OVERVIEW ON THE NEW GENERATION OF EXTRACTION TECHNIQUE: FABRIC SOLID-PHASE EXTRACTION

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Fabric phase sorptive extraction (FPSE) is a new-generation of sample preparation technique that effectively combines representative characteristics of solid-phase microextraction – SPME (equilibrium-based extraction) and solid phase extraction – SPE (exhaustive extraction). FPSE was introduced in 2014 by Kabir A. and Furon K.G. FPSE utilizes a fabric substrate (natural or synthetic such as cotton or polyester) that is chemically coated with a hybrid sorbent (organic-inorganic sol-gel). The entire assembly (fabric substrate coated with the sol-gel polymer) results in a fast and sensitive micro-extraction device. The FPSE development process can be described in 3 main steps: (1) Preparation of the fabric substrate for sol-gel coating, (2) preparation of the sol-solution for coating the substrate, and (3) formation of sol-gel coatings on the fabric substrate. Using this technique can be ensured a faster, cleaner, and with a high concentration of analyte solution. FPSE is a method that can be easily modified and used in different types of applications. For this reason~~,~~ FPSE is increasingly used in the scientific community dealing with sample pretreatment. By using this technique, promising results have been obtained both for the extraction and determination of certain analytes from environmental samples, as well as from other types of samples, with complex matrices (food and biological samples). This study aims to summarize the existing data on FPSE and to briefly present this innovative method.

Keywords: FPSE, fabric, microextraction

FABRIC PHASE SOLID EXTRACTION DESCRIPTION

Sample preparation is a very important and inevitable step in the chemical analysis workflow since it can easily influence the obtained results. Most of the analytical samples cannot be analyzed directly with an injection into the analytical instrument. Sample preparation may involve a series of steps that can include dissolution, extraction, reaction with some chemical species, filtering, dilution, or many other techniques, and it is considered to be the most time-consuming part of the whole analysis.

Lately, low-cost, fast, and environmentally friendly procedures became necessary in order to improve quality of life and protect the environment. Hence, scientists aim toward developing new analytical methodologies compliant with the principles of green analytical chemistry (GAC) (Armenta *et al*., 2015).

Different types of sorbent-based sorptive microextraction methods are used in analytical laboratories, such as: solid-phase microextraction (SPME) (Belardi and Pawliszyn, 1989; Arthur and Pawliszyn, 1990), stir bar sorptive extraction (SBSE) (Baltussen *et al*., 1999; David and Sandra, 2007), microextraction by packed sorbents (MEPS) (Abdel-Rehim, 2004) and solvent-based sorptive microextraction techniques e.g., single-drop microextraction (SDME) (Jeannot and Cantwell, 1996; Jeannot and Cantwell, 1997), dispersive liquid-liquid microextraction (DLLME) (Rezaee *et al*., 2006) and hollow-fiber microextraction (HF-LPME) (Pedersen-Bjergaard and Rasmussen, 1999; Shen and Lee, 2002).

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Fabric phase sorptive extraction (FPSE), is a new type of microextraction, developed by Kabir and Furton (Kabir and Furon, 2014). It utilizes sol-gel coating technology developed by Chong and co-workers (Chong *et al*., 1997) in order to create an inherently porous hybrid inorganic-organic sorbent material that is chemically bonded to the flexible and permeable substrate matrix, usually a fabric material.

The FPSE combines two extraction modes (SPME and SPE) into a single microextraction device. The procedure is based on the direct contact of the FPSE with the sample. Due to the created contact, the analytes are transferred onto the surface of FPSE, similarly to the direct-immersion SPME (equilibrium extraction mode). The extraction process may be facilitated by magnetic stirring, sonication etc. (Silva, 2017; Samanidou and Kabir, 2015).

The main steps of FPSE are presented in Figure 1.

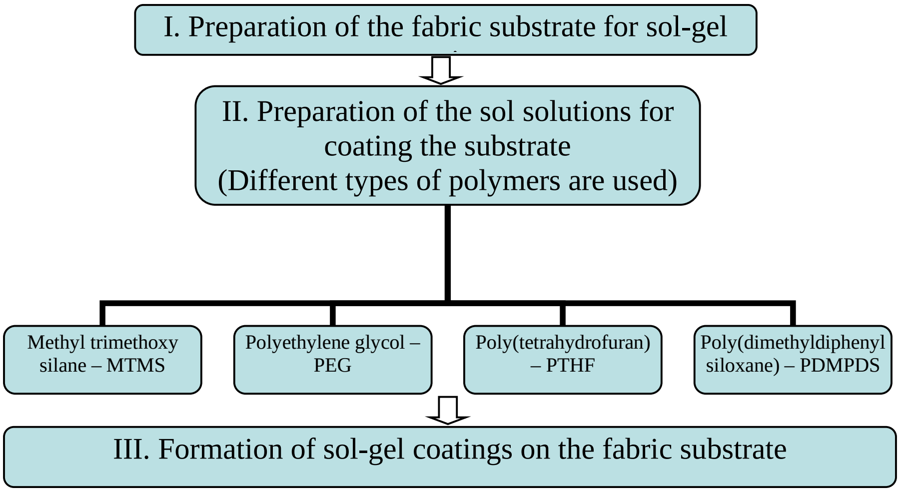

Figure 1. Main steps of FPSE

Currently, FPSE is considered to be the only microextraction technique that analyzes the substrate surface chemistry of the fabric to accomplish the overall selectivity and extraction efficiency of an FPSE membrane. Moreover, FPSE is the only microextraction technique that offers the possibility to use a complete range of sorbent chemistries such as polar, medium polar, nonpolar, cation exchanger, anion exchanger, mixed mode, zwitterionic, as well as zwitterionic mixed-mode sorbents (Kabir and Samanidou, 2021). It is important to note that all the before-mentioned sorbents can be coated on 100% cotton cellulose (hydrophilic), on fiberglass (neutral), or ~~on~~ polyester (hydrophobic) substrates.

Method development of fabric phase sorptive extraction is simple and straightforward. One of the big advantages is that FPSE does not require any sample pre-treatment process to reduce or minimize matrix interferents such as filtration or centrifugation (or any other type of pre-treatment process), and the FPSE membrane can be used directly with the sample, regardless of its complexity.

The extraction time is one of the most important factors that influence the extraction efficiency of an FPSE membrane. Generally, extraction efficiency is assessed between 0 and 60 min. The optimum time necessary for the desorption of the extracted analytes have been assessed in the range between 0 and 10 min.

Sample volume is another parameter in FPSE and depends on the availability and nature of the sample. The sample volume is directly proportional to the FPSE surface: for a smaller sample volume, a smaller FPSE membrane size can be used.

Table 1 presents the preparation of sol–gel sorbent coated FPSE membrane.

Table 1. Preparation of sol–gel sorbent coated FPSE membrane (adapted after Kabir and Samanidou, 2021)

Preparing the fabric substrate for sol-gel coating (Kabir *et al*., 2017; Kumar *et al*., 2014)	Preparing the sol-solution for coating the substrate (Kabir *et al*., 2013)	Formation of sol-gel coatings on the fabric substrate		
		Dip coating technology	Aging, thermal conditioning and cleaning	Cutting the FPSE membrane (Kabir and Samanidou, 2021)
Nonpolar analytes – polyester fabric	Sol-gel precursors: inorganic/organic modified	Coating the pretreated fabric with the sol-solution, typically 12h at room temperature	Conditioning under helium gas flow, typically for 24h at 50°C	Volume of sample<5mL – 1 cm diameter FPSE membrane
Medium-polar analytes – hydrophilic fabric: 100% cotton cellulose	Inorganic/organic active polymer	Drying the coated FPSE membrane in air, typically for 1h.	Cleaning the FPSE membrane.	5mL<Volume of sample<20 mL – 2.5cm x 2.0 cm size of FPSE membrane
Clean and activate the fabric surface	Compatible solvent system Acid catalyst and water			

FPSE technique extraction principle is analogous with solid phase microextraction (SPME), stir bar sorptive extraction (SBSE) and thin film microextraction (TFME) meaning direct immersion extraction.

The mass of the analyte extracted with FPSE (n), is proportional with the following parameters (Kabir and Samanidou, 2021):

- the coatings on the chosen substrate surface and the sample matrix (K_{es})
- the volume of the extracting phase (V_e)
- the volume of the sample (V_s)
- the initial concentration of the analyte (C_o)

The formula that can be used to express the mass of the extracted analyte is:

$$n = \frac{K_{es} V_e V_s C_o}{K_{es} V_e + V_s} \tag{1}$$

If the Sample volume if too large in comparison with the extracted sorbent volume (Ve<<Vs), the above equation can be expressed as:

$$n = K_{es} V_e V_s C_o \tag{2}$$

The extraction efficiency is influence by two factors: thermodynamic and kinetic factors (Lucena, 2012).

Many research groups have adopted this innovative sample preparation approach and have developed new analytical strategies with application in all analytical fields.

According to a review published by Kabir and Samanidou (2021), 66 papers have been published since 2014 to 2020 with an increased trend of publishing these works. In Table 2, some of the FPSE technique applications are presented.

Table 2. Applications of the FPSE Technique (Adapted after Zilfidou *et al.*, 2018)

Type of technique	Fabric substrate	Sol-Gel coating	Sample	Reference
FPSE-HPLC-UV	Cellulose	PEG	Tap-Pond-Reclaimed Water Substituted phenols	Kabir *et al.*, 2017
FPSE-HPLC-FLD	Cellulose	PTHF	Ground-River-Drinking, WWTP, Hospital wastewater Estrogens	Kumar *et al.*, 2014
FPSE-HS-GC-MS	Fiber glass	PDMDPS	Environmental air Sexual pheromone	Alcudia-León *et al.*, 2017
FPSE-HPLC-UV	Cellulose	PTHF	Industrial-Ground water, Borcher-Oakay alloy Heavy metal ions	Heena Kaur *et al.*, 2017
FDSE-FI-FAAS	Polyester	PDMDPS	River-Coastal-Ditch water Toxic metals	Anthemidis *et al.*, 2016
DFPSE-LC-MS/MS	Cellulose	PEG	River water, Effluent/influent wastewater Pharmaceuticals Personal care products	Lakade *et al.*, 2016
Stir-FPSE-UPLCDAD	Cellulose	PEG	River-Stream water Herbicides	Roldán-Pijuán *et al.*, 2015
SE/GC-MS	Cellulose	CW / PTHF / PDMS	Vegetable samples organophosphorus pesticides	Kaur *et al.*, 2019

CONCLUSION

The ability to use the same FPSE membrane in SPME or SPE modes is a unique concept that allows the extraction to be performed while maintaining the performance characteristics of the extraction, such as robustness, specificity and efficiency.

FPSE can be successfully used with any chromatographic techniques, such as liquid and gas chromatography coupled with various detectors depending on the needs of the analysis. This new generation technique found applications in the analysis of drugs, pharmaceuticals, and other chemical compounds that are mainly found in environmental samples as well as in food samples and biological fluids.

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