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Determination of polycyclic aromatic hydrocarbons in food samples by automated on-line in-tube solid-phase microextraction coupled with high-performance liquid chromatography-fluorescence detection

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ABSTRACT

A simple and sensitive automated method, consisting of in-tube solid-phase microextraction (SPME) coupled with high-performance liquid chromatography-fluorescence detection (HPLC-FLD), was developed for the determination of 15 polycyclic aromatic hydrocarbons (PAHs) in food samples. PAHs were separated within 15 min by HPLC using a Zorbax Eclipse PAH column with a water/acetonitrile gradient elution program as the mobile phase. The optimum in-tube SPME conditions were 20 draw/eject cycles of 40 μL of sample using a CP-Sil 19CB capillary column as an extraction device. Low- and high-molecular weight PAHs were extracted effectively onto the capillary coating from 5% and 30% methanol solutions, respectively. The extracted PAHs were readily desorbed from the capillary by passage of the mobile phase, and no carryover was observed. Using the in-tube SPME HPLC-FLD method, good linearity of the calibration curve ($r > 0.9972$) was obtained in the concentration range of 0.05–2.0 ng/mL, and the detection limits ($S/N = 3$) of PAHs were 0.32–4.63 pg/mL. The in-tube SPME method showed 18–47 fold higher sensitivity than the direct injection method. The intra-day and inter-day precision (relative standard deviations) for a 1 ng/mL PAH mixture were below 5.1% and 7.6% ($n = 5$), respectively. This method was applied successfully to the analysis of tea products and dried food samples without interference peaks, and the recoveries of PAHs spiked into the tea samples were >70%. Low-molecular weight PAHs such as naphthalene and pyrene were detected in many foods, and carcinogenic benzo[*a*]pyrene, at relatively high concentrations, was also detected in some black tea samples. This method was also utilized to assess the release of PAHs from tea leaves into the liquor.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of over 200 different compounds containing two or more fused aromatic rings made of carbon and hydrogen atoms [1,2]. Most PAHs are chemically inert, hydrophobic, and soluble in organic solvents. PAHs are ubiquitous environmental pollutants, resulting from the incomplete combustion or pyrolysis of organic matter during industrial processing and various human activities [1]. These compounds are widely present in the environment due to their hydrophobic properties, allowing their adsorption onto atmospheric particles and direct deposition in sediments, soils and plants. Consequently, environmental PAHs can be introduced into the food chain by both plants and animals. Also, food can become contaminated during thermal treatments that occur in processes of food preparation and manufacture (drying and smoking) and cooking (roasting, baking, and frying) [1–3]. PAHs have been detected in various food samples, including tea [4], roasted coffee [5], fruits [6], vegetables [6,7], oils [8–12], milk [13–15], smoked cheese [16,17], smoked meat [18], and smoked fish [19–22], at ng/g concentrations. Food is the major source of exposure to environmental PAHs (>70%) in persons who are nonsmokers and nonoccupationally exposed [22–25]. The multiple sources of human exposure, however, make it difficult to assess the contribution due to food intake.

These contaminant PAHs are of considerable interest because some are highly carcinogenic and/or genotoxic in laboratory animals and have been implicated in breast, lung, and colon cancers in humans [1,26–28]. Based on epidemiological data and its mutagenicity, carcinogenicity, and mode of action, benzo[*a*]pyrene (BaP), originally classified as a probable human carcinogen (Group 2A), has been recently reclassified by the WHO International Agency for Research on Cancer (IARC) as a human carcinogen (Group 1). Dibenz[*a*,*h*]anthracene (DahA) is another Group 2A carcinogen, whereas chrysene, benz[*a*]anthracene

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(BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), and indenol[1,2,3-c,d]pyrene (IP) are possible human carcinogens (Group 2B) [1]. Thus, exposure to PAHs is a significant public health problem. Various recent epidemiological studies have also an association between dietary exposure to PAHs and an increased risk of some human cancers [26,29]. Legal regulation is limited, partly because of the difficulty of defining safe levels of these complex mixtures. To minimize harmful effects on human health, a European Union (EU) recommendation highlighted 15 PAHs as carcinogenic following the opinion of the Scientific Committee on Food. An EU regulation (Commission Regulation No. 208/2005) set limits only for BaP as a marker for the carcinogenic risk of PAHs. The threshold level for oils, edible fats, and fresh fish was set at 2 ng/g, the maximum level for smoked meat and fish products was set at 5 ng/g, and the levels for mollusks, bivalves, and infant foods were set at 10 ng/g. According to the opinion of the Scientific Committee on Food of the EU, which concluded that a safe threshold of exposure for PAHs in food could not really be defined, monitoring programs should not only control compliance with regulations, but should also control the actual presence of these different substances. Due to the recognized adverse effects of PAHs and the need for regulatory control, monitoring of their levels in food samples are important in evaluating the risks associated with human consumption of various foods. Therefore, a sensitive, selective, and simple method is needed to determine the presence and contents of PAHs in food samples.

PAHs in food samples have been analyzed by high-performance liquid chromatography (HPLC) with ultraviolet (UV) [2,4,10] or fluorescence detection (FLD) [2,5–8,13,16,19,20,23–25], gas chromatography–mass spectrometry (GC–MS) [9,12,14,15,17,18,21,30], and GC–MS–MS [11,22]. HPLC-FLD methods are sensitive and the most widely used assays, and GC–MS and GC–MS–MS methods are also specific and sensitive, with their use becoming increasingly widespread. GC–MS combined with the use of isotopically labeled internal standards ensures exact quantification and unambiguous structural identification [11]. Most of these methods, however, require sample preparation steps, such as extraction, concentration, and isolation, to enhance the sensitivity and selectivity of their detection. For example, liquid–liquid extraction [8,13,24,25] with several organic solvents, pressurized liquid extraction [5,11,21], gel permeation or open-column chromatography [4,6,18,24], and solid-phase extraction (SPE) [5,7,9,10,16,18,25] have been used as cleanup procedures. Most of these sample preparation techniques are complicated and time consuming, and require large volumes of organic solvents. Complicated pretreatment methods may introduce errors, and the use of large volumes of organic solvents may pose a health hazard to those performing the analyses and contributes to environmental pollution. In contrast, several solid-phase microextraction (SPME) techniques coupled with GC–MS have been developed for the determination of PAHs in head space or direct immersion [12,14,15,17]. This method is simple, consumes low volumes of solvents, and is superior in extraction efficiency. However, head space SPME cannot be applied to the extraction of high-molecular weight PAHs, and direct immersion of SPME fibers into the sample solution can pollute the fibers with sample matrix. Therefore, it is important to develop an efficient sample pretreatment method. The use of automation will reduce both labor and costs, and a routine analysis method will facilitate the processing of large numbers of samples.

In-tube SPME [31], using an open tubular fused-silica capillary column with an inner surface coating as the SPME device, is simple and can be easily coupled on-line with HPLC and LC–MS. In-tube SPME allows convenient automation of the extraction process, which not only reduces the analysis time, but also provides better accuracy, precision, and sensitivity than manual off-line techniques. We have already developed an in-tube SPME method, coupled with HPLC [32,33] and LC–MS [34–36], for determination of various compounds in food samples. The details of the in-tube SPME technique and its applications have been summarized in some reviews [37–39]. The present study was performed to develop an automated on-line in-tube SPME/HPLC-FLD method for determination of PAHs in tea products and dried food samples. Furthermore, the release of PAHs from tea leaves into the liquor was studied using this method.

2. Experimental

2.1. Materials

Fig. 1 shows the structures of the 15 PAHs examined in this study. Naphthalene (Nap), phenanthrene (Phe), anthracene (Ant) and pyrene (Pyr) were purchased from Nacalai Tesque (Kyoto, Japan). Acenaphthene (Ace), fluorene (Flu), fluoranthene (Flt), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*ghi*]perylene (BghiP), indeno[1,2,3-*cd*]pyrene (IP) and dibenz[*a*,*h*]anthracene (DahA) were purchased from Wako Pure

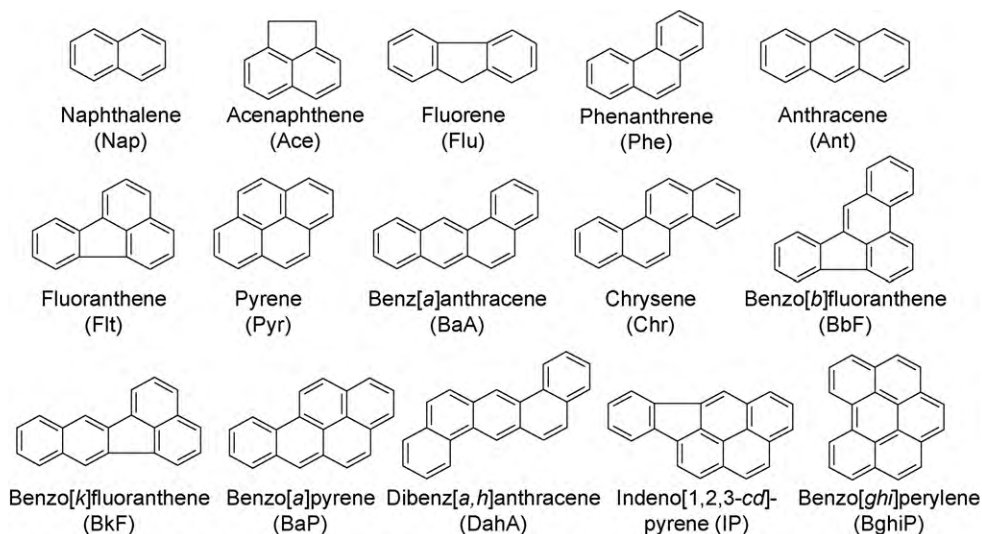

Fig. 1. Structures of the PAHs assayed in this study.

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