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ScienceDirect
Talanta 71 (2007) 751–757
Talanta
www.elsevier.com/locate/talanta

Analysis of polycyclic aromatic hydrocarbons in solid matrixes by solid-phase microextraction coupled to a direct extraction device

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Received 7 March 2006; received in revised form 3 May 2006; accepted 12 May 2006
Available online 19 June 2006

Abstract

Analysis of polycyclic aromatic hydrocarbons (PAHs) standards in model systems was carried out by solid-phase microextraction (SPME) coupled to a direct extraction device (DED) and subsequent gas chromatography/mass spectrometry (GC/MS). PAHs standard was added to gelatine systems at different concentrations. Extraction process was carried out by SPME-DED at 25 °C for 60 min. Polydimethylsiloxane 100 μm (PDMS 100 μm), divinylbenzene/polydimethylsiloxane 65 μm (DVB/PDMS 65 μm) and polyacrilate 85 μm (PA 85 μm) SPME fibres were tested. SPME-DED satisfactorily extracted PAHs with a molecular weight (MW) lower than 206 from the gelatine system. All fibres showed a good reproducibility (residual standard deviation (RSD) between 5.24% and 18.25%), linearity (regression coefficients between 0.8959 and 0.9983) and limit of detection (LOD) (between 0.008 and 0.138 ng mL^{-1}). Presence of PAHs in different smoked meat products was also tested by SPME-DED. Different low MW PAHs were satisfactorily detected from all the foodstuffs studied. SPME-DED appears as a rapid, non-destructive technique for primary screening of low MW PAHs in solid matrixes.

Keywords: SPME; PAHs; Direct extraction; Model systems; Smoked foods

1. Introduction

The relation between the presence of polycyclic aromatic hydrocarbons (PAHs) in foodstuffs and the development of mutagenic and carcinogenic processes is well known [1]. The occurrence of PAHs in foods may result from their sorption from a contaminated environment (unprocessed foods) or from technological processes (processed foods) [2]. PAHs have been found in charcoal-broiled meat, smoked/grilled foods, fats and oils, plant materials, seafood, liquid smokes and beverages [3].

Most methodologies for analysis of PAHs in food systems are laborious, time consuming and need organic solvents. Moreover, the sampling step may deteriorate the quality of several solid foods. Solid-phase microextraction (SPME) is an alternative technique that can overcome some of these disadvantages. SPME integrates sampling, extraction, concentration and sample introduction in a simple process, and uses no solvent during extraction [4]. Previous studies have demonstrated the feasibility of SPME for analysing PAHs in different types of samples, such as environmental [5–7], biological [8,9] and foodstuffs [10]. Nevertheless, a portion of sample is also needed for SPME analysis.

In previous papers we have described the use of a direct extraction device (DED) [11,12], which enables the introduction of the SPME fibre in the core of solid matrixes, allowing the analysis of volatile compounds from solid foods with no or little deterioration of the product. Such device (Fig. 1) has an internal chamber in which the SPME fibre is exposed. This small chamber has several holes that allow volatile compounds to equilibrate between the solid matrix and the internal headspace of the DED.

Extraction of volatile compounds from dry cured hams and pâté in one step, without sampling and thus, with only minor or none physical damage of the foodstuffs by SPME couple to DED has been previously reported [11,12]. Moreover, Ventanas and Ruiz [13] effectively extracted volatile nitrosamines by SPME-DED from solid model systems.

The aim of this work was to study the feasibility of using SPME-DED for extraction of PAHs from solid matrixes

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doi:10.1016/j.talanta.2006.05.037

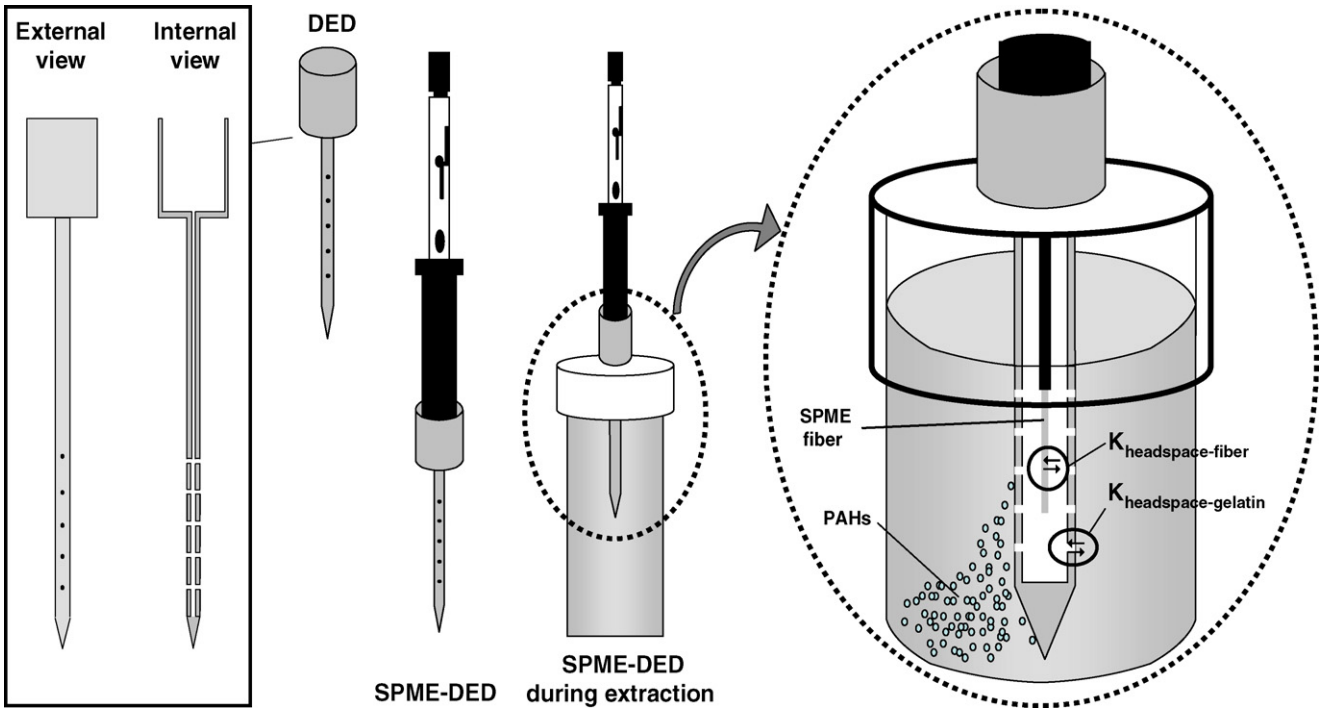

Fig. 1. Scheme of the use of SPME-DED in model systems of gelatine. An enlargement of a section of the gelatine shows the diffusion process of some PAHs from the matrix to the headspace of the DED. The equilibriums that are implied in the process are also showed.

mimicking solid foodstuffs and real smoked meat products and to compare different types of SPME stationary phases for extraction of these compounds from the model systems.

2. Experimental

2.1. Reagents and materials

PAHs standard was supplied by Sigma–Aldrich (QTM PAHs Mix, Sigma–Aldrich, St. Louis, USA). This solution contained 16 analytes: acenaphthene (AC), acenaphthylene (ACL), anthracene (AN), benz[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbFA), benzo[*ghi*]perylene (BghiP), 2-bromonaphthalene (2-BrNA), chrysene (CHR), dibenz[*ah*]anthracene (DBahA), fluoranthene (FA), fluorene (FL), indeno[1,2,3-*cd*]pyrene (IP), naphthalene (NA), phenanthrene (PHE) and pyrene (PY).

Methanol (HPLC grade) was obtained from Scharlau Chemie (Barcelona, Spain). Gelatine (300 bloom, A type) was supplied by Sigma–Aldrich (St. Louis, USA). SPME stationary phases were acquired from Supelco.

Smoked meats products were obtained in a small village from an area of Extremadura (Spain) in which home processing of this type of products is common. These products were: smoked tenderloin, smoked jowl, smoked dry cured sausage and smoked potato sausage. All of them had been directly exposed to the smoke for 30 days.

2.2. Preparation of PAHs standards

PAHs stock solution at 8 $\mu g\,mL^{-1}$ was prepared by diluting 4 μL of the PAHs standard (2000 $\mu g\,mL^{-1}$) in methanol.

PAHs standard working gelatines at different concentrations (0.1, 0.5, 1, 5 and 10 $ng\,mL^{-1}$) were prepared by addition of the appropriate volume of the PAHs stock solution to 32 mL of gelatine solutions contained in polypropylene tubes with polyethylene caps. Gelatine solutions (20%) were prepared by addition of the appropriate amount of gelatine to distilled water and microwave heating. The PAHs standard stock solution was added when the gelatine was at 60 °C. Working gelatines were immediately sealed, vortexed for 30 s and stored at 2–4 °C until analysis. Gelatines of each concentration were prepared in duplicate, except for the 10 $ng\,mL^{-1}$ ones, used for calculating the reproducibility, which were prepared in quintuplicate. Analysis of PAHs in gelatines by SPME-DED was carried out within 3 days after preparation.

2.3. SPME-DED extraction of PAHs

PAHs were extracted from gelatines by directly inserting the DED into the core of the gelatine and subsequent introduction of the SPME fibre into the DED following the procedure previously described [12]. In order to control the temperature, tubes containing the gelatines were kept in a thermostatised water bath at 25 °C. Extraction time was 60 min. Fig. 1 shows the DED, the way in which it is coupled to SPME, and how SPME-DED is used to extract PAHs from gelatines.

Different SPME stationary phases were tested: polydimethylsiloxane 100 μm (PDMS 100 μm), divinylbenzene/polydimethylsiloxane 65 μm (DVB/PDMS 65 μm) and polyacrilate 85 μm (PA 85 μm). Parameters studied for each fibre were: efficacy, reproducibility, linearity and limit of detection (LOD).

PAHs from smoked meat products were extracted following a procedure similar to that used for gelatines, directly inserting