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Stir-bar supported micro-solid-phase extraction for the determination of polychlorinated biphenyl congeners in serum samples

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ABSTRACT

In present work, a new configuration of micro-solid phase extraction was introduced and termed as stir-bar supported micro-solid-phase extraction (SB-μ-SPE). A tiny stir-bar was packed inside the porous polypropylene membrane along with sorbent material and the edges of membrane sheet were heat sealed to secure the contents. The packing of stir-bar inside the μ-SPE device does not allow the device to stick with the wall or any corner of the sample vial during extraction, which is, however, a frequent observation in routine μ-SPE. Moreover, it enhances effective surface area of the sorbent exposed to sample solution through continuous agitation (motion and rotation). It also completely immerses the SB-μ-SPE device in the sample solution even for non-polar sorbents. Polychlorinated biphenyls (PCBs) were selected as model compounds and the method performance was evaluated in human serum samples. After extraction, samples were analyzed by gas chromatography mass spectrometry (GC–MS). The factors that affect extraction efficiency of SB-μ-SPE were optimized. Under optimum conditions, a good linearity (0.1–100 ng mL^{-1}) with coefficients of determinations ranging from 0.9868 to 0.9992 was obtained. Limits of detections were ranged between 0.003 and 0.047 ng mL^{-1}. Acceptable values for inter-day (3.2–9.1%) and intra-day (3.1–7.2%) relative standard deviations were obtained. The optimized method was successfully applied to determine the concentration of PCB congeners in human serum samples.

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1. Introduction

Despite of all major advancements in analytical instrumentation, sample preparation is an unavoidable step prior to instrumental analysis. It is because original samples are sometimes composed of matrix which is not compatible with the components of the instrument or too dilute that target compounds cannot be detected directly by the instrument or too dirty that matrix components can interfere with analysis. Sample preparation generally involves sample clean-up, removal of interferences and preconcentration of target compounds [1]. Solid-phase extraction (SPE) and liquid–liquid extraction (LLE) are most commonly used sample preparation methods but they consume large amounts of chemicals and hazardous organic solvents. Moreover, they are laborious because of extended multistep extraction procedures [2]. The trend has been shifting toward miniaturized sample preparation methods. Over the last two decades, number of microextraction methods have been introduced including solid phase microextraction [3], liquid-phase microextarction [4,5], dispersive solid phase extraction [6], dispersive liquid–liquid microextraction [7] and many of their modifications [8,9]. These methods overcome disadvantages of conventional SPE and LLE. In addition, these methods are comparatively simple, cost effective, efficient, green, and easy to perform.

Micro-solid phase extraction (μ-SPE) was introduced by Basheer et al., in 2006 [10]. Since then, μ-SPE has been extensively used in environmental [11,12], biological [13,14] and food [15,16] analysis. This approach involves packing of small quantity of sorbent material inside a porous membrane, whose ends are heat sealed. This sorbent containing bag is then placed inside the sample solution and allowed to tumble freely using magnetic stirrer. After extraction, the analytes are desorbed from the packed sorbent in suitable desorption solvent by ultrasonication. Although, in μ-SPE, a stir-bar is placed inside the sample solution to agitate the solution by magnetic stirring but it has been frequently observed that μ-SPE device sticks to the one wall of the sample vial or floats over the sample solution, which allows the μ-SPE device to extract only on the surface of the sample solution. Polypropylene (PP) is most commonly used membrane for fabrication of μ-SPE devices. Due to its hydrophobic nature [17], μ-SPE devices do not get enough wettability even after conditioning in the organic solvent for longer periods of time. This poor wettability, in turn, does not allow μ-SPE

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device to sink completely inside the sample solution. The device can completely sink only in the case when water penetrates inside the membrane and adsorbed by the sorbent [18]. However, such penetration and adsorption of water are not possible due to the hydrophobic PP membrane. As a result, μ-SPE device keeps floating near the surface. This can be seen in a figure of μ-SPE device given in a published work [19]. In order to solve this problem, we have proposed a simple modification in μ-SPE device where a tiny stir-bar is packed inside the μ-SPE device along with sorbent. In this way, packed stir-bar does not allow the membrane to float over surface or stick to any wall of the glass vial. In a recent paper, Naing et al. reported the use of a magnetic sorbent in μ-SPE to avoid the need of a separate stir bar [20]. In the present work, the inserted stir-bar prevents the μ-SPE device to be too buoyant, and allows the device to be in a continuous state of motion and rotation, which in turn increases the effective surface area of the sorbent exposed to the target compounds in the sample solution.

Although stir-bar sorptive extraction (SBSE), is a well-established micro-extraction technique but it has limitation that only few materials can be coated over the stir-bar. Thickness and stability of the coating are very critical in order to evaluate reproducibility of SBSE. Most commonly used PDMS coated stir-bars can only be employed for extraction of non-polar or weekly polar target compounds [21]. However, our proposed stir-bar supported micro-solid phase extraction (SB-μ-SPE), has flexibility for selection of sorbent. Sorbent can be selected according to the nature of target compounds and then an accurate amount can easily be packed inside the membrane along with stir-bar.

To evaluate the performance of SB-μ-SPE, determination of PCBs in serum samples were investigated. PCBs were widely used for industrial applications before 1970. Although, they were banned in the 1970s [22] still their measurable concentrations have been reported in the environment. They are persistent in nature and have an ability to accumulate in tissues and biological matrix [23]. Their presence in body fluids such as blood has been linked with different carcinogenic [24] and non-carcinogenic [25] disorders. Hence, it is highly desirable to develop sensitive analytical methods to monitor PCBs in environmental and biological matrices.

2. Experimental

2.1. Chemicals and reagents

Accruel polypropylene sheet membrane (pore size of 0.2 μm, 157 μm thickness) was purchased from Membrana (Wuppertal, Germany). HPLC-grade solvents (methanol, toluene, acetonitrile and *n*-hexane) were obtained from Fisher (Loughborough, UK). The PCB congeners mixture (100 $\mu g\, mL^{-1}$) was purchased from Restek (Bellefonte, US). Stock solution of PCBs mixture (10 $\mu g\, mL^{-1}$) was prepared in methanol and stored at −4 °C and working solutions (0.1–100.0 $ng\, mL^{-1}$) were freshly prepared before experiments. C_{18} column packing material (average particle size: 12 μm; surface area; 180 m^2/g) was obtained from Sigma-Aldrich. Muti-wall carbon nanotubes (MWCNTs) (outer diameter: 20–30 nm, length 10–30 μm and purity >95%) were purchased from Cheap Tubes Inc. (Cambridgeport, USA). Coconut activated carbon was purchased from Cenapro Chemical Corporation (Mandauae City, Philippines).

2.2. Serum samples and standard solutions

Real pooled human serum was used for method development and it was obtained from a local laboratory. Research ethics regarding use of human biological samples were taken into account while collection of the samples. The blood samples were extracted from volunteers by venipuncture in sterilized blood tubes. Serum was separated by centrifugation at 6000 rpm for 12 min and collected together in 50 mL glass bottles equipped with Teflon caps. Collected serum was stored at −20 °C prior to use. The serum samples used for method optimization were free of PCBs. Optimization experiments were carried out with 10 times diluted serum samples spiked at 25 $ng\, mL^{-1}$. Serum samples were also collected from individual patients to test the applicability of the method. Standard safety protocols were adopted for handling and disposing of biological samples.

2.3. Gas chromatography–mass spectrometric (GC–MS) analysis

The separation and quantitation of target compounds were performed on a Shimadzu (Kyoto, Japan) QP2010 GC–MS. The system was equipped with a Shimadzu AOC–20 s auto sampler and AOC-20 auto injector. Rxi-5 Sil MS column with thickness of 0.25 μm, length of 30.0 m and diameter of 0.25 mm (Restek, Bellefonte, US) was used for separation of target compounds. The high purity helium gas was employed as carrier gas at flow rate of 1.01 $mL\, min^{-1}$. The GC injection port temperature was kept 250 °C and all the samples were injected in splitless mode. The opening time of split vent was 1.0 min. The GC–MS interface temperature was 220 °C and ion source temperature was 200 °C. The oven temperature was programmed as follows: initial temperature was 40 °C and held for 1 min; then increased to 100 °C at 10 °C/min and held for 2 min; then increased to 165 °C at 10 °C/min and held for 0 min; then increased to 190 °C at 6 °C/min and held for 3 min; after that it was increased to 220 °C at 3 °C/min and held for 3 min; and finally increased to 240 °C at 2 °C/min and held for 1 min. Total run time was 46.67 min. For qualitative analysis, data acquisition was performed in scan mode to confirm the retention times of target compounds. For quantitative analysis, selective ion monitoring (SIM) mode was employed. Selected target ions are listed in Table 1.

2.4. SB-μ-SPE procedure

SB-μ-SPE device was fabricated by packing a tiny stir-bar (7 mm × 2 mm) and accurately weighed amount of sorbent into a porous polypropylene (PP) membrane envelope whose edges were heat sealed. Briefly, PP flat membrane sheet was cut into rectangular pieces with dimensions of 1.6 cm by 2.0 cm. The shorter length was folded and heat sealed with an electrical heat sealer. One of the two remaining open edges was heat sealed to give it a shape of an envelope with one open edge. The sorbent and tiny stir bar were added from the last open edge that was finally heat sealed to give SB-μ-SPE device.

Before extraction, SB-μ-SPE device was conditioned in toluene for 1 min. For extraction, SB-μ-SPE device was placed inside a glass vial containing 5 mL of sample or spiked matrix solution. This vial was placed on a magnetic stirrer. The SB-μ-SPE device was stirred in the sample solution for an optimum extraction time. SB-μ-SPE device was taken out of the sample solution, and dried with the help of lint free tissue. The device was then inserted into an Eppendorf vial and 250 μL of desorption solvent were added. Analytes were then effectively desorbed or eluted by using ultra-sonication for an optimum desorption time. After desorption, 1 μL of extract was injected into GC–MS.

3. Results and discussion

3.1. Optimization of SB-μ-SPE

The factors that affect the extraction efficiency of SB-μ-SPE were optimized by using real human serum samples spiked at 25 $ng\, mL^{-1}$.

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