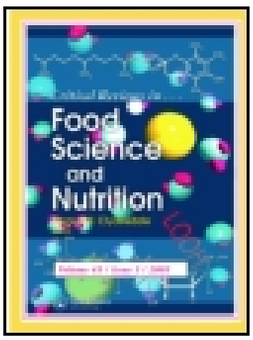

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REVIEW

Current trends in sample preparation by solid-phase extraction techniques for the determination of antibiotic residues in foodstuffs: a review

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ABSTRACT

The presence of antibiotic residues in foodstuff has been of growing concern in recent years. They are associated with several adverse effects on human health such as the transmission of antibiotic-resistant pathogenic bacteria through the contaminated food, weakness of the immune system, allergic or toxic reactions and imbalance of the gut microbiota. Therefore, monitoring of the levels of antibiotic residues in animal-derived food is necessary to guarantee the safety of food products as well as the public health. Since the residual antibiotics in the foodstuff are in trace levels which are often lower than the limits of detection of analytical instruments, the sample preparation before the analysis is very important. This step is an essential part of an analytical process, especially for the extraction of chemical residues from a sample, preconcentration of the extract and elimination of any matrix interferences that may affect the selectivity, sensitivity and the overall performance of the analytical methods. Solid-phase extraction (SPE) is one of the most widely used techniques for the sample preparation that provides an efficient and reproducible method for selective concentration of target analytes in complex matrices. The objective of this research was to provide an updated overview of the recent trends in SPE techniques over the past five years. Different variations of this method, including solid-phase microextraction, stir bar sorptive extraction, matrix solid-phase dispersion, micro-solid-phase extraction, dispersive micro solid-phase extraction, magnetic solid-phase extraction, and molecularly imprinted solid-phase extraction are also given in the present study. The review is focused on recent developments and innovations in the SPE which tries to improve the efficiency, safety and performance of sample preparation.

KEYWORDS

Solid-phase extraction; food; antibiotic residue; sample preparation

Introduction

Antibiotics are widely used in veterinary medicine for the prevention and treatment of microbial infections or diseases and as dietary supplements in livestock husbandry (Bittencourt et al. 2012; Javadi and Khatibi 2017; Karageorgou et al. 2018). However, the excessive and inconsiderate use of them may leave residues in animal-derived foods, that may have several adverse effects on the human health (Javadi, Mirzaie, and Khatibi 2011b; Bittencourt et al. 2012; Ramatla et al. 2017; Karageorgou et al. 2018). In recent years, the association between the use of antibiotics in animal breeding and the occurrence of antimicrobial resistance in humans has become a great threat to public health (Javadi and Khatibi 2017; Pérez-Rodríguez et al. 2018). The presence of sub-therapeutic levels of antimicrobials in foodstuff for long periods can lead to the prevalence of drug-resistant strains of pathogenic bacteria (Kabir, Locatelli, and Ulusoy 2017; Ramatla et al. 2017). Furthermore, human exposure to significant levels of antibiotic residues in food may lead to the weakness of the immune system, allergic or toxic reactions in susceptible individuals, disturbance of the intestinal microbiota, tissue damage and neurological disorders (Javadi, Mirzaie, and Khatibi 2011a; Kabir, Locatelli, and Ulusoy 2017; Ramatla et al. 2017; Bitas et al. 2018).

Due to the discovery of new resistant strains of bacteria over time, the pressures on the diagnostic laboratories to determine the veterinary antimicrobials in foodstuff have been increased in recent years. In order to guarantee the food safety and protect human health from the adverse effects of potentially dangerous antibiotics, governmental authorities have established monitoring programs to detect antibiotic residues in the foodstuff (Khatibi and Javadi 2009; Bittencourt et al. 2012; Karageorgou et al. 2018; Pérez-Rodríguez et al. 2018). The maximum residue limits (MRL) has been adopted for residues of veterinary drugs in foodstuffs of animal origin (Bittencourt et al. 2012; Chang et al. 2019). MRLs are legally permitted or recognized as acceptable drug residue in food that may be ingested daily without having any toxicological hazard to human health. The MRL levels, expressed in mg/kg or μg/kg, are set up for several animals species and target tissues such as muscle, liver,

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kidney, fat, milk, egg and, in a few cases, honey (Pérez-Rodríguez et al. 2018; Chang et al. 2019).

In recent years, various analytical methods such as enzyme-linked immunosorbent assay (ELISA), capillary electrophoresis (CE), thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC), gas chromatography coupled to mass spectrometry (GC-MS) and liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) have been developed for detection of drug residues in complex matrices (Chen et al. 2015; Galvidis, Lapa, and Burkin 2015; Thangadurai 2015; Liu et al. 2017; Paul et al. 2017; Zhou et al. 2017; Song et al. 2018; Liyong He, Huang, et al. 2019; Lan et al. 2019). However, the antibiotic residues are present in low concentrations which are often lower than the limits of detection (LODs) of the analytical instruments (Alampanos, Samanidou, and Papadoyannis 2019). Furthermore, the separation and quantitative analysis of drug residues in the food samples can be affected by the complex matrix and impurities such as protein and fat (Lan et al. 2019). Therefore, the sample pretreatment is a vital part of the analytical process, especially for the extraction of chemical residues from the sample, preconcentration of the extract to isolate the target analytes and eliminate any matrix interferences that may affect the selectivity, sensitivity and the overall performance of an analytical technique (Kinsella et al. 2009; Bitas et al. 2018).

Solid-phase extraction (SPE) is one of the most widely used techniques for the extraction of veterinary drug residue (Huang et al. 2016; Cunha and Fernandes 2018; Alampanos, Samanidou, and Papadoyannis 2019). In this technique, the separation of analyte carried out based on solid-liquid phase equilibrium and low-pressure liquid chromatography (Pérez-Rodríguez et al. 2018). This technique can be applied in three types of manual, the semi-automatic or the automatic (Alampanos, Samanidou, and Papadoyannis 2019).

The main steps of a basic SPE procedure are included: the activation of sorbent phase, percolation/sorption of the analyte in the sample matrix (liquid solution) into the sorbent, removal of the matrix interferences (clean-up) and elution and concentration of the analyte with an appropriate technique (Pérez-Rodríguez et al. 2018). However, the mechanisms for the extraction can be varied based on the nature of sorbent (Cunha and Fernandes 2018).

SPE technique is a safe, efficient and reproducible method for the separation of antibiotic residues. It has easy automation and provides a selective concentration of the analyte (Bogialli et al. 2007; Pérez-Rodríguez et al. 2018). Besides these advantages, compared with modern techniques, SPE is a solvent and time-consuming multi-step process (Vas and Vékey 2004; Alampanos, Samanidou, and Papadoyannis 2019). In this technique, the concentration step is necessary which may lead to the loss of volatile components. It also has difficulties in providing consistent flow and plugging of cartridges, especially in automation (Vas and Vékey 2004; Kinsella et al. 2009).

In order to overcome the above drawbacks, novel SPE methods have been developed using a variety of different sorbents to preconcentrate the target analytes (Dmitrienko et al. 2014; Lan et al. 2019).

The current trends in food sample preparation are going toward the development of new techniques that are faster, cheaper, require less amount of organic solvents, lower mass of sample to analyze and are amenable to automation and provide simultaneous extraction of multiple analytes from a sample (Kinsella et al. 2009; Lan et al. 2019).

This study aimed to review the most recently published articles about the use of SPE techniques for the determination of antibiotic residues in foodstuff over the past five years. The main variations of this technique applied nowadays are summarized in Table 1. Also, the advantages and limitations of solid-phase extraction techniques are presented in Table 2. The current review will focus on recent developments and innovations in SPE which tries to improve the efficiency, safety and performance of sample preparation.

Solid-phase microextraction

Since SPE is time-consuming and has an extensive procedure, novel solid-phase microextraction (SPME) methods have been developed to overcome the drawbacks of SPE (Jafari and Hamidi 2018; Alampanos, Samanidou, and Papadoyannis 2019). In recent years, SPME was very popular because of its proven advantages such as easy miniaturization, high sensitivity, convenient automation, short extraction time, cost minimization and easy coupling with chromatographic instruments. This technique is suitable for different varieties of organic and inorganic substances in any one of their three kinds of physical states (Bogialli et al. 2007; Kumar and Malik 2009; Souza-Silva, Gionfriddo, and Pawliszyn 2015; Kabir, Locatelli, and Ulusoy 2017; Jafari and Hamidi 2018; Alampanos, Samanidou, and Papadoyannis 2019).

The miniaturization of sample preparation in this technique is reduced labor-intensive manual operations which enhance the overall performance of the analytical method (Kabir, Locatelli, and Ulusoy 2017). In comparison with the conventional SPE technique, less solvent is consumed to achieve the pure extracts using SPME (Bogialli et al. 2007; Kumar and Malik 2009; Lan et al. 2019). Moreover, according to the principles of Green Analytical Chemistry (GAC) and the need for environmental-friendly techniques, SPME methods have received more interest than other techniques of antimicrobial extraction (Filippou, Bitas, and Samanidou 2017; Alampanos, Samanidou, and Papadoyannis 2019).

The mechanism of SPME involves two main steps: (1) Adsorption of analytes from the sample matrix into the sorbent phase (2) Desorption of analytes into the suitable mobile phase for the analysis which is usually performed by LC, GC and HPLC (Lum, Tsoi, and Leung 2014; Delafiori, Ring, and Furey 2016; Filippou, Bitas, and Samanidou 2017; Niu et al. 2018; Pérez-Rodríguez et al. 2018).

Since the stationary phase should have the highest affinity to the selected analytes, the choice of proper sorbent with the desired properties is very difficult (Kumar and Malik 2009; Lum, Tsoi, and Leung 2014; Souza-Silva, Gionfriddo,

Table 1. Examples of recent solid-phase extraction methods used for the analysis of antibiotic residues in the foodstuff.

Food Sample	Analytes	Type of SPE	Type of adsorbent	Detection system	LODs	LOQs	Recovery (%)	RSD%	Linear dynamic range	References
Milk	TC OTC DOX	MSPE	β-CD functionalized silica-coated magnetic GO	HPLC-UV	1.8–2.9 μg/L	6.1–9.7 μg/L	70.6-121.5	<8.8	10.0–200.0 μg/L	(Al-Afy et al. 2018)
Honey	TC	Micro-SPE	Electrospun polyethylene terephthalate nanofibers doped with GO nanoparticles	HPLC-UV	15.3 μg/kg	47.1 μg/kg	89–94	<4.1	10–5000 μg/ kg	(Arabsorkhi and Sereshti 2018)
	Cefotaxime				3 μg/kg	10 μg/kg	95–98	<5.3		
Milk	Ciprofloxacin, Enrofloxacin, Marbofloxacin	MEPS	C8	UHPLC–PDA	0.010- 0.015 mg/mL	0.032–0.048 mg/mL	79- 88	2.4-3.6	0.001-1 mg/mL	(Aresta, Cotugno, and Zambonin 2019)
Honey	SAs	MISPE	MIP	HPLC–MS/MS	0.004–1.050 μg/kg	0.014–3.499 μg/kg	84.3-104.7	<11.6	1–60 mg/kg	(Baeza Fonte, Rodríguez Castro, and Liva-Garrido 2018)
Pork muscle, Minced pork,	TCs	MSPE	Eu- and Tb-coated magnetic nanocomposite	UHPLC-FLD	1.0- 3.8 ng/mL	–	65.0 – 102.6	≤15.4	2–10000 ng/mL	(Castillo-Garcia, Aguilar-Caballos, and Gomez-Hens 2015)
Chicken, pork, ground mix, Chicken muscle	Qs				0.25- 1.2 ng/mL		61.2- 98.5		0.5–2000 ng/mL	
Milk	FQs	Multiple monolithic fiber SPME	Poly(apronal-co-divinylbenzene/ ethylenedimethacrylate) monolith	HPLC/MS-MS	0.0019 – 0.018 μg/kg	0.0062 – 0.059 μg/kg	74.5-116	0.9 – 9.5	0.005- 50.0 μg/kg	(Chen and Huang 2016)
Honey					0.0010-0.0028 μg/kg	0.0033 – 0.0092 μg/kg				
Milk	CPs	Hollow fiber SPME	GO	HPLC-PDA	0.01– 0.02 μg/mL	0.03–0.06 μg/mL	71–108	2.6-8.6	0.05–10 μg/mL	(Chen and Ye 2016)
Honey	FQs	d-SPE	β-CD/ATP composite	HPLC-UV	0.30-3.95 μg/L	1.00-7.24 μg/L	83.6–88.6	<7.4	10–1500	(Cui et al. 2015)
Honey	Qs	d-SPME	Two-dimensional nanostructured Zn Al-LDH	HPLC-UV	3.0-5.0 ng/g	10-20 ng/g	74.1-88.9	2.4-7.9	10-2000 ng/g	(Di et al. 2019)
Infant formula	PCs	MISPE	MIP	HPLC-MS/MS	0.7- 23.6 μg/kg	2.4- 78.4 μg/kg	60- 91	–	–	(Díaz-Bao et al. 2015)
Milk	Qs	d-SPE	PSA	UHPLC-ESI-MS/MS	0.2-0.6 ng/g	0.6-2.0 ng/g	96.8-104.5	0.5-6.2	–	(Dorival-García et al. 2016)
	β-lactams				0.1-0.4 ng/g	0.3-1.3 ng/g	94.9-103.8	1.6-7.1		
Chicken Muscle and Liver	FQs	SBSE	GO/PEG composite	HPLC-FLD	0.0045–0.0079 μg/g	–	82.01-111	4.6–12.1	0.02–500 μg /L	(Fan et al. 2015)
							89.0 – 113			
Milk	SAs	MSPE	Fe_3O_4/reduced GO-CNTs	HPLC-UV	0.35–1.32 μg/L	1.16–4.40 μg/L	88.4–105.9	0.74–5.38	5–500 μg/L	(Feng et al. 2016)
Milk	DOX OTC TMP PC-G	MSPE	Magnetic mesoporous PANI coated with hydrophilic monomers and casein	HPLC-DAD	–	8.09-9.63 ng/mL	93.16-100	1.40-7.62	8-1000 ng/mL	(Florez, Dutra, and Borges 2019)
Milk	SAs	MSPE	p-Tolyl-functionalized magnetic CTNs	LC–HRMS	2–10 ng/L	10–30 ng/L	81.3–108.9	<6.9	–	(Fu et al. 2019)
Milk	Amoxicillin Ampicillin Cloxacillin	Micro-SPE	GO–starch–based nanocomposite	HPLC–UV	0.8–1.5 μg/kg	2.7–5.0 μg/kg	83-105	3.4-7.3	3–1000 μg/kg	(Golzari Aqda et al. 2019)
Egg	SDZ	MISPE	MIP microspheres	HPLC-DAD	0.05-0.06 μg/L	0.17-0.20 μg/L	78.22–86.10	2.60–5.03	0–200 μg/L	(He et al. 2016)
Milk, Chicken muscle, Egg	FQs	d-SPE	Magnetic graphene	HPLC–UV	0.05–0.3 ng/g	0.2–0.8 ng/g	82.4–108.5	1.6-3.4	0.2–2000 ng/mL	(He et al. 2017)
Milk, Fish	Kanamycin	SBSE	Thiol Kana aptamer	ELISA	0.3 pg/mL	–	89.5-106	<4.7	0.8 pg/mL–10 ng/mL	(He, Huang, et al. 2019)
Pork muscle	β-lactams	MSP	Oasis HLB	UPLC-MS/MS	0.02-0.63 mg/kg	0.07-0.97 mg/kg	92 – 111	<12	0.5-100 mg /kg	(Huang et al. 2016)
Milk	Sulfamethoxazole	d-SPE	Butylamide silica	CE	0.05 mg/l	0.10 mg/l	73to 85	1.85-2.3	0.10-34.0 mg/l	(Islas et al. 2016)
Milk	Cloxacillin	MISPE	MIP	electrochemical nanosensor based on a screen-printed electrode	36 nM	–	98.6- 101.8	4.3-5.3	110–750 nM	(Jafari et al. 2019)
Milk	SAs	d-SPME	MIL-101(Cr)@GO	UHPLC-MS/MS	0.012-0.145 μg/L	0.039- 0.491 mg/L	79.83 – 103.8	<10	0.10-50 μg/L	(Jia et al. 2017)
Milk, Pork meat, Chicken meat, Pork liver and kidney, Egg	FQs	96-well plate Micro-SPE	Sulfonated-PANI/PAN NFsM	UPLC-MS/MS	0.012-0.06 μg/kg	0.04-0.2 μg/kg	84.5-110.7	<12.8	0.04-600.0 μg/kg	(Jian et al. 2019)

(*continued*)

Table 1. Continued.

Food Sample	Analytes	Type of SPE	Type of adsorbent	Detection system	LODs	LOQs	Recovery (%)	RSD%	Linear dynamic range	References
Pork and chicken meat, Clam	TC DTC OTC Chloroteracycline	Accelerated solvent extraction and Micro-SPE	Copper(II) isonicotinate	HPLC-UV	7.4–16.3 ng/g	24.7–53.8 ng/g	92 – 105	<9.3	0.005 – 1.0 mg/kg	(Jiao, Zhu, and Yao 2015)
Milk	β-Lactams Chloramphenicol	MSPD	Plexa and QuECheRS	HPLC-DAD	1-7 µg/kg	–	81.8 – 116.9	<10.7	20–2000 µg/ kg	(Karageorgou et al. 2018)
Beef and chicken muscle	β-Lactams TCs MAs FQs	SPME	PAN / hydrophilic-lipophilic balance	LC-MS/MS	–	≤10 ng/g	70 – 120	≤25	–	(Khaled, Singh, and Pawliszyn 2019)
Milk	Cephalexin	MISPE	Molecular imprinted polymer	HPLC-UV	–	–	91.78–93.25	–	–	(Lata et al. 2015)
Milk	SAs	MSPE	$CoFe_2O_4$-graphene	HPLC-UV	<1.59 µg/L	<4.81 µg/L	62.0 – 104.3	<14.0	0.02-50.00 mg/L	(Li et al. 2015)
Honey	AMs	d-SPE	PVA-coated core-shell MNPs	HILIC-MS/MS	0.993-1.23 µg/kg	3.11- 4.12 µg/kg	82.9 – 100.7	<12.8	20-4000 µg/kg	(Li et al. 2018)
Honey	MAs	SPME	MIP	HPLC/ESI-MS/MS	1.1–5.1 ng/g	0.01–0.2 ng/g	79.8–98.1	≤8.6	0.05–100 ng/g	(Liu et al. 2019)
Milk					1.9–15.8 ng/g	3.3-15.8 ng/g	73.4–96.1			
Milk	Penicilloic Acid Penilloic Acid	MSPD	MIP	HPLC-MS	0.04 mg/g 0.05 mg/g	0.13 mg/g 0.17 mg/g	79.8-90.3 77.4-86.2	5.2-7.4 3.1-6.4	0.04 – 4 mg/g	(Luo, Xie, et al. 2015)
Egg, milk, milk powder	TCs	MISPE	MIP hybrid composite	RP-HPLC-UV	0.76–1.13 µg/kg	2.53–3.77 µg/kg	85.3 to 98.3	≤5.3	5.0–500 µg/kg	(Lv et al. 2015)
Fish muscle	Qs SAs MAs Pyrimethamine	SPME	(MOF) MIL-101(Cr)-NH_2 fiber	LC-MS/MS	0.2 – 1.1 ng/g	0.6 – 3.7 ng/g	–	1.5 – 8.3	10-50000 ng /L	(Mondal et al. 2019)
Honey	AMs	MISPE	MIP	CZE-MS/MS	0.4-28.5 µg/kg	1.4-94.8 µg/kg	88.2-99.8	<8	1.4-800 mg/kg	(Moreno-González et al. 2015)
Milk, Chicken meat	SAs	Magnetic Micro-SPE	TMCNTs	HPLC-DAD	0.02–1.5 µg/L	0.08–5.0 µg/L	80.7–116.2	0.3–7.7	0.1–500 µg/L	(Nasir et al. 2019)
Honey	TCs	SPME	Poly (muconic acid-*co*-divinylbenzene/ ethylenedimethacrylate) monolith	HPLC-MS/MS	7.3-17.1 ng/kg	24.1-56.4 ng/kg	70.5-111.0	<10	0.05-100.0 µg/kg	(Pei and Huang 2017)
Milk	Qs	SBSE	PEG modified silicone	UHPLC-MS/MS	0.3-1.0 µg/kg	0.5-4.0 µg/kg	88-114	<15	0.5 – 150 µg/kg	(Rodríguez-Gómez et al. 2018)
Shrimp	Chloramphenicol Thiamphenicol Florfenicol	Ultrasound-assisted MSPD	Lichrolut C18	HPLC-DAD	–	–	89.1-120.6 81.3-114.5 72.0-103.3	<13.6	50-1000 µg/kg	(Samanidou and Makrygianni 2015)
Milk	Chloramphenicol	MISPE	Sol–gel silica based inorganic polymeric sorbent	LC-UV LC-MS	17 µg/kg 0.1 µg/kg	50 µg/kg 0.3 µg/kg	85-106	<13	50-5000 µg/kg	(Samanidou et al. 2016)
Infant formula powder	FQs	MISPE	Molecularly imprinted hybrid monoliths	LC/MS-MS	0.19–1.24 µg/kg	0.63–4.13 µg/kg	82.91–102.00	1.04–7.39	5–400 µg/kg	(Shao et al. 2019)
Fish muscle	SAs	MSPD	HLB	LC–MS/MS	2.3-16.4 µg/kg	6.9-54.7 µg/ kg	70.6–95.5	1.4–10.3	0.1-100 ng/mL	(Shen et al. 2016)
Milk	SAs	In-tube SPME	Graphene-embedded porous polymer	CE-LIF	0.25–0.47 µg/L	0.78–1.54 µg/L	91.1-94.6	≤1.14	2.0–500.0 µg/L	(Shuo et al. 2018)
Milk	Ampicillin	MISPE	MIP	HPLC-UV	10.7 µg/L	35.8 µg/L	>98	<7	100-500 µg/kg	(Soledad-Rodríguez et al. 2017)
Pork, bovine and chicken muscles	MAs	MISPE	MIP	LC–MS/MS	0.1-0.4 µg/kg	0.3 – 1.0 µg/kg	60.7-100.3	<14	0.1-0.4 µg/kg	(Song et al. 2016)
Pork meat	MAs	d-SPE	MIP	LC–MS/MS	0.2–0.5 µg/kg	0.5–2.0 µg/kg	68.6-95.5	<8	5-100 µg/kg	(Song et al. 2018)
Fish	Enrofloxacin	MISPE	Hollow MIPs	HPLC-UV	0.24 ng/mL	–	68.88-100.29	1.6-4.4	0.5-16.0 ng/mL	(Tang et al. 2016)
Milk	SAs	MSPE	Magnetic hyper crosslinked polystyrene (HCP/Fe_3O_4)	HPLC–AD	2.0–2.5 ng/mL	6.0–7.5 ng/mL	84–105	3-10	10.0–400 ng/mL	(Tolmacheva et al. 2016)
Honey	TC	MSPE	Fe_3O_4/aptamer nanoparticles	HPLC-UV	2.5 µg/L	10 µg/L	82.9-107.3	≤7.6	10.0-3000.0 mg/L	(Tu et al. 2019)
Milk	Cloxacillin Oxacillin Dicloxacillin	MISPE	MIP beads	HPLC- DAD	1.6-1.9 µg/kg	5.3–6.3 µg/kg	99–102	<9	7.5-480 µg/kg	(Urraca et al. 2016)

Meat-based baby food	Fleroxacin Norfloxacin Ofloxacin	Magnetic Micro-SPE	Zr-Fe-C MNPs	HPLC-FLD	3.0 mg/L 1.5 mg/L 1.5 mg/L	10 mg/L 5 mg/L 5 mg/L	86-111 90-122 88-116	≤9.8 ≤9.8 ≤9.9	10-1000 mg/L 5-1000 mg/L 5-1000 mg/L	(Vakh et al. 2018)
Milk, Chicken meat, Beef, pork	Benzyl-PC	MISPE	MIP	LC–MS/MS	6.2-14.4 μg/kg	–	96.2-108.20	–	0.5–10 mg/kg	(Van Royen et al. 2016)
Milk	TCs	MEPS	Graphene	HPLC-MS/MS	0.03-0.21 μg/L	0.05-0.9 μg/L	87.9-118.4	<19	15-110 μg/L	(Vasconcelos Soares Maciel et al. 2018)
Milk	SAs	MSPE	GO-based magnetic nanocomposite (Fe_3O_4@GO)	HPLC–MS/MS	0.02-0.13 μg/L	0.07-0.43 μg/L	73.4-97.4	≤8.2	2.0-100.0 μg/L	(Wang et al. 2016)
Pork meat	FQs SAs TCs	MSPD	MIP	UPLC-PDA	0.5–3.0 ng/g	1.5–6.0 ng/g	74.5–102.7	≤3.8	2–1000 ng/mL	(Wang, Zhang, et al. 2017a)
Chicken breast	Metronidazole Chloramphenicol Tinidazole Sulfamethoxazole	d-SPME	MIL-101(Cr)@GO	HPLC–MS/MS	0.77 ng/kg 0.08 ng/kg 0.71 ng/kg 1.02 ng/kg	2.55 ng/kg 0.26 ng/kg 2.37 ng/kg 3.40 ng/kg	91.5 – 102.3 91.1-95.6 95.2-100.3 88.9-98.0	2.2-4.9 2.1-5.2 2.0-4.3 1.6-3.7	10–1000 ng/kg 1–100 ng/kg 10–1000 ng/kg 10–1000 ng/kg	(Wang, Zhang, et al. 2017b)
Egg	Chloramphenicol Florfenicol Thiamphenicol	MISPE	Magnetic mesoporous dual-template MIPs (Fe_3O_4@$mSiO_2$ @DMIP)	HPLC-UV	0.16 μg/kg 0.08 μg/kg 0.08 μg/kg	0.5 μg/kg 0.27 μg/kg 0.27 μg/kg	88.2- 94.1 85.6- 94.4 83.3- 93.8	4.7-7.9 2.8- 5.9 5.9- 7.5	–	(Wei et al. 2016)
Milk	TCs	MSPE	GO/nZVI	HPLC-MS/MS	8.05–83.19 ng/L	17.42–182.75 ng/L	84.2–105.5	≤9.7	0.03–100 μg/L	(Wei, Wu, and Zhu 2017)
Egg	FQs	MSPE	Fe_3O_4–MoS_2	HPLC-UV	0.2-5.0 μg/L	0.7-17 μg/L	88.6-96.6	<5	2.5-300 μg/L	(Wu et al. 2019)
Chicken and pork meat, Shrimp	SAs	MSPE	Fe_3O_4@JUC-48 nanocomposite	HPLC-DAD	1.73- 5.23 ng/g	3.97-15.89 ng/g	76.1-102.6	<4.5	3.97–1000 ng/g	(Xia et al. 2017)
Chicken thigh meat pork shrimp	SAs	MSPE	Fe_3O_4@JUC-48	HPLC-DAD	1.73-5.23 ng/g	3.97-15.89 ng/g	76.1-102.6	<4.5	3.97–1000	(Xia et al. 2017)
Milk	Erythromycin TC Chloramphenicol	MISPE	Molecular imprinted polymer	HPLC-ELSD	10 μg/kg 20 μg/kg 10 μg/kg	–	77.82-87.08 81.02-88.17 72.94-83.57	1.21 4.09 4.37	10-600 μg/kg 20-600 μg/kg 10-1000 μg/kg	(Xie et al. 2018)
Milk	Oxacillin Cloxacillin Dicloxacillin	d-SPME	COU-2	HPLC-UV	2.0–3.3 μg/L	6.0–10.0 μg/L	80.3–99.5	6.2–8.8	10–5,000 μg/L	(Yahaya et al. 2015)
Chicken and pork Meat fish	FQs	SBSE	Dual-template MIP	HPLC-DAD	0.1-0.3 ng/g	0.4-0.9 ng/g	67.4-99.0	<6.9	1-1000 ng/mL	(Yang et al. 2017)
Milk	Qs	SBS Micro-extraction	Monoclonal antibody	HPLC-FLD	0.05-0.1 ng/g	0.2-0.3 ng/g	11.8-40.0	≤12.5	0.1-100 ng/mL	(Yao et al. 2015)
Milk Pork Fish	FQs	MSPE	Fe_3O_4@MCM-48 nanocomposite	HPLC–MS/MS	0.7–6.0 ng/L	2.5–20.0 ng/L	75.0– 104.7	<10	5-1000 ng/L	(Yu et al. 2019)
Chicken muscle, Egg	Nitroimidazoles Nitrofurans Chloramphenicol	d-SPE	C18-diatomaceous earth	UHPLC-MS/MS	0.05-0.2 μg/kg	0.1-0.5 μg/kg	86.4-116.7	≤20%.	–	(Zhang, Wang, et al. 2017)
Milk	Chloramphenicol	MISPE	MIP	LC-MS/MS	0.02 μg/L	0.08 μg/L	96.04-108.68	<7.97	0.1–2 ng/mL	(Zhao et al. 2017)
Beef, chicken, pork, sea bass, pork liver, milk, egg, shrimp	SAs	MISPE	SDZ@MIP microspheres with surface-grafted PHEMA	HPLC–MS/MS	0.02-0.1 μg/L	0.03-0.5 μg/L	63.49-115.72	1.64-4.68	0.001-2.5 μg/L	(Zhao et al. 2018)
Chicken, egg	FQs	Magnetic solid-phase extraction	g-C_3N_4/Fe_3O_4/MoS_2 nanocomposite	HPLC-UV	0.5-2.0 μg/L	1.7-6.7μg/L	89.3-99.6	<4.5	2-300 μg/L	(Zhao et al. 2019)

*AD: Amperometric detection; ATP: Attapulgite; Benzyl-PC: Benzylpenicillin; CE-LIF: Capillary electrophoresis -laser induced fluorescence; CNT: carbon nanotube; CoFe2O4: cobalt ferrite; CPs: cephalosporins; CZE: Capillary zone electrophoresis; DAD: Diode array detection; DMIP: Dummy-template molecularly imprinted polymer; DOX: Doxycycline; d-SPE: Dispersive solid-phase extraction; d-SPME: Dispersive solid-phase microextraction; DTC: Deoxytetracycline; ELISA: Enzyme-linked immunosorbent assay; ELSD: Evaporative light scattering detection; ESI: Electrospray ionization; Eu: Europium; Fe3O4: Iron (II, III) oxide; FLD: Fluorescence detection; FQs: Fluoroquinolones; g-C3N4: Graphitic carbon nitride; GO: Graphene oxide; HLB: Hydrophilic-lipophilic balance; h-MIPs: Hollow molecularly imprinted polymers; HPLC: High-performance liquid chromatography; HRMS: High-resolution mass spectrometry; LC: Liquid chromatography; LODs: Limits of detection; LOQs: Limits of quantification; MA: macrolid; MEPS: Microextraction by packed sorbent; Micro-SPE: Micro-solid-phase extraction; MIP: Molecularly imprinted polymer; MISPE: Molecularly imprinted solid-phase extraction; MSPE: Magnetic solid phase extraction; MOF: Metal organic framework; MoS_2: Molybdenum disulfide; MS/MS: Tandem mass spectrometry; MS: Mass spectrometry; mSiO2: Mesoporous silica; MSPD: Matrix solid-phase dispersion; NFsM: Nanofiber mats; nZVI: Nanoscale zero-valent iron; OTC : Oxytetracycline; PAN: Polyacrylonitrile; PANI: Polyaniline; PC: Penicillin; PDA: Photo Diode Array detection; PEG: Polyethyleneglycol; PHEMA: Poly(2- hydroxyethyl methacrylate; PSA: Primary-secondary amine; PS-DVB: Polystyrene-divinylbenzene; PVA: Polyvinyl alcohol; Qs: Quinolones; QuECheRS: Quick, easy, cheap, effective, rugged and safe; RP-HPLC: Reversed phase-high performance liquid chromatography; RSD: Relative standard deviations; SA: Sulfonamide; SBSE: Stir-bar sorptive extraction; SDZ: Sulfadiazine; SiO2: Silicon dioxide; SPE: Solid-phase extraction; SPME: Solid-phase microextraction; Tb: Terbium; TC: Tetracycline; TMCNT: Thiol-functionalized magnetic carbon nanotube; TPM: Trimethoprim; UHPLC: Ultra-high-performance liquid chromatography; UPLC: Ultra-performance liquid chromatography; UV: Ultraviolet detection; Zn Al-LDH: Zinc-aluminum layered double hydroxide; β-CD: β-cyclodextrin

Table 2. The advantages and disadvantages of solid-phase extraction techniques for determination of antibiotic residues in foodstuff*.

Method	Advantages	Disadvantages	References
SPME	• Easy miniaturization • High sensitivity • Convenient automation • Short extraction time • Ability to evaluate the samples in small sizes • Cost minimization • Easy coupling with chromatographic instruments • Reduced labor-intensive manual operations • Low solvent consumption • Performing of the sampling and extraction only in a single step	• Difficulties in the choice of proper sorbent with the desired properties • Low robustness • Instability and swelling of the stationary phase when exposed to organic solvents • Limited loading of analyte into the sorbent • High variability between the results of different runs and batches • Low thermal stability of physically holding sorbent • Slow diffusion of the analytes into viscous sorbents • The short lifetime of the physically holding sorbent • Lower extraction of target analytes due to the drag of matrix interferences	(Perez-Rodriguez et al., 2018, Ridgway, Lalljie, and Smith 2007, Alampanos, Samanidou, and Papadoyannis 2019, Bogialli et al. 2007, Kabir, Locatelli, and Ulusoy 2017, Souza-Silva, Gionfriddo, and Pawliszyn 2015, Kumar and Malik 2009, Jafari and Hamidi 2018)
SBSE	• Higher sorbent loading in SBSE than of SPME • Higher sensitivity than of SPME • Selective extraction of target analytes by the use of appropriate sorbent	• Availability of the sorbent phase only in the form of PDMS or PEG in PDMS • The limited spectrum of analyte polarities for the used sorbents • Strong matrix effects • Slow diffusion of analyte during extraction • Long extraction time • The necessity for high control of the extraction conditions	(Hamidi, Alipour-Ghorbani, and Hamidi 2018, Kabir, Locatelli, and Ulusoy 2017, Dmitrienko et al. 2014, Perez-Rodriguez et al., 2018, Gilart et al. 2014)
MSPD	• Simplicity • Rapidness • Having a selective approach • Performing of the disruption, extraction, and cleaning-up in only a single step • Low solvent consumption • No need for multiple extractions • High surface area for the interactions between the sorbent and analytes • Easy combination with automated extraction or clean-up systems	• The difficulty of automation • Time-consuming procedure in the extraction of multiple samples • Activation of anhydrous sorbents at high temperatures	(Perez-Rodriguez et al., 2018, Ridgway, Lalljie, and Smith 2007, Lozowicka et al. 2012, Dmitrienko et al. 2014, Marazuela and Bogialli 2009, Bitas et al. 2018)
Micro-SPE	• High recovery of the target analyte • Performing of the extraction and concentration of analytes in a single step • Short time for sample preparation • Low solvent consumption	• The limited number of available stationary phases • Fragility of fiber • Possibility of analyte carryover	(Płotka-Wasylka et al. 2015b, Lashgari, Basheer, and Kee Lee 2015, Kanimozhi et al., 2011)
d-SPE	• Extremely fast extraction procedure • Simplicity • Low cost • High recovery of analytes • Reproducibility to different types of samples and analytes	• The decrease in the analyte recovery by matrix interferers • The need for additional clean-up steps to reduce the amount of interferers	(Fontana et al. 2011, Islas et al. 2017, Bitas et al. 2018, Marazuela and Bogialli 2009, Saha et al. 2018, Kinsella et al. 2009)
d-SPME	• Simplicity • Cheapness • Easy procedure • Rapid mass transfer • High extraction efficiency • Short equilibrium time • Highly compatible with HPLC • Minimal solvent use • High capacity and dispersibility of sorbent in liquid samples	• Impaired dispersion of sorbent in the sample solution by addition of salt • Lower dispersion of sorbent at high pH values	(Perez-Rodriguez et al., 2018, Liu et al. 2015, Asfaram et al. 2015, Alampanos, Samanidou, and Papadoyannis 2019, Asgharinezhad et al. 2015)
MSPE	• Easy to perform • Rapidness • Cheapness • Environmental-friendly • High extraction efficiency • Convenient and quickly separation of sorbents from the sample solution	• Difficulties in the synthesis of the magnetic composites • The need for large sorbent and solution volume in the elution step	(Perez-Rodriguez et al., 2018, Cheng et al. 2012, Rodriguez et al. 2010, Filippou, Bitas, and Samanidou 2017, Płotka-Wasylka et al. 2015a, Herrero-Latorre et al. 2015)

(*continued*)

Table 2. Continued.

Method	Advantages	Disadvantages	References
	• Reusability of magnetic adsorbents • A possible use for the preparation of samples in large volume		
MEPS	• Low solvent consumption • The use of sorbents in small volumes • Performing the analyte extraction only in one single device • Injection of the extract directly into the HPLC system without additional treatments	• Long time required for the pre-analytical steps	(Alampanos, Samanidou, and Papadoyannis 2019, Kabir, Locatelli, and Ulusoy 2017, Filippou, Bitas, and Samanidou 2017, Moein, Abdel-Rehim, and Abdel-Rehim 2015, Kole et al. 2011)
MISPE	• Easy to perform • Low cost • High analyte retention • high selectivity and sensitivity • The possibility of sorbent reuse • Proper stability of sorbent in a different temperature, pH and solvents • The possibility of performing in offline and online modes	• Possibility for the leaching or remaining of the analyte in the MIP • Polymer swelling in unfavorable solvents • Slow binding kinetics • Sample contamination by template bleeding • Difficulties with removing the template from polymer • Lack of reproducibility • Nonselective hydrophobic interactions in aqueous media • Problems in the selection of sorbents for new analytes • Possibility of inconsistent molecular recognition	(Perez-Rodriguez et al., 2018, Andrade-Eiroa et al. 2016, Buszewski and Szultka 2012, Cunha and Fernandes 2018, Turiel and Martín-Esteban 2010, Kinsella et al. 2009, Marazuela and Bogialli 2009)

*__d-SPE:__ Dispersive solid-phase extraction; __d-SPME:__ Dispersive solid-phase microextraction; __HPLC:__ High-performance liquid chromatography; __MEPS:__ Microextraction by packed sorbent; __Micro-SPE:__ Micro-solid-phase extraction; __MIP:__ Molecularly imprinted polymer; __MISPE:__ Molecularly imprinted solid-phase extraction; __MSPE:__ Magnetic solid phase extraction; __MSPD:__ Matrix solid-phase dispersion; __PDMS:__ Polydimethylsiloxane; __PEG:__ Poly ethylene glycol; __SBSE:__ Stir-bar sorptive extraction; __SPME:__ Solid-phase microextraction

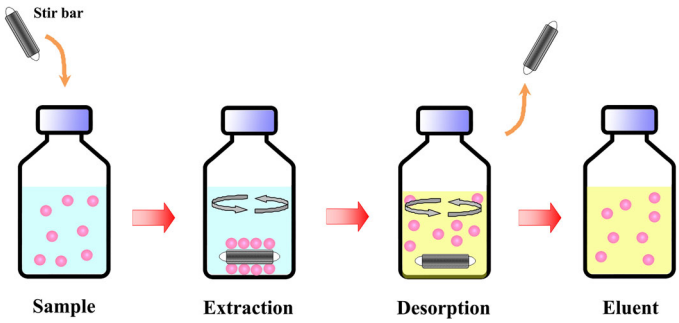

Figure 1. The main steps of stir bar sorptive extraction.

and Pawliszyn 2015; Delafiori, Ring, and Furey 2016; Filippou, Bitas, and Samanidou 2017; Niu et al. 2018). The commonly used adsorbents in this method are included as divinyl benzene (DVB), polydimethylsiloxane (PDMS), carboxen (CAR), polyacrylate, polyethylene glycol (PEG) and Carbowax (CW) supported on a solid matrix. In order to improve the efficiency and selectivity of isolation, new materials such as graphene and graphene oxide, carbon nanotubes, molecularly imprinted polymers (MIPs) and metallic nanoparticles have also been developed in recent years (Alampanos, Samanidou, and Papadoyannis 2019; Lan et al. 2019).

Different types of SPME such as in-tube SPME, fiber SPME, in vivo SPME, in-tip fiber SPME, immunoaffinity solid-phase microextraction have been emerged and used for clean-up purposes (Marazuela and Bogialli 2009; Lum, Tsoi, and Leung 2014; Delafiori, Ring, and Furey 2016; Filippou, Bitas, and Samanidou 2017; Niu et al. 2018).

The main drawbacks of SPME which limit its application for the analysis of antimicrobials in food, are included as (1) the limited number of commercially available stationary phases, (2) instability and swelling of the stationary phase when exposed to organic solvents, (3) limited loading of analyte into the sorbent, (4) high variability between the results of different runs and batches, (5) the low thermal stability of physically holding sorbent, (6) long extraction equilibrium time due to the slow diffusion of the analytes into viscous sorbents, and (7) the short lifetime of the physically holding sorbent (Marazuela and Bogialli 2009; Souza-Silva, Gionfriddo, and Pawliszyn 2015; Kabir, Locatelli, and Ulusoy 2017; Alampanos, Samanidou, and Papadoyannis 2019). Despite these drawbacks, SPME protocols are developing in recent years and the obtained results were very promising.

Mondal et al. (2019) developed an SPME method using MIL-101(Cr)NH2 as an adsorbent to extract antibiotic residues from tilapia fish. Four classes of antibiotic residues (quinolones, sulfonamides, macrolides and pyrimethamine) were analyzed by LC-MS/MS. The extraction efficiencies of the custom-made fiber were higher than those of the commercial C18, PDMS, PDMS/divinylbenzene and polyacrylate fibers. The MIL-101(Cr)NH2-polyacrylonitrile fiber also showed good reproducibility which made it an ideal sorbent for the extraction of antibiotics in fish muscle.

The SPME method has been compared with two well-documented sample preparation techniques including solvent extraction (SE) and quick, easy, cheap, effective, rugged and safe (QuEChERS) for quantitative analysis of different

veterinary antibiotics in chicken and beef tissue. The SPME exhibited considerably fewer matrix effects than the other two methods (Khaled, Singh, and Pawliszyn 2019)

Xu et al. (2016) developed a miniaturized SPE method to the determination of tetracyclines (TCs) in honey and milk using the extraction sorbent based on chitosan-modified graphitized multiwalled carbon nanotubes. The analytes were extracted from the samples with a mixture of acetonitrile and acetic acid. The target compounds were determined by ultra-high-performance liquid chromatography and quadrupole time-of-flight mass spectrometry (UHPLC-Q-TOF/MS). Excellent recoveries and a relatively strong enrichment capacity were obtained for residual TCs determined by the used method.

A novel sorbent phase based on poly (muconic acid-*co*-divinylbenzene/ethylene methacrylate) monolith was synthesized and used for SPME of TCs residues in honey samples. The analytes were analyzed by HPLC-MS/MS. Under the optimized conditions, the fabricated adsorbent had proper sensitivity for monitoring trace TCs (Pei and Huang 2017).

Shuo et al. (2018) developed an in-tube SPME method based on graphene-embedded porous polymer monolithic column for the determination of SAs residues from milk samples. In-tube SPME in combination with capillary electrophoresis-laser induced fluorescence (CE-LIF) was able to detect an amount of 3.7 ng/mL sulfamethazine in the milk which was much lower than the MRL.

SPME was also applied to monitor the fluoroquinolones (FQs) in milk and honey samples using poly(apronal-*co*-divinylbenzene/ethylene methacrylate) monolith. In comparison with previous techniques, the developed method exhibited satisfactory sensitivity, high cost-effectiveness, simplicity and minimal use of the organic solvent (Chen and Huang 2016).

An effective and sensitive SPME method was developed by Chen and Ye (2016) to determine six cephalosporins (CPs) (cefadroxil, cephapirin sodium, cefixime, cefuroxime sodium, cefoxitin sodium and ceftiofur hydrochloride) in milk samples. Analytes were adsorbed by graphene oxide-reinforced hollow fiber and analyzed using high-performance liquid chromatography-photodiode array detection (HPLC-PDA). A satisfactory accuracy and precision were achieved using the developed procedure in milk samples with low LODs (ranging from 0.01 to 0.02 μg/mL), as well as recovery levels (between 71% and 108%).

Stir bar sorptive extraction

Stir bar sorptive extraction (SBSE) is a novel technique for the preparation of food samples in which glass magnetic stirrer bars coated with PDMS are used as the sorbent (Dmitrienko et al. 2014). Since the sorbent loading in SBSE is substantially higher than of SPME, this technique has been developed to increase the sensitivity of SPME. In order to extract the target analyte, the stir bars are directly placed inside the aqueous sample and mixed on a magnetic stirrer for a specific time. After the analyte extraction, the stir bars are recovered from the sample solution, washed with deionized water, dried and the extracted analytes are desorbed (Figure 1). Twister® is the trade name of commercially available SBSE devices (Dmitrienko et al. 2014; Kabir, Locatelli, and Ulusoy 2017).

The main drawback of this technique is that only PDMS and PEG in PDMS are available as the sorbent phase. Due to the high viscosity of these phases, analyte diffusion is also slowed down during extraction which leads to increased extraction time (Gilart et al. 2014; Kabir, Locatelli, and Ulusoy 2017).

In several studies, this method was used for the isolation of Qs from meat (Yang et al. 2017), milk (Yao et al. 2015; Rodríguez-Gómez et al. 2018), chicken muscle and liver (Fan et al. 2015).

A rapid and sensitive method was developed by Rodríguez-Gómez et al. (2018) for the quantitative monitoring of seventeen Qs in cows' milk. The residues were concentrated by SBSE based on PDMS and PEG-modified silicone. The best extraction yield was determined by PEG at pH 6. Aliquots of 5 g of milk were mixed with acetonitrile (3.75 mL) and precipitation solution (3.75 mL). The mixture was centrifuged at 4050 × g for 10 min and the supernatant was separated. The acetonitrile was evaporated using a vacuum centrifugal evaporator. For SBSE, the twister and NaCl were added to the sample. The suspension was stirred (600 rpm, room temperature) for 15 h. Following the analyte extraction, the stir-bar was removed from the sample, rinsed with water and dried. Subsequently, the extracted residues were desorbed using methanol (0.5 mL) in an ultrasound bath. The eluent was dried under nitrogen gas at room temperature, and the sample was re-dissolved in the initial mobile phase (100 μL) and centrifuged at room temperature at 16,300 ×g for 5 min. Finally, the analysis was carried out by UHPLC-MS/MS system.

Fan et al. (2015) successfully developed a sensitive method for the quantitative monitoring of five FQs in chicken muscle and liver using SBSE coupling to high-performance liquid chromatography-fluorescence detector (HPLC-FLD). The analytes were concentrated by graphene oxide/polyethyleneglycol (GO/PEG) composite as the stir bar coating. The used GO/PEG composite showed higher extraction efficiency for five FQs than graphene oxide/polyaniline composite and PDMS. Under the optimized experimental conditions, the LODs of the proposed method for five FQs were achieved within the range of 0.0045–0.0079 μg/L.

A dual-template molecularly imprinted polymer-coated stir bar was prepared as the adsorbent of FQs by Yang et al. 2017. After optimization of the extraction procedure, the stir bar was used for the extraction of the nine FQ residues in the meat before the analysis with HPLC. High recoveries (>90%) and enrichment factors (33–47 folds) for the drugs were observed using this method.

Yao et al. (2015) also proposed a sensitive, selective and reproducible method for the detection of 11 quinolones (Qs) in bovine milk by immunoaffinity-SBSE combined with liquid chromatography and fluorescence detection (LC-FLD). For the first time, a broad-specificity monoclonal antibody was immobilized on a glass bar for the production

of a reusable immunoaffinity stir bar. The stir bars were placed into the milk samples, and the mixture was shaken for 30 min followed by analysis with HPLC-FLD. The LODs for each Qs were between 0.05 and 0.1 ng/g.

A novel SBSE protocol extraction was designed to minimize the complex matrix interference to the determination of kanamycin in milk and fish samples using a microfluidic chip-based ratiometric aptasensor. Briefly, a gold stir bar (0.25 mm diameter, 3 cm length) was immersed in the 3-mercaptopropyl-tri-methoxy silane (1%). The stir bar was then pulled out and rinsed with PBS. In the end, the stir bar was placed into the solution containing gold nanoparticles (AuNPs) for 6 h at 4 °C. The stir bar was immersed into thiol Kana aptamer (10 μM) for 6 h at 4 °C. The stir bar was rinsed with PBS to remove uncombined aptamers. The AuNPs modified stir bar was immersed in the thiol Kana aptamer solution in PBS buffer (2:8) for 6 h at 4 °C. The stir bar was rinsed with PBS to remove uncombined aptamers after completing the reaction. Finally, 3 mL of the spiked sample was mixed with a stir bar modified with the aptamer for 30 min at 30 °C. Afterward, the above solution (15 μL) was mixed with the circular DNA template (10 μL) and *Bacillus stearothermophilus* DNA Polymerase (Bst DNA polymerase) (8 U) at 37 °C for 30 min. Finally, the analytes were detected using a commercial ELISA kit (Liyong He, Huang, et al. 2019).

Matrix solid-phase dispersion

Matrix solid-phase dispersion (MSPD) is a widely applied technique for the extraction of antimicrobials from solid and semi-solid food products with both high and low-fat contents (Marazuela and Bogialli 2009; Dmitrienko et al. 2014; Pérez-Rodríguez et al. 2018). MSPD provides a simple and selective approach for the sample homogenization, disruption, extraction and cleaning-up in only a single step which results in a rapid pretreatment and lower solvent consumption (Marazuela and Bogialli 2009; Bitas et al. 2018; Perez-Rodriguez et al., 2018; Pérez-Rodríguez et al. 2018).

This technique consists of a mechanical blending of the sample with a bulk dispersing agent which improves the complete disruption of the sample matrix (Marazuela and Bogialli 2009; Dmitrienko et al. 2014; Pérez-Rodríguez et al. 2018). Thus, the surface area for sample extraction as well as the interactions between the sorbent material and the analytes are increased by this method. The extraction and clean-up processes are performed in an SPE cartridge using a suitable solvent or a sequence of solvents (Marazuela and Bogialli 2009; Bitas et al. 2018).

The MSPD can be used in combination with automated extraction or clean-up systems like pressurized liquid extraction or SPE (on-line or off-line formats) (Marazuela and Bogialli 2009).

In recent years, the MSPD method was used to extract SAs from fish (Shen et al. 2016), chicken, bovine and pork tissue (Wang et al. 2015; Geng Nan Wang, Zhang, et al. 2017). Also, the effectiveness of different sorbents is compared (Shen et al. 2016).

An MSPD procedure for the extraction of SAs from fish tissue was developed by Shen et al. (2016) using hydrophilic-lipophilic balance (HLB) material as sorbent and a micro-scale pipette tip (PT) as the cartridge. The extract was eluted with a mixture of methanol/water/ammonia (50/49/1, v/v/v). The analytes were determined using LC-MS/MS. The mean recoveries for most SAs in the range of 70.6–95.5%. Also, precision and accuracy ranged between 1.4 and 10.3%, respectively. This method not only needed the minimal volume of HLB sorbent (0.3 mL) and solvents (4.8 mL for LC) but also a short time for the procedure (5 min for PT-MSPD and 8 min for LC). In this work, several solid support materials including both polar and nonpolar, such as C18, neutral alumina, Florisil PR and multi-walled carbon nanotubes were evaluated and HLB had the best extraction efficiencies followed by neutral alumina. The satisfactory performance and high-throughput capability of the developed method made it a suitable approach for widespread drug residue analysis.

Wang et al. (2015) defined a simple protocol included a combined MSPD-homogeneous ionic liquid microextraction (HILME) for the extraction of SAs from chicken, bovine and pork tissue samples. The ionic liquid was used as an extraction solvent in HILME and elution solvent in MSPD. A tissue sample was mixed with silica gel (1 g) and 1-butyl-3-methylimidazolium tetrafluoroborate ([C4MIM][BF4]) (200 μL). The mixture was then transferred into a glass column containing absorbent cotton layers. The analytes were eluted by pure water and mixed with 0.45 g of NaCl and 1 mL of ammonium hexafluorophosphate (2.4 M). The mixture was centrifuged at 5 °C (10,000 rpm, 5 min). The supernatant was removed, and the remaining ionic liquid phase was mixed with acetonitrile (300 μL) and injected to high-performance liquid chromatography with diode-array detection (HPLC-DAD).

A molecularly imprinted polymer-based MSPD (MMIP-MSPD) was also developed by Geng Nan Wang, Zhang, et al. (2017) for the simultaneous determination of antibiotics in pork meat. Pipemidic acid, sulfabenzamide and chlortetracycline were used to synthesize a novel mixed-template MIP (MMIP) for the determination of FQs, for SAs and TCs, respectively. The extraction procedure carried out by the MMIP-MSPD method followed by ultra-performance liquid chromatography (UPLC). The proposed MSPD procedure proved to be a rapid, simple, specific and sensitive method for multi-determination of the residues of FQs, TCs and SAs.

Karageorgou et al. (2018) developed an MSPD procedure to extract the residues of the β-lactam group and chloramphenicol from fortified raw milk samples using Plexa as a sorbent. After the MSPD, the analytes were detected by the HPLC-diode array. The extraction efficiency was increased after ultrasonic treatment by QuEChERS in MSPD format.

A UPLC–MS/MS method based on MSPD was developed by Huang et al. (2016) for the simultaneous determination of 15 β-lactams in pork muscle tissue. For this purpose, the homogenized pork muscle (2 g) was mixed with Oasis HLB (3 g) as the dispersion adsorbent. After homogenization of

the mixture, it was transferred into a glass column. The column was washed with n-hexane, and the analytes were eluted by acetonitrile/water (50:50, v/v) both containing 0.1% formic acid. Ethyl acetate (6 mL) was added to the elution and vortexed for 1 min. The final extract was dried under the stream of nitrogen, and dissolved into acetonitrile/water (10:90, *v/v*) before the analysis of UPLC-MS/MS. Under the optimized condition, LODs and limits of quantification (LOQs) for the analyzed residues were in the range of 0.02-0.63 µg/kg and 0.07–0.97 µg/kg, respectively. Also, satisfactory recovery values were obtained for all drugs (92–111%) and the relative standard deviations (RSDs) were lower than 12%.

A simple and rapid sample preparation procedure was proposed for the determination of degradation products of penicillin (penicilloic acid and penilloic acid) in milk using selective surface molecularly imprinted matrix solid-phase dispersion (SMIPs-MSPD). The SMIPs were synthesized using modified silica gel as support, methanol and acetonitrile (1:1, v/v) as a solvent, penicilloic acid as template molecule and methacrylic acid as a functional monomer for pre-polymerisation. In order to polymerize the SMIPs, ethylene glycol dimethacrylate and azobisisobutyronitrile were added as crosslinker monomer and initiator at 60 °C, respectively. Finally, the target analytes were extracted using the synthesized sorbent and MSPD technique. Analysis of residues was performed by HPLC. The authors also compared SMIPs with commercial SPE adsorbents, and they found that SMIPs-MSPD can selectively extract the target analytes. Also, it can simplify and accelerate the sample cleanup and improve recovery values (Zhimin Luo, Xie, et al. 2015).

Micro-solid-phase extraction

Micro-solid-phase extraction (Micro-SPE), also known as porous membrane-protected SPE, is one of the newest techniques for preconcentration and extraction of target analytes in food samples which can be used as an alternative method to multistep SPE (Kanimozhi et al., 2011; Dmitrienko et al. 2014; Lashgari, Basheer, and Kee Lee 2015).

The main advantages associated with the use of Micro-SPE include the high recovery of analyte (depending on the matrix and the analyte type), the extraction and concentration of the target analyte in a single step, short time for sample preparation, the minimal usage of the solvent and high level of the analyte concentration (Kanimozhi et al., 2011; Lashgari, Basheer, and Kee Lee 2015; Płotka-Wasylka et al. 2015).

A typical Micro-SPE procedure involves the following steps: (1) package of sorbent phase in small bags made of porous polypropylene; (2) diffusion of analytes through the membrane and their absorbance to the sorbent phase. There is no need for vacuum pressure for the loading or elution process in this method (Lashgari, Basheer, and Kee Lee 2015; Płotka-Wasylka et al. 2015; Alampanos, Samanidou, and Papadoyannis 2019).

Jiao, Zhu, and Yao (2015) developed a novel sample preparation technique for the extraction of tetracycline (TC), oxytetracycline (OTC), deoxytetracycline (DTC), chlortetracycline (CTC) in the tissues of pork, chicken meat and clam. The enrichment and cleaning-up were carried out by the Micro-SPE method. The sorbent was packed in an enclosed microporous polypropylene membrane package (1.0 cm length × 0.8 cm width). Under the optimized conditions, LODs and LOQs were 7.4–16.3 ng/g and of 24.7–53.8 ng/g, respectively. The recovery levels of selected residues were between 92–105%.

The graphene oxide–starch-based nanocomposite was used in Micro-SPE by Golzari Aqda et al. (2019) for the extraction of amoxicillin, ampicillin and cloxacillin residues from cow milk samples. The extracted analytes were determined by HPLC–UV. Using the porous hydrogel based on starch nanocomposite as the sorbent phase, high extraction efficiencies and acceptable relative recovery (in the range of 83–105%) was obtained for the analyzed residues.

Jian et al. (2019) proposed a high-throughput 96-well plate micro-SPE method combined with UPLC-MS/MS for multi-residue detection of FQs in various food samples with animal origin (milk, pork and chicken muscle, pork liver and kidney and egg). They prepared a novel sulfonated-polyaniline/polyacrylonitrile nanofiber mats (sulfonated-PANI/PAN NFsM) as the sorbent. The homogenized sample (0.5 ± 0.01 g) was mixed with EDTA–McIlvaine's buffer (2.5 mL). After sonication (10 min) and centrifugation (10,000 rpm for 5 min) of the mixture, the supernatant (2.5 mL) was transferred to the pre-conditioned 96-well plate Micro-SPE cartridges and adsorbed on sulfonated-PANI/PAN NFsM. The mixture of formic acid and acetonitrile (10%) was used for the elution of analytes. The extract was evaporated to dryness and dissolved in 0.2% formic acid/water (0.1 mL) before the analysis by UPLC-MS/MS. The sulfonated-PANI/PAN NFsM exhibited large adsorption capacity for the analytes, excellent efficiency and proper reusability. Compared with the conventional methods, this procedure had several advantages such as lower sample size (0.5 g), lower consumption of the organic solvent (0.7 mL), lower sorbent use (5.0 mg), shorter extraction time (0.2 min per sample) and high sensitivity (0.012–0.06 µg/kg).

Electrospun polyethylene terephthalate nanofibers doped with graphene oxide nanoparticles (GO-PET) was synthesized and used as the sorbent in Micro-SPE for determination of cefotaxime and TC residues in honey. HPLC system was used for the analysis of analytes. The honey samples (5 g) were dissolved in distilled water (5% w/v) at 50 °C for 10 min and centrifuged at 4000 rpm for 15 min. The final solution was filtered by a filter paper before the extraction. The GO-PET (40 mg) was dissolved in the solution and vortexed for 10 min. Then, the sorbent was collected from the solution and transferred into a test tube. Methanol (400 µL) was added to the sorbent, and it was shaken for 1 min. Afterward, the extract was evaporated until the dryness. The extract was redissolved in methanol (200 µL) before the analysis with HPLC. The proposed Micro-SPE procedure using GO-PET had a proper precision (RSD%) for the detection

of cefotaxime and TC in comparison with other usual methods (Arabsorkhi and Sereshti 2018).

Dispersive-SPE

Dispersive-SPE (d-SPE) is a technique in which the sorbent is dispersed in an appropriate solvent containing the sample. The sorbent removes matrix interferences by leaving them in the matrix while the desired analytes adsorb on the sorbent (Kinsella et al. 2009; Marazuela and Bogialli 2009). After the extraction is completed, the sorbent is separated by filtration or centrifugation and the previous step was repeated using an appropriate solvent for the elution of analytes (Bitas et al. 2018; Soares Maciel et al., 2018).

The extent of SPE applications is limited by the sorbent type and the properties of sample ingredients. The tightly packed SPE cartridges can increase the time of extraction and backpressure while the d-SPE doesn't have the same problems and the sorbent is directly mixed with the sample solution and not packed into a cartridge (Marazuela and Bogialli 2009; Bitas et al. 2018; Saha et al. 2018). This technique is extremely fast, simple, practical and inexpensive with high recovery and reproducibility for many analytes which can be determined by LC- and GC analysis (Kinsella et al. 2009).

Several authors have recently used the d-SPE procedure for the isolation of antibiotic residues from animal-derived food. A d-SPE protocol has been developed for the multiclass extraction of antibiotics, including β-lactams, Qs, SAs and sulfonamide potentiators from animal tissues. The method involved solvent extraction by Na_2EDTA (0.1 M) and 1% acetic acid in acetonitrile (v/v) using a d-SPE clean-up with C18 sorbent. The final determination of the residues was carried out by ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) (Luo, Xie, et al. 2015).

Also, Zhang, Wang, et al. (2017) reported a d-SPE method for the extraction of nitroimidazoles, nitrofurans and chloramphenicol in the chicken tissue and egg. The spiked samples were treated with hydrochloric acid (0.2 M, 10 mL) and 2-nitrobenzaldehyde in methanol (0.1 M, 200 µL) followed by a clean-up step with the mixture of C18 (4 g) and diatomaceous earth (4 g) and hexane (10 mL). The analysis was carried out by UHPLC-MS/MS. The authors have reported that the accuracy of method was high enough with mean recoveries ranged from 86.4% to 116.7% and interday precision was lower than 18%. The LOQs (ranged from 0.1 to 0.5 µg/kg) were also satisfactory.

A novel dispersive sorbent based on β-cyclodextrin (β-CD) and attapulgite (ATP) (β-CD/ATP composite) was prepared by bonding β-CD to modified ATP and used for the extraction of Qs (ciprofloxacin, norfloxacin, ofloxacin and gatifloxacin) from honey samples. The honey sample (10 g) was diluted with deionized water to 100 mL. β-CD/ATP composite particles (4 mg), as the sorbent, was added to the sample (5.0 mL). The mixture was vortexed for 1 min and placed in an ultrasonic bath for 1 min. The suspension was centrifuged (at 4000 rpm for 8 min) and the sample solution carefully separated. Then, 200 mL of 40% ammonia in methanol (v/v) was used as the eluent. In the end, the resulting extract (10 mL) was injected into the high-performance liquid chromatography with ultraviolet detection (HPLC–UV) for analysis. The authors emphasized that β-CD/ATP composite has a high adsorption capacity for Qs and the LODs (0.30–3.95 mg/L) and recovery values of 83.6–88.6% for the target analytes were satisfactory (Cui et al. 2015).

A new d-SPE procedure based on CE was proposed for the detection of sulfamethoxazole in milk samples. Butylamide silica particles were synthesized and used as the sorbent phase. The residues were extracted by adding acetic acid 2% (v/v) to the sample and heating for 5 minutes (65 °C) followed by adsorption of the analytes on sorbent particles. The developed d-SPE method showed proper average recoveries ranged from 73% to 85% with a limit of detection (LOD) of 0.05 mg/L (Islas et al. 2016).

Dorival-García et al. (2016) also used a new sensitive, selective and accurate method for the simultaneous determination of quinolone and β-lactam residues in raw cow milk by ultrasound-assisted extraction and d-SPE before UHPLC – MS/MS analysis. The extraction was performed by adding a mixture of acetonitrile/methanol/McIlvaine buffer solution (60:25:15; v/v/v). The analytes were adsorbed using PSA (primary-secondary amine) sorbent before the analysis by ultra-high-performance liquid chromatography-electrospray ionization–tandem mass spectrometry (UHPLC-ESI-MS/MS). Satisfactory recovery rates (96.0–104.5%) and low LOQs (0.3–2.0 ng/g) were obtained by this method. The authors reported that the used preparation protocol was more laborious and time-consuming with multi-step transfers during the extraction.

Dispersive solid-phase microextraction

The concept for the development of dispersive solid-phase microextraction (d-SPME) is similar to those of SPME and SBSE techniques (Pérez-Rodríguez et al. 2018). The d-SPME is performed by the addition of dispersive solid sorbent particles in the sample solution and the adsorption of the target analytes on the particles. The sorbent particles containing the adsorbed analytes are then separated by centrifugation or filtration. Finally, the analytes are eluted with a small volume of a suitable organic solvent. This technique provides a simple and fast method for sample preparation with high extraction efficiency that is highly compatible with HPLC. In comparison with other techniques like classic SPE, this procedure is a simple, fast, cheap, low time-consuming method with minimal solvent consumption which is following GAC principles (Asgharinezhad et al. 2015; Pérez-Rodríguez et al. 2018; Alampanos, Samanidou, and Papadoyannis 2019).

In order to provide fast and accurate adsorption and elution, the materials used as the sorbent in d-SPME method should have a large surface area, high capacity and dispersibility in liquid samples (Asfaram et al. 2015; Asgharinezhad et al. 2015). Some materials such as the carbon nanotubes

(CNTs), graphene, fullerene and magnetic nanoparticles (MNPs) have been used as a solid-phase sorbent in this technique (Asgharinezhad et al. 2015; Alampanos, Samanidou, and Papadoyannis 2019). Despite d-SPME has been known as a promising technique for sample preparation, it has limited usage in the analysis of foodstuff (Liu et al. 2015; Pérez-Rodríguez et al. 2018).

A novel procedure for the extraction of oxacillin, cloxacillin and dicloxacillin in milk samples has been developed by Yahaya et al. (2015) using an ordered mesoporous carbon, COU-2 as the dispersive micro-solid phase. The extraction protocol included several simple steps. COU-2 sorbent (75 mg) and sodium chloride (NaCl) (1 g) were added to the diluted milk sample (20 mL). The suspension was vortexed to facilitate the dispersion of COU-2 in the sample. Then, it was centrifuged (at 1790 × g force for 2 min) and the sorbent phase (COU-2) was separated from the sample solution. The sorbent was mixed with methanol (100 µL) in a tube and sonicated for 3 min. After the filtration of the solution through a syringe filter (0.2 µm), the extract was analyzed by the HPLC system. Under the optimized condition, the developed method showed low LODs (2.0–3.3 µg/L), a good reproducibility (RSD = 6.2–8.8%) and high recovery values (80.3–99.5%) for residues of penicillins in milk.

Recently, nanomaterials such as carbon nanotubes and graphene oxide metal organic frameworks have been synthesized and used as adsorbents in the d-SPME method (Di et al. 2019).

MIL-101(Cr)@GO nanocomposite was used as a sorbent in a d-SPME procedure for the extraction of SAs in milk (Jia et al. 2017) and chicken breast (Yudan Wang, Zhang, et al. 2017). Jia et al. 2017 synthesized the MIL-101(Cr)@GO composite by hydrothermal method. The composite was prepared using the graphite oxide (0.566 g), chromium nitrate nonahydrate (4 g), trimesic acid (1.66 g) and hydrofluoric acid (450 µL, 40%, w/w). Under the optimized conditions, the LODs were ranged between 0.012 and 0.145 µg/L. The recoveries were between 79.83% and 103.8% with RSDs lower than 10% ($n = 3$). The authors compared MIL-101(Cr)@GO with conventional adsorbents such as MIL-101(Cr), MIL-100(Fe) and activated carbon. They reported that MIL-101(Cr)@GO has remarkable advantages including lower solvent consumption, satisfactory extraction time and lower LODs. The same adsorbent was used by Wang, Zhang, et al. 2017b for the concentration of sulfamethoxazole and chloramphenicol. Also, the optimal extraction was obtained by combining d-SPME with microwave-assisted extraction. It was proved that the proposed approach with HPLC–MS/MS is an efficient and reliable method for the detection of analytes in chicken breast.

A novel and green d-SPME method was developed based on a two-dimensional nanostructured zinc-aluminum layered double hydroxide (Zn Al-LDH) for the extraction of acidic Qs from honey. The residues were determined by HPLC-UV. The main advantage of the developed method was that Qs was efficiently extracted from honey samples without the consumption of organic solvents. Using the zinc and aluminum layered double hydroxides as a dissolvable sorbent, there was no need for the elution of analytes in the extraction procedure which result in short extraction time. After the optimization of key parameters influencing the extraction efficiency, low LODs (3.0–5.0 ng/g), good precision (RSD < 9.1%) and acceptable LOQs (ranged from 10 to 20 ng/g) were achieved by this method (Di et al. 2019).

Magnetic solid-phase extraction

Magnetic solid-phase extraction (MSPE) is an SPE-based method that employs magnetic-nanoparticle-based sorbent for the chemical separation of analytes. Magnetic sorbent particles are usually polymerized in the presence of magnetite. This method is used for the concentration of different organic and inorganic analytes and their isolation from complex matrixes (Rodriguez et al. 2010; Cheng et al. 2012; Bitas et al. 2018; Alampanos, Samanidou, and Papadoyannis 2019).

The mechanism of MSPE procedure includes three main steps. In the first step, the magnetic sorbent particles are dispersed into the sample solution, and the target analytes are adsorbed on the surface of the magnetic particles. The magnetic particles are removed from the suspension using a magnet. Finally, the analytes are eluted from the collected particles using a suitable solvent (Figure 2). In this method, the ratio between surface area and the volume of sorbent phase is very important, because an increase in this ratio can improve the extraction efficiency (Rodriguez et al. 2010; Cheng et al. 2012; Herrero-Latorre et al. 2015; Bitas et al. 2018; Pérez-Rodríguez et al. 2018; Alampanos, Samanidou, and Papadoyannis 2019).

MSPE has known as a green, easy, fast, cheap and environmental-friendly technique which demands less analysis time and provides satisfactory recoveries of analytes (in the range of 82.5–103% depending on the type of matrix and analyte) (Rodriguez et al. 2010; Herrero-Latorre et al. 2015; Płotka-Wasylka et al. 2016; Filippou, Bitas, and Samanidou 2017).

One of the main advantages of this method is that the sorbents can be quickly separated from the sample solution using an external magnet. Due to the use of an external magnetic field, this method doesn't involve the problem of column packing (Yu, Bekele, and Pieper 2017).

Since MSPE provides a high extraction efficiency, it has been attracted great interest in the preparation of complex samples in recent years (Cheng et al. 2012; Pérez-Rodríguez et al. 2018).

Due to the low cost and low toxicity, iron (II, III) oxide (Fe_3O_4) is the most commonly used magnetic material in MSPE that is available with inorganic or organic coatings such as silica, chitosan, polypyrrole or alumina. (Karami-Osboo et al. 2015; Tolmacheva et al. 2016; Bitas et al. 2018; Alampanos, Samanidou, and Papadoyannis 2019). Recently, Fe_3O_4 has been used for the synthesis of various magnetic nano-adsorbent and further development of potential MSPE applications in the foodstuffs (Xia et al. 2017; Tu et al. 2019; Yu et al. 2019; Yanfang Zhao et al. 2019).

Yanfang Zhao et al. (2019) developed a new molybdenum disulfide-based core-shell magnetic nanocomposite (Fe_3O_4@MoS_2) for the extraction of SAs in the food samples. The nanocomposite was synthesized as an adsorbent by

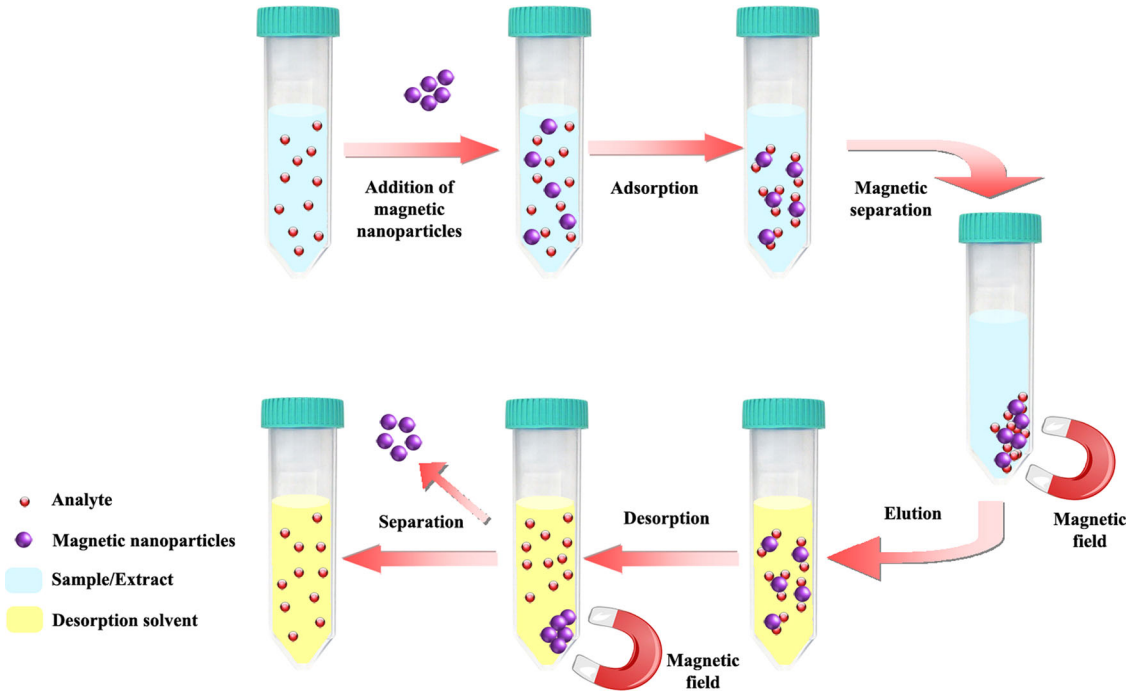

Figure 2. Schematic illustration of the main steps in Magnetic solid-phase extraction.

the hydrothermal method. The residues of SAs were quantified by HPLC-MS/MS. The synthesized nanocomposites had a remarkable adsorption affinity toward the SAs. The satisfactory repeatability and reproducibility (RSD <10%) and acceptable recoveries (within the range of 80.2–108.6%) were obtained for SAs determination in milk, pork meat and fish samples.

A similar protocol was used with Yu et al. (2019) to determine the FQs residues by HPLC-MS/MS. The milk, pork and fish meat were prepared by MSPE using Fe_3O_4@MoS_2 The developed MSPE protocol based on magnetic molecular sieve sorbent showed an acceptable performance for the concentration of FQs in food samples. The same sorbent phase was used by Wu et al. (2019) for the extraction of five FQs (lomefloxacin, ciprofloxacin, ofloxacin, sparfloxacin and enrofloxacin) in eggs before analysis with HPLC-UV.

Bingxin Zhao et al. (2019) synthesized a ternary nanocomposite (g-C_3N_4/Fe_3O_4/MoS_2) by a hydrothermal method as an adsorbent for the preconcentration of trace FQs (enoxacin, ofloxacin, prulifloxacin, gatifloxacin, difloxacin, tosufloxacin) in chicken tissue and egg. After HPLC-UV analysis, high recovery rate, good linear range, low LODs and high sensitivity were achieved by the proposed method.

Tu et al. (2019) applied a novel aptamer-based adsorbent for the MSPE of TCs from honey samples. The Fe_3O_4/aptamer sorbent was synthesized by the immobilization of aptamers on the surface of Fe_3O_4 magnetic nanoparticles. Since the aptamer was specific to the target analytes, the Fe_3O_4/aptamer had better adsorption capability than of Fe_3O_4 and most traditional sorbents.

Another MSPE protocol was used for the extraction of SAs from the samples of pork, chicken and shrimp tissues. The procedure was carried out using magnetic Fe_3O_4@JUC-48 nanocomposite as the sorbent particle. The residues were extracted from the tissue samples (2 g) using acetonitrile (20 mL). Fe_3O_4@JUC-48 (25 mg) was added to the sample extract (8 mL) and vortexed for 8 min. The magnetic sorbent particles were collected using an external magnet. Methanol and Acetic acid (95:5, v/v; 0.8 mL) were used for the elution of targeted analytes. The analysis was carried out with HPLC-DAD. In comparison with classic sample preparation methods, the used protocol had higher sensitivity and better recovery that consumed lower time and solvent usage. The proposed MSPE protocol combined with HPLC showed high sensitivity with low LODs (1.73–5.23 ng/g), acceptable recoveries (76.1–102.6%) and high precision (RSD < 4.5%) (Xia et al. 2017).

In several studies, magnetic nanocomposites based on graphene and its derivatives were successfully used as sorbent phase in MSPE method (Li et al. 2015; Wang et al. 2016; He et al. 2017; Wei, Wu, and Zhu 2017; Feng et al. 2019). Graphene has several beneficial characteristics such as ultrahigh surface area, high capacity for analyte absorption, high stability, high hydrophobicity and excellent resistance in acidic or alkaline solutions (He et al. 2017). In an MSPE protocol by magnetic graphene particles, the extraction method exhibited high absorption capacities (>6800 ng) enrichment factors (68–79-fold) for seven FQs in bovine milk, chicken muscle and egg samples. Also, this adsorbent had good reusability for at least 40 times (He et al. 2017).

In other research, a magnetic graphene-based composite ($CoFe_2O_4$-graphene) has been developed for the extraction and preconcentration of SAs residues in milk samples. Briefly, the milk sample (1.5 mL) was dissolved in perchloric acid ($HClO_4$) solution (15%, 0.2 mL) to precipitate its

protein content. The mixture was centrifuged (at 14,000 rpm for 5 min) and the supernatant was separated and diluted with deionized water (100 mL). The sample extract (8 mL) was mixed with the magnetic sorbent (15 mg). The suspension was shaken for 20 min and vortexed for 2 min. The magnetic sorbents were collected using an external magnet. The analytes were eluted with a solution of acetic acid in methanol (5%, 0.5 mL) before analysis with HPLC-UV. Under the optimal condition, the acceptable LODs (less than 1.59 µg/L) and good reproducibility were achieved by the developed method (Li et al. 2015). Using the graphene oxide (GO), several novel adsorbents such as magnetic graphene oxide nanocomposite (Fe_3O_4@GO) (Wang et al. 2016), Fe_3O_4/reduced graphene oxide-carbon nanotubes (Feng et al. 2019), β-cyclodextrin functionalized silica-coated magnetic graphene oxide (Fe_3O_4@SiO_2@GO-β-CD) (Al-Afy et al. 2018) and graphene oxide/nanoscale zero-valent iron (GO/nZVI) (Wei, Wu, and Zhu 2017) has also been developed for the concentration of SAs and TCs in the milk samples.

Tolmacheva et al. (2016) were reported a convenient and efficient method MSPE method for the extraction of SAs in milk samples. A magnetic hyper cross-linked polystyrene composite was synthesized and used as the sorbent material. The milk sample (25 mL) was mixed with the magnetic sorbent (20 mg). The suspension was vortexed for 10 min. After the collection of the magnetic sorbent, the analytes were eluted with acetonitrile and sonicated for 5 min. The eluate was analyzed by high-performance liquid chromatography—amperometric detection (HPLC-AD). The results showed acceptable recoveries (ranging from 84% to105%) with a satisfactory LODs (2.0–2.5 ng/mL) for target analytes in milk.

A new analytical method used for the simultaneous determination of DOX, OXT, trimethoprim (TPM) and penicillin G (PC-G) in the cow milk sample. The residues were extracted using the MSPE method and analyzed with HPLC. A new restricted access material based on magnetic mesoporous polyaniline coated with hydrophilic monomers and casein (RA-MMPAni-HM-CAS) was synthesized as the sorbent for the analytes. The recovery value for TPM, DOX and OXY in milk was 100%, while this value was about 93.16% for PC-G. The used MSPE-HPLC method also showed good linearity, robustness, accuracy and precision for the detection of antibiotics in milk (Florez, Dutra, and Borges 2019).

Milk samples were also prepared by MSPE using amino terminated carbon nanotubes (Fu et al. 2019) and laccaic acid-loaded magnetite nanocomposite (Yu and Fan 2017) for the extraction and preconcentration of SAs and TCs, respectively. The extracted antibiotics were analyzed by LC-high resolution mass spectrometry (LC–HRMS) and HPLC-UV, respectively. The evaluation of both extraction methods showed that the proposed procedures had an acceptable performance for the extraction of target analytes.

Vakh et al. (2018) developed an automated magnetic d-SPME method in a fluidized reactor for the extraction of FQs (fleroxacin, norfloxacin and ofloxacin) in meat-based baby food samples. Zr-Fe-C magnetic nanoparticles were used as the sorbent for the sample concentration. The magnetic nanoparticles were floated in the sample solution by air-bubbling. In this method, the sample solution was injected into the fluidized reactor, and the nanoparticles were separated from the sample matrix using a magnetic field. After the elution step by KOH solution in methanol (0.02 mol/L), the residues were determined by HPLC-FLD. Since, the procedure performed in a miniaturized fluidized reactor, lower sample volume and less magnetic nanoparticles were consumed by this method compared to a magnetic bar stirring in a syringe.

Nasir et al. (2019) used thiol-functionalized magnetic carbon nanotubes (TMCNTs) as the adsorbent in the magnetic micro-SPE of SAs in milk and chicken meat samples before the analysis with HPLC-DAD. The 3-mercapto-propyl-trimethoxy-silane (MPTS) was used as silane coupling agents of thiol in the synthesis of TMCNTs. The optimized TMCNTs were then employed for the extraction of SAs in milk and chicken meat samples. Briefly, the spiked sample was mixed with TMCNTs sorbent and vortexed for 2 min. After extraction, the sorbent particles were separated using an external magnet. TMCNTs were dried at room temperature and dissolved in acetonitrile and 1% ammonium hydroxide. Finally, the sorbent particles were separated by a magnet, and the clean extract was injected into the HPLC-DAD system. Under optimized extraction conditions, good linearities (0.1–500 µg/L with r2 $\geq$ 0.9950), low LODs (0.02–1.5 µg/L), excellent recovery values (80.7–116.2%) and good RSDs (0.3–7.7%, $n = 15$) were obtained. Using the TMCNTs as a sorbent phase in magnetic Micro-SPE, the sample preparation and HPLC analysis were performed only within 30 min. The proposed method had some advantages such as minimum usage of sorbent and solvent, rapid analysis, lower cost, improved sensitivity and simplicity compared to those reported in the literature.

Microextraction by packed sorbent

Microextraction by packed sorbent (MEPS) essentially is the miniaturized form of the classic SPE. The essential steps in the MEPS protocols are included as the conditioning of the sorbent phase, sample loading, washing and elution of targeted analytes (Figure 3) (Kole et al. 2011; Moein, Abdel-Rehim, and Abdel-Rehim 2015; Filippou, Bitas, and Samanidou 2017).

In recent years, several types of materials have been used as the packing sorbents which are included: C18 (octadecyl), C2 (ethyl), C8 (octyl), mixed-mode C8 and ion exchange (SCX), mixed-mode M1 (80% C8 and 20% SCX with sulfonic acid bonded silica), silica-based sorbents, polystyrene, porous graphitic carbon, polystyrene-divinylbenzene (PS-DVB), molecularly imprinted polymers (MIPs) and metal organic framework (MOF)-based MIPs (Alampanos, Samanidou, and Papadoyannis 2019, Kabir, Locatelli, and Ulusoy 2017).

MEPS is a promising technique in sample preparation that is compatible with the standards of GAC. The use of this method has some advantages such as small volumes of sorbents, low solvent consumption, and the small volume of

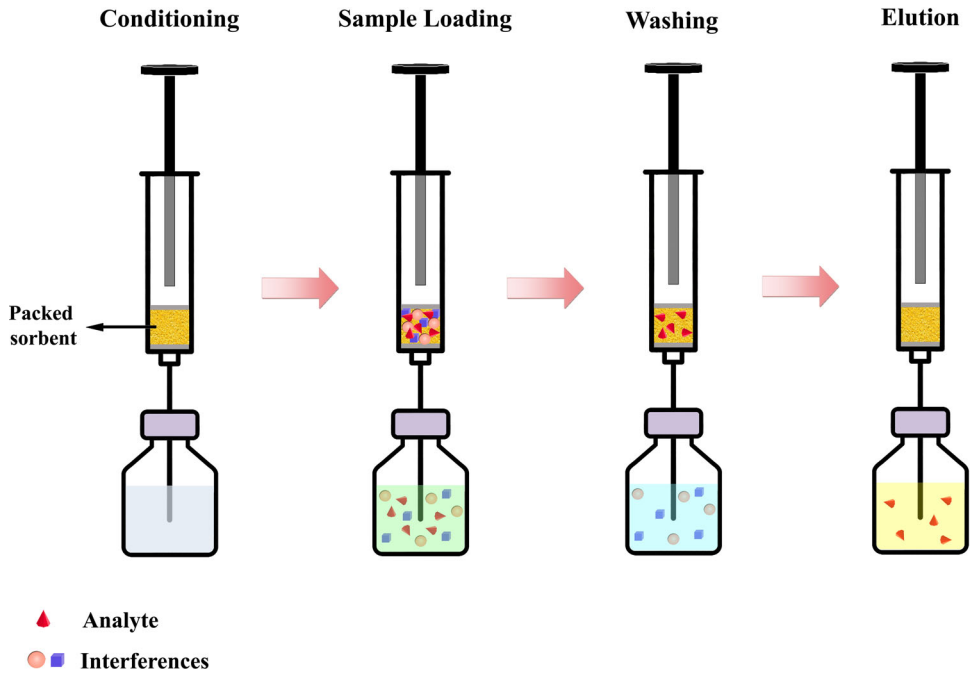

Figure 3. Micro-extraction by packed sorbent.

sample. Moreover, the extraction of analytes is carried out only in one single device and the extract can be directly injected into the HPLC system without additional treatments (Kole et al. 2011; Moein, Abdel-Rehim, and Abdel-Rehim 2015; Filippou, Bitas, and Samanidou 2017; Kabir, Locatelli, and Ulusoy 2017; Alampanos, Samanidou, and Papadoyannis 2019).

Despite these benefits, due to the required long time for the pre-analytical steps, the application of this technique in the preparation of food and food supplements are relatively limited in recent years.

Aresta, Cotugno, and Zambonin (2019) proposed a new, easy and rapid MEPS combined with UHPLC-PAD for the simultaneous determination of three FQs (ciprofloxacin, enrofloxacin and marbofloxacin) in bovine milk. Before the extraction, the milk sample was diluted with a saturated ammonium sulfate solution (1:2). The sample solution was centrifuged (at 13.000 × g for 15 min) and the supernatant was collected. The eVol-MEPS device with a replacement needle was used for sample concentration. The MEPS removable needle contained C8 as the packing sorbent which was reusable for at least 90–120 samples. In order to extract the target analytes, the sorbent was preconditioned with acetonitrile (4 × 50 mL) and water (4 × 50 mL). The supernatant of the sample was passed through the sorbent (5 × 50 mL). The washing step was carried with water (50 mL) and the analytes were eluted with a 0.4% formic acid and acetonitrile solution (50:50, v/v) (3 × 50 mL). The eluent was directly injected into the UHPLC system. The optimized procedure provided a simple analyte preconcentration, a short time for the elution (<8 min) and acceptable sensitivity for the determination of the residues.

Another protocol used graphene particles supported on silica as the sorbent for the determination of TCs in milk. Compared to commercial sorbent, the developed sorbent exhibited better results performance in the extraction of target analytes. Under optimized conditions, LOQs for the selected drugs were ranged from 0.05 to 0.9 µg/L and the accuracy levels were between from 87.9 to 118.4% (Vasconcelos Soares Maciel et al. 2018).

Xinda Zhang, Wang, et al. (2017) described a new, selective and sensitive method for the extraction of QNs in milk. The method was based on immunoaffinity microextraction in a packed syringe followed by analysis with LC-FLD. The glass microbeads (0.2 g) bounded with a quinolone monoclonal antibody filled into the syringe. Methanol was dissolved in phosphate-buffered saline (9:1, v/v) and used for the elution of analytes. The LODs and LOQs were in the range of 0.05–0.1 ng/g and 0.15 to 0.3 ng/g, respectively. This IA-MEPS method has several advantages such as simplicity, low cost and low volume of organic solvent use.

Molecularly imprinted solid-phase extraction

Molecularly imprinted polymers (MIPs) are synthetic cross-linked polymers that exhibit high affinity and selectivity toward a target analyte or a class of structurally related analytes in the presence of other compounds with similar physicochemical properties (Figure 4) (Kinsella et al. 2009; Turiel and Martín-Esteban 2010; Cunha and Fernandes 2018; Alampanos, Samanidou, and Papadoyannis 2019).

MIPs are commonly used as the selective sorbents in SPE, so-called molecularly imprinted solid-phase extraction (MISPE), which adsorb the target analytes by various types of interactions including covalent, non-covalent and semi-covalent (Kinsella et al. 2009; Marazuela and Bogialli 2009; Cunha and Fernandes 2018).

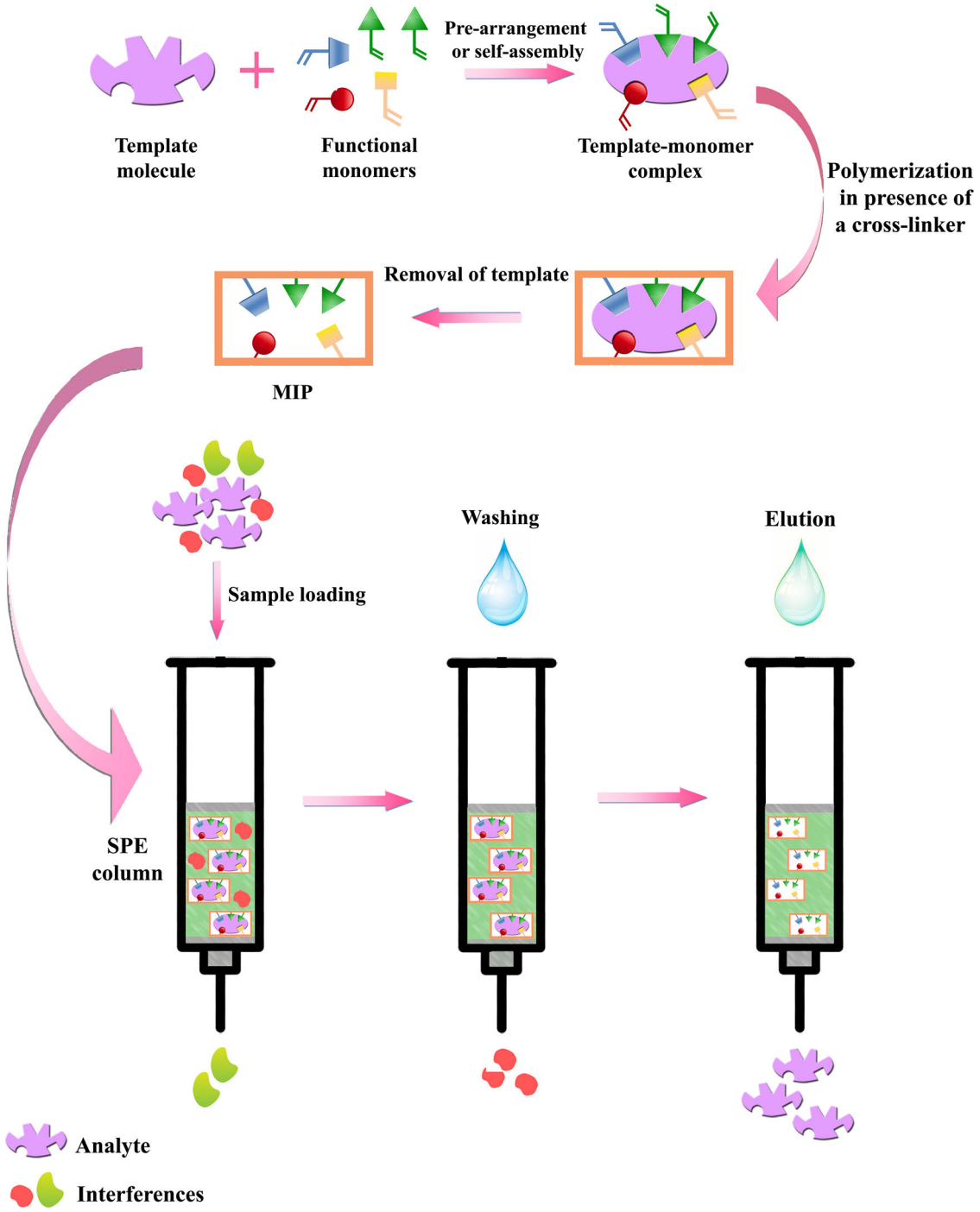

Figure 4. General scheme for the synthesis of molecularly imprinted polymer and selective extraction of a target analyte.

Compared to conventional SPE methods, this procedure has several advantages, such as high selectivity and sensitivity and proper stability in a different temperature, pH, or used solvent. MISPE can also be used as offline and online modes (Turiel and Martín-Esteban 2010; Cunha and Fernandes 2018).

The main drawbacks of this method are the potential leaching or remaining of the analyte in the MIP, polymer swelling in unfavorable solvents, slow binding kinetics, sample contamination by template bleeding and the binding site heterogeneity which result in inconsistent molecular recognition (Kinsella et al. 2009; Marazuela and Bogialli 2009; Cunha and Fernandes 2018).

In recent years, numerous studies have been carried out about the utilization of MISPE and MIPs for the extraction of the TCs (Lv et al. 2015; Feng et al. 2016; Alampanos, Samanidou, and Papadoyannis 2019; Jinxing He, Huang, et al. 2019), amphenicols (Samanidou et al. 2016; Wei et al. 2016; Zhao et al. 2017; Xie et al. 2018), β-lactams (Díaz-Bao et al. 2015; Lata et al. 2015; Urraca et al. 2016; Van Royen et al. 2016; Soledad-Rodríguez et al. 2017; Jafari et al. 2019), SAs (He et al. 2016; Baeza Fonte, Rodríguez Castro, and

Liva-Garrido 2018; Zhao et al. 2018), FQs (Tang et al. 2016; Shao et al. 2019), aminoglycosides (Moreno-González et al. 2015) and MAs (Song et al. 2016; Liu et al. 2019).

Several MIP-SPE procedures combined with HPLC have been used for determining β-lactam residues in the foodstuff. One of these methods made use of a class-selective imprinted polymer for application in milk samples. 2-Biphenylylpenicillin was used as a template molecule, N-(2-aminoethyl) methacrylamide as a functional monomer and trimethylolpropane trimethacrylate as a cross-linker. The MIPs were synthesized in the form of microspheres and porous silica beads (40–75 µm) and used as sacrificial scaffolds. A selective washing by acetonitrile-water (20:80 v/v) and elution by 0.05 mol/L tetrabutylammonium in methanol provided an efficient and accurate MISPE method for the concentration of target analytes in milk (Urraca et al. 2016).

Baeza et al. (2016) evaluated several functional monomers and cross-linkers to prepare the MIPs with the highest selectivity for the simultaneous extraction of cephalexin, cefquinome, cefazolin, cephalonium, cephapirin and ceftiofur from the milk samples. The new MIPs were synthesized based on non-covalent imprinting approach in the form of spherical microparticles using the sodium 7-(2-biphenylylcarboxamido)-3-methyl-3-cepheme-4-carboxylate as the synthetic surrogate molecule. In this case, the functional monomer consisted of N-3,5-bis(trifluoromethyl)phenyl-N′-4-vinyl phenyl urea (VPU) and divinylbenzene in a 1:2:20 molar ratio. In the optimized MISPE method, the washing step was performed by methanol/2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) buffer (0.1 M, pH 7.5) (2:98, *v/v*), followed by elution with trifluoroacetic acid in methanol (0.1:99.9, *v/v*). The residues were determined by UHPLC–MS/MS. The developed MISPE method provided a selective multi-residual extraction of cephalosporins particularly from the foodstuff.

Application of a molecularly imprinted polymer hybrid composite material followed by a reversed-phase HPLC for determination of TCs in egg, milk and milk powder was reported by Lv et al. (2015). The use of tetracycline as the template, methacrylic acid as a functional monomer, tetraethoxysilane as the inorganic precursor and methacryloxypropyltrimethoxysilane as the coupling agent allowed the preparation of novel MIPs to be used as SPE sorbent. The developed MIP-SPE method exhibited better clean-up efficiency and higher recovery values compared to conventional cartridges.

Song et al. (2018) synthesized a class-specific macrolide (MA) MIP for the extraction of seven MAs in pork tissue. The analytes were extracted with a mixture of 1% acetic acid in acetonitrile, followed by blending with the synthesized polymer. The analytes were eluted from the sorbents using the solution of acetic acid in methanol (10%) and ultrasonication for 10 min. Fast adsorption kinetics and good imprinting effects for MAs residues were observed by the prepared MIP microspheres.

Jinxing He, Huang, et al. (2019) synthesized a three-dimensional carbon nanocomposite of graphene oxide (GO) and carbon nanotube (CNT) as a hydrophilic tetracycline-imprinted polymer with high selectivity by a green synthesis method of freeze-drying. The synthesized material was for MISPE of TCs residues in milk, chicken and fish samples before the analysis with HPLC. The synthesized adsorbent could concentrate high similar structural analogs of TC and OTC with super selectivity. The maximum adsorption capacity for TC by the developed MIP was 3-fold higher than OTC. The results showed good recoveries and LODs for the TCs residues by this method.

A novel hollow molecularly imprinted polymers (h-MIPs) was developed by Tang et al. (2016) consisting of $K_2Ti_4O_9$ as a sacrifice matrix for selective extraction of enrofloxacin in fish samples. The h-MIPs showed a fast adsorption kinetic (~10 min), good selectivity factor (2.4) and a high capacity for the adsorption of a target analyte.

Conclusions

This article presents an overview of recent progress in solid-phase extraction technology for the determination of antibiotic residues in foodstuffs. Therefore, different varieties of this technology were reviewed. During the past years, great progress has been made in chromatographic technologies and mass spectrometers design. However, the sample preparation remains crucial and the most challenging step in the analytical procedures.

In the area of antimicrobial residues, there is an increasing trend toward the improvement of the sensitivity and efficiency of the extraction method. Moreover, based on the principles that govern the concept of green analytical chemistry, the use or generation of hazardous materials and solvents by analytical procedures should be reduced or eliminated. Therefore, scientists have focused on the development of the more environmentally friendly and miniaturized variations of the SPE technique in recent years. This technology has evolved to simple, rapid and one-step sample preparation procedures that require smaller sample sizes, less solvent volume, low cost per analysis, less toxic organic solvents and low cost for the equipment and automation.

Future studies on antimicrobial extraction by SPE technique should focus on the development and further application of new sorbent materials, further automation and miniaturization, multi-analyte extraction in a single step and easier online coupling with the analytical instruments.

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No potential conflict of interest was reported by the authors.

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