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典型有机磷酸酯阻燃剂分析方法研究进展

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摘要: 有机磷酸酯(OPEs)是一类重要的有机磷阻燃剂,近些年逐渐取代了溴代阻燃剂,广泛应用于各行各业,也因此导致在多种环境介质中有较高的暴露量和潜在风险。已有研究表明,OPEs 具有一定的毒理效应,对人体及其他生物均有潜在危害。本文综述了近年来国内外 OPEs 的检测技术,详述了不同环境介质 OPEs 的前处理方法。结果表明,目前固相萃取(SPE)和固相微萃取(SPME)仍是水样前处理的主要方法;对于固体样品,加速溶剂萃取/加压液相萃取(ASE/PLE)和微波辅助萃取(MAE)应用较多;虽然大气样品仍以固体吸附剂方式为主,但已向在线一体化方向发展;而生物样品的前处理方法多与水样和固体样品方法相似;但是对于复杂环境介质中 OPEs 样品的前处理较为困难,方法有待改善;气相色谱-质谱联用(GC-MS)和气相色谱-氮磷检测器(GC-NPD)对弱极性和易挥发的 OPEs 分析效果好,而强极性和难挥发的 OPEs 多用液相色谱-质谱联用(LC-MS);气相色谱-质谱串联(GC-MS/MS)、液相色谱-质谱串联(LC-MS/MS)和高效液相色谱-质谱串联(UPLC-MS/MS)等对多种复杂的环境介质中的 OPEs 均有较好的检测分析效果,但并未普及。最后,对 OPEs 分析测试方法的发展趋势提出了展望。

关键词: 有机磷酸酯;阻燃剂;前处理方法;检测分析方法
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Research Progress on Analysis Methods of Typical Organophosphate Esters（OPEs）Flame Retardants

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Abstract: Organophosphate esters (OPEs) are an important class of organophosphorus flame retardants (OPFRs), which have gradually replaced brominated flame retardants (BFRs) in recent years, and been widely used in a wide range of industries, thus leading to the higher exposure and potential risks in various environment media. Previous studies showed that OPEs have certain toxicological effects and are potentially harmful to human body and other organisms. In this paper, the detecting techniques of OPEs in recent years were reviewed, and the pretreatment method of OPEs in different environmental media were described respectively in details. The results indicated that

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solid phase extraction (SPE) and solid phase micro extraction (SPME) were still the main methods for water sample analysis, and accelerated solvent extraction/pressurized liquid extraction (ASE/PLE) and microwave aided extraction (MAE) were mostly used in solid samples. Although for the atmosphere sample analysis solid adsorbents were mainly applied, the online integration for the air samples have been developed. The pretreatment methods of biological samples were similar to those of water and solid samples. However, it was difficult to analyze OPEs in complex environmental medium, so the methods needed to be improved. In addition, the weakly polar and volatile OPEs were analyzed well with GC-MS/GC-NPD, while the strongly polar and difficultly volatile OPEs were detected by LC-MS. The GC-MS/MS, LC-MS/MS and UPLC-MS/MS were all suitable for the detection and analysis of OPEs in various complex environmental media. Finally, we prospected the development trend of OPEs related analytical test methods in the future.

Keywords: OPEs; flame retardants; pretreatment methods; detection and analysis methods

阻燃剂作为一种功能性材料,可有效地抑制易燃物质燃烧,也可以减缓火势的蔓延,抑制火势传播,是目前应用较为广泛的一类助剂,多用于建筑材料、家具、电子产品、纺织品以及塑料等产品[1-2]。根据分子结构的不同,阻燃剂主要包括有机阻燃剂和无机阻燃剂[3],其中无机阻燃剂有氢氧化物、硼酸盐、氧化锑及无水碳酸镁等无机化合物[3-4],而应用最广的是有机阻燃剂,包含氯系阻燃剂、溴系阻燃剂和有机磷阻燃剂(organophosphorus flame retardants, OPFRs)等。

由于溴代阻燃剂(brominated flame retardants, BFRs)对人类和动物具有很大的毒性[5],2009 年斯德哥尔摩公约将四溴联苯醚、五溴联苯醚、六溴联苯醚和七溴联苯醚列入持久性有机污染物(POPs)[6],欧美及日本等陆续停止对 BFRs 的使用,随后全球范围陆续响应。OPFRs 作为一种新型阻燃剂,与 BFRs 相比,具有高阻燃性、产生毒物少、热稳定性强、良好的增塑性及产物腐蚀性小等特点[1],因此,OPFRs 逐步取代三氧化铝和 BFRs,并广泛应用于建筑材料、电子设备及家具等材料[7-8]。

OPFRs 主要分为有机磷酸酯(organophosphate esters, OPEs)和磷杂环化合物[1],且以物理方式添加于各种材料,而不是化学键结合的形式[9],由此易通过磨损或挥发而进入环境介质,如水体、土壤、大气及生物体内[10-15]。其中 OPEs(结构式如图 1 所示)是目前应用更为广泛的一类 OPFRs。根据取代基的不同,OPEs 主要分为烷基阻燃剂、芳香基阻燃剂和卤代烷基阻燃剂,较为常用的共 28 种(如表 1 所示)[16-17]。由于 OPEs 广泛用于各个行业,由此造成环境中含量日益增加,对生态稳定和人类健康的初期毒理效应逐步显露。已有研究显示,OPEs 具有急性毒性[18-19]、生殖与发育毒性[15,20-22]、神经毒性[23-26]、基因毒性与致突变性[27-30]、内分泌干扰[31-33]及心脏和肝毒性[34-36]。同时也有研究对不同环境介质中 OPEs 的主要成分及其含量进行检测分析,但缺乏系统性综述。鉴于此,本文综述了近年来 OPEs 分析测试的前处理及检测方法,为后续研究提供方法基础,并对未来检测分析方法的研究进行展望。

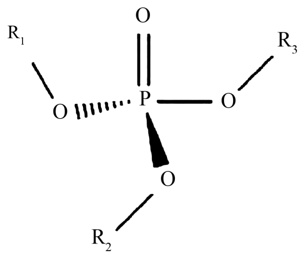

图 1　有机磷酸酯阻燃剂(OPEs)结构式

注:R_1、R_2 和 R_3 均是取代基。

Fig. 1　Molecular structure of organophosphate esters (OPEs) flame retardants

Note: R_1, R_2 and R_3 are all substituted bases.

1　有机磷酸酯前处理方法(Pretreatment methods of organophosphate esters)

含不同取代基的 OPEs 具有不同的同分异构体,导致其物理化学性质千差万别;不同的环境介质,其前处理方法也具有很大的区别。一般的前处理方法可归纳为:匀浆或研磨、提取、净化和浓缩等,其中关键步骤为提取和净化[37]。

1.1　水样前处理方法

水环境是 OPEs 的主要存在介质,已检测出多种 OPEs[38-43],理化性质差异较大,因此 OPEs 的提取

表1 常用的有机磷酸酯阻燃剂种类和结构

Table 1 Types and structures of organophosphate flame retardants commonly used

类别 Types	中文名称 Chinese name	英文名称 English name	缩写 Abbreviation	分子式 Formulae
烷基取代的有机磷酸酯 Alkyl substituted OPEs	磷酸三甲酯	Tris(methyl) phosphate	TMP	$C_3H_9O_4P$
	磷酸三乙酯	Tris(ethyl) phosphate	TEP	$C_6H_{15}O_4P$
	磷酸三丙酯	Tris(propyl) phosphate	TPP	$C_9H_{21}O_4P$
	磷酸三异丙酯	Tris(isopropyl) phosphate	TIPP	$C_9H_{21}O_4P$
	磷酸三正丁酯	Tris(butyl) phosphate	TNBP	$C_{12}H_{27}O_4P$
	磷酸三异丁酯	Tris(isobutyl) phosphate	TIBP	$C_{12}H_{27}O_4P$
	磷酸三己基酯	Tris(hexyl) phosphate	THP	$C_{18}H_{39}O_4P$
	磷酸三(2-乙基己基)酯	Tris(2-ethylhexyl) phosphate	TEHP	$C_{24}H_{51}O_4P$
	2-乙基己基二苯基磷酸酯	2-Ethylhexyl diphenyl phosphate	EHDPP	$C_{20}H_{27}O_4P$
	磷酸三(丁氧基乙基)酯	Tris(2-butoxyethyl) phosphate	TBOEP	$C_{18}H_{39}O_7P$
芳香基取代的有机磷酸酯 Aromatic substituted OPEs	磷酸三苯酯	Tris(phenyl) phosphate	TPHP	$C_{18}H_{15}O_4P$
	磷酸三甲苯酯	Tris(cresyl) phosphate	TCP	$C_{21}H_{21}O_4P$
	三邻甲苯磷酸酯	Tris(orthocresyl) phosphate	TOCP	$C_{21}H_{21}O_4P$
	三对甲苯磷酸酯	Tris(methylphenyl) phosphate	TMPP	$C_{21}H_{21}O_4P$
	磷酸甲酚二苯酯	Cresyl diphenyl phosphate	CDP	$C_{19}H_{17}O_4P$
	磷酸三异丙基苯酯	Tris(4-isopropylphenyl) phosphate	TIPPP	$C_{27}H_{33}O_4P$
	三(4-丁基苯基)磷酸酯	Tris(4-butylphenyl) phosphate	TBPP	$C_{30}H_{39}O_4P$
	三(3,5-二甲基苯基)磷酸酯	Tris(3,5-dimethylphenyl) phosphate	TDMPP	$C_{24}H_{27}O_4P$
	双酚 A 双(二苯基)磷酸酯	Bisphenol A bis(diphenyl phosphate)	BPA-BDPP	$C_{39}H_{34}O_8P_2$
	间苯二酚双(二苯基)磷酸酯	Resorcinol bis(diphenyl phosphate)	RBDPP	$C_{30}H_{24}O_8P$
	三苯基氧化膦	Triphenylphosphine oxide	TPPO	$C_{18}H_{15}OP$
卤代烷基取代的有机磷酸酯 Halogenated alkyl substituted OPEs	磷酸三(2-氯乙基)酯	Tris(chloroethyl) phosphate	TCEP	$C_6H_{12}Cl_3O_4P$
	磷酸三(2-氯丙基)酯	Tris(chloropropyl) phosphate	TCPP	$C_9H_{18}Cl_3O_4P$
	磷酸三(1-氯异丙基)酯	Tris(2-chloroisopropyl) phosphate	TCIPP	$C_9H_{18}Cl_3O_4P$
	磷酸三(2,3-二氯异丙基)酯	Tris(2,3-dichloropropyl) phosphate	TDCPP	$C_9H_{15}Cl_6O_4P$
	磷酸三(1,3-二氯异丙基)酯	Tris(1,3-dichloroisopropyl) phosphate	TDCIPP	$C_9H_{15}Cl_6O_4P$
	磷酸三(2,3-二溴丙基)酯	Tris(2,3-dibromopropyl) phosphate	TDBPP	$C_9H_{15}Br_6O_4P$
	磷酸三(三溴新戊基)酯	Tris(tribromoneopentyl) phosphate	TTBNPP	$C_{15}H_{24}Br_9O_4P$

也各有特点。水环境中 OPEs 的提取技术目前主要包括：液液萃取(liquid liquid extraction, LLE)、固相萃取(solid phase extraction, SPE)、固相微萃取(solid phase micro extraction, SPME)、液相微萃取(liquid phase micro extraction, LPME)、分散液液微萃取(dispersive liquid liquid micro extraction, DLLME)和膜辅助萃取(membrane assisted extraction, MAE)等。

SPE 常根据 OPEs 的理化性质和后续检测方法选取合适的吸附剂和洗脱剂，是目前萃取净化水样中 OPEs 常用的前处理方法。Bacaloni 等[42]利用基质加标测试 Oasis HLB 小柱、Bakerbond (Hydrophilic-DVB)小柱及 LC-18 小柱，对水样中 6 种烷基 OPEs、3 种芳香基 OPEs 和 3 种氯代 OPEs 均有良好的萃取效果，Bakerbond (Hydrophilic-DVB)小柱萃取过程快，以及对 TCP 的回收率最高(82%)；但三者对强极性、强亲水性和强挥发性的 TMP 回收率较低，分别为 23%、35% 和 20%。Wang 等[43]研究 5 种 SPE 小柱萃取水样中 12 种 OPEs 的效果，结果显示，除了 TMP 和弱极性及难挥发的 TEHP 之外，绝大多数 OPEs 回收率均较高，但是 HLB 却表现出对

TEHP 更好的萃取效果。何丽雄等[44]则比较了 4 种洗脱剂和 3 种聚合物型 SPE 小柱对水样中 7 种 OPEs 萃取效果，研究表明，选取 HLB 小柱和乙酸乙酯，无论强疏水性还是强亲水性 OPEs，均有良好的回收率和重复率。由此看出，耐酸碱和强稳定性的 HLB 小柱是 SPE 柱中对水样中 OPEs 的萃取效果更好的固相萃取柱，应用范围也更普遍。

SPME 是以 SPE 为基础发展而来，且克服了 SPE 的缺点，其关键技术在于石英纤维上的涂层。罗庆等[39]以聚二甲基硅氧烷-二乙烯苯（PDMS-DVB）作为 SPME 的纤维涂层，并且通过控制实验条件满足：pH＝4、NaCl 浓度为 25%、5% 乙腈加入样品溶液、萃取时间为 50 min、萃取温度为 40 ℃、搅拌速度为 600 $\mathrm{r\cdot min^{-1}}$，此法可实现对水样中 13 种 OPEs 均有良好的萃取效果，其回收率 68.2% ~ 90.3%，检出限为 1.1 ~ 27.3 $\mathrm{ng\cdot L^{-1}}$。Rodriguez 等[45]使用同样的纤维涂层萃取水样中 9 种 OPEs，除了 TEHP 回收率为 26.7%，其余均达到 86% ~ 119%，基质效应明显。也有一些学者自制一些纤维涂层以应用于 SPME，如新型离子液体（[AMIM]、$[BF_4]$）涂层和氧化石墨烯涂层，对水样中 OPEs 的萃取效果优于 PDMS-DVB 纤维涂层[46-47]。但是由于制备时存在一些误差，而导致其应用受到限制。LPME 作为一种新萃取技术，弥补了 SPME 的缺点，同时也可作为一种绿色化学材料，可有效减少有害溶剂的消耗[48]。

Ellis 等[49]将 MAE 和 SPME 结合来萃取废水中 OPEs，对 TEHP 萃取效果明显，并且加入 NaCl 后，水相基质对 PDMS-DVB 纤维涂层的作用力降低，从而加大 TNBP、TBOEP 的回收率。García-López 等[50]提出 DLLME 萃取水样中 10 种 OPEs，向含有 20% NaCl 的 10 mL 样品溶液中加入含有 2% 的 1,1,1-三氯乙烷的 1 mL 丙酮溶液，萃取效果明显，且方法快速易行，但是对于污水等复杂水样中 TIBP 和 TEHP 存在明显的基质抑制效应。薄膜辅助溶剂萃取（membrane assisted solvent extraction, MASE）以环己烷为萃取剂提取污水中 OPEs，除了对极性较强的 TCEP 回收率仅为 5%，其余均具有较高的回收率，且基质效应弱于 SPE[51]。聚丙烯微孔膜辅助液-液微萃取技术（microporous membrane liquid-liquid extraction, MMLLE）除了 TCEP 和 TEHP 回收率仅为 2% 和 4%，其余多数 OPEs 回收率较高，也存在复杂水样对 TEHP 的基质抑制效应[52]。同时也应注意水样中天然有机物对萃取效果的影响[53]。

目前水样中 OPEs 的前处理是一稳多元的发展趋势，常用的仍是 SPE，其次 SPME，伴随着多种新型的前处理方法，也可多种方法联用，弥补传统方法的不足，同时满足复杂水样的萃取要求。

1.2　固体样品前处理方法

固体样品是一类较复杂的环境样品，已在污泥、沉积物、土壤和塑料等中检出 OPEs[11,54-67]。若萃取基质简单的固体样品，可直接检测分析；若萃取某些基质复杂的，则需经过净化，去除干扰，降低基质效应，进而提高仪器灵敏度和准确度，方可检测分析。目前，固体样品前处理主要向减少使用有机溶剂和简化净化步骤的方向发展。固体样品中 OPEs 提取技术主要有：索氏提取（Soxhlet extraction, SE）、超声波萃取（ultrasonic extraction, UE）、加压液相萃取（pressurized liquid extraction, PLE）或加速溶剂萃取（accelerated solvent extraction, ASE）和微波辅助萃取（microwave aided extraction, MAE）。

SE 是一种传统的、公认的经典方法，Lee 等[54]和 Hu 等[55]采用 SE 对沉积物 OPEs 萃取，回收率分别为 67% ~125% 和 79.5% ~123.3%，而检出限分别为 0.02 ~1.44 $\mathrm{ng\cdot g^{-1}}$ 和 0.0054 ~0.098 $\mathrm{ng\cdot g^{-1}}$。温家欣[56]以乙酸乙酯为萃取剂用氧化铝-硅胶柱进行 SE 萃取，分析土壤中 OPEs，除了 TMP 和 TEP，其余 OPEs 回收率为 64.2% ~ 91.7%，相对标准偏差（RSD）为 1.91% ~14.9%。Wang 等[57]则利用涡旋和超声波萃取对土壤中 12 种 OPEs 进行萃取，只有 TPP 没检测出，TEP 和 TNBP 回收率分别为 94% 和 75%，其余回收率均为 100%，可能由于 OPEs 与土壤颗粒结合力强，延长了其半衰期，从而提高了检测频率。除此，超声波萃取也应用于萃取污泥和沉积物中 OPEs[58-59]。

ASE/PLE 作为一种极具发展前途的新型的样品前处理方法，可选取恰当的溶剂从固体或半固体样品中快速高效地萃取 OPEs。Marklund 等[60]将含有 12 种 OPEs 的污泥样品置于乙酸乙酯中，ASE 的回收率为 97% ~117%，检出限为 0.2 ~5.1 $\mathrm{ng\cdot g^{-1}}$。李成辉等[61]以丙酮/二氯甲烷（体积比 1∶1）为萃取剂，ASE 萃取污泥中 OPEs，不仅降低了基质效应，也提高了回收率。ASE/PLE 也可用于萃取塑料材料及沉积物中 OPEs[62-63]，也有研究将 ASE 和 SPE 相结合共同萃取和浓缩污泥中 OPEs，比 UE 具有更好的萃取效果[64]。MAE 是近年一种比较新型的前

处理技术，与望秀丽等[62]的研究仅限于聚氯乙烯(PVC)塑料不同，周小丽等[65]以乙腈为萃取剂，利用MAE对多种塑料材料中7种OPEs萃取，效果好，其加标回收率为85.9%～95.2%，RSD(n=9)均小于8%。因此，实验中含有OPEs的样品应存放在不锈钢容器、不透光的玻璃容器或聚四氟乙烯容器中，使用前用极性或非极性有机溶剂冲洗，保证无OPEs，避免外来干扰[40]。MAE作为一种较经典的萃取方法，适合固体和半固体样品处理，如沉积物[66-67]。

固体样品常含有复杂的有机质，比如污泥、沉积物和土壤等，是众多污染物的“汇”和“源”，成分复杂，会对OPEs的萃取产生干扰，导致SE、UE萃取效果不理想，而ASE/PLE通常具有较好的效果，且高效快速。而与ASE相比，MAE更适于萃取多种塑料材料中OPEs。

1.3 大气样品前处理方法

OPEs在空气中的主要存在形式是悬浮分子态和附着在大气颗粒物表面，其中又以后者占主导[9,68]。采集大气样品时，常用过滤材料或固体吸附剂采集大气颗粒物，固体吸附剂同时富集附着在颗粒物表面和气态的OPEs[9]。其中提取方法有SPE、SPME、MAE、SE、UE和PLE/ASE等。

作为常用的固体吸附方式，SPE分为SPE膜和SPE小柱，其中SPE膜具有更大的比表面积，样品流速更快。聚氨酯泡沫(polyurethane-foam plugs, PUFs)也可作为固体吸附剂，可对挥发性或半挥发性的气态有机物吸附[9]。但SPE膜和PUFs在解吸时比SPE小柱耗用更多有机溶剂，可能导致稀释的提取物及与初级提取蒸发浓缩相关的潜在程序性空白问题[69-70]。SPE小柱洗脱OPEs之前用非极性溶剂冲洗吸附剂，省去净化步骤，大大降低最终提取物的复杂性，而缺点在于比PUFs和反相吸附剂膜具有更高的空气阻力[71]。Tollback等[72]利用C8 Empore SPE膜，通过SPE与LC-MS单通道在线解吸大气样品中OPEs，甲醇解吸，可获得挥发性TMP，并且该法采样时间短且易进行大量富集，取得较高的回收率。Wong等[73]选用玻璃纤维滤膜(glass fiber filter, GFF)和PUFs分别采集室内室外大气样品，对于室外样品用SE(石油醚与丙酮体积比4:1)提取PUFs中OPEs，用UE(萃取剂为二氯甲烷)提取GFF中OPEs，随后用二氧化硅柱进行分馏净化，己烷洗脱萃取柱；而采集室内样品的PUFs和GFF均用超声波浴提取，之后提取物溶剂换为异辛烷，并用硫酸钠净化萃取柱，此法对室外室内样品均有较好的提取效果。Carlsson等[68]对SE和UE作对比，并选用二氯甲烷作萃取剂，对大气样品中OPEs进行提取，SE对TBOEP回收率仅为37%，UE的回收率超过95%，可能由于TBOEP吸附在仪器的玻璃表面和器皿上导致SE效果较低。

SPME近年来也被用于大气样品中OPEs的萃取，可直接将萃取纤维暴露于气样中，且大气中OPEs浓度与SPME纤维暴露时间是其富集能力主要因素[67,74]。Salamova等[75]用石英纤维滤膜富集美国5个地区的大气样品，SE提取样品中12种OPEs，旋转蒸发降低提取物体积，再在硅胶柱上分馏纯化，结果表明，烷基和氯代OPEs在5个地区均检出，芳香基OPEs只在部分地区检出，且城镇地区的检出浓度高于乡村及偏远地区，这可能与烷基和氯代OPEs的挥发性高且在城镇应用范围广有关。

低密度聚乙烯薄膜(low density polyethylene sheets, LDPES)可采集大气中疏水性化合物，并且与其他被动采样相比，更简单易行和价廉，同时也无需复杂的净化技术[76-79]。Khairy和Lohmann[79]利用LDPES对埃及亚历山德里亚室内室外大气样品进行采集，UE提取后用硅胶进行纯化和分级，从而获得较好的提取效果，其回收率为74%～101%，重现性可达18%～25%。

与人体暴露密切相关的灰尘，采集后的萃取和净化方法常与固体样品类似。Wang等[57]用同样的方法萃取灰尘中12种OPEs，除了TPP未检出，其余OPEs均≥82%。李静等[80]以乙酸乙酯/丙酮(体积比3:2)为萃取剂，利用UE和SPE萃取净化灰尘中10种OPEs，回收率为51.4%～123.5%，其中TEP的为51.4%。Garcia等[81]以丙酮为MAE的萃取剂，并用Oasis HLB与硅胶柱净化，得到的回收率为85%～104%，RSD为3%～11%。基质固相分散萃取(matrix solid phase dispersion extraction, MSPDE)也可用于灰尘样品中OPEs提取，且最佳萃取剂为丙酮，此时可获得良好的萃取效果，其加标回收率为80%～116%，重现性较好(RSD<11%)[82]。

1.4 生物样品前处理方法

OPEs通过物理方式添加于材料中，因此易释放到环境中，被生物摄取吸收后进入食物链，且具有生物积累效应[14]。生物样品相对比较复杂，OPEs即存在于生物液体样品(尿液、血液或蛋液)[7,13,15,83-87]，也

存在于生物固体样品(脂肪或组织)[6,13,84,88−90]。因此,其前处理包括了水样和固体样品的前处理方法,过程也大致相似。但生物样品需要最初的预处理,尤其水生生物样品,清除水样或固体中 OPEs 的干扰;对于血液样品,根据血清和血浆等不同的要求进行前处理;对于生物固体样品,应先除去样品中水分,避免干扰,降低误差;同时多数生物样品较脆弱且易受污染,因此前处理前后必须做好预防措施。

LLE 可对部分生物液体样品进行萃取,比如 Sundkvist 等[13]以乙醚/己烷(体积比 7∶10)为萃取剂,萃取牛奶中 12 种 OPEs,并经凝胶渗透层析法(gel permeation chromatography, GPC)净化,回收率为 50% ~110%。同样魏莱等[15]以正己烷/二氯甲烷(体积比 1∶1)为萃取剂对鸟卵的蛋液进行萃取,随后超声混匀、离心,再用 NH$_2$ 固相萃取柱净化,之后洗脱萃取柱,测得 9 种 OPEs 加标回收率为 76% ~106%,仅 TPHP 为 52%。SPE 也常用于生物样品中 OPEs 的萃取净化。Schindler 等[7]采用 SPE 两步法萃取尿液中 4 种 OPEs,并获得较高的回收率,也首次检测到人体尿液中 OPEs 的代谢产物,且回收率高达 79% ~113%,具有高重现性、高选择性和高灵敏度,此法常用于尿液中 OPEs 的萃取。He 等[83]以 StrataX-AW 小柱为萃取柱和乙腈/水(体积比 1∶1)为萃取剂,萃取儿童尿液中 9 种 OPEs,除了 TNBP 未能检测出,其余均有少量检测,可能是 OPEs 在人体内得到降解,转化为相应的代谢产物。Choo 等[84]先超声混匀血样,后在二氯甲烷和甲醇条件下用 SPE (Oasis HLB)萃取,其中 TDCIPP、TEHP 和 TCP 未能检出,其余均有较高的回收率(45% ~100%),检出限为 0.08 ~0.82 ng·mL^{-1}。SPME 也可萃取生物样品中 OPEs,如血样,但其回收率较低[85]。MMLLE 作为一种新型液相萃取技术,也可萃取血样中 OPEs,并通过控制萃取时间或调整装置均可获得较高的回收率[86−87]。

而对于生物固体样品前处理,赵赛等[88]用振荡-超声-离心方法萃取美人蕉的根、茎及叶中 8 种 OPEs,经 Florisil-Carbon GCB 柱串联富集净化,其加标回收率分别为 67.34% ~ 138.81%、63.98% ~ 120.4% 和 61.33% ~146.38%,满足分析要求。Zhao 等[89]则用超声-振荡-离心方法萃取无脊椎软组织和鱼类肌肉组织中 OPEs,NH$_2$-SPE 柱净化,进而取得高回收率。Choo 等[84]也利用 UE 对鱼类的肌肉、性腺和肝脏中 OPEs 进行提取,随后离心,N$_2$ 浓缩,HLB 柱净化,其中 TDCIPP 和 TCP 均未有检出,且肝脏中 TBOEP、TEHP(性腺也未检出)和 TPHP 也未检出。Sundkvist 等[13]用 ASE 萃取鱼类肌肉组织中 OPEs,过滤后用 GPC 净化,其加标回收率为 64% ~ 110%,检出限 0.05 ~11 ng·g^{-1},其中 TDCIPP(11 ng·g^{-1})和 TBEP(23 ng·g^{-1})的回收率更高;此外该法在富含脂肪的鱼类和贻贝样品中回收率更高,平均值为 132%。与 Sundkvist 等[13]的研究相比,Kim 等[90]经硅胶柱净化后,OPEs 萃取回收率为 58.1% ~ 114%。MSPDE 可同时提取和纯化目标物,适于固体和半固体样品,Campone 等[6]又对其进行了优化,使鱼肉组织样品经无水硫酸钠和硅酸镁载体分散均匀,后移至活性氧化铝 SPE 小柱中,用正己烷/二氯甲烷(体积比 1∶1)冲洗样品中脂质,再用正己烷/丙酮(体积比 6∶4)洗脱,OPEs 的回收率达 70% ~ 110%。Ma 等[91]建立 MAE-GPC-SPE-GC/MS 综合检测方法,该法可有效地萃取鱼、鸟及家禽中 14 种 OPEs,有较好的检出限。

文中涉及的常见样品中 OPEs 前处理方法的主要原理、优劣性及适用范围,总结于表 2 中。

表 2　常用的环境样品中 OPEs 前处理方法

Table 2　OPEs pretreatment method commonly used in environmental samples

名称 Name	主要原理 Main principle	优势 Advantage	局限性 Limitation	适用性 Applicability
液液萃取 Liquid liquid extraction (LLE)	有机溶剂对样品中各种待测组分进行数次提取 Use the organic solvents to extract the various components	勿需任何特殊仪器,且样品过滤与否均可处理 Require no special instruments, whether filter the sample or not, it can be processed.	有机溶剂耗量大,有害,易产生乳化,二次污染,难自动化 Large organic solvent consumption, harmful, easy emulsification, secondary pollution, difficult automation.	水样、牛奶、蛋液等 Water sample, milk, egg liquid, etc.

续表2

名称 Name	主要原理 Main principle	优势 Advantage	局限性 Limitation	适用性 Applicability
固相萃取 Solid phase extraction (SPE)	分为吸附和洗脱,多孔固相吸附剂选择性地吸附样品溶液中待测组分,后脱附,达到分离富集 During adsorption and elution, the porous solid phase adsorbent selectively adsorbs the components in the sample solution, and then elute, separate and concentrate.	SPE柱和膜种类多,溶剂耗量少,对强极性和弱极性均有较好的效果,应用范围广 Many types of SPE column and membrane, less solvent consumption, extract chemicals with strong or weak polarity well, a wide range of applications.	未过滤的样品可能导致堵塞,而过滤则可能使颗粒与疏水性OPEs结合,堵塞滤膜,降低回收率,减少柱使用寿命 Unfiltered samples may cause blockages, while filtration may cause the particles to bind to the hydrophobic OPEs, which clogs the membrane, reduces the recovery rate and the column life.	多种水样、大气、尿液、血液等 A variety of water samples, atmosphere, urine, blood, etc.
固相微萃取 Solid phase micro extraction (SPME)	石英纤维涂层插入样品中,待测组分通过扩散、吸附、浓缩和解吸进行分析 Quartz fiber coating is inserted into the samples and the components are analyzed by diffusion, adsorption, concentration and desorption.	集采样、萃取、浓缩、进样于一体,无需过滤水样、无需溶剂、操作简便快速、易自动化 Set sampling, extraction, concentration, injection in one, no need to filter water sample, no solvent, simple and fast operation, easy to be automated.	纤维涂层种类少,装置昂贵,选择性差 Less fiber coating type, expensive equipment, poor selectivity	水样、大气、血液等 Water sample, atmosphere, blood, etc.
索氏提取 Soxhlet extraction (SE)	利用溶剂回流和虹吸原理,纯溶剂萃取样品中目标物 Using solvent reflux and siphoning, the target substance is extracted by pure solvent.	能耗低,萃取效率高,设备简单 Low energy consumption, high extraction efficiency and simple equipment	萃取时间较长、消耗的有机溶剂多,操作复杂,不易自动化 Long extraction time, the high consumption of organic solvents, complex operation, difficult automation.	固体、大气颗粒物 Solid, atmospheric particulate
超声波萃取 Ultrasonic extraction (UE)	固体样品在超声波的空化作用下,在溶剂中分散、乳化,提取所需成分 Under the cavitation of ultrasonic wave, solid samples are dispersed and emulsified in the solvent to extract required components.	萃取时间短、产率高、无需加热 Short extraction time, high yield, no heating	在超声波条件下更易挥发和降解,造成萃取效果降低 More volatile and degradable under ultrasonic conditions, resulting in reduced extraction	固体、大气颗粒物、生物固体 Solid, atmospheric particulate, biological solid
加速溶剂萃取 Accelerated solvent extraction (ASE)	待测物对有机溶剂有较高的亲和力,增温或加压将其从样品中萃取出 The analytes have a high appetency for organic solvents, which are extracted from the samples by increasing temperature and pressure.	有机溶剂耗量少,降低基质效应,快速高效,回收率高,重现性好,易全自动化 Less organic solvent consumption, reduce matrix effect, fast and efficient, high recovery, good reproducibility, easy to be fully automated.	能耗高,成本较高,装置需耐高温、高压 High energy consumption, high cost, high temperature and high pressure resistance	固体、生物固体 Solid, biological solid

续表2

名称 Name	主要原理 Main principle	优势 Advantage	局限性 Limitation	适用性 Applicability
微波辅助萃取 Microwave aided extraction (MAE)	微波反应器中,样品浸于适合溶剂,进而待测组分迅速溶出 In a microwave reactor, the sample is immersed in a suitable solvent, and the target substance is rapidly dissolved.	溶剂用量少,萃取时间短,高效率,可同时处理多个样品,高灵敏度 Low organic solvent consumption, short extraction time, high efficiency, handle simultaneously multiple samples, high sensitivity.	对弱极性OPEs的萃取效果较低 Low extraction effect on weakly polar OPEs	固体、生物固体 Solid, biological solid
基质固相分散萃取 Matrix solid phase dispersion extraction (MSPDE)	样品与固体材料一起研磨后作填料装柱,不同溶剂淋洗,使待测物洗脱出 The samples are ground with solid materials to pack column, and the analytes are eluted with different solvents.	萃取条件温和、有机溶剂耗量少,可减少样品损失,易自动化 Mild extraction conditions, low organic solvents consumption, reduce sample loss, easy to be automated.	基质效应干扰,分散剂缺乏选择性,对分散剂和洗脱剂要求高 Matrix effect, dispersant lacks selectivity and high requirement for dispersant and eluent.	固体、生物固体 Solid, biological solid

2　有机磷酸酯检测方法(Detection method of organophosphate esters)

目前,OPEs检测分析的常用方法包括气相色谱法(gas chromatography, GC)和液相色谱法(liquid chromatography, LC)。由于OPEs的理化性质千差万别,多数具有一定的挥发性,因此分析方法仍以GC为主。但是与GC相比,LC对于部分极性更强和难挥发的OPEs具有更好的检测效果。

2.1　气相色谱及其联用技术

GC作为目前常用的OPEs检测方法,同时结合合理的前处理方法、程序升温控制、选择性检测器以及大体积进样量,可有效地提高检出限。目前常用检测器主要有氮磷检测器(nitrogen phosphorus detecter, NPD)和电子轰击离子化-质谱(electron impact ionization mass spectrometry, EI-MS)[2,9,40,69]。EI-MS对于磷酸酯类化合物的低质量数离子的检测易受基质干扰,分辨率较差,常用作OPEs的定性分析,而具有强选择性和高灵敏度的NPD常用于OPEs定量分析[2,37,69]。GC-NPD常用氮气作载气,因为氢气对磷酸盐有一定降解作用[68]。研究表明,GC-NPD在检测各种环境介质中的OPEs时具有较好的检出限[45,50,74,81-82,86]。Campone等[6]采用GC-NPD对前处理后的鱼肉组织样品进行定量检测分析,检出限为0.2~3.1 $\mathrm{ng \cdot g^{-1}}$。但是GC-NPD存在稳定性较差的问题,可能是NPD在使用过程中铷珠会降解,需定期更换[9,37]。因此,Gao等[46]采用与NPD相似灵敏度和选择性的火焰光度检测器(flame photometric detecter, FPD)来检测水样中7种OPEs,最优化后,方法检测限(MDL)为0.7~11.6 $\mathrm{ng \cdot L^{-1}}$。

GC-MS是目前最常用的GC检测分析方法,能有效地减弱分析过程中基质效应的影响,且多数在选择性离子检测(selected ion monitoring, SIM)-电子轰击离子化(electron impact ionization, EI)模式下可提供较好的灵敏度及选择性,而化学电离下GC-MS对多数OPEs不太有效[40],可应用于水样[38,44]、固体[55,57,58-59,65]、大气[68,76]和生物[87,91]样品中。何丽雄等[44]在SIM模式下用GC-EI-MS对各类水中7种氯代和非氯代OPEs进行检测,均有较好的检出限。同样方式,秦宏兵等[38]对地表水中6种OPEs进行检测,由于TBOEP离子化效率随浓度增加而增大,使其线性相关系数较低,需采用二次线性回归校准,除了TBOEP定量限为32 $\mathrm{ng \cdot L^{-1}}$,其余均低于5 $\mathrm{ng \cdot L^{-1}}$。除了EI,也有研究采用电子捕获负电离(electron capture negative ionization, ECNI)做离子源在SIM模式下通过GC-MS检测沉积物中OPEs,其灵敏度较高[56]。近年来,电感耦合等离子体质谱法(inductively coupled plasma-mass spectrometry, ICP-MS)因其在其他干扰物存在下也具有良好的选择性和灵敏度,能提供简单的色谱图,检出限与NPD和EI-MS相似,是良好的替代品,越来越多地应用于测定样品中OPEs[49,66,85]。但是因其存在多原子物质在

m/z为31的同质元素($^{15}N^{16}O^+$和$^{14}N^{16}O^1H^+$)的干扰而需要安装碰撞反应池,导致成本增加,也因此限制了其推广[9,66,69]。也有研究将飞行时间(time of flight, TOF)作质量分析器,建立GC-TOF-MS对废水中OPEs的检测分析方法[49]。

基于复杂的样品介质,需要更高选择性的检测器,因此串联MS逐渐应用于复杂样品中OPEs的检测[7,39,54,79-80,84]。罗庆等[39]选用多重反应监测(multiple reaction monitoring, MRM)模式下的GC-EI-MS/MS检测水样中13种OPEs,测得3倍和10倍信噪比的检出限(LOD)和定量限(LOQ)分别为1.1～27.3 ng·L^{-1}和3.7～90.1 ng·L^{-1}。Quintana等[69]采用正离子化学电离(positive chemical ionization, PCI)结合GC-MS/MS检测样品中OPEs,其成本与GC-EI-MS相似,检出限低于50倍,虽选择性高于GC-NPD,但检出限略高。

2.2　液相色谱及其联用技术

由于GC普遍具有色谱峰拖尾现象,尤其对TBOEP和TPPO,这严重影响GC的使用[37]。鉴于此,以液体为流动相的LC在OPEs的检测分析中的应用日益增多。与GC相比,LC一般只与MS联用检测OPEs,且更适于高沸点、热不稳定、极性强和难挥发的OPEs[2,37,67]。同时与SIM模式下的GC-EI-MS/MS和GC-PCI-MS/MS相比,在MRM模式下LC-MS/MS有更好的灵敏度和选择性,并且水样可以直接检测,不需要转移到有机溶剂中[69]。

目前,LC-MS的离子源普遍采用电喷雾离子化(electrospray ionization, ESI),且多数在正电离模式下检测分析OPEs,色谱柱主要以C18或C8柱为主,而流动相常用甲醇、乙腈或乙酸。Tollback等[72]在MRM模式下,分别用C18和C8柱,采用SPE-LC-ESI-MS检测大气中7种OPEs,结果表明,C8柱对多数极性OPEs分离效果强于C18柱,且使用高采样流可提高灵敏度(MDL为0.4～19 pg·m^{-3}),将分析范围扩大到挥发性最强的OPEs。一些研究显示,LC-MS/MS和UPLC-MS/MS可快速高效地分析复杂基质样品中OPEs,也能提高检测的灵敏度,多用于水样[41-43,51]、固体[61,63-64]以及生物样品中[83,89-90]。Martinez-Carballo等[41]先分别用LLE萃取水样和UE萃取沉积物,随后LC-ESI-MS/MS在21 min内完成对提取物中9种OPEs的检测,水体的LOQ为2.6～13 ng·L^{-1},沉积物的为0.48～11 μg·kg^{-1},但其中只有TCEP和TNBP的信噪比高于3。He等[83]以甲醇和乙酸为流动相采用LC-ESI-MS/MS检测尿液中OPEs及其代谢产物,除了TNBP未能检出,其余OPEs的MDL为0.017～4.9 ng·g^{-1},而代谢物的最高MDL为7.8 ng·g^{-1}。Giulivo等[63]在选择反应监测(selective reaction monitoring, SRM)模式和加热电喷雾电离源(heated-electrospray ionisation source, H-ESI),用LC-MS/MS检测3条河流中沉积物和鱼类中OPEs,有较好的检出限,其中鱼类检出限明显高于沉积物。Wang等[43]同样在SRM模式下,建立了以C8为色谱柱的UPLC-ESI-MS/MS分析方法,在11 min内完成水样中12种常见的OPEs的检测,定量下限为2～6 ng·L^{-1}。该法具有高灵敏度和高通量的优点,并且从强极性和挥发性的TMP到疏水性和非挥发性的TEHP均有较好的检测,也是首次确定空白污染物主要来源于有机流动相,并发现与甲醇相比,乙腈更易去除空白污染。

ESI离子源虽然是目前应用比较多的一类电离模式,对极性的OPEs检测效果好,但是也存在信号强弱易受样品基质的影响,严重影响LC-MS/MS的检测分析。鉴于此,Quintana和Reemtsma[51]将MASE与LC-MS/MS相结合,对废水中7种非离子态的氯代和非氯代OPEs进行检测分析,有效地削弱了样品基质效应,且效果优于SPE-LC-MS/MS,MDL为1～25 ng·L^{-1}。也有研究表明,大气压化学电离(atmospheric pressure chemical ionization, APCI)在正电离模式下,比ESI更能有效地减弱复杂样品的基质效应,尤其适用于弱极性的OPEs[67,92]。

由于GC-MS对于多数三酯类OPEs都适用,目前仍是主流方法,且对于复杂基质的环境介质可用GC-MS/MS进行检测,均能实现较低的LOD。但是对于二酯类和单酯类OPEs,LC-MS具有更好的优势,尤其对含有复杂基质的样品,LC-MS/MS具有更低的LOD和更高的选择性[69]。

3　结论与展望(Conclusion and prospect)

目前,国内外已有大量关于不同环境介质中OPEs的前处理方法和检测分析方法的研究,GC-NPD虽然检测限较低,但稳定性较差,可选用优化后的FPD和ICP-MS检测;GC-MS也是应用较多的技术,有良好的选择性和灵敏度。由于GC常用于弱极性和挥发性OPEs的分析,而强极性和难挥发的OPEs可选用LC-MS或UPLC-MS,同时复杂的环境基质常在MRM模式下检测分析。LC-MS/MS和GC-MS/MS的研究虽然相对比较完善,但应用仍受到

一定的限制,包括 UPLC-MS/MS 的应用也未得到普及。OPEs 作为一种新型的阻燃剂,针对未来 OPEs 相关分析方法可从以下几个方面进行深入研究。

(1)改善人类社会生活各种复杂环境介质中 OPEs 的前处理和检测方法及技术,以及完善人体及其他生物体内 OPEs 及其代谢产物的提取—净化—检测系统,比如三类废水、农业生产及城市生活的土壤、大气、污泥和沉积物,血液、体液、尿液、动植物体组织和器官及其排泄物等。

(2)建立健全样品在线提取—净化—检测一体化系统,结合微萃取技术以及高效的检测技术,快速高效地检测环境介质中 OPEs,简化检测系统,提高检测的准确性、精确性和选择性,提高检测系统普及性,实现全自动化。

(3)完善和发展 GC-MS/MS、LC-MS/MS 和 UPLC-MS/MS 等检测方法,开展高效新技术的研究,将其应用于各种环境介质中,实现同时对多种环境介质的检测分析,弥补传统技术的劣势并发展优势,解决环境基质干扰效应和空白污染的问题,提高适应性、选择性和灵敏度,降低检出限,逐步取代 GC-MS 和 GC-NPD 的应用。

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