannot & Cantwell, 1996; Liu & Dasgupta, 1996). It is a simple, low cost and fast extraction technique that incorporates sampling, concentration and sample introduction into a single step. First in 1996, Das Gupta and Cantwell demonstrated the separation and preconcentration of analytes in single drop of organic solvent from aqueous solution and termed the technique as a single drop microextraction (SDME). Then Pedersen-Bjergaard and Rasmussen (1999) introduced the hollow fibre liquid-phase microextraction (HF-LPME) where the organic solvent is put into the hollow fibre for isolation and concentration of analytes. This technique gave higher sensitivity and better precision because the organic phase is protected by a fibre and can avoid the dissolution of the organic phase observed in the SDME technique. However, all these sample preparations require more amount of sample solution (≈1–10 mL) and it is better to have a small volume of sample in the economical point of view. Recently, drop-to-drop solvent microextraction (DDSME) has been developed where the micro amount of sample solution (15–30 μL) is being used for the extraction of analytes from biological and food samples (Shrivas & Wu, 2007; Wu, Yen, & Chin, 2006). However, the enrichment factor obtained by this technique for the extraction of biological sample is not good due to the short extraction time. Thus, the method is modified very little by using hollow fibre-assisted with ultrasound irradiation during the extraction of analyte molecules from sample solution. Thus, this technique best fits to separate and preconcentrate the analytes from nightshade vegetable and commercial food products. The parameters which affect the extraction efficiency of nicotine from sample solution are investigated.

2. Experimental

2.1. Reagents and solution preparations

The entire reagents used were of analytical reagent grade. Toluene and iso-propanol were purchased from Mallinckrodt (Paris, KY, USA). Sodium chloride, chloroform, iso-butene, sodium chloride and n-hexane were purchased from Merck (Darmstadt, Germany). About 10 μL microsyringe (10F, SGE Australia) with blunt tip was used for the UA-HF-LPME based extraction of analytes from sample solution. All the extractions were carried out using an accurel Q3/2 polypropylene hollow fibre membrane (Wuppertal, Germany) with a 0.2 μm pore size, 600 μm internal diameter and 200 μm wall thickness. An ultrasonic bath (Branson-200, Taiwan) was used for the ultrasonication process. The generator of this apparatus has an output of 30 W and frequency of 50/60 kHz. A hollow fibre was cut into 1.0 cm segments and the approximate internal volume of each segment could contain 2.5 μL of organic solvent for the extraction of analytes. The hollow fibre was ultrasonically cleaned in acetone and air-dried before use. Stock solution of nicotine was prepared by dissolving 1 mg of substance in 10 mL of methanol. Working standard solutions were prepared from diluting the stock solution with deionised water.

2.2. Sample collection and preparation

Different types of nightshade vegetables including potatoes, tomatoes, eggplants, peppers, etc., were collected in prewashed polyethylene bottles from local market of Rajnandgaon, India during March, 2008. The samples were washed with deionised water in order to remove the external contamination. About 10 g of each sample was crushed with mortar and pestle by manual operation. The juice was separated from fruits with a mechanical press and centrifuged in order to clarify the sample solution. A small amount of vegetable juice was sufficient for the determination of nicotine in these samples. The commercial products of potato, tomato and pepper were also collected from the local market for the analysis of nicotine. A 5 g of commercial food products was diluted in deionised water according to the concentration of nicotine present in the samples. Separated sample was filtered with Whatmann No. 41 filter paper and 30 μL aliquot of sample solution was used for the determination of nicotine using a UA-HF-LPME/GC–MS technique.

2.3. Procedure for the extraction of nicotine from sample solution by using UA-HF-LPME in GC–MS

A 10 μL microsyringe filled with 1.5 μL of organic solvent (acceptor phase) was inserted into the hollow fibre to impregnate the acceptor phase. Next, the other end of the segment was heat-sealed by a hot nipper. A 100 μL vial (containing 30 μL of nicotine, 10 ng g^{-1}) was placed on ultrasonic water bath for the extraction of target compound. The organic solvent in the syringe was injected completely into the hollow fibre. The fibre, together with the tip of microsyringe needle was placed into the sample solution. Ultrasonic bath was switched onto start the extraction, allowing the sampling process for 10 min. After the completion of extraction time, the solvent in hollow fibre was retracted back into the microsyringe and the hollow fibre was discarded. The acceptor phase enriched with nicotine was injected into a GC system for analysis of nicotine. The schematic diagram for the performance of UA-HF-LPME is shown in Fig. 1.

2.4. Procedure for the extraction of nicotine from sample solution by using DDSME in GC–MS

The procedure for the DDSME separation and preconcentration of analytes from sample solution was described elsewhere in the literature (Shrivas & Wu 2007; Wu et al., 2006). A 30 μL sample solution containing nicotine (10 ng g^{-1}) was added into a 100 μL vial. A specified volume of organic solvent was drawn into the microsyringe before the extraction. The microsyringe fixed with stand and clamps was then inserted through the septum of the sample vial to extract the nicotine from sample solution. The plunger was pushed down to expose the 1.5 μL of organic solvent into the aqueous sample solution for 10 min extraction time. When the extraction time was finished, the drop was retracted back into the microsyringe and injected directly into the GC inlet for further analysis.

2.5. Gas chromatography mass spectrometry

A Varian 3800 GC/Saturn 2000 ITMS system fitted with a SPB-5 column (30 m, 0.25 mm i.d., 0.25 μm film thickness) (Supelco,

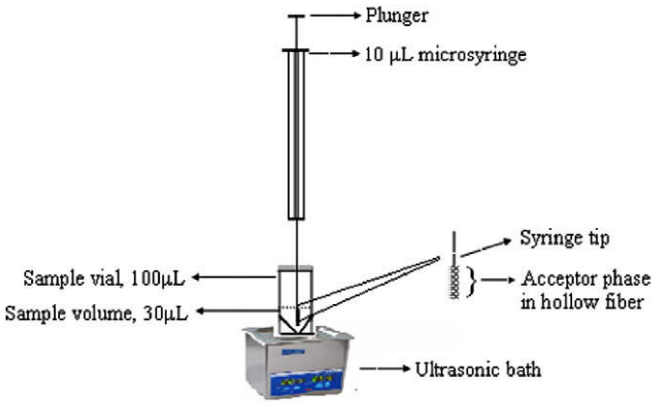

Fig. 1. Schematic diagram for the operation of UA-HF-LPME.