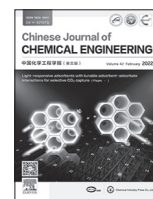




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Review

Development trend and prospect of solid phase extraction technology

Chao Zhang^{1,3}, Huifang Xing^{2,4}, Liangrong Yang^{2,4,*}, Pengfei Fei¹, Huizhou Liu^{1,2,3,4,*}¹ National Science Library, Chinese Academy of Sciences, Beijing 100190, China² College of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China³ Department of Library, Information and Archives Management, School of Economics and Management, University of Chinese Academy of Sciences, Beijing 100190, China⁴ Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

Solid phase extraction is widely used in sample pretreatment, concentration and analysis processes due to high selectivity and suitability for low concentration sample system. In this review, we systematically summarized and discussed the development trends of solid phase extraction by bibliometrics method. By analyzing papers output scale, the research and development direction of solid phase extraction technology is prospected. We also give an overview on current strategies of novel solid phase extraction from the separation medium and separation technology. The paper aims to describe the global research profile and the development trends of solid phase extraction, to help researchers to accurately grasp the research trend and to provide support for scientific research institutions to formulate scientific policies and strategic plans. Furthermore, the prospect of the development and application of solid phase extraction is also discussed.

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1. Introduction

Low-concentration complex systems widely exist in the fields of health, resources and environment. For example, extraction of pharmaceutical products, extraction of rare and precious metals, water purification, etc. are all related to low-concentration complex systems [1,2]. Therefore, the separation of low-concentration complex systems has a great impact on the national industrial structure and national economy. However, the properties of low concentration of target substance and large number of similar components will lead to low separation efficiency, high cost, complicated steps and other problems. In 2016, a comment published in *Nature* listed seven technologies that need to be developed urgently in the field of chemical separation. Among them, three technologies are widely used in the separation and extraction of low-concentration complex solution targets [3]. From the above, the efficient, accurate and controllable separation of target substances in low-concentration and large-volume complex solutions is a world frontier topic in the field of chemical separation science.

Extraction technology is especially suitable for the separation of target substances in large-scale complex systems due to its good selectivity and ease for large-scale continuous production. However, the extractant amount used for many low-concentration target substances isolation is very small, which causes the difficulty in mix and dispersion, leading to the low separation efficiency. Moreover, intense stirring usually causes emulsification and loss of organic solvent with high energy consumption. Solid phase extraction (SPE) is currently being used as an enrichment technique when low concentration analytes have to be recovered. The basic principle of SPE is the transfer of targets from the aqueous phase to the active sites of the adjacent solid phase [4] (Fig. 1). SPE for both high enrichment factor and operation flexibility, have some processing advantages such as quick absorption kinetics, extractant can be reused, organic reagent consumption, produce less waste, failure material easy curing. It is widely used in the separation some key species analysis, concentration and environment water pollution treatment processes due to its selectivity and suitability for targets isolation from low concentration and trace system [5,6].

In order to accurately understand the development status of solid phase extraction, and draw the “topographic map” of the development trend of solid phase extraction technology, this work comprehensively analyzed the development trend of solid phase extraction by bibliometrics methods based on the data of

* Corresponding authors at: College of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

E-mail addresses: lryang@ipe.ac.cn (L. Yang), hzliu@ipe.ac.cn (H. Liu).

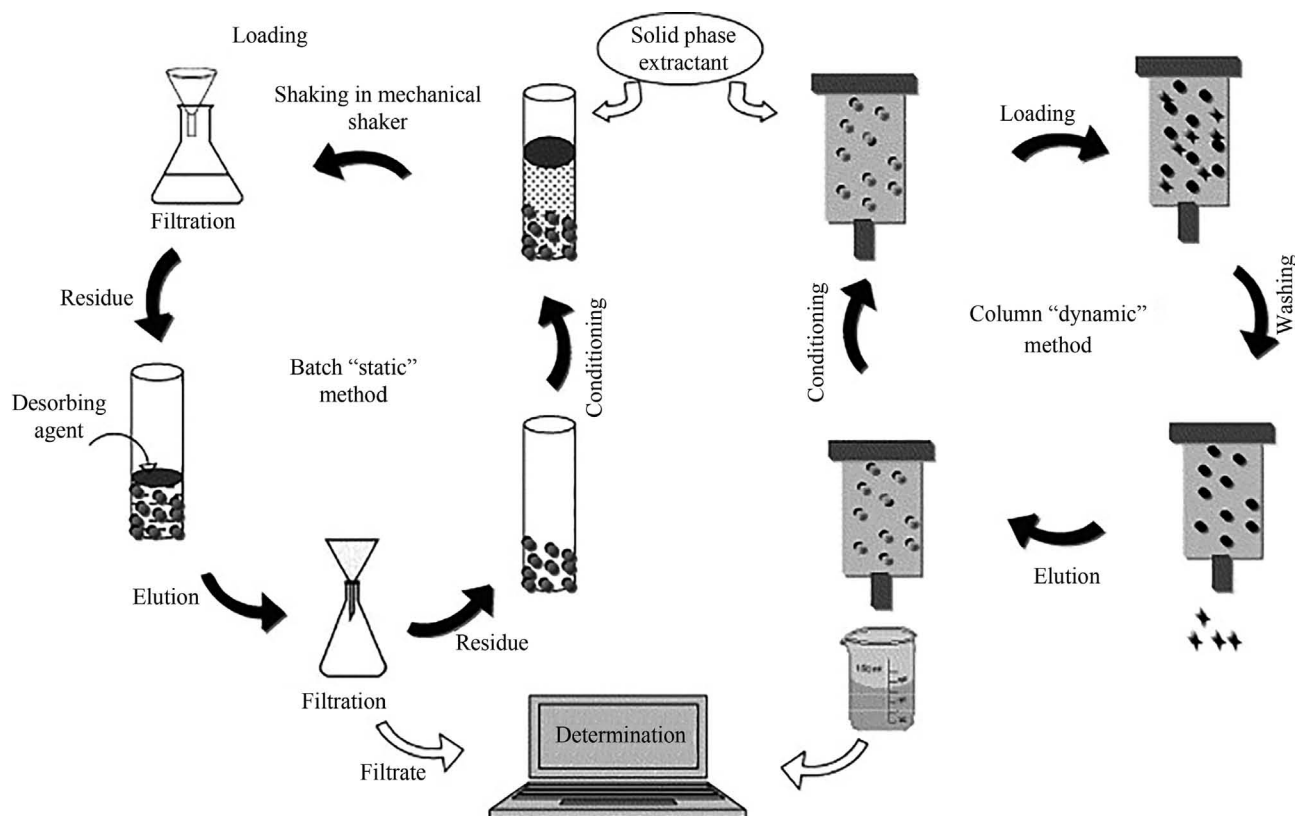


Fig. 1. Principle of solid phase extraction [4].

SCI-EXPANDED of Clarivate Analytics Web of Science (WoS) [7–9], which provides reference for scientific research managers to understand the development trend and competitiveness of solid phase extraction technology.

2. Analysis of SCI Papers Output

In order to retrieve the research articles related to “solid phase extraction”, a search strategy was constructed according to the search terms (TS = “solid phase extraction” or “solid phase micro-extraction” or “solid phase microextraction”). A total of 63,428 articles were screened in ISI Web of Science-SCI database according to the Article and Review (search time: July 2020). The retrieved data were analyzed by Excel, Derwent Data Analyzer (DDA) and other tools.

2.1. Research trend analysis

Looking at the chronological distribution of SCI articles on solid phase extraction (Fig. 2), the international community began to systematically study solid phase extraction in the late 1980s. Before 1985, research on solid phase extraction was carried out sporadically. For example, Broich *et al.* used the term liquid–solid extraction for the first time when extracting excessive amounts of drugs from urine in 1971 [10]; in 1972, Hoffman *et al.* used liquid–solid extraction to extract drugs from bile [11]. In 1978, Gorky University of the former Soviet Union published research results on “Mathematical Model of Solid Phase Extraction Kinetics”, which is the first article on solid phase extraction in the world [12]. Since 1983, due to the appearance of bonded silica gel, various commercial small columns represented by Sep-Pak of Waters have entered the market, making solid phase extraction method have made great progress and the amount of literature has soared [13]. Since

1997, the average annual number of articles published has exceeded 1000, and in 2013, the number of articles published has exceeded 4000. The global research on solid phase extraction has reached a considerable scale and developed rapidly.

2.2. Country (region) analysis

A total of more than 130 countries and regions in the world have carried out solid phase extraction research, and the top 20 countries are ranked in Fig. 3. The top ten countries are China, the United States, Spain, Iran, Italy, Germany, Japan, Brazil, Poland and Canada. The top ten countries and regions account for more than 70% of the total number of articles published.

China has an absolute advantage in the research on this topic, accounting for 25% of all articles. The United States ranked second by a large gap. Spain came in third with 5462 articles. Except for China, the United States and Spain, which have published more than 5000 articles, Iran has published more than 4000 articles, while other countries in the top 10 have published about 2000 articles, forming a big gap with the above countries.

From the perspective of research area, Europe has a relative advantage in the field of solid phase extraction. China, Iran and Japan are among the top ten Asian countries and regions, accounting for more than 36% of the total number of articles published.

2.3. Author affiliation distribution

2.3.1. Global institutions analysis

The top 20 institutions involved in the research articles on solid phase extraction published worldwide have published more than 300 articles, and 5 institutions have published more than 500 articles (Table 1). Among the top 20 institutions, China has 7, Spain has 5, Iran has 2, and the countries with 1 institution are Philippines,

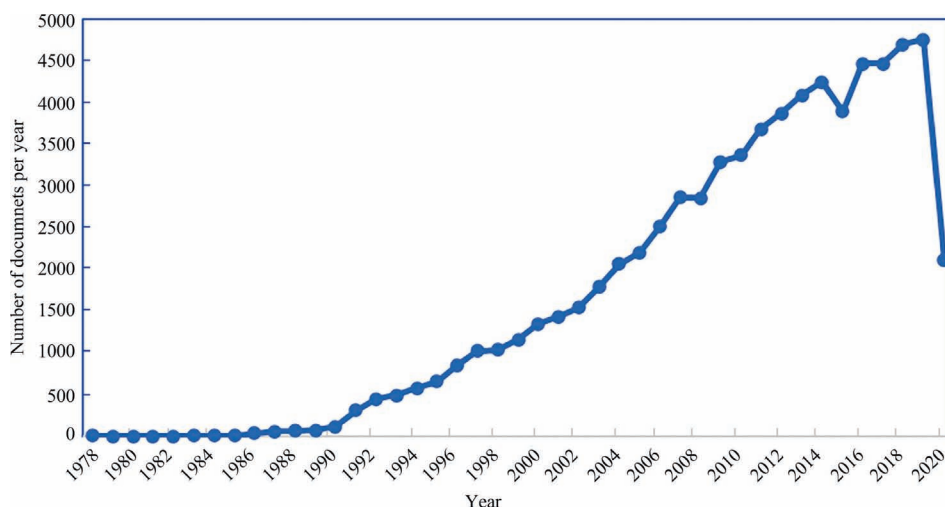


Fig. 2. Annual publications of SCI articles on solid phase extraction.

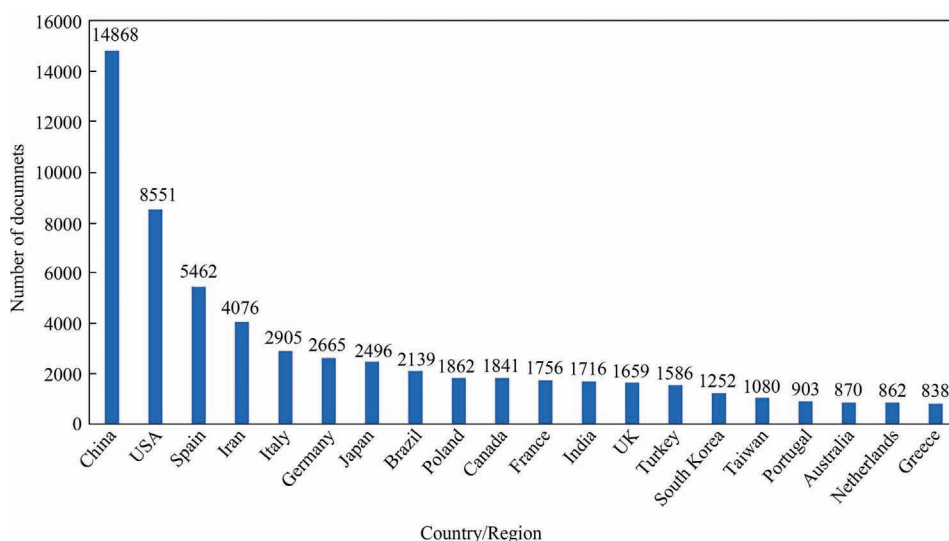


Fig. 3. Distribution of SCI articles in solid phase extraction research country (region).

Table 1

Distribution of global research institutions for SCI articles on solid phase extraction research

	Author affiliation	Publications	Country (Region)
1	Chinese Acad Sci	1750	China
2	Islamic Azad Univ	801	Iran
3	CSIC	675	Spain
4	Wuhan Univ	635	China
5	Univ Waterloo	549	Canada
6	Erciyes Univ	494	Turkey
7	China Agr Univ	462	China
8	Univ Sao Paulo	443	Philippines
9	Univ Porto	432	Portugal
10	Chinese Acad Agr Sci	425	China
11	Univ Valencia	419	Spain
12	Univ Santiago de Compostela	383	Spain
13	Univ Tehran	370	Iran
14	Sun Yat Sen Univ	362	China
15	Univ Cordoba	362	Spain
16	Jilin Univ	353	China
17	Univ Barcelona	337	Spain
18	Zhejiang Univ	330	China
19	Univ Bologna	321	Italy
20	Aristotle Univ Thessaloniki	307	Greece

Note: Take the top 20 institutions for analysis.

Canada, Portugal, Turkey, Greece and Italy. The top five institutions are Chinese Academy of Sciences, Islamic Azad University, CSIC, Wuhan University and University of Waterloo. The Chinese Academy of Sciences has 1750 articles, which is in the first research echelon in this research field. Islamic Azad University, CSIC, Wuhan University and Waterloo University all published more than 500 articles, which are in the second research echelon. Yeshiva University, China Agricultural University, University of Sao Paulo, University of Porto, Chinese Academy of Agricultural Sciences and University of Valencia have all published more than 400 articles, which are in the third research echelon in this research field. The rest of the institutions published more than 300 articles, belonging to the fourth echelon.

2.3.2. Distribution of institutions in China

In the SCI articles on solid phase extraction, 7 research institutions in China have entered the top 20 in the world. Among the top ten research institutions in China (Table 2), except for the Chinese Academy of Sciences and the Chinese Academy of Agricultural Sciences, the other 8 institutions are all universities, namely Wuhan University, China Agricultural University, Sun Yat-sen University, Jilin University, Zhejiang University, Fudan University,

Table 2
Distribution of SCI articles on solid phase extraction research in China

	Author affiliation	Publications
1	Chinese Acad Sci	1750
2	Wuhan Univ	635
3	China Agr Univ	462
4	Chinese Acad Agr Sci	425
5	Sun Yat Sen Univ	362
6	Jilin Univ	353
7	Zhejiang Univ	330
8	Fudan Univ	300
9	Sichuan Univ	252
10	Peking Univ	247

Sichuan University and Peking University. The above-mentioned top ten research institutions have all published more than 200 articles. In Chinese Academy of Sciences, Lanzhou Institute of Chemical Physics, Research Center for Eco-Environmental Sciences, Yantai Institute of Coastal Zone Research, Dalian Institute of Chemical Physics, Institute of Chemistry and Institute of Process Engineering have carried out extensive research in the field of solid phase extraction. The Chinese Academy of Sciences is far ahead of other institutions in the number of articles published by 1750 SCI articles.

2.3.3. Country cooperation analysis

It is found that many countries have carried out extensive cooperation in the field of solid phase extraction. In addition to cooperating with their own research institutions, international cooperation has also been carried out extensively.

Research institutions in the United States have relevant cooperation with the top 20 countries/regions, especially with China. In addition, the United States has carried out extensive cooperation with Britain, Canada, Germany, Spain and Japan. Apart from United States, China has closer cooperation with Britain, Canada and South Korea (see Fig. 4).

2.4. Journal analysis

More than 200 journals have published articles on solid phase extraction, mainly focusing on biochemical research methods, molecular biology, chemical analysis and other research fields. The top five journals with the largest number of articles are *Journal of Chromatography A* (5377), *Talanta* (2342), *Analytica Chimica Acta*

(2245), *Journal of Chromatography B-analytical Technologies in the Biomedical and Life Sciences* (2240) and *Journal of Separation Science* (1810). Among the top ten journals, the journal with the highest impact factor is *Analytical Chemistry* published in the United States with an impact factor of 6.350 (see Table 3).

2.5. Highly cited articles

There are 416 highly cited articles in the field of solid phase extraction. According to the order of cited frequency, the top 20 articles are selected as follows. Germany has 4 articles, Britain has 3 articles, Portugal and China has 2 articles respectively, and Australia, the Netherlands, Romania, the United States, Japan, Cyprus, Iran, Israel and Italy each has 1 article. Kuemmerer and Klaus of Germany published the article in *Chemosphere* in 2009 with the highest citation frequency. The article summarizes the research status of antibiotic enrichment and influence in the environment and analysis methods for antibiotic content determination [14]. Until now, it has been cited by more than 1900 institutions in 75 countries and regions with 1848 citations.

In the field of solid phase extraction research, there are two highly cited articles published in China. Both articles are about the pretreatment of complex matrix samples published by Professor Chen Lingxin of Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences in *Chemical Society Reviews* [15,16]. The articles were published in 2011 and 2016 respectively, with 1098 and 744 citations respectively, ranking third and ninth respectively. Although China has produced many research results in solid phase extraction research, its influence and attention in this research field need to be further strengthened (see Table 4).

2.6. Analysis of citation frequency of country (region)

The citation frequency of solid phase extraction research articles published in the world is analyzed, and the citation frequency of each article is calculated by cumulative addition of countries/regions (Table 5). The total number of citations and the number of citations per article indicate the influence of the research. Among them, the total number of citations indicates the influence of the country/region in the research field, and the number of citations per article indicates the degree of attention paid to published articles.

Judging from the total frequency of citations, the top ten are China, the United States, Spain, Germany, Iran, Canada, Italy, Britain, France and Japan. China has been cited 273,824 times, ahead of other countries/regions. The citation frequency of all articles is 18.42, ranking 18th in the world. Although Canada has only 1841 published articles, ranking 10th, the average citation frequency of published articles in Canada is 42.09, ranking first.

Table 3
Distribution of SCI articles published in solid phase extraction research periodicals

	Journal Title	Publications	Impact factor ^①
1	<i>Journal of Chromatography A</i>	5377	3.858
2	<i>Talanta</i>	2342	4.916
3	<i>Analytica Chimica Acta</i>	2245	5.256
4	<i>Journal of Chromatography B-analytical Technologies in the Biomedical and Life Sciences</i>	2240	2.813
5	<i>Journal of Separation Science</i>	2063	2.516
6	<i>Analytical and Bioanalytical Chemistry</i>	1810	3.286
7	<i>Food Chemistry</i>	1652	5.399
8	<i>Journal of Agricultural and Food Chemistry</i>	1543	3.571
9	<i>Analytical Chemistry</i>	1326	6.350
10	<i>Analytical Methods</i>	1240	2.378

^① Journal Impact Factor Data Source: JCR Science Edition 2018.

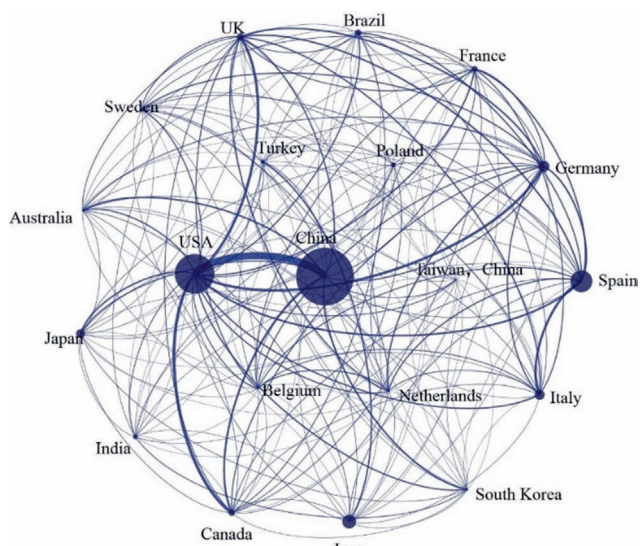


Fig. 4. Cooperation distribution of solid phase extraction research institutions.

Table 4
SCI hot articles on solid phase extraction research

	First author	Journal	Citations	Country/Region
1	Kuemmerer, Klaus	<i>Chemosphere</i> . 2009, 75: 417–434.	1848	Germany
2	Zhu, Qi-Long	<i>Chem. Soc. Rev.</i> 2014, 43: 5468–5512.	1043	Japan
3	Chen, Lingxin	<i>Chem. Soc. Rev.</i> 2011, 40: 2922–2942.	1098	China
4	Van der Veen, Ike	<i>Chemosphere</i> . 2001, 13(4): 375–380.	1004	Netherlands
5	Petrie, Bruce	<i>Water Res.</i> 2015, 72, 3–27	809	United Kingdom
6	Michael, I.	<i>Water Res.</i> 2013, 47 (3), 957–995	770	Cyprus
7	Kasprzyk-Hordern, Barbara	<i>Water Res.</i> 2009, 43 (2), 363–380.	764	United Kingdom
8	Santos, Lucia H. M. L. M.	<i>J. Hazard. Mater.</i> 2010, 175 (1–3), 45–95.	757	Portugal
9	Chen, Lingxin	<i>Chem. Soc. Rev.</i> 2016, 45 (8), 2137–2211	744	China
10	Yuan, Jiayin	<i>Prog. Polym. Sci.</i> 2013, 38 (7), 1009–1036.	706	Germany
11	Rezaee, Mohammad	<i>J. Chromatogr. A</i> 2010, 1217 (16), 2342–2357.	697	Iran
12	Peng, Gang	<i>Nat. Nanotechnol.</i> 2009, 4 (10), 669–673.	607	Israel
13	Vandenberg, Laura N.	<i>Health Perspect.</i> 2010, 118 (8), 1055–1070.	692	United States
14	Kuemmerer, Klaus	<i>J. Environ. Manage.</i> 2009, 90 (8), 2354–2366.	661	Germany
15	Lapworth, D. J.	<i>Environ. Pollut.</i> 2012, 163, 287–303.	639	United Kingdom
16	Homem, Vera	<i>J. Environ. Manage.</i> 2011, 92 (10), 2304–2347.	633	Portugal
17	Ignat, Ioana	<i>Food Chem.</i> 2011, 126 (4), 1821–1835.	588	Romania
18	Loos, Robert	<i>Environ. Pollut.</i> 2009, 157 (2), 561–568.	579	Italy
19	Watkinson, A. J.	<i>Sci. Total Environ.</i> 2009, 407 (8), 2711–2723.	567	Australia
20	Fromme, Hermann	<i>Int. J. Hyg. Environ. Health.</i> 2009, 212 (3), 239–270.	565	Germany

Table 5
Citation status of solid phase extraction SCI articles in countries/regions

	Country/Region	Publications	Total cites		Citations per paper	
			Times cited	Sort	Citations	Sort
1	China	14,868	273,824	1	18.42	18
2	USA	8551	269,603	2	31.53	8
3	Spain	5462	189,341	3	34.67	5
4	Iran	4076	81,883	5	20.09	15
5	Italy	2905	75,995	7	26.16	11
6	Germany	2665	93,912	4	35.24	4
7	Japan	2496	53,442	10	21.41	13
8	Brazil	2139	40,321	11	18.85	17
9	Poland	1862	35,888	13	19.27	16
10	Canada	1841	77,495	6	42.09	1
11	France	1756	55,684	9	31.71	7
12	India	1716	29,248	15	17.04	19
13	UK	1659	63,585	8	38.33	3
14	Turkey	1586	32,206	14	20.31	14
15	South Korea	1252	20,437	20	16.32	20
16	Taiwan	1080	24,881	18	23.04	12
17	Portugal	903	24,648	19	27.30	10
18	Australia	870	26,836	17	30.85	9
19	Netherlands	862	35,945	12	41.70	2
20	Greece	838	27,295	16	32.57	6

Note: Take the top 20 countries/regions in the number of articles published for analysis, calculate the cumulative total number of citations and the number of citations per article published by the countries/regions, and sort them.

The bubble chart is made by using the country name, the number of articles published and the citation frequency of the top 10 countries in the number of articles published, and the bubble size indicates the citation frequency of the articles published (Fig. 5). Compared with developed countries in America and Europe, the citation frequency of articles in Asian countries is relatively low.

2.7. Keywords analysis of research topics

According to the retrieved literature, the keywords are analyzed by DDA analysis tools to eliminate invalid concepts, and the high-frequency keywords involved in the research on solid phase extraction technology are obtained. The topic keywords are screened and analyzed according to the clustered research topics.

Table 6 lists the top 20 keywords ranked by word frequency in the papers published in solid phase extraction from 1981 to 2020. Topic keywords are divided into four research directions:

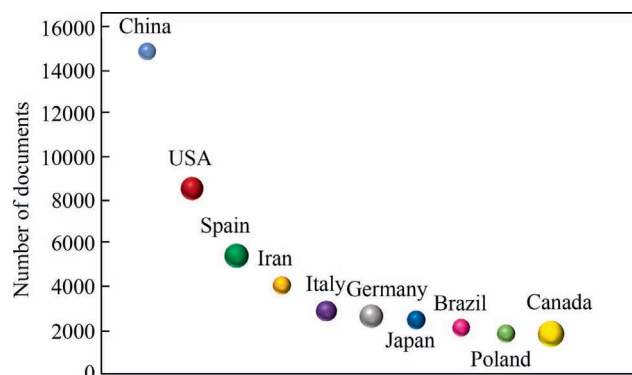


Fig. 5. Number of articles published in the top 10 countries of solid phase extraction SCI articles-analysis of citation frequency of all articles (circle size indicates citation frequency).

separation technology, separation medium, instrumental analysis methods and separation object. Among them, the technologies mainly include SPE, solid phase microextraction (SPME), magnetic solid phase extraction (MSPE), dispersive solid phase extraction (DSPE), etc. The separation mediums mainly involve molecularly imprinted polymers, ionic liquids, graphene/graphene oxide and

Table 6

Analysis of topic frequency words in research field of solid phase extraction separation technology

Subject classification	High-frequency keywords	Word frequency
Separation Technologies	SPE	8876
	SPME	5741
	Dispersive solid extraction	1365
	Magnetic solid-phase extraction	1237
Separation medium	Molecularly imprinted polymers	1855
	Ionic liquid	915
	Graphene (Graphene oxide)	885
	Metal-organic frameworks	420
	Carbon nanotubes	839
Instrumental analysis methods	HPLC	4671
	GC-MS	3893
	LC-MS	3127
	Mass spectrometry	2216
	Gas chromatography-mass spectrometry	1866
	QuEChERS	604
Objects	Pesticides	2346
	Volatile Compounds	1946
	Polycyclic aromatic hydrocarbons	1203
	Antibiotics	481

metal-organic frameworks (MOFs), etc. Instrumental analysis methods mainly refer to high performance liquid chromatography, gas chromatography, mass spectrometry, a quick, easy, cheap, effective, rugged, and safe method for pesticide residue analysis (QuEChERS), etc. The separation objects include pesticides, volatile compounds, polycyclic aromatic hydrocarbons antibiotics, etc.

Fig. 6 shows the trend of the frequency of keywords in the field of separation medium (a), separation technology (b), instrumental analysis methods (c) and separation object (d). From the data of Fig. 6(a), the use of MOFs or graphene (graphene oxide) as SPE separation medium is an emerging hot spot in recent 10 years. The use of molecularly imprinted polymers, ionic liquids and carbon nanotubes as separation medium has maintained a high degree of research interest for nearly two decades. From Fig. 6(b), the research on solid-phase microextraction has lasted for nearly 30 years. Besides, dispersive solid phase extraction and magnetic solid phase extraction have been the research hotspots in the past decade. The data in Fig. 6(c) indicates SPE has been widely used in HPLC, GC-MS, LC-MS and other instrumental analysis methods. In recent years, with increasing attention to environmental pollution, the use of solid-phase extraction technology for the detection of volatile organics, pesticides and polycyclic aromatic hydrocarbons is also been the focus of attention. (Fig. 6(d)).

3. Novel Solid Phase Extraction Technology

3.1. Separation medium

3.1.1. Metal-organic frameworks (MOFs)

MOFs are porous polymeric materials consisting of metal ions as a center and an organic ligand as a repeating, or more precisely, bridging unit [17]. Due to their wide range of structures and func-

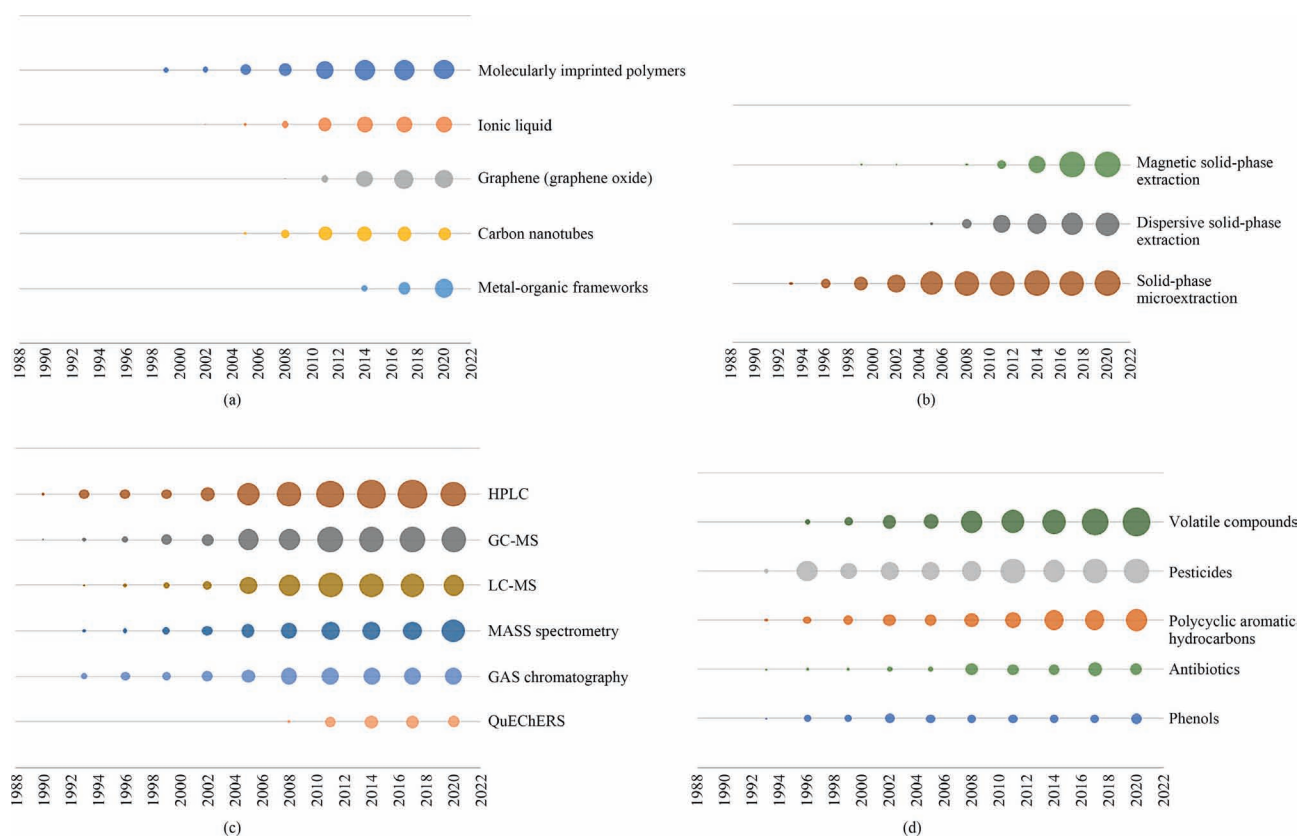


Fig. 6. The trend of the frequency of keywords in the field of separation medium and separation technology (a: separation medium; b: separation technology; c: instrumental analysis methods; d: separation object). The keywords frequency is represented by the circles 'size'.

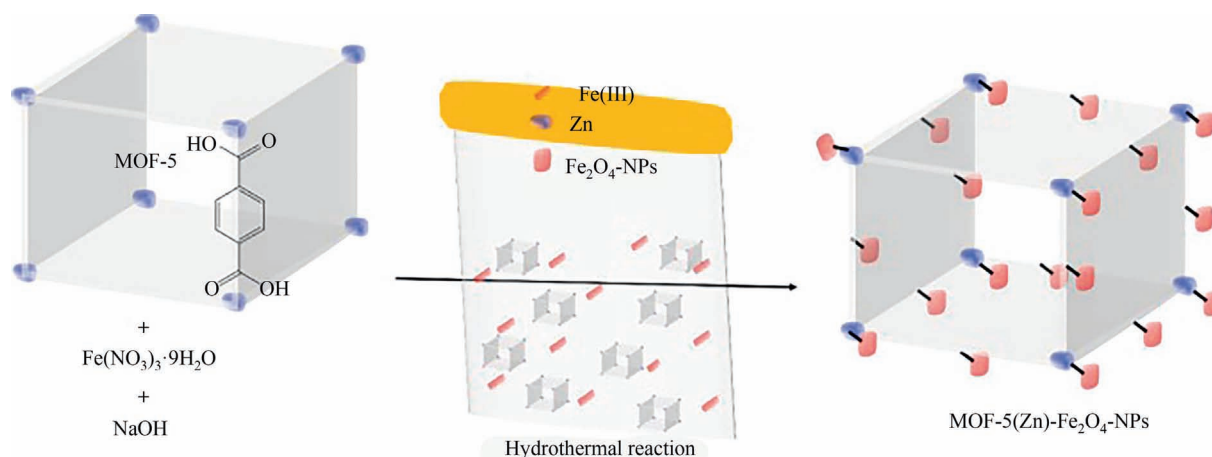


Fig. 7. All steps for MOF-5(Zn)-Fe₂O₄ single bond NPs [21].

tionalties, MOFs have been widely accepted for applications which include gas storage, separations, catalysis and drug delivery [18]. In recent years, the application of MOFs in different SPE technologies has been widely explored, such as in classical SPE, magnetic SPE and dispersive SPE [19]. Ghiasvand *et al.* synthesized a MIL-101 (Cr) nanocomposite that intercalated with polyaniline (PANI) and doped with SiO₂ nanoparticles used for the accurate determination of phenolic antioxidants in plant and food samples [20]. Bahrani *et al.* combined the Fe₂O₄ nanoparticles and MOF-5 to prepare a novel magnetic sorbent for determination of colchicine in complex matrices (Fig. 7). Xinpeng Dai *et al.* prepared MIL-101(Cr) as a SPE sorbent for the determination of sulphonamides in environmental water samples coupling with UPLC-MS/MS [22]. The utilization of MOFs in SPE notably enhances the extraction efficiency and reduces the analysis time for specific analytes compared to previous procedures.

3.1.2. Graphene/Graphene oxide

Graphene (G) and Graphene oxide (GO) seem to be ideal sorbents in SPE because of their huge surface area and the hexagonal arrays of carbon atoms in G sheets that are ideal for strong interactions with other molecules. G and GO have received much attention for their many potential applications in classical SPE of both organic compounds and metal species [23].

The application of G as a sorbent is limited due to its lower water dispersibility. GO overcomes this limitation and is more frequently used in sample preparation. For instance, GO was applied as material in the SPE combined with electromembrane extraction followed by capillary electrophoresis for the determination of chlorphen oxyacid herbicides in environmental water samples [24].

In order to solve the problem of G or GO being difficult to be separated from the mother solution, the synthesis of various kinds of magnetic nanoparticles (Ni, CoFe₂O₄, Fe₃O₄) combined with functional G and GO as adsorbents have been also proposed [25]. For example, Geng *et al.* synthesized GO/Fe₃O₄ nanocomposites with tunable GO/Fe₃O₄ ratio and achieved an exceptionally high yield [26]. Akamine *et al.* introduced an innovative GO-Fe₃O₄ based MSPE method to extract gingerols from ginger-derived commercial formulations (Fig. 8) [27].

3.1.3. Ionic liquids

Ionic liquids (ILs)-based sorbents have high extraction capacity, improved selectivity and very low limits of detection and limits of quantitation compared to the commercial sorbents. ILs are often associated silica, molecular imprinted polymer, carbon nanotubes,

graphene oxide and magnetic materials in SPE process [28] (Fig. 9). Immobilized materials have higher extraction efficiency and adsorption capacity, stronger extraction selectivity. In recent years, they have been widely used for the separation of bioactive compounds [29], drug molecules [30] and organic pesticides [31]. For example, Yang *et al.* applied the oil-soluble 1-butyl-3-methylimidazolium α -aminohydrocinnamic acid ([C₄C₁im] [Phe]) to prepare surfaces of MIPs in acetonitrile for the selective recognition of L-Phe [32]. Ge *et al.* developed a novel and fast preconcentration approach-ionic liquid-dispersive liquid-liquid microextraction combined with micro-solid phase extraction for antidepressant drugs in water [33]. The authors synthesized an ionic liquid mediated sol-gel sorbents for hollow fiber solid-phase microextraction for extraction of the pesticides: diazinon, fenitrothion, malathion, fenvalerate, phosalone and tridemorph from human hair and water samples [34].

3.1.4. Molecularly imprinted polymers

In recent years, molecularly imprinted polymers (MIPs) have attracted much attention due to their outstanding advantages, such as predetermined recognition ability, stability, relative ease and low cost of preparation, and potential application to a wide range of target molecules [35]. MIPs were most frequently utilized as affinity-based separation media for sample preconcentration and separation, via molecularly imprinted solid-phase extraction (MISPE) and molecularly imprinted solid-phase micro-extraction (MISPME) (Fig. 10) [15].

MIPs based solid phase extraction can be used in environmental, bioanalytical, food and pharmaceutical fields. For example, Hu *et al.* prepared M-CCNs@MIP for highly selective adsorption of fluoroquinolones from water [37]. Cheng *et al.* developed a high-performance liquid chromatograph equipped with a UV method based on molecularly imprinted-solid phase extraction for preconcentration, cleanup and determination of ceftiofur sodium in food samples [38].

3.2. Separation technology

3.2.1. Magnetic solid phase extraction technology for high efficiency separation

In 1996, Towler *et al.* used manganese dioxide-coated magnetite as a sorbent for the separation of radium, lead, and polonium from seawater samples. The term of magnetic solid-phase extraction (MSPE) was first introduced by Šafařík and Šafaříková in 1999. They used a reactive copper-phthalocyanine dye, which was immobilized on fine silanized magnetite particles and mag-

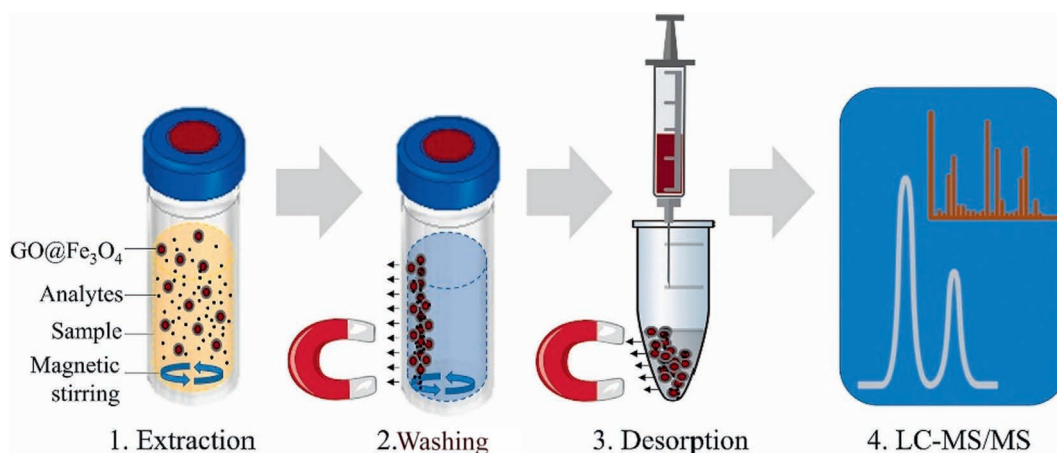


Fig. 8. Main steps of the analytical procedure for GO-Fe₃O₄ based MSPE of gingerols [27].

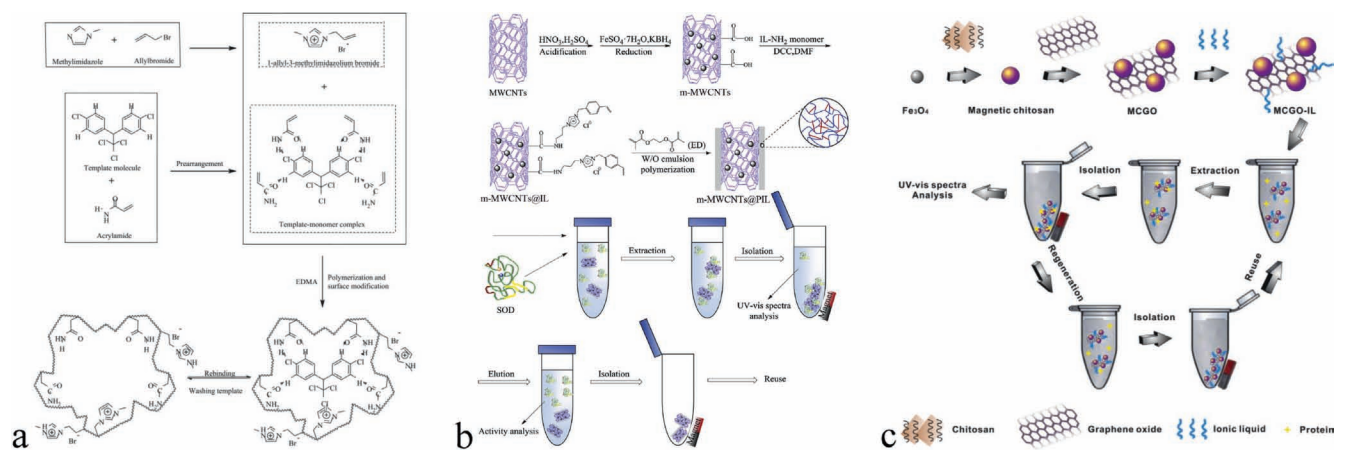


Fig. 9. (a) Schematic illustration of IL and IL-MIPs formation; (b) Preparation of m-MWCNTs@PIL and the application for the MSPE of Cu, Zn-SOD; (c) Preparation of MCGO-IL and its application in MSPE of protein [28].

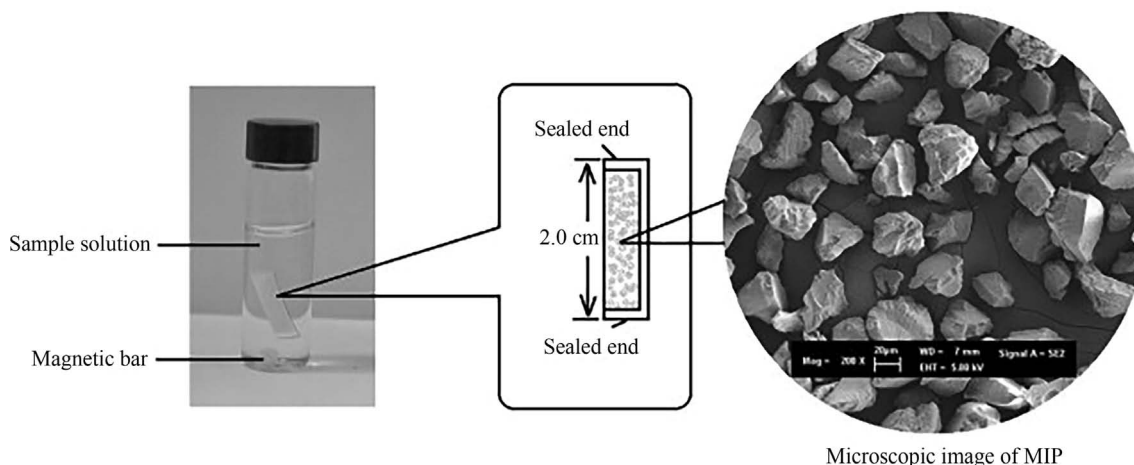


Fig. 10. Schematic diagram and microscopic image of MIP sorbent used [36].

netic charcoal for the separation and preconcentration of organic compounds with planar molecular structures (such as safranin O and crystal violet) [39].

In MSPE technique, magnetic adsorbents are directly dispersed into sample solutions, and this dispersive extraction mode can enhance the contact area between adsorbents and analytes. As a

result, the extraction efficiency of MSPE is superior to that of typical SPE (Fig. 11). Magnetic adsorbents, commonly consisting of magnetic carriers and functionalities, play a vital role in the MSPE technique since they not only influence extraction efficiency but also settle on the sensitivity and selectivity of the method [41]. Therefore, MSPE has been extensively applied in several fields,

such as wastewater treatment [42–47], food analysis [41,48], and biomedicine [49–51].

3.2.2. Dispersive solid phase extraction

Dispersive solid phase extraction (DSPE) is another form of SPE in which the adsorbent is exposed to the analytes via dispersion process to provide a large surface area and high sorption capacity. It has surged in popularity since 2003, when it was reported by Anastassiades *et al.* as an effective clean-up procedure in pesticide extraction from produce [52]. DSPE possess several benefits including short equilibrium time, no need for conditioning stage, and high extraction recovery [53]. A significant increasing attention to DSPE can be observed in recent years. It has been used in the extraction, isolation, and clean-up of several compounds present in complex matrices, as in the analysis of veterinary drugs [54], water analysis [55] and pesticide residues [56].

More recently, dispersive micro-solid phase extraction (D- μ -SPE) has been widely developed as a simple and miniaturized modification of DSPE [57]. Compared with DSPE, D- μ -SPE can be

performed by trapping the target analytes in the sorbents. After extraction, the sorbent containing the target analytes is isolated by centrifugation or filtration, which leads to the advantages of higher extraction efficiency and enrichment factor, less solvent consumption and lower sample solution consumption [57,58]. A schematic illustration of D-m-SPE procedure is illustrated in Fig. 12.

3.2.3. Electric and ultrasonic field-assisted solid phase extraction technology

The electric field-assisted extraction process is a new type of separation technology that improves the separation efficiency by applying an electric field to enhance the mass transfer. It has the advantages of simple liquid extraction operation, good enrichment effect, and electric field can accelerate mass transfer and enhance selectivity. In recent years, electric field-assisted solid phase extraction (E-SPE) technology got more attention because the electric field can strengthen the mass transfer, effectively shorten the extraction time, and can selectively extract the separated

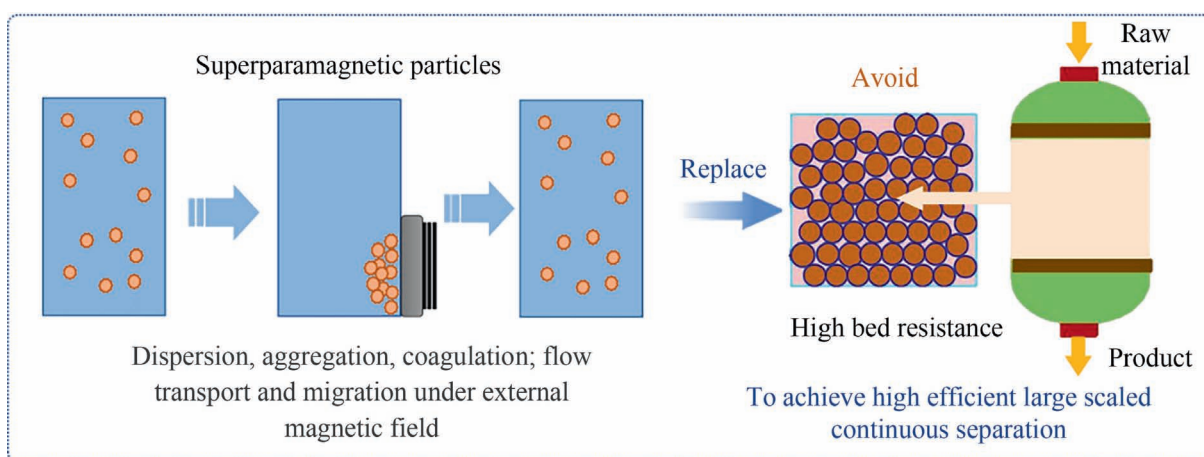


Fig. 11. Magnetic responsive solid phase extraction technology [40].

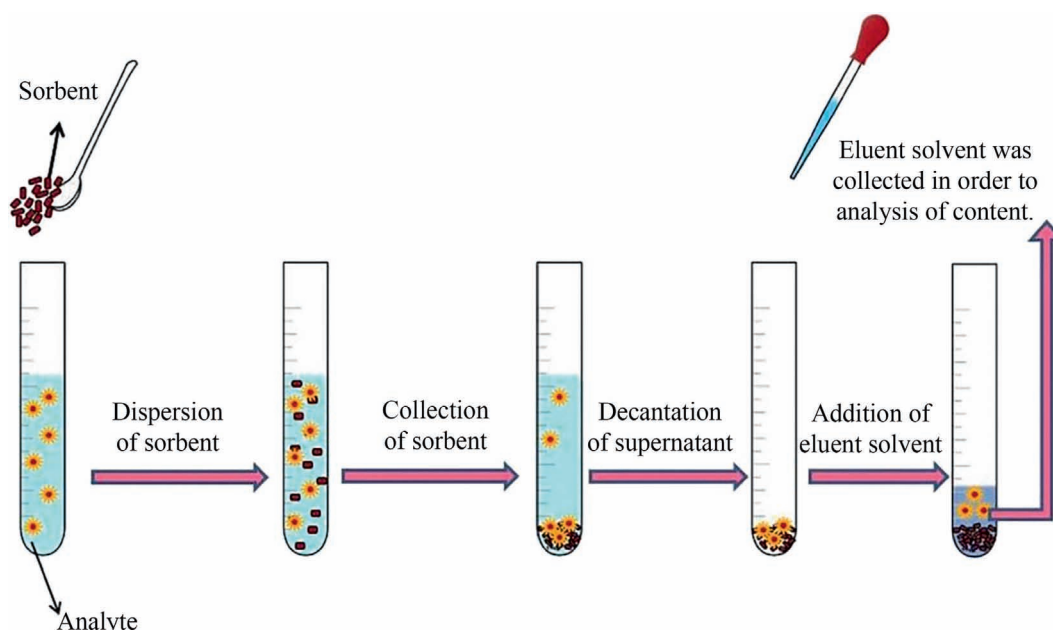


Fig. 12. Schematic illustration of D-m-SPE procedure [57].

substances of the opposite charge by adjusting the electric field parameters. Su *et al.* used poly(vinyl)ferrocene-functionalized electrodes to selective electrochemical remove of anionic chromium and arsenic oxyanions, under a range of different concentrations and electrolyte conditions [59]. Bagheri *et al.* prepared polyamide nanofibers using magnetic and electric field-enhanced electrospinning technology for on-line solid phase extraction and high-performance liquid chromatography to obtain good separation effects, and achieved the integration of extraction, enrichment and detection [60].

In recent years, ultrasonic-assisted extraction has also received more and more attentions. Ahmadi *et al.* used $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{C}_8/\text{NH}_2$ magnetic particles to achieve the extraction and separation of imipramine and norimipramine in human plasma with the assistance of ultrasound [61]; Sereshti *et al.* used graphene oxide as a nano-adsorbent for solid-phase microextraction to achieve simultaneous detection of theobromine, theophylline and caffeine in different brewed tea samples under high-performance liquid chromatography-UV combined conditions. The ultrasonic field assisted in the extraction process effectively increased the rate of adsorption and desorption [62].

4. Conclusion and Outlook

Through the bibliometric analysis of scientific research output in the field of solid phase extraction, it is found that solid phase extraction is widely used in the field of detection, but rarely used in the commercial separation. The precise, efficient, and controllable separation for low-concentration complex systems is the world's frontier subject and important development direction of separation science and technology in the future [3]. The current research still needs to be further strengthened in the following aspects. Firstly, for the highly selective and precise separation of large molecules such as proteins and enzymes in biological products, aptamer, the new type of ligand with high selective binding ability to targets, has been developed and widely investigated due to its advantages of universality and stability. While, it is necessary to increase research efforts to expand the target nucleic acid aptamer library. Besides, the high tunability and diverse structures of MOF facilitate its application in the field of solid phase extraction separation. However, increase the stability of MOFs is still a great challenge as the most stable MOFs are still not comparable with other porous materials including zeolites, mesoporous silica, and porous carbons. Thus, more efforts should be done on this aspect. Moreover, for the sort of GO materials, unavoidable agglomerations of GO layers in the process of preparation and modification of graphene-based materials will lead to the small surface area of obtained graphene and graphene-based materials and the loss of GO layers during application. Therefore, developing monodispersed single layer graphene or graphene-based materials is still a critical issue. For the IL community using in separation processes, to develop continuous purification processes, intensified regimes able to be scaled-up, feasible processes for solvent and material recycling, and processes with low energy and solvent consumption, effluent discharge and material disposal needs to take into account. What's more, the adsorption with a high selectivity usually leads to difficulty in desorption. Thus, in the future, both selective adsorption and controllable desorption with a mild condition should be considered. More green and efficient methods such as electrochemistry or bionics have provided ideas to solve this problem. In addition, due to the simple structure and the similar properties with adjacency of metal ions, the highly selective solid phase extraction for metal ions separation is still a research difficulty, such as alkali metal ions' highly selective adsorption and separation. Difficulty in desorption and ease to dissolve limits the

application of inorganic solid phase extraction adsorbent. While for the organic adsorbents, selectivity still needs to be improved. It is necessary to further study the selective interaction mechanism and influence of the structural interface on separation efficiency from the molecular mesoscopic scale for the more precise and highly efficient separation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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