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Comparison of fully-automated headspace single drop microextraction and headspace solid phase microextraction techniques for rapid analysis of No. 6 solvent residues in edible oil

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ABSTRACT

Rapid, automated and solvent-free are the developing trends of sample preparation technique. In this study, fully-automated microextraction techniques, including headspace solid-phase microextraction (HS-SPME) and static headspace single drop microextraction (HS-SDME), coupled with GC/MS were investigated and compared for rapid analysis of No. 6 solvent residues in edible oil. With the use of Gerstel MultiPurpose autosampler, sample extraction, injection and analysis procedures can be automatically carried out. Under the optimized extraction conditions, the developed methods presented shorter analysis time, lower limits of detections (LODs) and satisfied precisions (RSDs <6.8%). The LODs of HS-SPME (0.1 $\mu g \cdot g^{-1}$) and HS-SDME (1 $\mu g \cdot g^{-1}$) are much lower than traditional headspace (HS) method (7 $\mu g \cdot g^{-1}$). Moreover, the LOD of the automated HS-SPME–GC/MS method can be lowered to 0.005 $\mu g \cdot g^{-1}$ under splitless mode, due to the solvent-free and less sample introduction nature, and satisfied results were obtained for the analysis of edible oil sample.

1. Introduction

Sample preparation step is the key process in the analysis of food sample, which involves an extraction procedure for the isolation and enrichment of target analytes from sample matrix. Extraction technologies have been developed to address the need for a reduction in solvent use, miniaturization, and automation [1]. As solventless or solvent-free technique, solid-phase microextraction (SPME) and single drop microextraction (SDME) have been widely applied on the sampling and sample preparation of complex matrix samples [2–6], especially in food sample analysis [7–9].

An important practical aspect of implementing the microextraction in analytical laboratories is the automation of these techniques [10]. Over the past decade, the automation and optimization of SPME and SDME have obtained a lot of attention, which greatly enhanced and extended their applications [11–15].

The analysis of contaminations in edible oil is an important issue in the quality controls, due to the potential risks for public health. There have been some researches concentrated on esters of monochloropropanediol in edible oil [16], lard contamination adulterated in some edible oils [17], polycyclic aromatic hydrocarbons in edible oils [18], and solvent residues [19].

Solvents are widely used in the extraction of edible oils and the synthesis and crystallization of pharmaceuticals. In China, solvent for edible oil extraction is called No. 6 solvent oil, which is a mixture of light alkanes (C6), and separated from the raffinate oil [20]. Hexane is the main component of No. 6 solvent oil. Because of its high fat-solubility, hexane can be easily enriched in the human body and has toxicity to the nervous system. Hence, it is necessary to determine residual solvents in edible oils to confirm that the concentration levels of these compounds are lower than the acceptable levels recommended by standard limitation of China [21].

In general, static headspace (HS) coupled with gas chromatography/mass spectrometry (GC/MS), is an appropriate method for the analysis of solvent residues [22,23]. In the standard method for the analysis of hygienic of edible oils of China, HS-GC is the recommended sample preparation method [24], and the European Pharmacopoeia also recommends gas chromatographic methods with static headspace injection to identify solvent residues in pharmaceuticals [25]. However, compared with HS-SPME and HS-SDME, HS has lower selectivity and sensitivity [26].

In HS-SPME and HS-SDME, the extraction phase, with either solid or liquid sorbents, is exposed to the headspace above a sample to trap and concentrate analytes from a static or dynamic HS process [26]. The

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preconcentration of the analytes helps to reduce the time consumption and achieve a lower limit of detection than HS, and the automation of HS-SPME and HS-SDME will make the whole analysis process more convenient.

In the present work, fully-automated microextraction techniques including HS-SPME and HS-SDME were established and applied to the analysis of No. 6 solvent residues in edible oils. Parameters influencing the extraction efficiency, such as extraction phase, extraction time and temperature as well as sample incubation time, were optimized, and the sensitivities and analysis time of HS-SPME, HS-SDME and traditional HS methods were compared.

2. Experimental section

2.1. Chemicals and supplies

The standard solution of No. 6 solvent oil (dissolved in N,N-dimethylacetamide, 10 mg/mL) was purchased from Academy of State Administration of Grain (Beijing China). N,N-Dimethylacetamide (A.R.) was purchased from Guangzhou Chemical Reagent Company (Guangzhou, China). 1-octanol (99%) and undecane (99%) were purchased from Anpel Company (Shanghai, China).

SPME fibers, 65 μm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) and 100 μm Polydimethylsiloxane (PDMS), were obtained from Supelco (Bellefonte, PA, USA). Hamilton Model 701N 10 μL syringe (26s gauge, style bevel tip for autosampler) was purchased from Hamilton (Reno, NV, USA). Headspace 1 mL syringe was purchased from Gerstel (Gerstel GmbH, Mülheim an der Ruhr, Germany). The 20 mL vials with magnetic snap caps and PTFE coated silicone septa (Supelco, Bellefonte, PA, USA) were used for the automated analysis.

2.2. Instruments

The experiments were carried out on an Agilent 6890N GC equipped with a 5975 MSD (Agilent Technologies, CA, USA), and a split/splitless injector was used for sample introduction. Chromatographic separation was carried out with a HP-5MS capillary (30 m × 0.25 mm × 0.25 μm). The automated sample preparation procedure was performed with a Gerstel MultiPurpose autosampler (MPS, Gerstel GmbH, Mülheim an der Ruhr, Germany).

In GC analysis, injector temperature was set at 250 °C. Helium was used as carrier gas at a constant flow rate of 1.2 mL/min. The oven temperature was set at 50 °C for 10 min. As mentioned above, No. 6 solvent oil is a mixture of light alkanes (C6). In this work, five substances were detected in the standard solution of No. 6 solvent oil, which were 2-methylpentane, 3-methylpentane, n-hexane, methylcyclopentane and cyclohexane.

2.3. Headspace procedure (standard method of China)

Fifty-microliter standard solution of No. 6 solvent oil (10 mg/mL) was dissolved in 5 g edible oil as the working solution (10 μg/g). For headspace, the 20 mL sample vial, which contained the working solution, was incubated in the agitator for 30 min at 50 °C. After that, 100 μL headspace gases were transferred into the GC injector for analysis with headspace syringe. The procedure was conducted by the autosampler.

2.4. Automated HS-SPME procedure

A schematic diagram of automated HS-SPME procedure was shown in Fig. 1. The 20 mL sample vial, which contained the working solution, was placed in the sample tray (A), and then was transferred by mechanical arm of the autosampler from the sample tray to the agitator with a temperature controller, shaken for 2 min at 30 °C 500 rpm (B). Afterward, the SPME fiber fixed on the mechanical arm was exposed to headspace of the sample vial for extraction (C1). After 10 min extraction time, the fiber was withdrawn and introduced into the GC injector for desorption and analysis. The entire procedure was conducted by the autosampler.

2.5. Automated HS-SDME procedure

For HS-SDME, the automation program was modified based on the program reported in 2007 [13]. The schematic diagram of automated HS-SDME procedure was shown in Fig. 1. The 20 mL sample vial, which contained 5 g 10 μg/g No. 6 solvent oil solution (dissolved in the edible oil), was placed in the sample tray (A), and then was transferred by mechanical arm of the autosampler from the sample tray to the agitator with a temperature controller, shaken for 4 min at 30 °C 500 rpm (B). The Hamilton 701 10 μL syringe (bevel tip), filled with

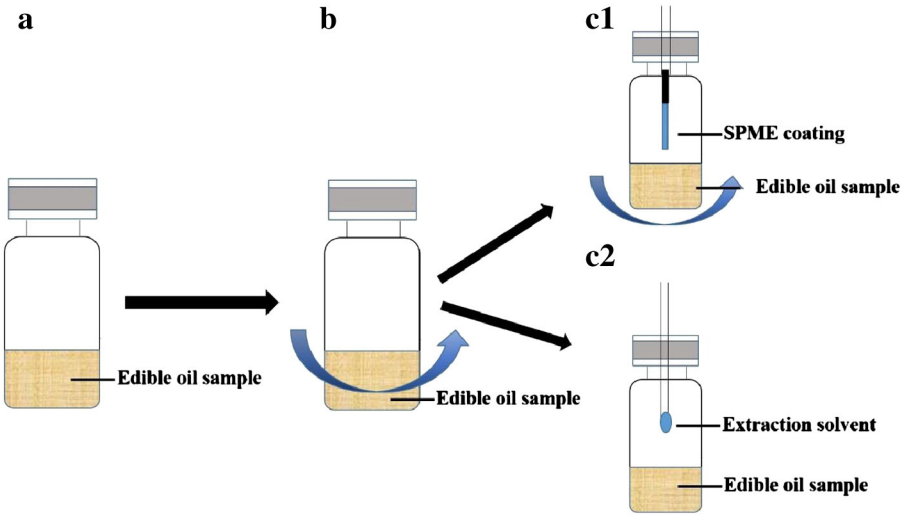

Fig. 1. The schematic diagram of automated HS-SPME procedure and HS-SDME procedure. (A) 20 mL vials were placed in the sample tray of autosampler; (B) the vial was transferred into the agitator shaken by the mechanical arm of autosampler; (C1) SPME fiber fixed on the mechanical arm was exposed in the headspace of the vial for extraction; (C2) extraction solvent was slowly exposed in the headspace of the vial for extraction.