Chapter

Online Automated Micro Sample Preparation for High-Performance Liquid Chromatography

Hiroyuki Kataoka, Atsushi Ishizaki and Keita Saito

Abstract

Sample preparation is one of the most labor-intensive and time-consuming operations in sample analysis. Sample preparation strategies include the exhaustive or non-exhaustive extraction of analytes from matrices. Online coupling of sample preparation with the separation system is regarded as an important goal. In-tube solid-phase microextraction (SPME) is an effective sample preparation technique that uses an open tubular fused-silica capillary column as an extraction device. In-tube SPME is useful for trace enrichment, automated sample cleanup, and rapid online analysis. Moreover, this method can be used to determine the analytes in complex matrices by direct sample injection or merely by simple sample treatment such as filtration. In-tube SPME is frequently combined with high-performance liquid chromatography (HPLC) using online column-switching techniques. Various operating systems and new sorbent materials have been reported to improve extraction efficiency, such as sorption capacity and selectivity. This chapter discusses efficient micro sample preparation techniques for HPLC, especially online automated in-tube SPME.

Keywords: sample preparation, online automated analysis, column switching, in-tube solid-phase microextraction, high-performance liquid chromatography

1. Introduction

Sample analysis consists of various analytical steps, including sampling, sample preparation, separation, detection and data analysis. One of the most important steps is sample preparation, which involves the extraction, isolation and concentration of target analytes from complex matrices. Sample preparation [1–18] is the most labor-intensive and error-prone process in analytical methodology and markedly influences the reliability and accuracy of analyte determination. In addition, sample preparation requires large amounts of sample and organic solvents, and is therefore difficult to automate. An ideal sample preparation technique should be simple and fast; be specific for analytes through the efficient removal of coexisting components; provide high sample throughput; utilize fewer operation steps to minimize analyte losses; and be solvent-free, inexpensive, and compatible with chromatography systems. Online automated sample preparation [19–29], in which sample preparation is directly connected to chromatographic separation systems, eliminates further sample handling between the trace-enrichment and separation
steps. Online automated sample preparation methods usually improve data quality, increase sample throughput, reduce costs, and improve the productivity of personnel and instruments.

In-tube solid-phase microextraction (SPME), using a capillary tube as an extraction device, was introduced by Eisert and Pawliszyn [30] to overcome the problems inherent to conventional fiber SPME. These drawbacks included fragility, low sorption capacity, bleeding from thick-film coatings on fibers, limited effectiveness for extraction of weakly volatile or thermally labile compounds not amenable to gas chromatography (GC) or GC-mass spectrometry (MS), and reduced stability in solvents used in high performance liquid chromatography (HPLC). In-tube SPME was also developed to completely automate the sample preparation process and to enable direct online coupling of in-tube SPME with HPLC using capillary column switching systems [31].

This chapter reviews the configurations and characteristics of in-tube SPME technology and discusses current and future directions, including the strategies involved in extraction efficiency and method development. The details of in-tube SPME have been described in well documented reviews [27, 32–50].

2. Configurations of in-tube SPME

In-tube SPME is an efficient sample preparation technique for extraction in capillary columns using stationary phases coated on the inner wall of the capillary or on the surface of the packing material (Figure 1). Various in-tube SPME capillary devices have been developed, such as inner wall-coated fused-silica open tubular (Figure 1A), fiber-packed (Figure 1B), sorbent-packed (Figure 1C), and rod-type porous monolith (Figure 1D) capillaries [16, 31]. The capillaries are easily fixed with the autosampler injection system, and are generally reusable without plugging or breaking the column and without exfoliation of coating materials.

![Figure 1](image)

**Figure 1.** Capillary devices for in-tube SPME: (A) polymer coated, (B) sorbent-packed, (C) fiber-packed, and (D) monolith capillary tubes.
2.1 Operating systems of in-tube SPME

Flow-through systems (Figure 2), in which sample solutions are continuously passed in one direction through a capillary column; or as repeated draw/ejection systems (Figure 3), in which sample solutions are repeatedly aspirated and dispensed from a capillary column, are used as an operating system of in-tube SPME [18]. These systems are operated by column switching techniques under computer control.

In flow-through systems, the complete analytical system consists of an automatic six-port valve, two pumps (a sample pump and a wash pump) and a liquid chromatography (LC) system. A capillary column is installed in the six-port valve or sometimes placed in the loop. Although one or two six-port valves are available, one valve mode is used more frequently than others. The procedure consists of four steps, conditioning, extracting, washing and desorbing. After conditioning of capillary column with water, the aqueous sample is pumped through the column under the load position (Figure 2A). Remaining matrix and residues in capillary are removed by washing with water. After switching the six-port valve to the injection position, the LC mobile phase is passed through the column (dynamic desorption), with the flow-rate of the LC pump (Figure 2B). The desorbed analytes are subsequently transferred to the analytical column for separation and detection. The flow-through extraction system, however, may include systematic troubles, such as contamination of the switching valve by sample matrix [18, 31, 37, 41].

Repeated draw/ejection systems include the placement of a capillary column for extraction between the injection loop and the injection needle of the autosampler. Since the sample solution moves only in the capillary, the metering pump and switching valve are not contaminated by sample matrix [18, 31, 37, 41]. A built-in UV diode array detector (DAD) or fluorescence detector (FLD) between the HPLC and the MS can enhance the multidimensional and simultaneous multi-detections, improving analyte identification. During the extraction and concentration step (Figure 3A), the injection syringe is programmed to repeatedly draw and eject sample solution from the vial until the concentration of the analyte reaches distribution equilibrium between the sample solution and the stationary phase. After switching the six-port valve to the injection position, the extracted analytes can be directly desorbed from the capillary coating by LC mobile phase flow (dynamic

![Schematic diagrams of a flow-through extraction system used for online in-tube SPME. (A) Load position (extraction), and (B) injection position (desorption).](image-url)
desorption) or by an aspirated desorption solvent (static desorption) (Figure 3B) [31]. The desorbed analytes are subsequently transferred to an LC column. The computer controls the drawing and ejection of sample solution; switching of the valves; control of peripheral equipment, such as the HPLC and MS; and analytical data processing, thus reducing labor and enhancing precision. In addition, the autosampler can automatically process a large number of samples without carry-over, because the injection needle and capillary column are washed in methanol and the mobile phase before the sample is extracted.

### 2.2 Extraction sorbent materials

The amount of analyte extracted into the stationary phase of the capillary during in-tube SPME is dependent on the characteristics of the capillary coating and the target analyte. Among the commercially available GC capillary columns, silica modified columns have been found more suitable for the analysis of nonpolar compounds. Porous polymer type capillary columns such as Supel-Q PLOT (divinylbenzene polymer, film thickness 17 μm) have shown better extraction efficiencies due to their large surface area for most organic compounds than other liquid-phase type capillary columns, such as CP-Sil 5CB (100% polydimethylsiloxane, film thickness 5 μm), Quadrex 007–5 (5% phenyl polydimethylsiloxane, film thickness 12 μm), CP-Sil 19CB (14% cyanopropyl phenyl methylsilicone, film thickness 1.0 μm), and CP-Wax 52CB (polyethylene glycol, film thickness 1.2 μm). CP-Sil 19CB was superior for extraction of polyaromatic hydrocarbons, although the film layer was thin. In contrast, some compounds were effectively extracted with other PLOT type coatings, including Carboxen-1006 PLOT (carboxen molecularsives, film thickness 17 μm) and CP-Pora PLOT amine (basic modified styrene divinylbenzene polymer, film thickness 10 μm).

Several unique phases and technical solutions have been developed to improve extraction efficiency and selectivity when extended to microscale applications.

---

**Figure 3.** Schematic diagrams of a draw/eject extraction system used for online in-tube SPME (reproduced from Ref. [37]). (A) Extraction and concentration step, and (B) desorption and injection step.
These include polypyrrole (PPY) coated capillaries; PEEK tube capillaries packed with molecularly imprinted polymer (MIP) particles; and highly biocompatible SPME capillaries packed with alkyl-diol-silica (ADS) particles as restricted access media (RAM); immunosorbents; ionic liquids; monolithic materials; carbon nanomaterials; silica-coated magnetite; and temperature responsive polymers. Novel extraction sorbent materials for in-tube SPME are shown in Figure 4.

For example, chemically or electrochemically deposited PPY coatings have higher extraction efficiencies than commercial GC coatings due to the various types of interactions (e.g., $\pi-\pi$, polar, hydrogen bonding, and ionic interactions) between these multifunctional PPY coatings and the analytes. Capillary tubes have been coated with MIP, consisting of cross-linked synthetic polymers produced by copolymerizing a monomer with a cross-linker in the presence of a template molecule (Figure 4A), and PEEK tubes have been packed with MIP particles. By removing the template after polymerization, it is possible to leave open sites of a specific size and shape suitable for binding the same or similar chemicals in a sample.

![Figure 4](image.png)

**Figure 4.** Novel extraction sorbent materials for in-tube SPME (reproduced from Ref. [37, 42, 84]). (A) Molecularly imprinted polymers, (B) restricted access media, (C) immunosorbents, (D) monolithic polymers, (E) carbon nanotubes, (F) silica-coated magnetite, and (G) temperature responsive polymers.
MIPs recognize chemicals through combination of shape, hydrogen bonding, and hydrophobic and electrostatic interactions [16, 18, 31]. RAM materials possess defined diffusion barriers with small sized pores and biocompatible outer particle surfaces (Figure 4B). The bifunctionality of ADS particles used as a RAM SPME device can prevent fouling of the capillary by protein adsorption while simultaneously trapping the analytes in the hydrophobic porous interior. Furthermore, a simple SPME device has been fabricated for use in online immunoaffinity capillaries packed with immuno-sorbent materials, consisting of covalently immobilized antibodies (Figure 4C).

An alternative approach consists of in-tube SPME using monolithic capillary columns comprised of one piece of organic polymer or silica rods with a unique flow-through double-pore structure (Figure 4D). Monoliths are also highly permeable to liquids and biological samples, enabling reduced solvent use, varied support formats, and/or automation. Monolithic capillaries are especially suitable for in-tube SPME media due to the low pressure drop, allowing a high flow-rate to achieve high throughput and a total porosity greater than that of particle-packed capillaries. Hydrophobic main chains and acidic pendant groups of poly (methacrylic acid-ethylene glycol dimethacrylate) enhance the ability to extract basic analytes from aqueous matrices. The physicochemical properties of graphene-based sorbents and carbon nanotubes (Figure 4E) enable their use in extraction, with these combinations showing excellent results when used for in-tube SPME. In addition, various cationic, anionic and zwitterionic liquid-mediated sol–gel coatings have been developed for effective in-tube SPME.

Other innovative extractive phases that enhance the affinity of the analytes include silica magnetite (SiO$_2$–Fe$_3$O$_4$; Figure 4F) and poly (N-isopropylacrylamide; Figure 4G), which have been used in new microextraction processes involving magnetism and thermal energy, respectively. Magnetic and temperature controlled in-tube SPME are performed using flow-through systems, due to the need for additional equipment providing a magnetic or thermal field, which is easier to implement using flow-through devices. Other techniques include wire-in-tube SPME, using modified capillary columns with inserted stainless steel wires, and fiber-in-tube SPME, using PEEK tubes packed with fibrous rigid-rod heterocyclic polymers. These methods increase extraction efficiency by reducing capillary volume or increasing the extracting surface and have shown improved extraction efficiency when extended to microscale applications.

### 3. Method development and characteristics of in-tube SPME

#### 3.1 Optimization of in-tube SPME

In-tube SPME depends on the distribution coefficient of each analyte. Extraction conditions may be optimized by increasing the distribution factor in the stationary phase. The selectivity and efficiency of extraction depend on the type of stationary phase and on the internal diameter, length, and film thickness of the capillary column. Sorption equilibrium is attained by optimizing various extraction parameters for each type of analyte. These parameters include extraction rate, sample volume, sample pH, flow-rate, number of draw/eject cycles (only draw/eject system), and desorption conditions. As described in the preceding section, the choice of capillary coating is important for optimizing extraction selectivity and efficiency. Generally, low and high polarity columns selectively retain hydrophobic and hydrophilic compounds, respectively. Stationary phase consisting of a thicker film and longer column can extract larger amounts of compound, but quantitative desorption of compounds from capillary columns may be difficult. PLOT-type
columns have a larger adsorption surface area and thicker film layer than liquid-phase-type columns, enabling more analytes to be extracted [16, 18].

Generally, the optimal length and internal diameter of a capillary column used in combination with HPLC is 20–80 cm and 0.25 or 0.32 mm, respectively. Although thick-film capillaries often show higher sample capacity and extraction sensitivity, it is extremely difficult to reliably bind thicker chemical coatings to the inner surfaces of fused-silica capillary tubes using conventional approaches. In contrast, thin-film capillaries can minimize the time to reach extraction equilibrium due to their low sample capacity. Capillary columns with chemically bonded or cross-linked liquid phases are very stable in water and organic solvents and can prevent loss of phase by LC mobile phase [18].

The volume of sample passed through a capillary is usually 0.2–2 mL in flow-through extraction systems, and their optimum extraction flow rates are 0.25–4 mL/min depending on the volume of the column. Although increases in the number and volume of draw/eject cycles can enhance extraction efficiency in draw/ejection systems, peak broadening is often observed [16]. Optimal conditions for a capillary column of inner diameter 0.25 mm and length 60 cm include a draw/ejection volume of 30–40 μL, a draw/ejection flow rate of 50–100 μL/min and 10–15 draw/ejection cycles. Below this rate, extractions require an inconveniently long time, and above this rate, bubbles form on the inside of the capillary, reducing extraction efficiency. Furthermore, the extraction efficiency of the analyte to the stationary phase varies with the pH of the sample solution. The presence of hydrophilic solvents such as methanol in the sample reduces the extraction efficiency. The analyte extracted on capillary coatings can be easily desorbed statically or dynamically without carryover [18].

3.2 Characteristics of the in-tube SPME technique

Table 1 summarizes the characteristics of in-tube SPME. The main advantage is that the series of processes can be automated, which enables continuous extraction,
desorption and injection with column switching using a standard autosampler, and online coupling with the LC system [16, 18, 31]. In-tube SPME may be suitable for the determination of polar and thermolabile compounds. Compared with manual techniques, automated sample-handling procedures not only shorten the total analysis time but are more accurate and precise. Automated techniques are also suitable for miniaturization, high-throughput performance, and online coupling with analytical instruments, and reduce the consumption of solvent. Online procedures can limit contact with dirty and hazardous samples, reducing sample contamination and loss. Online column-switching systems are highly sensitive due to pre-concentration resulting from the injection of large sample volumes into the extraction support without loss of chromatographic performance. The main disadvantage is that the capillaries tend to clog, which may be avoided by removing interfering phases such as particles or macromolecules by filtration or centrifugation before extraction. Although the absolute recovery rate of the in-tube SPME method is generally low, it can be extracted and concentrated reproducibly using an autosampler, and all extracts can be introduced into the LC column [16, 18, 31].

The online in-tube SPME method can be applied to polar and nonpolar compounds in liquid samples, and can be coupled with various analytical methods, such as HPLC and LC–MS. Early applications of online in-tube SPME have involved draw/eject extraction systems and commercially available open-tubular GC capillaries such as Supel Q PLOT and Carboxen 1006 PLOT capillaries. The subsequent development of various operating systems and new sorbent materials improved extraction efficiency, such as sorption capacity and selectivity, and extended the range of applications. Last decade, numerous applications of online in-tube SPME methods have been reported to many types of pharmaceutical and biomedical [86, 89–124], food [125–137], and environmental [138–178] analyses.

4. Conclusions and future directions

The online in-tube SPME techniques described in this chapter have many desirable features for automated separation of analytes, using column-switching techniques. These methods are especially well suited to the analysis of samples requiring significant cleanup and concentration to improve their selectivity and sensitivity, as well as being useful for high-throughput sampling. Since the in-tube SPME method using capillaries as an extraction device is useful for online sample preparation to extract and concentrate polar and non-polar compounds from aqueous solution, it has become an effective technique for convenient analysis of a wide variety of compounds in complex matrices such as biological, pharmaceutical, food and environmental samples [31]. Furthermore, various operating systems and new sorbent materials have been developed to improve extraction efficiency and sorption capacity and selectivity, and to extend the range of applications. These include MIPs, RAM, immunosorbents, monolithic materials, carbon nanoparticles, ionic liquids, temperature responsive polymers and magnetic hybrid adsorbents.

The main future direction in sample preparation is the development of more sensitive and selective extraction sorbents [31]. Chiral active phases, ionic liquids, dendrimers, aptamer modified sorbents, magnetic materials, temperature responsive materials may be available as new polymer devices for effective sample preparation. Furthermore, biomimetic coating materials including ultrasound and light responsive polymers may be available as a selective extraction device in the future. These customized coating materials, differing in type, shape, and size, are expected to result in highly efficient extraction of various samples. Biocompatible RAM and monolithic sorbents are useful for direct analysis, without pre-treatment other than
dilution and centrifugation of biological samples. As another future direction, better integration of sampling/sample preparation and instrumental analysis will allow wider use of automated online analysis. Especially, the use of column-switching systems involving microextraction techniques and/or microdevices will offer convenient integration of sample preparation with various analytical instruments such as HPLC as well as other chromatographic systems, electrophoresis, direct MS, etc.

Finally, this chapter provides an overview of the configurations and characteristics of in-tube SPME technology for online automated micro sample preparation for HPLC. We hope that this chapter will serve as a guide to choosing the most effective sample preparation techniques for the analysis of various complex samples.

Acknowledgements

This work was supported by a Grant-in-Aid for Basic Scientific Research (C, No. 17 K08259).

Conflict of interest

The authors declare no conflict of interest.

Author details

Hiroyuki Kataoka*, Atsushi Ishizaki and Keita Saito
School of Pharmacy, Shujitsu University, Nishigawara, Okayama, Japan

*Address all correspondence to: hkataoka@shujitsu.ac.jp

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
References

[1] Pawliszyn J, Lord H. Handbook of Sample Preparation. Hoboken: John Wiley & Sons; 2010

[2] Papadoyannis IN, Samanidou VF. Sample preparation for HPLC. In: Cazes J, editor. Encyclopedia of Chromatography. 3rd ed. Vol. III. Broken Sound Parkway: CRC Press; 2010. pp. 2090-2105

[3] Ashri NY, Abdel-Rehim M. Sample treatment based on extraction techniques in biological matrices. Bioanalysis. 2011;3:2003-2018

[4] Samanidou V, Kovatsi L, Fragou D, Rentifis K. Novel strategies for sample preparation in forensic toxicology. Bioanalysis. 2011;3:2019-2046

[5] Singleton C. Recent advances in bioanalytical sample preparation for LC-MS analysis. Bioanalysis. 2012;4:1123-1140

[6] Pawliszyn J. Comprehensive Sampling and Sample Preparation: Analytical Techniques for Scientists. Vol. 1-4. Burlington: Academic Press; 2012

[7] Namera A, Saito T. Recent advances in unique sample preparation techniques for bioanalysis. Bioanalysis. 2013;5:915-932

[8] Lundanes E, Reubsæt L, Greibrokk T. Chromatography: Basic Principles, Sample Preparations and Related Methods. Weinheim: Wiley-VCH; 2013

[9] Martín-Esteban A. Sample preparation for chromatographic analysis. Advances in Chromatography. 2014;51:215-240

[10] Bylda C, Thiele R, Kobold U, Volmer DA. Recent advances in sample preparation techniques to overcome difficulties encountered during quantitative analysis of small molecules from biofluids using LC-MS/MS. Analyst. 2014;139:2265-2276

[11] Melnyk A, Wolska L, Namieśnik J. Coacervative extraction as a green technique for sample preparation for the analysis of organic compounds. Journal of Chromatography. A. 2014;1339:1-12

[12] Ribeiro C, Ribeiro AR, Maia AS, Gonçalves VM, Tritan ME. New trends in sample preparation techniques for environmental analysis. Critical Reviews in Analytical Chemistry. 2014;44:142-185

[13] Voglardi S, Tucci M, Stocchero G, Ferrara SD, Favretto D. Sample preparation methods for determination of drugs of abuse in hair samples: A review. Analytica Chimica Acta. 2015;857:1-27

[14] Rejczak T, Tuzimski T. Recent trends in sample preparation and liquid chromatography/mass spectrometry for pesticide residue analysis in food and related matrixes. Journal of AOAC International. 2015;98:1143-1162

[15] Raynie DE. Trends in sample preparation. LCGC North America. 2016;34:174-188

[16] Kataoka H. Sample preparation for liquid chromatography. In: Fanali S, Haddad PR, Poole CF, Riekkola ML, editors. Handbooks in Separation Science: Liquid Chromatography. 2nd ed. Vol. 2. Amsterdam: Elsevier; 2017. pp. 1-37. ISBN: 978-0-12-805392-8

[17] Barchanska H, Danek M, Sajdak M, Turek M. Review of sample preparation techniques for the analysis of selected
classes of pesticides in plant matrices. Critical Reviews in Analytical Chemistry. 2018;48:467-491

[18] Kataoka H. Pharmaceutical analysis/sample preparation. In: Worsfold P, Townshend A, Poole C, Miró M, editors. Encyclopedia of Analytical Science. 3rd ed. Vol. 8. Amsterdam: Elsevier; 2019. pp. 231-255. DOI: 10.1016/B978-0-12-409547-2.14358-6

[19] Wells DA. High throughput bioanalytical sample preparation: Methods and automation strategies. In: Progress in Pharmaceutical and Biomedical Analysis. Vol. 5. Amsterdam: Elsevier; 2003

[20] Zheng N, Jiang H, Zeng J. Current advances and strategies towards fully automated sample preparation for regulated LC-MS/MS bioanalysis. Bioanalysis. 2014;6:2441-2459

[21] Helle N, Baden M, Petersen K. Automated solid phase extraction. Methods in Molecular Biology. 2011;747:93-129

[22] Marquet P. LC-MS vs. GC-MS, online extraction systems, advantages of technology for drug screening assays. Methods in Molecular Biology. 2012;902:15-27

[23] Pan J, Zhang C, Zhang Z, Li G. Review of online coupling of sample preparation techniques with liquid chromatography. Analytica Chimica Acta. 2014;815:1-15

[24] Rogeberg M, Malerod H, Roberg-Larsen H, Aass C, Wilson SR. On-line solid phase extraction-liquid chromatography, with emphasis on modern bioanalysis and miniaturized systems. Journal of Pharmaceutical and Biomedical Analysis. 2014;87:120-129

[25] Mueller DM. The current role of on-line extraction approaches in clinical and forensic toxicology. Bioanalysis. 2014;6:2261-2274

[26] Wei D, Li M, King KW, Yang L. Online and automated sample extraction. Bioanalysis. 2015;7:2227-2233

[27] Barreiro JC, Luiz AL, Maciel SC, Maciel EV, Lanças FM. Recent approaches for on-line analysis of residues and contaminants in food matrices: A review. Journal of Separation Science. 2015;38:1721-1732

[28] Peng J, Tang F, Zhou R, Xie X, Li S, Xie F, et al. New techniques of on-line biological sample processing and their application in the field of biopharmaceutical analysis. Acta Pharmaceutica Sinica B. 2016;6:540-551

[29] Fumes BH, Andrade MA, Franco MS, Lanças FM. On-line approaches for the determination of residues and contaminants in complex samples. Journal of Separation Science. 2017;40:183-202

[30] Eisert R, Pawliszyn J. Automated in-tube solid-phase microextraction coupled to high-performance liquid chromatography. Analytical Chemistry. 1997;69:3140-3147

[31] Kataoka H. Recent advances in online column-switching sample preparation. In: Boyd R, Davies P, Decker M, et al., editors. Chemistry, Molecular Sciences and Chemical Engineering. Amsterdam: Elsevier; 2018. pp. 1-43. DOI: 10.1016/B978-0-12-409547-2.14547-0

[32] Kataoka H, Lord HL, Pawliszyn J. Applications of solid-phase microextraction in food analysis. Journal of Chromatography. A. 2000;880:35-62

[33] Lord H, Pawliszyn J. Microextraction of drugs. Journal of Chromatography. A. 2000;902:17-63
[34] Kataoka H. Automated sample preparation using in-tube solid-phase microextraction and its application—A review. Analytical and Bioanalytical Chemistry. 2002;373:31-45

[35] Lord HL. Strategies for interfacing solid-phase microextraction with liquid chromatography. Journal of Chromatography. A. 2007;1152:2-13

[36] Pragst F. Application of solid-phase microextraction in analytical toxicology. Analytical and Bioanalytical Chemistry. 2007;388:1393-1414

[37] Kataoka H, Ishizaki A, Nonaka Y, Saito K. Developments and applications of capillary microextraction techniques: A review. Analytica Chimica Acta. 2009;655:8-29

[38] Kataoka H. Recent developments and applications of microextraction techniques in drug analysis. Analytical and Bioanalytical Chemistry. 2010;396:339-364

[39] Kataoka H. New trends in sample preparation for analysis of plant-derived medicines. Current Organic Chemistry. 2010;14:1698-1713

[40] Campíns-Falcó P, Verdú-Andrés J, Sevillano-Cabeza A, Herráez-Hernández R, Molins-Legua C, Moliner-Martínez Y. In-tube solid-phase microextraction coupled by in valve mode to capillary LC-DAD: Improving detectability to multiresidue organic pollutants analysis in several whole waters. Journal of Chromatography. A. 2010;1217:2695-2702

[41] Kataoka H, Saito K. Recent advances in SPME techniques in biomedical analysis. Journal of Pharmaceutical and Biomedical Analysis. 2011;54:926-950

[42] Kataoka H. Current developments and future trends in solid-phase microextraction techniques for pharmaceutical and biomedical analyses. Analytical Sciences. 2011;27:893-905

[43] Kataoka H. Solid-phase microextraction: Biomedical applications. In: Jan Reedijk J, editor. Chemistry, Molecular Sciences and Chemical Engineering. Oxford: Elsevier, Academic Press; 2014. pp. 1-15

[44] Padrón ME, Afonso-Olivares C, Sosa-Ferrera Z, Santana-Rodríguez JJ. Microextraction techniques coupled to liquid chromatography with mass spectrometry for the determination of organic micropollutants in environmental water samples. Molecules. 2014;19:10320-10349

[45] Queiroz ME, Melo LP. Selective capillary coating materials for in-tube solid-phase microextraction coupled to liquid chromatography to determine drugs and biomarkers in biological samples: A review. Analytica Chimica Acta. 2014;826:1-11

[46] Kataoka H. SPME techniques for biomedical analysis. Bioanalysis. 2015;7:2135-2144

[47] Moliner-Martínez Y, Herráez-Hernández R, Verdú-Andrés J, Molins-Legua C, Campíns-Falcó P. Recent advances of in-tube solid-phase microextraction. Trends in Analytical Chemistry. 2015;71:205-213

[48] Kataoka H, Ishizaki A, Saito K. Solid-phase microextraction for pharmaceutical and biomedical analysis. Analytical Methods. 2016;8:5773-5788

[49] González-Fuenzalida RA, Moliner-Martínez Y, Molins-Legua C, Campíns-Falcó P. Miniaturized liquid chromatography coupled on-line to in-tube solid-phase microextraction for characterization of metallic
nanoparticles using plasmonic measurements. A tutorial. Analytica Chimica Acta. 2019;1045:23-41

[50] Eugenia M, Queiroz C, de Souza ID, Marchioni C. Current advances and applications of in-tube solid-phase microextraction. Trends in Analytical Chemistry. 2019;111:261-278

[51] Augusto F, Carasek E, Silva RG, Rivellino SR, Batista AD, Martendal E. New sorbents for extraction and microextraction techniques. Journal of Chromatography. A. 2010;1217:2533-2542

[52] Fumes BH, Silva MR, Andrade FN, Nazario CED, Lanças FM. Recent advances and future trends in new materials for sample preparation. Trends in Analytical Chemistry. 2015;71:9-25

[53] Maciel EVS, de Toffoli AL, Lanças FM. Current status and future trends on automated multidimensional separation techniques employing sorbent-based extraction columns. Journal of Separation Science. 2018;42:258-272

[54] Tamayo FG, Turiel E, Martín-Esteban A. Molecularly imprinted polymers for solid-phase extraction and solid-phase microextraction: Recent developments and future trends. Journal of Chromatography. A. 2007;1152:32-40

[55] Pichon V. Selective sample treatment using molecularly imprinted polymers. Journal of Chromatography. A. 2007;1152:41-53

[56] Hagiwara J. Molecularly imprinted polymers as affinity-based separation media for sample preparation. Journal of Separation Science. 2009;32:1548-1565

[57] Turiel E, Martín-Esteban A. Molecularly imprinted polymers for sample preparation: A review. Analytica Chimica Acta. 2010;668:87-99

[58] Moein MM, Abdel-Rehim M. Molecularly imprinted polymers for on-line extraction techniques. Bioanalysis. 2015;7:2145-2153

[59] Sarafraz-Yazdi A, Razavi N. Application of molecularly-imprinted polymers in solid-phase microextraction techniques. Trends in Analytical Chemistry. 2015;73:81-90

[60] Speltini A, Scalabrini A, Maraschi F, Sturini M, Profumo A. Newest applications of molecularly imprinted polymers for extraction of contaminants from environmental and food matrices: A review. Analytica Chimica Acta. 2017;974:1-26

[61] Ansari S, Karimi M. Recent progress, challenges and trends in trace determination of drug analysis using molecularly imprinted solid-phase microextraction technology. Talanta. 2017;164:612-625

[62] Cassiano NM, Barreiro JC, Moraes MC, Oliveira RV, Cass QB. Restricted-access media supports for direct high-throughput analysis of biological fluid samples: Review of recent applications. Bioanalysis. 2009;1:577-594

[63] Yang SH, Fan H, Classon RJ, Schug KA. Restricted access media as a streamlined approach toward on-line sample preparation: Recent advancements and applications. Journal of Separation Science. 2013;36:2922-2938

[64] Hennion MC, Pichon V. Immuno-based sample preparation for trace analysis. Journal of Chromatography. A. 2003;1000:29-52

[65] Liu R, Liu JF, Yin YG, Hu XL, Jiang GB. Ionic liquids in sample preparation. Analytical
and Bioanalytical Chemistry. 2009;399:871-883

[66] Ho TD, Canestraro AJ, Anderson JL. Ionic liquids in solid-phase microextraction: A review. Analytica Chimica Acta. 2011;695:18-43

[67] Mei M, Huang X, Chen L. Recent development and applications of poly (ionic liquid)s in microextraction techniques. Trends in Analytical Chemistry. 2019;112:123-134

[68] Saunders KC, Ghanem A, Boon HW, Hilder EF, Haddad PR. Separation and sample pre-treatment in bioanalysis using monolithic phases: A review. Analytica Chimica Acta. 2009;652:22-31

[69] Xu L, Shi ZG, Feng YQ. Porous monoliths: Sorbents for miniaturized extraction in biological analysis. Analytical and Bioanalytical Chemistry. 2011;399:3345-3357

[70] Samanidou VF, Karageorgou EG. An overview of the use of monoliths in sample preparation and analysis of milk. Journal of Separation Science. 2011;34:2013-2025

[71] Bunch DR, Wang S. Applications of monolithic solid-phase extraction in chromatography-based clinical chemistry assays. Analytical and Bioanalytical Chemistry. 2013;405:3021-3033

[72] Nema T, Chan EC, Ho PC. Applications of monolithic materials for sample preparation. Journal of Pharmaceutical and Biomedical Analysis. 2014;87:130-141

[73] Fresco-Cala B, Cárdenas S. Potential of nanoparticle-based hybrid monoliths as sorbents in microextraction techniques. Analytica Chimica Acta. 2018;1031:15-27

[74] Lucena R, Simonet BM, Cárdenas S, Valcárcel M. Potential of nanoparticles in sample preparation. Journal of Chromatography. A. 2011;1218:620-637

[75] Tian J, Xu J, Zhu F, Lu T, Su C, Ouyang G. Application of nanomaterials in sample preparation. Journal of Chromatography. A. 2013;1300:2-16

[76] Scida K, Stege PW, Haby G, Messina GA, García CD. Recent applications of carbon-based nanomaterials in analytical chemistry: Critical review. Analytica Chimica Acta. 2011;691:6-17

[77] Xu L, Qi X, Li X, Bai Y, Liu H. Recent advances in applications of nanomaterials for sample preparation. Talanta. 2016;146:714-726

[78] Zhang BT, Zheng X, Li HF, Lin JM. Application of carbon-based nanomaterials in sample preparation: A review. Analytica Chimica Acta. 2013;784:1-17

[79] Jakubus A, Paszkiewicz M, Stepnowski P. Carbon nanotubes application in the extraction techniques of pesticides: A review. Critical Reviews in Analytical Chemistry. 2017;47:76-91

[80] Song XY, Chen J, Shi YP. Different configurations of carbon nanotubes reinforced solid-phase microextraction techniques and their applications in the environmental analysis. Trends in Analytical Chemistry. 2017;86:263-275

[81] Segro SS, Tran MP, Kesani S, Alhendal A, Turner EB, Malik A. Sol-gel microextraction phases for sample preconcentration in chromatographic analysis. Journal of Separation Science. 2010;33:3075-3096

[82] Zhao L, Qin H, Wu R, Zou H. Recent advances of mesoporous materials in sample preparation. Journal of Chromatography. A. 2012;1228:193-204

[83] de Toffoli AL, Maciel EVS, Fumes BH, Lanças FM. The role of
graphene-based sorbents in modern sample preparation techniques. Journal of Separation Science. 2018;41:288-302

[84] Moliner-Martínez Y, Prima-Garcia H, Ribera A, Coronado E, Campins-Falcó P. Magnetic in-tube solid phase microextraction. Analytical Chemistry. 2012;84:7233-7240

[85] Herrero-Latorre C, Barciela-García J, García-Martín S, Peña-Crecente RM, Otárola-Jiménez J. Magnetic solid-phase extraction using carbon nanotubes as sorbents: A review. Analytica Chimica Acta. 2015;892:10-26

[86] Shamsayei M, Yamini Y, Asiabi H, Safari M. On-line packed magnetic in-tube solid phase microextraction of acidic drugs such as naproxen and indomethacin by using Fe₃O₄@SiO₂@layered double hydroxide nanoparticles with high anion exchange capacity. Mikrochimica Acta. 2018;185:192

[87] Yu QW, Ma Q, Feng YQ. Temperature-response polymer coating for in-tube solid-phase microextraction coupled to high-performance liquid chromatography. Talanta. 2011;84:1019-1025

[88] Yang Y, Rodriguez-Lafuente A, Pawliszyn J. Thermoelectric-based temperature-controlling system for in-tube solid-phase microextraction. Journal of Separation Science. 2014;37:1617-1621

[89] Melo LP, Queiroz RH, Queiroz ME. Automated determination of rifampicin in plasma samples by in-tube solid-phase microextraction coupled with liquid chromatography. Journal of Chromatography. B, Analytical Technologies in the Biomedical and Life Sciences. 2011;879:2454-2458

[90] Chaves AR, Silva BJ, Lanças FM, Queiroz ME. Biocompatible in-tube solid phase microextraction coupled with liquid chromatography-fluorescence detection for determination of interferon α in plasma samples. Journal of Chromatography. A. 2011;1218:3376-3381

[91] Caris JA, Silva BJ, Moisés EC, Lanchote VL, Queiroz ME. Automated analysis of lidocaine and its metabolite in plasma by in-tube solid-phase microextraction coupled with LC-UV for pharmacokinetic study. Journal of Separation Science. 2012;35:734-741

[92] Chaves AR, Queiroz ME. Immunoaffinity in-tube solid phase microextraction coupled with liquid chromatography with fluorescence detection for determination of interferon α in plasma samples. Journal of Chromatography. B, Analytical Technologies in the Biomedical and Life Sciences. 2013;928:37-43

[93] Chaves AR, Queiroz MEC. In-tube solid-phase microextraction with molecularly imprinted polymer to determine interferon alpha 2a in plasma sample by high performance liquid chromatography. Journal of Chromatography. A. 2013;1318:43-48

[94] SantosMG, TavaresIMC, BarbosaAF, Bettini J, Figueiredo EC. Analysis of tricyclic antidepressants in human plasma using online-restricted access molecularly imprinted solid phase extraction followed by direct mass spectrometry identification/quantification. Talanta. 2017;163:8-16

[95] Wang R, Li W, Chen Z. Solid phase microextraction with poly(deep eutectic solvent) monolithic column online coupled to HPLC for determination of non-steroidal anti-inflammatory drugs. Analytica Chimica Acta. 2018;1018:111-118

[96] Souza ID, Hantao LW, Queiroz MEC. Polymeric ionic liquid open tubular capillary column for on-line in-tube SPME coupled
with UHPLC-MS/MS to determine endocannabinoids in plasma samples. Analytica Chimica Acta. 2019;1045:108-116

[97] Wang R, Chen Z. Boronate affinity monolithic column incorporated with graphene oxide for the in-tube solid-phase microextraction of glycoproteins. Journal of Separation Science. 2018;41:2767-2773

[98] Wang C, Zhou W, Liao X, Zhang W, Chen Z. An etched polyether etherketone tube covered with immobilized graphene oxide for online solid phase microextraction of quaternary alkaloids prior to their quantitation by HPLC-MS/MS. Microchimica Acta. 2017;184:2715-2721

[99] Zheng MM, Wang ST, Hu WK, Feng YQ. In-tube solid-phase microextraction based on hybrid silica monolith coupled to liquid chromatography-mass spectrometry for automated analysis of ten antidepressants in human urine and plasma. Journal of Chromatography. A. 2010;1217:7493-7501

[100] Shamsayei M, Yamini Y, Asiabi H. Polythiophene/graphene oxide nanostructured electrodeposited coating for on-line electrochemically controlled in-tube solid-phase microextraction. Journal of Chromatography. A. 2016;1475:8-17

[101] Asiabi H, Yamini Y, Seidi S, Ghahramanifard F. Preparation and evaluation of a novel molecularly imprinted polymer coating for selective extraction of indomethacin from biological samples by electrochemically controlled in-tube solid phase microextraction. Analytica Chimica Acta. 2016;913:76-85

[102] Asiabi H, Yamini Y, Shamsayei M. Development of electrochemically controlled packed-in-tube solid phase microextraction method for sensitive analysis of acidic drugs in biological samples. Talanta. 2018;185:80-88

[103] Saito K, Yagi K, Ishizaki A, Kataoka H. Determination of anabolic steroids in human urine by automated in-tube solid-phase microextraction coupled with liquid chromatography-mass spectrometry. Journal of Pharmaceutical and Biomedical Analysis. 2010;52:727-733

[104] Kataoka H, Inoue T, Ikekita N, Saito K. Development of exposure assessment method based on the analysis of urinary heterocyclic amines as biomarkers by on-line in-tube solid-phase microextraction coupled with liquid chromatography-tandem mass spectrometry. Analytical and Bioanalytical Chemistry. 2014;406:2171-2178

[105] Mizuno K, Kataoka H. Analysis of urinary 8-isoprostane as an oxidative stress bio marker by stable isotope dilution using automated online in-tube solid-phase microextraction coupled with liquid chromatography-tandem mass spectrometry. Journal of Pharmaceutical and Biomedical Analysis. 2015;112:36-42

[106] Kataoka H, Mizuno K, Oda E, Saito A. Determination of the oxidative stress biomarker urinary 8-hydroxy-2'-deoxyguanosine by automated on-line in-tube solid-phase microextraction coupled with liquid chromatography-tandem mass spectrometry. Journal of Chromatography. B, Analytical Technologies in the Biomedical and Life Sciences. 2016;1019:140-146

[107] He J, Liu Z, Ren L, Liu Y, Dou P, Qian K, et al. On-line coupling of in-tube boronate affinity solid phase microextraction with high performance liquid chromatography-electrospray
ionization tandem mass spectrometry for the determination of cis-diol biomolecules. Talanta. 2010;82:270-276

[108] Ahmadi SH, Manbohi A, Heydar KT. Electrochemically controlled in-tube solid phase microextraction of naproxen from urine samples using an experimental design. Analyst. 2015;140:497-505

[109] Wang S, Xu H. Inorganic-organic hybrid coating material for the online in-tube solid-phase microextraction of monohydroxy polycyclic aromatic hydrocarbons in urine. Journal of Separation Science. 2016;39:4610-4620

[110] Luo X, Li G, Hu Y. In-tube solid-phase microextraction based on NH₂-MIL-53(Al)-polymer monolithic column for online coupling with high-performance liquid chromatography for directly sensitive analysis of estrogens in human urine. Talanta. 2017;165:377-383

[111] Saito A, Hamano M, Kataoka H. Simultaneous analysis of multiple urinary biomarkers for the evaluation of oxidative stress by automated online in-tube solid-phase microextraction coupled with negative/positive ion-switching mode liquid chromatography-tandem mass spectrometry. Journal of Separation Science. 2018;41:2743-2749

[112] Yasuhara R, Ebara K, Saito K, Kataoka H. Automated analysis of salivary stress-related steroid hormones by online in-tube solid-phase microextraction coupled with liquid chromatography–tandem mass spectrometry. Analytical Methods. 2012;4:3625-3630

[113] Kataoka H, Ebara K, Yasuhara R, Saito K. Simultaneous determination of testosterone, cortisol, and dehydroepiandrosterone in saliva by stable isotope dilution on-line in-tube solid-phase microextraction coupled with liquid chromatography-tandem mass spectrometry. Analytical and Bioanalytical Chemistry. 2013;405:331-340

[114] Moriyama E, Kataoka H. Automated analysis of oxytocin by on-line in-tube solid-phase microextraction coupled with liquid chromatography-tandem mass spectrometry. Chromatography. 2015;2:382-391

[115] Ishizaki A, Uemura A, Kataoka H. A sensitive method to determine melatonin in saliva by automated online in-tube solid-phase microextraction coupled with stable isotope-dilution liquid chromatography-tandem mass spectrometry. Analytical Methods. 2017;9:3134-3140

[116] Kataoka H, Inoue T, Saito K, Kato H, Masuda K. Analysis of heterocyclic amines in hair by on-line in-tube solid-phase microextraction coupled with liquid chromatography-tandem mass spectrometry. Analytica Chimica Acta. 2013;786:54-60

[117] Yamamoto Y, Ishizaki A, Kataoka H. Biomonitoring method for the determination of polycyclic aromatic hydrocarbons in hair by online in-tube solid-phase microextraction coupled with high performance liquid chromatography and fluorescence detection. Journal of Chromatography. B, Analytical Technologies in the Biomedical and Life Sciences. 2015;1000:187-191

[118] Inukai T, Kaji S, Kataoka H. Analysis of nicotine and cotinine in hair by on-line in-tube solid-phase microextraction coupled with liquid chromatography-tandem mass spectrometry as biomarkers of exposure to tobacco smoke. Journal of Pharmaceutical and Biomedical Analysis. 2018;156:272-277
[119] Chen D, Ding J, Wu MK, Zhang TY, Qi CB, Feng YQ. A liquid chromatography-mass spectrometry method based on post column derivatization for automated analysis of urinary hexanal and heptanal. Journal of Chromatography. A. 2017;1493:57-63

[120] Ying LL, Ma YC, Xu B, Wang XH, Dong LY, Wang DM, et al. Poly(glycidyl methacrylate) nanoparticle-coated capillary with oriented antibody immobilization for immunospecific in-tube solid phase micro-extraction: Preparation and characterization. Journal of Chromatography. A. 2017;1509:1-8

[121] Hakobyan L, Tolos JP, Moliner-Martinez Y, Molins-Legua C, Ramos JR, Gordon M, et al. Determination of meropenem in endotracheal tubes by in-tube solid phase microextraction coupled to capillary liquid chromatography with diode array detection. Journal of Pharmaceutical and Biomedical Analysis. 2018;151:170-177

[122] Wang S, Hu S, Xu H. Analysis of aldehydes in human exhaled breath condensates by in-tube SPME-HPLC. Analytica Chimica Acta. 2015;900:67-75

[123] Li Y, Xu H. Development of a novel graphene/polyaniline electrodeposited coating for on-line in-tube solid phase microextraction of aldehydes in human exhaled breath condensate. Journal of Chromatography. A. 2015;1395:23-31

[124] Hu Y, Song C, Li G. Fiber-in-tube solid-phase microextraction with molecularly imprinted coating for sensitive analysis of antibiotic drugs by high performance liquid chromatography. Journal of Chromatography. A. 2012;1263:21-27

[125] Wang J, Zhao Q, Jiang N, Li W, Chen L, Lin X, et al. Urea-formaldehyde monolithic column for hydrophilic in-tube solid-phase microextraction of aminoglycosides. The Journal of Chromatography A. 2017;1485:24-31

[126] Pang J, Yuan D, Huang X. On-line combining monolith-based in-tube solid phase microextraction and high-performance liquid chromatography-fluorescence detection for the sensitive monitoring of polycyclic aromatic hydrocarbons in complex samples. Journal of Chromatography. A. 2018;1571:29-37

[127] Wang J, Jiang N, Cai Z, Li W, Li J, Lin X, et al. Sodium hyaluronate-functionalized urea-formaldehyde monolithic column for hydrophilic in-tube solid-phase microextraction of melamine. Journal of Chromatography. A. 2017;1515:54-61

[128] Wu F, Wang J, Zhao Q, Jiang N, Lin X, Xie Z, et al. Detection of trans-fatty acids by high performance liquid chromatography coupled with in-tube solid-phase microextraction using hydrophobic polymeric monolith. Journal of Chromatography. B, Analytical Technologies in the Biomedical and Life Sciences. 2017;1040:214-221

[129] Wang T, Chen YH, Ma JF, Hu MJ, Li Y, Fang JH, et al. A novel ionic liquid-modified organic-polymer monolith as the sorbent for in-tube solid-phase microextraction of acidic food additives. Analytical and Bioanalytical Chemistry. 2014;406:4955-4963

[130] Asabi H, Yamini Y, Seidi S, Esrafil J, Rezaei F. Electroplating of nanostructured polyaniline-polypyrrole composite coating in a stainless-steel tube for on-line in-tube solid phase microextraction. Journal of Chromatography. A. 2015;1397:19-26

[131] Ishizaki A, Saito K, Hanioka N, Narimatsu S, Kataoka H. Determination monolithic column for hydrophilic in-tube solid-phase microextraction of aminoglycosides. The Journal of Chromatography A. 2017;1485:24-31
of polycyclic aromatic hydrocarbons in food samples by automated on-line in-tube solid-phase microextraction coupled with high-performance liquid chromatography-fluorescence detection. Journal of Chromatography. A. 2010;1217:5555-5563

[132] Ishizaki A, Saito K, Kataoka H. Analysis of polycyclic aromatic hydrocarbons contamination in tea products and crude drugs. Analytical Methods. 2011;3:299-305

[133] Ying LL, Wang DY, Yang HP, Deng XY, Peng C, Zheng C, et al. Synthesis of boronate-decorated polyethyleneimine-grafted porous open tubular capillaries for enrichment of polyphenols in fruit juices. Journal of Chromatography. A. 2018;1544:23-32

[134] Andrade MA, Lanças FM. Determination of ochratoxin A in wine by packed in-tube solid phase microextraction followed by high performance liquid chromatography coupled to tandem mass spectrometry. Journal of Chromatography. A. 2017;1493:41-48

[135] Saito K, Ikeuchi R, Kataoka H. Determination of ochratoxins in nuts and grain samples by in-tube solid-phase microextraction coupled with liquid chromatography-mass spectrometry. Journal of Chromatography. A. 2012;1220:1-6

[136] Wu F, Xu C, Jiang N, Wang J, Ding CF. Poly (methacrylic acid-co-diethenyl-benzene) monolithic microextraction column and its application to simultaneous enrichment and analysis of mycotoxins. Talanta. 2018;178:1-8

[137] Wang X, Ma Q, Li M, Chang C, Bai Y, Feng Y, et al. Automated and sensitive analysis of 28-epihomobrassinolide in Arabidopsis thaliana by on-line polymer monolith microextraction coupled to liquid chromatography-mass spectrometry. Journal of Chromatography. A. 2013;1317:121-128

[138] Poorahong S, Thammakhet C, Thavarungkul P, Kanatharana P. Online in-tube microextractor coupled with UV-vis spectrophotometer for bisphenol A detection. Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances and Environmental Engineering. 2013;48:242-250

[139] Feng J, Wang X, Tian Y, Luo C, Sun M. Basalt fibers grafted with a poly(ionic liquids) coating for in-tube solid-phase microextraction. Journal of Separation Science. 2018;41:3267-3274

[140] González-Fuenzalida RA, López-García E, Moliner-Martínez Y, Campíns-Falcó P. Adsorbent phases with nanomaterials for in-tube solid-phase microextraction coupled on-line to liquid nanochromatography. Journal of Chromatography. A. 2016;1432:17-25

[141] Saito K, Uemura E, Ishizaki A, Kataoka H. Determination of perfluorooctanoic acid and perfluorooctane sulfonate by automated in-tube solid-phase microextraction coupled with liquid chromatography-mass spectrometry. Analytica Chimica Acta. 2010;658:141-146

[142] Vitta Y, Moliner-Martínez Y, Campíns-Falcó P, Cuervo AF. An in-tube SPME device for the selective determination of chlorophyll a in aquatic systems. Talanta. 2010;82:952-956

[143] Bagheri H, Piri-Moghadam H, Es'haghi A. An unbreakable on-line approach towards sol-gel capillary microextraction. Journal of Chromatography. A. 2011;1218:3952-3957
Biochemical Analysis Tools - Methods for Bio-Molecules Studies

[144] Moliner-Martínez Y, Molins-Legua C, Verdú-Andrés J, Herráez-Hernández R, Campíns-Falcó P. Advantages of monolithic over particulate columns for multiresidue analysis of organic pollutants by in-tube solid-phase microextraction coupled to capillary liquid chromatography. Journal of Chromatography. A. 2011;1218:6256-6262

[145] Prieto-Blanco MC, Moliner-Martínez Y, López-Mahía P, Campíns-Falcó P. Ion-pair in-tube solid-phase microextraction and capillary liquid chromatography using a titania-based column: Application to the specific lauralkonium chloride determination in water. Journal of Chromatography. A. 2012;1248:55-59

[146] Kataoka H, Shiba H, Saito K. Automated analysis of oseltamivir and oseltamivir carboxylate in environmental water samples by online in-tube solid-phase microextraction coupled with liquid chromatography–tandem mass spectrometry. Analytical Methods. 2012;4:1513-1518

[147] Prieto-Blanco MC, Moliner-Martínez Y, Campíns-Falcó P. Combining poly(dimethyl-diphenylsiloxane) and nitrile phases for improving the separation and quantitation of benzalkonium chloride homologues: In-tube solid phase microextraction-capillary liquid chromatography-diode array detection-mass spectrometry for analyzing industrial samples. Journal of Chromatography. A. 2013;1297:226-230

[148] Masiá A, Moliner-Martínez Y, Muñoz-Ortuño M, Pico Y, Campíns-Falcó P. Multiresidue analysis of organic pollutants by in-tube solid phase microextraction coupled to ultra-high performance liquid chromatography-electrospray-tandem mass spectrometry. Journal of Chromatography. A. 2013;1306:1-11

[149] Prieto-Blanco MC, Moliner-Martínez Y, López-Mahía P, Campíns-Falcó P. Determination of carbonyl compounds in particulate matter PM2.5 by in-tube solid-phase microextraction coupled to capillary liquid chromatography/mass spectrometry. Talanta. 2013;115:876-880

[150] Moliner-Martínez Y, Vitta Y, Prima-Garcia H, González-Fuenzalida RA, Ribera A, Campíns-Falcó P, et al. Silica supported Fe3O4 magnetic nanoparticles for magnetic solid-phase extraction and magnetic in-tube solid-phase microextraction: Application to organophosphorous compounds. Analytical and Bioanalytical Chemistry. 2014;406:2211-2215

[151] González-Fuenzalida RA, Moliner-Martínez Y, Prima-Garcia H, Ribera A, Campins-Falcó P, Zaragozá RJ. Evaluation of superparamagnetic silica nanoparticles for extraction of triazines in magnetic in-tube solid phase microextraction coupled to capillary liquid chromatography. Nanomaterials. 2014;4:242-255

[152] Ahmadi SH, Manbohi A, Heydar KT. Electrochemically controlled in-tube solid phase microextraction. Analytica Chimica Acta. 2015;853:335-341

[153] Moliner-Martínez Y, Serra-Mora P, Verdú-Andrés J, Herráez-Hernández R, Campíns-Falcó P. Analysis of polar triazines and degradation products in waters by in-tube solid-phase microextraction and capillary chromatography: An environmentally friendly method. Analytical and Bioanalytical Chemistry. 2015;407:1485-1497

[154] Zhang J, Zhang W, Bao T, Chen Z. Polydopamine-based immobilization of zeolitic imidazolate framework-8 for in-tube solid-phase microextraction.
Journal of Chromatography. A. 2015;1388:9-16

[155] Pla-Tolós J, Moliner-Martínez Y, Molins-Legua C, Herráez-Hernández R, Verdú-Andrés J, Campíns-Falcó P. Selective and sensitive method based on capillary liquid chromatography with in-tube solid phase microextraction for determination of monochloramine in water. Journal of Chromatography. A. 2015;1388:17-23

[156] Tan F, Zhao C, Li L, Liu M, He X, Gao J. Graphene oxide based in-tube solid-phase microextraction combined with liquid chromatography tandem mass spectrometry for the determination of triazine herbicides in water. Journal of Separation Science. 2015;38:2312-2319

[157] Sun M, Feng J, Bu Y, Luo C. Nanostructured-silver-coated polyetheretherketone tube for online in-tube solid-phase microextraction coupled with high-performance liquid chromatography. Journal of Separation Science. 2015;38:3239-3246

[158] Sun M, Feng J, Bu Y, Luo C. Highly sensitive copper fiber-in-tube solid-phase microextraction for online selective analysis of polycyclic aromatic hydrocarbons coupled with high performance liquid chromatography. Journal of Chromatography. A. 2015;1408:41-48

[159] Feng J, Sun M, Bu Y, Luo C. Development of a cheap and accessible carbon fibers-in-poly(ether ether ketone) tube with high stability for online in-tube solid-phase microextraction. Talanta. 2016;148:313-320

[160] Bu Y, Feng J, Sun M, Zhou C, Luo C. Facile and efficient poly(ethylene terephthalate) fibers-in-tube for online solid-phase microextraction towards polycyclic aromatic hydrocarbons. Analytical and Bioanalytical Chemistry. 2016;408:4871-4882

[161] Bu Y, Feng J, Sun M, Zhou C, Luo C. Gold-functionalized stainless-steel wire and tube for fiber-in-tube solid-phase microextraction coupled to high-performance liquid chromatography for the determination of polycyclic aromatic hydrocarbons. Journal of Separation Science. 2016;39:932-938

[162] Sun M, Feng J, Bu Y, Luo C. Ionic liquid coated copper wires and tubes for fiber-in-tube solid-phase microextraction. Journal of Chromatography. A. 2016;1458:1-8

[163] Bu Y, Feng J, Tian Y, Wang X, Sun M, Luo C. An organically modified silica aerogel for online in-tube solid-phase microextraction. Journal of Chromatography. A. 2017;1517:203-208

[164] Bu Y, Feng J, Wang X, Tian Y, Sun M, Luo C. In situ hydrothermal growth of polyaniline coating for in-tube solid-phase microextraction towards ultraviolet filters in environmental water samples. Journal of Chromatography. A. 2017;1483:48-55

[165] Mei M, Huang X. Online analysis of five organic ultraviolet filters in environmental water samples using magnetism-enhanced monolith-based in-tube solid phase microextraction coupled with high-performance liquid chromatography. Journal of Chromatography. A. 2017;1525:1-9

[166] Serra-Mora P, Jornet-Martinez N, Moliner-Martinez Y, Campins-Falcó P. In tube-solid phase microextraction-nano liquid chromatography: Application to the determination of intact and degraded polar triazines in waters and recovered struvite. Journal of Chromatography. A. 2017;1513:51-58

[167] Wang X, Pan L, Feng J, Tian Y, Luo C, Sun M. Silk fiber for in-tube solid-phase microextraction to detect aldehydes by chemical derivatization.
Biochemical Analysis Tools - Methods for Bio-Molecules Studies

[168] Wang X, Feng J, Bu Y, Tian Y, Luo C, Sun M. Mesoporous titanium oxide with high-specific surface area as a coating for in-tube solid-phase microextraction combined with high-performance liquid chromatography for the analysis of polycyclic aromatic hydrocarbons. Journal of Separation Science. 2017;40:2474-2481

[169] Feng J, Wang X, Tian Y, Luo C, Sun M. Poly(ionic liquids)-coated stainless-steel wires packed into a polyether ether ketone tube for in-tube solid-phase microextraction. Journal of Separation Science. 2017;40:4773-4779

[170] Feng J, Tian Y, Wang X, Luo C, Sun M. Basalt fibers functionalized with gold nanoparticles for in-tube solid-phase microextraction. Journal of Separation Science. 2018;41:1149-1155

[171] Feng J, Mao H, Wang X, Tian Y, Luo C, Sun M. Ionic liquid chemically bonded basalt fibers for in-tube solid-phase microextraction. Journal of Separation Science. 2018;41:1839-1846

[172] Wang X, Feng J, Tian Y, Luo C, Sun M. Co-Al bimetallic hydroxide nanocomposites coating for online in-tube solid-phase microextraction. Journal of Chromatography. A. 2018;1550:1-7

[173] Feng J, Wang X, Tian Y, Bu Y, Luo C, Sun M. Electrophoretic deposition of graphene oxide onto carbon fibers for in-tube solid-phase microextraction. Journal of Chromatography. A. 2017;1517:209-214

[174] Jillani SMS, Alhooshani K. Urea functionalized surface-bonded sol-gel coating for on-line hyphenation of capillary microextraction with high-performance liquid chromatography. Journal of Chromatography. A. 2018;1543:14-22

[175] Pang J, Mei M, Yuan D, Huang X. Development of on-line monolith-based in-tube solid phase microextraction for the sensitive determination of triazoles in environmental waters. Talanta. 2018;184:411-417

[176] Prieto-Blanco MC, López-Mahía P, Campín-Falcó P. On-line analysis of carbonyl compounds with derivatization in aqueous extracts of atmospheric particulate PM10 by in-tube solid-phase microextraction coupled to capillary liquid chromatography. Journal of Chromatography. A. 2011;1218:4834-4839

[177] Fernández-Amado M, Prieto-Blanco MC, López-Mahía P, Muniategui-Lorenzo S, Prada-Rodríguez D. Ion-pair in-tube solid phase microextraction for the simultaneous determination of phthalates and their degradation products in atmospheric particulate matter. Journal of Chromatography. A. 2017;1520:35-47

[178] Ishizaki A, Kataoka H. A sensitive method for the determination of tobacco-specific nitrosamines in main- and side-stream smoke samples by online in-tube solid-phase microextraction coupled with liquid chromatography-tandem mass spectrometry. Analytica Chimica Acta. 2019;1075:98-105