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超分子溶剂-微萃取技术在食品及环境污染物检测中的应用进展

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摘　要: 随着人们对食品安全与环境质量关注度的不断提升, 高效精准的污染物检测技术至关重要。超分子溶剂-微萃取技术作为一种新兴的样品前处理手段, 凭借其高效、选择性好、环境友好等优势, 在食品及环境污染物检测领域展现出独特优势。该技术基于超分子溶剂(如环糊精、冠醚等主体分子形成的纳米/微米级溶剂)对特定污染物的选择性识别与富集能力, 通过微萃取操作实现样品中目标物的快速分离与浓缩。作为一种新型绿色溶剂, 超分子溶剂萃取效率高, 极性范围宽, 结构可设计, 兼具萃取和净化的效果, 在萃取分离领域应用广泛。本综述就超分子溶剂性质、超分子溶剂微萃取类型进行介绍, 重点对该技术在食品及环境污染物检测中的应用进行了较详细的综述, 并对该领域的工作进行了展望, 以期为超分子溶剂-微萃取技术的推广应用提供参考。

关键词: 超分子溶剂; 微萃取; 环境污染物; 绿色化学

Progress in the application of supramolecular solvent-microextraction technology in detection of food and environmental pollutants

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ABSTRACT: With the increasing attention to food safety and environmental quality, efficient and accurate pollutant detection technology is crucial. Supramolecular solvent microextraction technology, as an emerging sample pretreatment method, has demonstrated unique advantages in the field of food and environmental pollutant detection due to its high efficiency, good selectivity and environmental friendliness. This technology is based on the selective

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recognition and enrichment ability of specific pollutants by supramolecular solvents (such as nano/micro scale solvents formed by host molecules such as cyclodextrin and crown ether), and achieves rapid separation and concentration of target substances in samples through microextraction operations. As a new type of green solvent, supramolecular solvents have high extraction efficiency, wide polarity range, customizable structure, and both extraction and purification effects, making them widely used in the field of extraction and separation. This review introduced the properties of supramolecular solvents and types of supramolecular solvent microextraction, with a focus on the detailed application of this technology in the detection of food and environmental pollutants, and provided prospects for the work in this field, in order to provide reference for the promotion and application of supramolecular solvent-microextraction technology.

KEY WORDS: supramolecular solvent; microextraction; environmental pollutant; green chemistry

0　引　言

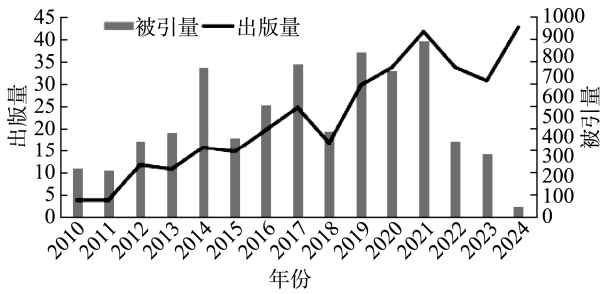
食品及环境污染物检测中, 样品分析过程主要包括样品采集、样品前处理、上机分析、数据处理及结果报告等步骤。而样品前处理是最烦琐、最耗时、最重要的步骤之一, 通过该步骤能够达到减少基质干扰、富集和浓缩目标分析物的目的[1−2]。目前主要的样品前处理技术为液相萃取和固相萃取, 均存在着耗时、不环保、成本高、操作复杂等缺点, 样品前处理方法正逐渐向着快速、绿色、简便、微型化、自动化方向发展。自 1990 年, ARTHUR 等[3]在固相萃取的基础上提出固相微萃取(solid-phase microextraction, SPME)技术以来, 微萃取技术便得到了不断的发展和应用。作为两种主要的微萃取技术, SPME 和液相微萃取(liquid phase microextraction, LPME)技术在食品和环境中的农药、真菌毒素、重金属等污染物的前处理中已有着广泛的应用。

2009 年, BALLESTEROS-GÓMEZ 等[4]首次引入了超分子溶剂(supramolecular solvents, SUPRASs)这一术语。SUPRASs 是由两亲性分子自组装和凝聚形成, 与水不混溶, 具有纳米结构的胶束聚集体; 具有环境友好、原料廉价、制备简单、提取效率高等优点。SUPRASs 与微萃取相结合, 能够充分发挥两者的优势, 形成了一种环境友好、快速简单、富集系数高的绿色新技术—超分子溶剂微萃取(supramolecular solvent microextraction, SSME)。2010 年, COSTI 等[5]首次将 SUPRAS 用于固体样品微萃取, 并测定鱼和贝类中恶喹酸和氟甲喹残留量, 此后 SSME 在各类污染物中的应用研究相继出现(图 1)。本文简要介绍 SUPRASs 及 SSME 类型, 重点综述 SSME 在食品及环境污染物检测中的应用, 以期为 SSME 的研究提供一些参考。

1　超分子溶剂概述

1.1　超分子溶剂的合成

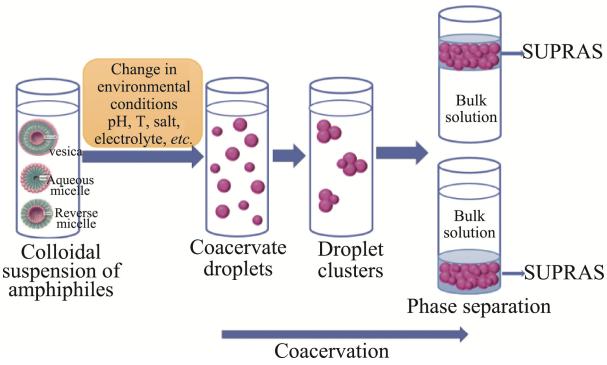
SUPRASs 的合成通常包括两个步骤(图 2): 首先, 两亲性分子在超过临界聚集浓度后会自主形成纳米结构(主要是囊泡、水相胶束和反向胶束 3 种结构); 然后, 在外界条件(如 pH、温度、溶剂、电解质)的诱导下, 生成的纳米结构三维聚集体会自组装形成更大的聚集体, 并絮凝从溶剂中分离, 即为 SUPRASs。



注: 图中的数据来自 Web of Science。

图 1　近年来 SSME 技术的发文数量和被引频率趋势

Fig.1　Trend of the number of published papers and citation frequency of SSME technology in recent years



注: Colloidal suspension of amphiphiles: 两亲性物质胶体悬浮液; vesica: 囊泡; Aqueous micelle: 水相胶束; Reverse micelle: 反向胶束; Change in environmental conditions pH, T, salt, electrolyte, *etc.*: 环境条件改变(pH、温度、盐浓度、电解质浓度等); Coacervate droplets: 凝聚液滴; Droplet clusters: 液滴聚集体; Bulk solution: 本体溶液; Phase separation: 相分离; Coacervation: 凝聚作用。

图 2　SUPRASs 合成的一般程序

Fig.2　General procedure of SUPRASs synthesis

1.2 超分子溶剂特点

SUPRASs 最突出的特点包括: 制备简单、提取效率高、绿色环保等。(1)大量的可结合位点。溶剂中含有高浓度的两亲性分子, 由此有大量的可结合位点, 少量的 SUPRASs 便可以获得高提取效率, 低体积便可达到高浓缩系数(通常为 100~500); (2)极性范围宽。两亲性分子具有亲水部分和疏水部分, 能够提供不同极性区, 可同时提取各种溶质; (3)表面积大。凝聚层液滴在 SUPRASs 中保持独立的个体(见图 2), 提供了大的表面积, 在萃取过程中能快速传质; (4)制备简单。两亲性分子廉价易得, SUPRASs 只需添加两亲性分子并提供絮凝条件就可制得; (5)绿色安全。与传统有机溶剂相比更加绿色环保, 不挥发、不可燃, 使用过程中安全性高。此外, SUPRASs 还具有限制进入的特性, 能够限制蛋白质和多糖等大分子物质的进入[6]。

SUPRASs 的萃取性能受两亲性分子和絮凝条件的影响, 因此通过调整两亲性分子和絮凝条件可以制备具有特定功能的 SUPRASs。ALGAR 等[7]通过改变羧酸烃链的长度和浓度以及四氢呋喃的浓度, 优化了 SUPRASs 非极性结构域的甲烷三基-π 氢键组成, 从而提高了对土壤中芳香化合物萃取效率。SÁNCHEZ-VALLEJO 等[8]分别以正辛醇和 1,2-辛二醇为原料合成了 7 种 SUPRASs, 用于树莓多酚的萃取, 其研究表示合成的 1,2-辛二醇海绵状结构的 SUPRASs 具有丰富的水互连通道, 对高极性多酚糖苷共轭物和低极性多酚有优异的提取性能。

目前, SUPRASs 应用最广泛的类型为反相胶束结构, 其次是囊泡结构, 水相胶束结构最少。反相胶束结构 SUPRASs 中, 均采用链烷酸或烷醇作为两亲性分子, 四氢呋喃作为凝聚剂。因此, 合成 SUPRASs 的原料类型还有待发展。ACCIONI 等[9]则用七氟丁酸作为两亲性分子制备 SUPRASs, 并用于提取氨基酸和寡肽, 其研究结果表明制备的 SUPRASs 对含有非极性脂肪族、环状和芳香族侧链取代基(log D>-3.62)的氨基酸和寡肽具有很好的提取效果。

1.3 超分子溶剂微萃取模式

本文将 SSME 分为 3 种模式: 基本模式、外力辅助模式和联用模式。在这 3 种模式中, 基本模式是最简单的, 主要是将 SUPRASs 与微萃取相结合, 如单滴微萃取(single drop microextraction, SDME)、LPME 和分散液液微萃取(dispersive liquid-liquid microextraction, DLLME)。但基本模式存在着提取效率低等问题, 为加快萃取速度, 研究人员陆续将涡旋辅助(vortex-assisted, VA)、超声波辅助(ultrasound-assisted, UA)、空气辅助(air assisted, AA)等外力辅助应用于 SSME: 这些辅助模式主要是通过增加 SUPRASs 和待测物质的接触面积, 或者改变目标物在样品与萃取相间的分配系数, 从而提高萃取效率。除以上单一的萃取模式, 目前还发展了与其他技术联用的模式: 如基于超临界流体萃取(supercritical fluid extraction, SFE)、磁纳米粒(magnetic nanoparticles, MNPs)、分散微固相萃取(dispersive micro-solid phase extraction, DMSPE)的联用模式。以下针对 SSME 在食品和环境中各种污染物检测中的应用进行简要阐述。

2 超分子溶剂微萃取应用

2.1 农兽药残留

近年来 SSME 在农兽药残留检测中的应用, 见表 1。农兽药残留涵盖了有机磷、有机氯、菊酯类、氨基甲酸酯等杀虫剂, 三唑类杀菌剂, 三嗪类和苯脲类除草剂, 硝基咪唑类、苯并咪唑类兽药, 仪器大多为 HPLC-UV/DAD。

COSTI 等[5]最早将 SSME 结合 LC-UV 应用到鱼贝类固体样品中氟甲喹和恶喹酸兽药残留检测: 400 μL SUPRAS 和 200 mg 切碎的样品混合后, 恒温到 15 ℃, 离心后取 SUPRAS 提取物上机分析; 在最佳条件下, 定量限为 5~22 μg/kg, 回收率为 99%~102%。该方法验证了 SUPRAS 在固体样品微萃取中的适用性, 简单快速、结果可靠、低成本, 为 SSME 在兽药残留中的应用奠定了基础。LI 等[14]用六氟异丙醇和辛醇制备了 SUPRAS, 结合 HPLC-UV 测定水样中氯酚, 富集倍数为 72~147, 回收率为 96.0%~107.9%。此外, 其制备的 SUPRAS 能排除蛋白质、多糖及腐殖物质等大分子物质, 而对分子量很小的氯酚不排阻, 彰显了从复杂基质中萃取小分子而排除大分子的应用潜力。

最初的 SSME 技术仅用于水样、果汁等简单基质, 而后逐步应用于果蔬、土壤等复杂基质。GORJI 等[10]以癸酸和 THF 制备 SUPRAS, 结合 HPLC-UV 检测了大米和蔬菜中噻螨酮和 4 种有机磷农药残留, 富集因子为 102~178, 检出限为 0.05~0.20 μg/kg, 回收率为 83.6%~105.0%; ANA 等[15]以 1-己醇和 THF 制备 SUPRAS, 结合 LC-MS/MS, 分析了水果、蔬菜中 4 种氯菊酯对映体, 检出限为 0.2~0.3 μg/kg, 符合相关农药残留标准。

2.2 SSME 在真菌毒素和食品添加剂检测中的应用

近年来 SSME 在真菌毒素和食品添加剂检测中的应用, 见表 2。

目前 SSME 技术在真菌毒素上的相关报道较少: GARCÍA-FONSECA 等[32]用十四烷酸和 THF 制备成 SUPRAS, 结合酶联免疫吸附, 测定小麦中黄曲霉毒素 B_1 和葡萄酒、香料中赭曲霉毒素 A, 回收率为 84%~96%, 与免疫亲和柱前处理技术相比, 两者均有相似的检出限和线性范围, 但后者不适用于香料, 更消耗有机溶剂, 因此该方法彰显出更大的应用潜力; CABALLERO-CASERO 等[33]利用 SUPRAS 限制进入的特性, 用癸酸和 THF 制备成 SUPRAS, 结合 HPLC-UV 测定了 5 种香料中赭曲霉毒素 A, 检出限为 0.5 mg/L, 回收率为 81%~101%, 该方法省去了免疫亲和柱净化, 节省了时间与成本, 也符合欧盟相关标准。

表 1　SSME 在农兽残留检测中的应用

Table 1　Application of SSME in the analysis of agricultural and veterinary residues

分析物	样品	SUPRAS	前处理方法	仪器方法	富集倍数	检出限	回收率/%	参考文献
4 种有机磷(乙硫磷、磷胺、二嗪磷、毒死蜱)	大米、蔬菜	癸酸/THF	VA-SSME[b]	HPLC-UV	102~178	0.05~0.205 μg/kg	83.6~105	[10]
二嗪磷、甲霜灵	果汁、水样	1-十二烷醇/甲苯	AA-DMSPE[c]	GC-FID	500	0.6~0.8 μg/L	85.0~96.6	[11]
3 种有机磷(杀螟硫磷、伏杀硫磷、毒死蜱)	茶饮	二-(2-乙基己基)磷酸/THF	SSME[a]	HPLC-UV	15~19	6~10 mg/L	77~98	[12]
4 种全氟化合物、5 种含氟农药	水样	十一烷醇/THF	VA-LLME[b]	UPLC-Q-Orbitrap HRMS	24.7~28.2	0.125~0.150 μg/L	82.9~105.9	[13]
氯酚	水样	六氟异丙醇/辛醇	VA-LLME[b]	HPLC-UV	72~147	0.38~0.57 ng/mL	96.0~107.9	[14]
氯菊酯	水果、蔬菜	1-己醇/THF	VA-SSME[b]	LC-MS/MS	-	0.2~0.3 μg/kg	93~107	[15]
啶酰菌胺、氟啶脲、氯氰菊酯和联苯菊酯	牛奶	壬醇/六氟异丙醇	LPME[a]	HPLC-UV	-	0.5~1.7 μg/L	80.8~111.0	[16]
5 种菊酯(氟氰戊菊酯、甲氰菊酯、苄呋菊酯、氯菊酯、氟氯氰菊酯)	烟草样品	十六烷基三丁基鏻四氟硼酸钠/柠檬酸钠	TRSUPRAS-DLLME[a]	HPLC-DAD	-	0.25~0.50 μg/L	91.6~100.2	[17]
多菌灵、氟虫腈、啶氧菌酯	水样	1-癸醇/THF	LPME[a]	HPLC-DAD	21.43–71.36	0.23~0.45 μg/L	93.5~110.0	[18]
甲萘威	果蔬、水样	庚醇/THF	VA-LLME[b]	UPLC-MS/MS	15	0.03 mg/L	90~102	[19]
草甘膦	黄瓜、西红柿	烷基多葡萄糖苷/1-庚酸	LPME[a]	HPLC-MS/MS	-	15 μg/kg	94~106	[20]
4 种三嗪除草剂(扑灭津、扑草净、特丁通、杀草净)	茶叶	[BMIM]PF_6/THF	DLLME[a]	HPLC-DAD	-	1.7~2.1 μg/kg	80.0~119.9	[21]
4 种苯脲除草剂(灭草隆、氯甲苯酮、异丙隆、绿谷隆)	水样、果汁、牛奶	三丁基(辛基)溴化膦/六氟磷酸铵	DLLME[a]	HPLC-DAD	37.1~72.8	0.13~0.19 μg/L	97.4~109.4	[22]
百草枯、敌草快	蔬菜	十二烷基硫酸钠/四丁基溴化铵	VA-LPME[b]	IP-RPHPLC-UV	22~26	1.5~2.8 g/L	95.0~106.7	[23]
5 种三唑类(腈菌唑、三唑酮、戊唑醇、己唑醇、丁硫克百威)	水样、果汁、豆奶	1-十二烷醇/1-十一烷醇	IS-CAE[b]	HPLC-UV	73~318	0.3~1.0 μg/L	77~117	[24]
4 种三唑类(腈菌唑、三唑酮、戊唑醇、己唑醇)	水、蜂蜜、豆浆	1-十二烷醇/十二烷基溴化磷三丁酯	PGS-SSME[b]	HPLC-UV	14~51	10~30 μg/L	60~114	[25]
6 种三唑类(腈菌唑、氟硅唑、戊唑醇、己唑醇、联苯三唑醇、烯唑醇)	饮料、水样	六氟异丙醇/十一醇	LPME[a]	HPLC-UV	-	1.0~5.0 μg/L	63.4~112.1	[26]
13 种硝基咪唑类	鱼血	1-辛醇/THF	VA-DLLME[b]	UPLC-MS/MS	-	0.05~0.2 μg/L	88.4~105	[27]
8 种苯并咪唑类	牛奶	己醇/THF	VA-LLME[b]	LC-MS/MS	-	0.03~0.14 μg/L	74~112	[28]
啶虫脒、嘧菌酯、联苯菊酯、多菌灵、毒死蜱、吡虫啉和戊唑醇	水样、谷物粉	1-癸醇/THF	VA-SSME[b]	HPLC-DAD	-	3 μg/L	80~112	[29]
5 种苯并咪唑类(噻苯达唑、阿苯达唑砜、奥芬达唑、阿苯达唑和芬达唑)	土壤	正癸醇/THF	SSME[a]	HPLC-UV	-	12.1~39.9 μg/kg	56.6~86.1	[30]
萘普生、酮洛芬	水样	甲基三辛基氯化铵/1-辛醇	VA-SS-DLLME[b]	HPLC-DAD	41~46	0.17~0.24 μg/L	93.6~101.4	[31]

注: a. 基本模式; b. 外力辅助模式; c. 联用模式; -表示文章中未提出; 表 2~4 同。高效液相色谱-紫外检测法(high performance liquid chromatography-ultraviolet, HPLC-UV); 气相色谱-氢火焰离子化检测器法(gas chromatography-flame ionization detector, GC-FID); 超高效液相色谱-四极杆-轨道阱高分辨质谱联用仪法(ultra-performance liquid chromatography-quadrupole-orbitrap high-resolution mass spectrometry, UPLC-Q-Orbitrap HRMS); 液相色谱-串联质谱法(liquid chromatography-tandem mass spectrometry, LC-MS/MS); 高效液相色谱-二极管阵列检测器法(high performance liquid chromatography-diode array detector, HPLC-DAD); 超高效液相色谱-串联质谱法(ultra performance liquid chromatography-tandem mass spectrometry, UPLC-MS/MS); 高效液相色谱-串联质谱法(high performance liquid chromatography-tandem mass spectrometry, HPLC-MS/MS); 离子对反相高效液相色谱-紫外检测法(ion pair-reverse phase high performance liquid chromatography-ultraviolet, IP-RPHPLC-UV)。

表 2 SSME 在真菌毒素、食品添加剂检测中的应用

Table 2 Application of SSME in the detection of mycotoxins and food additives

分析物	样品	SUPRAS	前处理方法	仪器方法	富集倍数	检出限	回收率/%	参考文献
赭曲霉毒素 A; 黄曲霉毒素 B1	葡萄酒、香料; 小麦	十四烷酸/THF	SSME[a]	ELISA	-	-	75~96	[32]
赭曲霉毒素 A	香料	癸酸/THF	VA-LPME[b]	LC-FLD	-	0.5 mg/L	81~101	[33]
亚硝酸盐	加工肉制品	癸酸/THF	VA-LPME[b]	UV-Vis	200	0.035 ng/mL	95.0~102.5	[34]
对羟基苯甲酸酯(6)	水样、药物、护理品	六氟异丙醇/Brij-35	LPME[a]	HPLC-DAD	26~193	0.042~0.167 g/L	90.2~112.4	[35]
苏丹红III	香料	1-癸醇/THF	UA-LLME[b]	UV-Vis	33	0.79 μg/L	87~102	[36]
苏丹红I	水样、辣椒	1-癸醇/THF	UA-LPME[b]	UV-Vis	-	1.74 μg/L	101~108	[37]
苏丹黑 B	黑米、黑豆、辣椒	1-辛醇/THF	VA-DLLME[b]	UV-Vis	55	9.01 μg/L	78.1~105.0	[38]
苏丹 I-IV 染料	红酒、饮料粉、辣椒酱、红辣椒	1-辛醇/THF	UA-SUPRAS[b]	HPLC-UV	-	0.48~0.63 ng/mL	90.6~102.5	[39]
苏丹 I、III、IV 染料	饮料、水样	六氟丁醇/法尼醇	VA-DLLME[b]	HPLC	-	0.8~3.1 ng/mL	93.9~122.1	[40]
苏丹 I-IV 染料	水、食品样品	1-癸醇/THF	表面活性剂介导 SSME[a]	HPLC-DAD	10~17	0.23~0.51 μg/L	81.8~109.0	[41]
亮蓝 FCF、靛蓝胭脂红、日落黄 FCF、苏丹 I-III	香料、棉花糖、水果味糖果、干果和巧克力糖衣丸	1-辛胺/百里香酚	VA-LPME[b]	HPLC-PDA	-	0.07~0.2 mg/kg	70~127	[42]
罗丹明 B	辣椒粉	1-戊醇	VA- DLLME[b]	UV-vis	16	0.008 mg/kg	95.0~115.2	[43]
罗丹明 B、甲基紫和荧光黑 T	食品、化妆品、水样	1-癸醇/四氢呋喃	VA-LLME[b]	UV-vis	15~20	0.480~0.511 μg/L	95~100	[44]
罗丹明 B、柯衣定	水样、饮料	六氟异丙醇/芳樟醇	VA-LLME[b]	HPLC	-	1.3~1.5 μg/L	84.4~109.1	[45]
阳离子染料	饮料、河水	香叶醇/六氟丁醇	VA-LLME[b]	HPLC-DAD	-	1~1.5 ng/mL	93.1~104.3	[46]
沙林、梭曼、甲基磷酸二甲酯	水样	聚氧乙烯单叔辛苯基醚/异辛烷	亲水胶束型 SSME[a]	GC–MS	-	0.2~0.8 ng/mL	80.7~89.3	[47]
马兜铃酸	马兜铃	六氟异丙醇/十一醇	VA-DLLME[b]	HPLC-DAD	-	0.3~3.1 ng/mL	92.8~100.6	[48]

注: 酶联免疫吸附测定法(enzyme-linked immunosorbent assay, ELISA); 液相色谱-荧光检测法(liquid chromatography-fluorescence detection, LC-FLD); 紫外-可见光谱法(ultraviolet-visible, UV-Vis); 高效液相色谱-光电二极管阵列检测器法(high performance liquid chromatography-photodiode array detector, HPLC-PDA); 气相色谱-质谱法(gas chromatography-mass spectrometry, GC-MS)。

食品添加剂在现代的食品工业中使用广泛, 主要有防腐剂、着色剂、抗氧化剂等 20 余种。但超量、超范围等违规使用对人体健康会造成潜在危害, 因此开发相关的快速简便检测方法也十分重要。ALTUNAY 等[34]利用癸酸和 THF 制备 SUPRAS, 结合紫外分光光度计检测了加工肉制品中亚硝酸盐含量, 富集倍数高达 200 倍, 检测结果与标准方法无显著差异, 结果准确可靠, 并具有快速、成本低、绿色等优点。CHEN 等[35]提出了一种基于六氟异丙醇/Brij-35 的新型 SUPRAS, 结合 HPLC-DAD 检测了水、药物和个人护理品中 6 种对羟基苯甲酸酯防腐剂, 检出限为 0.042~0.167 g/L, 回收率为 90.2%~112.4%。

工业染料等非食品添加剂在食品工业中的违法滥用时有发生, 科研人员对此进行了相关研究。SOYLAK 等[36]建立了 UA-SSME 结合分光光度法测定香料中苏丹红III的方法: 以 1-癸醇和 THF 制备 SUPRAS, 回收率为 87%~102%, 该法在复杂基质中展现了较好的回收率、重现性和选择性。BOGDANOVA 等[42]以 1-辛胺为两亲物, 麝香草酚为凝聚剂, 结合 HPLC-PDA 分析了香料、糖果中 6 种合成染料(亮蓝、靛蓝胭脂红、日落黄、苏丹红I、苏丹红II、苏丹红III), 检出限为 0.07~0.2 mg/kg, 结果满足欧盟食品检测的要求。

2.3 SSME 在重金属等元素检测中的应用

目前 SSME 常与火焰原子吸收(flame atomic absorption spectrometry, FAAS)和石墨炉原子吸收(graphite furnace atomic absorption spectrometry, GFAAS)等联用检测重金属等元素, 表 3 列出了 SSME 在重金属等元素检测中的主要应用。如 KHAN 等[49]首次将十一醇和 THF 制备的 SUPRAS 结合紫外分光光度计用于检测水样中的 Sb^{3+}, 检出限为 0.19 g/L, 回收率为 94%~101%, 该方法适用于各种环境水样。

表 3　SSME 在重金属等元素检测中的应用

Table 3　Application of SSME in the detection of heavy metals and other elements

分析物	样品	SUPRAS	前处理方法	仪器方法	富集倍数	检出限	回收率/%	参考文献
Sb^{3+}	水样	十一醇/THF	VA-LLME[b]	UV-Vis	15	0.19 g/L	94~101	[49]
Cr^{6+}、总铬	蔬菜、饮料、水样	1-癸醇/四丁基氢氧化铵	UA-DLLME[b]	FAAS	134	0.03 μg/L	94.0~105.5	[50]
总铅	食品	1-辛醇/THF	LLME[a]	FAAS	126	0.15 μg/L	91~104	[51]
Cu^{2+}	食品、水样	1-辛醇/THF	DMSPE[c]	GFAAS	280	0.2 ng/mL	92~96	[52]
Cu^{2+}	食品、水样	正丁醇/THF	LLME[a]	FAAS	60	1.4 g/L	>95	[53]
Cu	茴香茶	1-癸醇/THF	SA-LPME[b]	FAAS	-	1.91 μg/kg	80.2~111.8	[54]
U^{6+}	土壤、水样	十一烷醇/ THF	LLME[a]	UV-Vis	17	0.31 g/L	96~105	[55]
Th^{4+}	土壤、水样	1-癸醇/THF	LLME[a]	UV-Vis	40	0.40 μg/L	95~102	[56]
Hg	食品、水样	1-癸醇/THF	VA-LLME[b]	UV-Vis	100	0.30 μg/L	95.71~99.65	[57]
Hg	水、食品样品	1-癸胺/百里香酚	VA-LLME[b]	UV-Vis	114	0.6 μg/L	93.2~96.7	[58]
Hg^{2+}	蔬菜、水样	1-十一烷醇/四丁基氢氧化铵	UA-HLLME[b]	UV-vis	82	0.33 μg/L	96.4	[59]
Al^{3+}	食品、水样	十一醇/THF	UA-LPME[b]	UV-vis	50	1.2 μg/L	95~100	[60]
Al	水、头发样品	1-癸醇/THF	SSME[a]	UV-Vis	50	0.056 mg/L	92~110	[61]
Ni	蒲公英茶	1-癸醇/THF	LPME[a]	FAAS	-	25.86~497.64 μg/kg	86.0~131.8	[62]
As、Se	杏仁、核桃、开心果粉、水样	十一酸/四丁基氢氧化铵	AA-SFODME[b]	HG-AAS	103	0.07~0.09 μg/L	-	[63]
As(III)砷	水样、土壤	癸酸/THF	UA-DLLME[b]	GFAAS	60	0.2 ng/mL	91~105	[64]

注: 氢化物发生-原子吸收光谱法(hydride generation- atomic absorption spectrometry, HG-AAS)。

近年来, SSME 技术逐渐应用于复杂基质中重金属等元素的分析检测。TUZEN 等[50]建立了 UA-SUPRAS-DLLME-FAAS 方法对水、饮料及蔬菜中 Cr^{6+}和总铬进行了测定: 以 1-癸醇和四丁基氢氧化铵制备的 SUPRAS 作为萃取剂, 偶氮红为络合剂, 检出限为 0.03 μg/L, 富集倍数为 134, 回收率为 94.0%~105.5%; 同传统检测方法相比, 该方法富集倍数更高, 检出限更低。此外, ELIK[51]使用 1-辛醇和 THF 制备成 SUPRAS, 建立了一种基于液-液微萃取的新方法, 分析了蔬菜、烤肉制品等食品及水样中总铅, 该方法绿色高效, 适用于复杂基质样品中铬的测定。

KASHANAKI 等[52]将 SSME 与 DMSPE 技术联用, 建立了一种食品样品中超痕量铜离子的萃取新方法: 首先将样品中铜离子提取到 Al-Fu 纳米薄片上, 并用 THF 进行解吸; 接着将 THF 解吸液与 1-辛醇制备成 SUPRAS; 最后用 GFAAS 对铜离子进行检测。在最佳条件下, 可获得高达 280 的富集倍数, 检出限为 0.2 ng/mL。与其他方法相比, DMSPE-SSME 方法可有效净化样品、高效富集铜离子, 具有优异的选择性和更高的灵敏度, 该法也可用于各种基质中其他离子的萃取和预浓缩。

2.4　SSME 在新污染物检测中的应用

抗生素、持久性有机污染物(persistent organic pollutants, POPs)、环境内分泌干扰物(endocrine disrupting chemicals, EDCs)和微塑料(microplastics)是目前 4 大类典型新污染物, 具有以下几个共性特征: (1)多数为目前正在生产和应用的产品, 尚未有效控制其生产和排放; (2)污染正在发生, 环境介质中的存量较高, 对其环境行为缺乏足够认知; (3)缺乏毒性与健康风险数据, 缺乏全面的科学评估[65]。新污染物的来源广泛、种类繁多, 其在环境中的存在与迁移转化规律复杂多变, 给环境监测、风险评估和污染治理带来了前所未有的挑战。四环素、磺胺类药物等抗生素, 多环芳烃、全氟烷基酸等 POPs, 邻苯二甲酸酯、双酚 A、双酚 S 等增塑剂及雌激素等 EDCs, 均属于新污染物。SSME 在这些新污染物检测中的应用, 见表 4。

YANG 等[70]以正辛醇和四丁基溴化铵为原料制备 SUPRAS, 结合 LC-FLD, 用于食品中苯并芘的提取检测: 在优化条件下, 检出限为 0.11 μg/kg, 回收率为 89.86%~100.01%; 整个样品处理时间需 30 min, 与 GB 5009.27—2016《食品安全国家标准 食品中苯并(a)芘的测定》的传统处理方法相比, 该方法更简单快速, 可减少 60% 的处理时间。王春等[76]以正辛醇和 THF 制备 SUPRAS, 结合 UPLC-MS/MS 对食品接触材料中 8 种邻苯二甲酸酯类增塑剂进行了检测, 检出限为 0.1~1.0 μg/L, 回收率为 84.8%~117.5%, 该方法简单快速、结果准确可靠。除了以上两类新污染物, SSME 也同样适用于抗生素类污染物的

表 4 SSME 在新污染物检测中的应用

Table 4 Application of SSME in emerging contaminants detection

分析物	样品	SUPRAS	前处理方法	仪器方法	富集倍数	检出限	回收率/%	参考文献
4 种磺胺类(磺胺嘧啶、磺胺二甲氧嘧啶、5-甲氧基磺胺嘧啶、磺胺二甲嘧啶)	沉积物	六氟丁醇/香茅醇	VA-DME[b]	HPLC-DAD	-	30~60 ng/g	99.5~104.2	[66]
抗生素(7)	水样	无盐月桂酸/十二烷基三甲基氢氧化铵	MNP-LLME[c]	HPLC-UV	12~118	0.10~0.76 ng/mL	92.0~111.3	[67]
四环素类(5)	牛奶、鸡蛋、蜂蜜	双十二烷基二甲基溴化铵/十二烷基三甲基溴化铵	LPME[a]	HPLC	48~198	0.7~3.4 μg/L	61.4~130.3	[68]
3 种氟喹诺酮类(环丙沙星、达那沙星、恩诺沙星)	水样	癸酸/三辛基甲基氯化铵	VA-LLME[b]	HPLC-PDA	153~241	0.06~0.14 μg/L	99~101	[69]
苯并芘	食品	正辛醇/四丁基溴化铵	UA-SSME[b]	HPLC-FLD	-	0.11 μg/kg	89.86~100.01	[70]
多环芳烃(13)	茶叶	己酸/己酸钠	DLLME[a]	HPLC-FLD	38~46	0.02~0.04 μg/L	85~105	[71]
多环芳烃(7)	土壤	辛酸/THF	VA-LPME[b]	HPLC-FLD	-	0.07~0.4 μg/kg	89~117	[72]
多环芳烃(15)	苹果皮	癸酸/THF	SFE-SSME[c]	HPLC-FLD	138~196	0.34~1.27 μg/kg	60~78	[73]
氯代多环芳烃、多环芳烃	土壤	四氢呋喃/1-辛醇	SSME[a]	HPLC-FLD	-	0.07~2.30 μg/kg	76.5~105.3	[74]
全氟烷基酸、全氟烷基酸前体	螃蟹、虾、鱼	1-庚醇/THF	DLLME[a]	UPLC-MS/MS	-	0.03~0.15 ng/g	81.1~120.0	[75]
邻苯二甲酸酯(8)	食品接触材料	正辛醇/THF	VA-DLLME[b]	UPLC-MS/MS	-	0.1~1.0 μg/L	84.8~117.5	[76]
邻苯二甲酸酯(4)	婴儿食品	癸基葡萄糖苷/正庚醇	LPME[a]	HPLC-UV	-	10 μg/kg	85~93	[77]
邻苯二甲酸盐(4)	水样	十四烷基三甲基溴化铵/六氟异丙醇	DLLME[a]	RP-HPLC	75	0.3~0.6 μg/L	93.1~104.4	[78]
双酚 A、双酚 S	热敏纸	1-癸醇/乙醇	SFME 段塞流微萃取	ASAP-MS/MS	-	-	-	[79]
雌激素	牛奶样品	正辛醇/1-丁基-3-甲基咪唑鎓四氟硼酸盐	SS-VA-HF-LPME[b]	HPLC-DAD	330	0.10~0.22 ng/mL	-	[80]
雌激素	牛奶样品	正辛醇/1-丁基-3-甲基咪唑鎓四氟硼酸盐	SS-HF-LPME[b]	HPLC	334	0.10~0.22 ng/mL	88.30~93.93	[81]

注：高效液相色谱-荧光检测器法(high performance liquid chromatography-fluorescence detector, HPLC-FLD)；反相高效液相色谱法(reversed phase high performance liquid chromatography, RP-HPLC)；大气压固体分析探针-串联质谱法(atmospheric solids analysis probe-tandem mass spectrometry, ASAP-MS/MS)。

检测：SELAHLE 等[69]采用癸酸和三丙甲基氯化铵制备 SUPRAS，结合 HPLC-PDA 检测水样中 3 种氟喹诺酮类抗生素，检出限为 0.06~0.14 μg/L，富集倍数为 153~241，回收率为 99%~101%，此方法操作简便、精密度高，可有效从废水中提取抗生素。

在 SSME 过程中，离心步骤可以使含有目标分析物的 SUPRAS 相沉积在离心管的底部或顶部，但此过程往往耗时较长。相关研究表明将 MNPs 应用到 SSME 过程中，可以避免离心分离，从而提高效率。JIA 等[67]首次将无盐月桂酸与十二烷基三甲基氢氧化铵制备成 SUPRAS，联用疏水性 MNPs，并结合 HPLC-UV 分析水中磺胺类和氟喹诺酮类抗生素，检出限为 0.10~0.76 ng/mL，回收率为 92.0%~111.3%，提取时间仅需 3 min。该研究将 SSME 联合疏水性 MNPs，简化了萃取过程，缩短了萃取时间，且与离心辅助的 SSME 进行比较，该方法中所有分析物明显预浓缩，富集系数远高于离心辅助的 SSME。

GISSAWONG 等[68]探究了混合阳离子表面活性剂制作的 SUPRAS 在 LPME 中的适用性，采用双十二烷基二甲

基溴化铵和十二烷基三甲基溴化铵制备 SUPRAS, 结合 HPLC, 用于鸡蛋、牛奶和蜂蜜中 5 种四环素类的分析检测, 检出限为 0.7~3.4 μg/L, 回收率为 61.4%~130.3%。该方法简单、快速、环保, 制备的 SUPRAS 可在室温下保存 3 周, 为 SUPRAS 的合成提供了方向。

最近, TIMOFEEVA 等[71]开发了一种基于注射器的自动化 SS-DLLME 方法, 并成功地结合 HPLC-UV 测定茶叶中 13 种多环芳烃。该研究在流动系统的注射器中混合己酸、己酸钠与含水样品相, 自发相分离后得到含有目标分析物的超分子相。结果表明: SUPRAS 可有效提取多环芳烃, 并在注射器中快速相分离, 无需离心; 自动微萃取过程持续 4 min, 在最佳条件下检出限为 0.02~0.04 μg/L; 该方法简单、快速、自动化, 具有较高的再现性和可重复性。

3　结束语

与传统有机溶剂相比, SUPRAS 的优势在于提取效率高、制备简单、绿色环保, 可高效萃取环境样品和农产品等多种基质中的目标分析物, 且可以结合多种辅助手段及与其他技术联用, 适用于开发通用的样品前处理方式。与其他绿色萃取技术相比, SSME 也展现出独特的优势:

与离子液体萃取相比, SSME 的优势在于其不仅可实现更高效的预浓缩、且所采用 SUPRAS 组分(如天然表面活性剂、脂肪酸、醇)本身具有低毒性和较好的生物降解性。该技术在工艺实施过程中体现出低能耗、低成本、操作便捷等优点, 同时产生的废渣和需要的溶剂更少; 与超临界流体萃取相比, SSME 的优势在于其不仅具有高选择性、且操作流程简捷, 无需高压设备支持成本低、多功能萃取能力强、快速预浓缩效率高、极性物质提取能力强、萃取过程温和, 避免热敏性成分降解; 废渣和溶剂量少, 后续分离简便。

尽管 SSME 具有各种优点和很强的实用性, 但它也存在一些局限性: (1)一般 SUPRAS 的黏度都较高, 在分析前需要稀释, 会降低分析物的检测灵敏度, 且稀释过程中使用的有机溶剂也会造成环境问题; (2)目前 SUPRAS 基本上是由链烷醇/酸和 THF 制备的, 组成成分有待发展, 且 THF 具有一定毒性, 世界卫生组织将 THF 归类为 2 B 类致癌物; (3)SSME 过程中常需要通过离心的步骤促进相分离, 增加了时间; (4)在萃取完成后, SUPRAS 相与检测仪器设备的兼容问题也是目前的一大难题, 如 SUPRAS 的低挥发性造成无法用气相色谱进行分析。因此, 为推广 SSME 技术的应用, 今后还应加强以下方面的研究: (1)针对目标分析物的性质, 研发黏度较小、更加绿色安全的新型超分子溶剂; (2)丰富两亲性分子的种类, 探索适合复杂基质微萃取的替代溶剂, 使用表面活性离子液体作为两亲性分子可作为一个方向; (3)在 SSME 过程中建议引入铁磁流体。采用外加磁场进行相分离, 则可以避免离心过程的耗时, 提高萃取效率; (4)开发自动化 SSME 技术, 加强与其他检测技术的联用。此外, SSME 可与人工智能(artificial intelligence, AI)进行技术融合, 强化“AI+SSME+传感”三角架构, 实现溶剂设计-过程控制-数据分析闭环。SSME 还与其他先进技术的结合: (1)分子印迹超分子溶剂。通过在超分子溶剂中嵌入特异性识别位点, 实现对激素、抗生素等痕量污染物的靶向捕获; (2)微流控芯片集成。将超分子溶剂微萃取单元嵌入微流控平台, 实现“样品进-结果出”的单细胞代谢分析。随着对超分子溶剂的进一步研究, 相信 SSME 未来在食品和环境污染物等检测上的应用将会更加绿色化、自动化、微型化。

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