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加速溶剂萃取技术应用于二噁英检测的研究进展*

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摘要 加速溶剂萃取技术通过提高温度和压力对混合基质中的有机物进行自动萃取. 由于其具备有机溶剂用量少、萃取快速、样品回收率高等优点, 可被应用于二噁英分析的样品前处理过程中. 二噁英样品的提取效率与样品基质性质相关, 为保证提取回收率必须选择合适的提取条件. 本文从不同基质的角度综述了加速溶剂萃取技术在二噁英检测中的研究进展, 同时展望了该技术未来的发展趋势.

关键词 加速溶剂萃取技术, 二噁英, 样品前处理.

Research progress of accelerated solvent extraction (ASE) technology in the detection of dioxins

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Abstract Accelerated solvent extraction (ASE) technique extracts organic substances in mixed matrices at elevated pressure and temperature simultaneously. The technique could be used as sample pretreatment before dioxins analysis because it achieves high extraction efficiency with a less quantity of solvent within a short time. The extraction efficiency of dioxins is related to the properties of sample matrix. Therefore, in order to ensure the extraction recovery, the appropriate extraction conditions must be selected. This paper reviewed the progress of ASE technology in dioxin extraction and detection from different matrices. At the same time, the potential trend of this technology was also proposed.

Keywords accelerated solvent extraction, dioxin, sample pretreatment.

二噁英(dioxin)是一类持久性有机污染物(persistent organic pollutants, POPs), 由于氯原子的取代数目和位置不同^[1], 它包括 75 种多氯二苯并二噁英(polychlorinated dibenzo-p-dioxin, PCDDs)和 135 种多氯二苯并呋喃(polychlorinated dibenzofuran, PCDFs). 二噁英主要来源于废弃物焚烧等热处置过程和氯化化学工业过程而产生的副产物^[2-5]. 其中 17 种(2, 3, 7, 8 位全部被氯原子取代)二噁英类化合物被认为对人类健康有巨大的危害^[6-8]. 二噁英类化合物具有致癌、致畸、致突变作用^[9], 由于具有疏水性、亲

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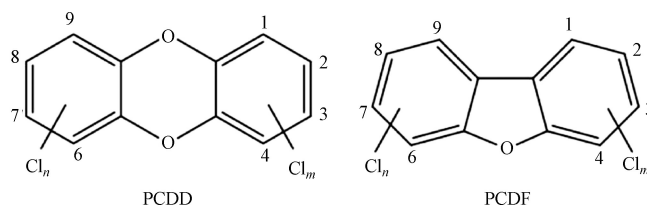
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脂性和高化学稳定性^[10], 能够通过沉降到水、土壤及沉积物等不同环境基质中, 经过生物积累等作用进入人体^[11-14], 威胁人类的生命健康. 因此 1998 年世界卫生组织(WHO)规定人体每日允许二噁英摄入量 $1-40 \text{ pg}\cdot\text{kg}^{-1}$ ^[15]. 2001 年二噁英被列入《关于持久性有机污染物的斯德哥尔摩公约》首批 POPs 清单. 随后, 世界各国对其在环境中的排放限值作出了规定. 欧盟将二噁英排放标准定为 $0.1 \text{ ng}\cdot\text{TEQ}\cdot\text{m}_N^{-3}$ ^[16], 我国在《危险废物焚烧污染控制标准》(GB18484-2001)中规定二噁英排放限值为 $0.5 \text{ ng}\cdot\text{TEQ}\cdot\text{m}_N^{-3}$, 在《生活垃圾焚烧污染控制标准》(GB 18485-2014)中将二噁英排放限值提升为 $0.1 \text{ ng}\cdot\text{TEQ}\cdot\text{m}_N^{-3}$, 监测二噁英的排放水平已成为环境监测的重要指标.

PCDD 和 PCDF 的化学结构式:



由于二噁英在环境中的含量很低, 同时其所处的基质对检测分析影响相对较大, 若要保证目标单体检测的灵敏度和准确度, 不能直接用气相色谱-质谱仪器进行检测分析. 必须对其进行样品前处理, 去除基质中的干扰物, 同时富集浓缩二噁英后才能进入仪器进行定性定量分析. 目前对于二噁英的样品前处理技术分为提取和净化两个步骤. 其中二噁英的主要提取技术主要为索氏提取法^[17-21, 22]和加速溶剂萃取法^[21, 23]. 索氏提取法(Soxxhlet extraction, SE)是传统的提取方法, 具有设备要求低和操作简单的特点, 但是索氏提取法耗时长(16—48 h), 有机溶剂消耗量大(160—350 mL)^[24-26]. 因此, Rübél 等^[27]提出了一种全新的萃取方法——加压溶剂萃取法(Pressurized liquid extraction, PLE), 也称为加速溶剂萃取(Accelerated solvent extraction, ASE). 该方法是通过提高温度(50—200 °C)和增加压力(1000—3000 psi)来对基质中的有机物进行自动萃取. 提高温度不仅能够加快分子的扩散速率, 还可以增加水的溶解度, 有利于萃取溶剂进入“水封微孔”提取目标物. 增加压力可以迫使萃取溶剂进入样品基体间隙中, 提取出其中的目标物. 基于高温高压条件, 萃取溶剂能与样品充分接触, 继而提高了萃取效率. 表 1 汇总了部分文献报道的不同基质中二噁英的提取技术的应用. 可以看出, 与索氏提取相比, 用 ASE 提取二噁英耗时短(0.8—1 h), 有机溶剂消耗少(15—160 mL). 为了实现快速在线检测, 目前已有文献报道将加速溶剂萃取技术应用于样品在线分离检测系统中, 并研制出了微型化的装置^[28-31]. 微池加速溶剂萃取的提取时间更短(15—60 s)、萃取溶剂更少(125 μL). 综上所述, 加速溶剂萃取法具有有机溶剂用量少、萃取时间短、样品回收率高等突出优点, 被美国环保局(EPA)推荐为固体废弃物中的二噁英检测的标准方法^[32], 我国也在《饲料中二噁英及二噁英类多氯联苯的测定同位素稀释-高分辨气相色谱/高分辨质谱法》(GB/T 28643-2012)和《食品中二噁英及其类似物毒性当量的测定》(GB 5009.205-2013)中推荐 ASE 作为饲料和食品中二噁英的提取方法.

本文主要综述了在不同基质中应用加速溶剂萃取技术提取二噁英的研究情况, 其中包括环境基质(水体^[33-34]、土壤及底泥沉积物^[35-42]、大气及废气^[43-47])、生物基质(生物^[48, 69-73]、人体血浆^[49, 79-82])、食品基质(食物^[50, 86-91]、饲料^[51, 88-90])等, 为进一步发展该技术应用用于不同基质中二噁英的检测提供参考.

表 1 不同基质中二噁英提取技术的应用

Table 1 Application of dioxin extraction technology in different matrices

样品基质 Sample matrix	萃取技术 Extraction technology	萃取时间/h Extraction time	萃取溶剂体积/mL Extraction solvent volume	回收率/% Recovery	仪器分析方法 Instrumental analysis method	文献 Ref.
土壤	索氏提取	18	250	68.0—85.0	GC/HRMS	[25]
废气	索氏提取	24	350	80.0—97.0	HRGC/HRMS	[19]
母乳	索氏提取	24	250	50.0—120.0	GC/HRMS	[22]
血清	索氏提取	48	160	66.2—95.2	HRGC/HRMS	[52]
烟道气	索氏提取	19	300	33.0—113.0	HRGC/HRMS	[84]

续表 1

样品基质 Sample matrix	萃取技术 Extraction technology	萃取时间/h Extraction time	萃取溶剂体积/mL Extraction solvent volume	回收率/% Recovery	仪器分析方法 Instrumental analysis method	文献 Ref.
底泥	索氏提取	16	250	55.0—86.0	HRGC/HRMS	[74]
底泥	索氏提取	48	350	52.0—104.0	HRGC/HRMS	[68]
鱼组织	索氏提取	24	—	60.0—120.0	GC/HRMS	[75]
松叶	索氏提取	24	—	46.0—116.0	HRGC/HRMS	[76]
水体	索氏提取	24	—	32.0—127.0	GC/HRMS	[77]
复合饲料	振荡提取	1	45	80.6—93.5	HRGC/HRMS	[92]
底泥	ASE	1	180	93.2—115.6	HRGC/HRMS	[35]
底泥	ASE	0.5	120	42.0—120.0	HRGC/HRMS	[78]
粉尘	ASE	0.2	35	96.0—121.0	HRGC/HRMS	[57]
水体	ASE	0.2	—	61.0—98.0	GC/HRMS	[34]
生肉	ASE	0.8	160	40.0—119.0	HRGC/HRMS	[93]
土壤	ASE	0.2	15	50.0—81.0	GC/MS	[25]
土壤	ASE	0.7	—	60.6—117.0	GC/MS	[83]
大气	ASE	0.5	—	55.7—94.1	HRGC/HRMS	[85]
肉类	ASE	0.2	—	81.0—97.0	GC/HRMS	[65]
树皮	ASE	0.4	—	70.0—95.0	GC-MS/MS	[6]
鱼组织	ASE	0.3	—	59.0—114.0	HRGC/HRMS	[69]

1 环境基质中二噁英的提取 (Extraction of dioxins from environmental matrix)

1.1 水体悬浮颗粒物中二噁英的提取

二噁英能与水中的悬浮固体颗粒结合, 水体中悬浮颗粒物中的二噁英可以通过滤膜后用 ASE 进行提取. Castro 等^[33]用玻璃纤维滤膜过滤湖水水样后, 将玻璃纤维滤膜转移至 ASE 萃取池中 (33 mL) 进行两次萃取, 两次的提取溶剂分别为甲醇和正己烷, 以 75 °C, 1500 psi, 100% 溶剂冲洗量, 提取和加热时间均为 5 min. 甲醇相的提取液再用正己烷提取, 并且过硅胶柱净化, 结合高分辨气相色谱与高分辨质谱 (HRGC/HRMS) 进行检测. 结果测得该湖的水样中二噁英含量为 163.3—2773.5 fg·L⁻¹. Youn 等^[34]用玻璃纤维滤膜和两种不同的 C18 固相萃取盘过滤水样, 将目标物保留在固相萃取盘中, 在 ASE 萃取池 (22 mL) 中加入硅藻土、富集了目标物的固相萃取盘、玻璃纤维滤膜, 在压力为 1500 psi, 温度为 150 °C 的条件下, 用甲苯对目标物提取 7 min, 进行两个循环. 将得到的提取液浓缩后用自动化多层硅胶柱净化待检测. 结果表明, 回收率在 61%—98% 之间, 能够满足 EPA1613 和 JISK0312 方法的要求. 该方法能够用于水样中二噁英的高通量分析, 并且相比于传统的抽滤水样-索氏提取-硅胶柱净化的方法, 将分析时间缩短至 3 d. Vandermarken 等^[94]比三十年间比利时沿海地区的悬浮颗粒物中二噁英的浓度, 采集海水中的悬浮颗粒物, 将其加入到 ASE 萃取池中 (33 mL), 用 1 : 1 (V/V) 的正己烷 : 丙酮在 125 °C, 1500 psi, 60% 溶剂冲洗量, 提取时间为 10 min, 加热时间为 6 min 的条件下进行两次循环萃取, 结合 Calux 生物测定法检测, 结果表明通过近年来不断减少二噁英排放量, 该海域中二噁英的浓度远低于三十年前.

1.2 土壤及底泥沉积物中二噁英的提取

排放进入大气的二噁英通过大气干沉降和湿沉降转移到地表, 进而进入土壤和水体中, 导致土壤和水体受到污染^[53]. 底泥沉积物是水体中二噁英最主要的“汇”, 而其中二噁英能够通过迁移分配等方式再次进入水体, 对水体的生态系统造成危害. 因此对土壤及底泥沉积物中二噁英的检测非常有必要. Chang 等^[54]对地震、海啸后的土壤中二噁英的含量进行检测. 在 ASE 萃取池 (66 mL) 中加入土壤样品, 萃取温度为 160 °C, 用甲苯作为提取溶剂, 加热时间和静态萃取时间分别为 8 min 和 20 min, 吹扫 150 s, 进行两次循环. 将 ASE 过程中获得的提取液过亚砷/银离子柱进行净化, 再经洗脱液淋洗, 可得到纯化的二噁英. 结合气相色谱-多光子电离-飞行时间质谱 (GC/MPI/TOFMS) 检测. 测得地震和海啸后的土

壤中二噁英含量较高, 为 0.01—11.64 $\text{pg}\cdot\text{g}^{-1}\cdot\text{TEQ}$. 该方法从提取 (1 h)、净化、检测 (45 min) 阶段都缩短了二噁英的分析周期, 在 3 d 之内能完成 7 个土壤样品的检测, 为发生自然灾害后的土壤中二噁英的检测提供安全快速高效的分析方法. 对于沉积物中二噁英的提取, Chuang 等^[55] 将沉积物样品与硅藻土混合, 并在萃取池 (33 mL) 中自下而上填充氧化铝 (分离二噁英与多氯联苯), 含 10% AgNO_3 的二氧化硅 (去除含硫化合物) 和酸性二氧化硅 (去除碱性化合物). 二氯甲烷作为提取溶剂连续提取 3 个循环, 每次循环提取时间为 10 min, 温度为 100 $^{\circ}\text{C}$, 吹扫时间为 60 s, 溶剂冲洗量为 100%. 结合免疫化学法 (ELISA) 和气相色谱/高分辨率质谱 (GC / HRMS) 分析, 沉积物中的二噁英回收率可达 $116\% \pm 11\%$. 该方法通过 ASE-ELISA 将样品处理量提升 3 倍以上, 并且成本大大降低. Aguiar 等^[56] 将沉积物样品与无水硫酸钠混合置于 ASE 萃取池 (100 mL) 中, 分别由下至上加入用甲苯预先清洗的二氧化硅, 氧化铝和弗洛里硅土 (Florisil), 萃取池内部吸附剂填充如图 1. 该萃取在 100 $^{\circ}\text{C}$ 和 1500 psi (溶剂冲洗量为 50%) 的条件下, 进行 2 个循环. 该方法用于分析表层沉积物中的二噁英回收率为 84%. 该法对于沉积物类的较脏样品中的二噁英有较好提取和净化能力, 将提取和净化步骤合二为一, 大大节省了前处理时间, 每个样品的前处理时间降至 2.5 h, 还将有机溶剂的使用量减少到 100 mL 以下, 为以后检测二噁英开辟了一条快速高效便捷的道路.

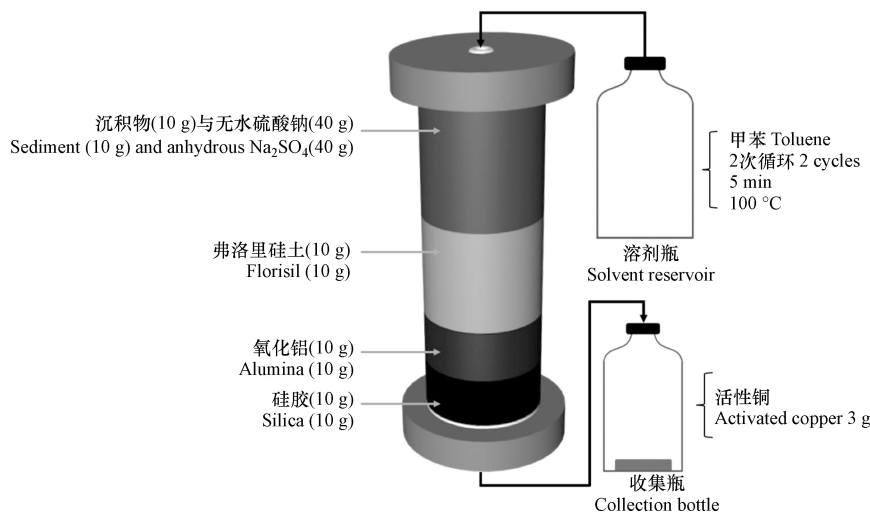


图 1 加速溶剂萃取沉积物中多氯代二苯并对二噁英/呋喃和多氯联苯^[56]

Fig.1 Accelerated solvent extraction of polychlorinated dibenzo-p-dioxin/furan and PCB in sediments^[56]

1.3 大气及粉尘中二噁英的提取

大气及粉尘中的二噁英一般采用大流量主动采样器采集. Klees 等^[57] 用索氏提取法和加速溶剂萃取法对街道粉尘中的二噁英的提取做了对比. 首先将一部分采集到的街道粉尘样品放置到 ASE 萃取池 (22 mL) 中, 温度范围为 100—160 $^{\circ}\text{C}$, 以甲苯作为萃取溶剂在 110 bar 的压力下, 加热和提取时间为 5 min, 吹扫时间为 60 s, 溶剂冲洗量为 60%, 得到的萃取液氮吹浓缩. 另一部分的样品则经过索氏提取的方法提取. 根据 EN 1948-2 的方法, 将 ASE 和 SE 的萃取液过硅胶柱净化, 用气相色谱-高分辨质谱 (GC/HRMS) 检测. 结果测得采用 ASE 法的二噁英回收率在 96%—121% 之间, 而采用索氏提取法的二噁英回收率在 81%—112% 之间. 经过比对, ASE 在对于粉尘中二噁英的提取能够替代索氏提取法, 表现出较高回收率和提取效率, 且大大节省了样品前处理时间. 中国科学院生态环境研究中心张庆华课题组^[58-59] 根据美国 EPA TO-9A 中的方法对天津市空气中的二噁英进行采样, 用玻璃纤维滤膜 (GFF) 和聚氨酯泡沫 (PUF) 分别采集颗粒物相和气相中的二噁英. 将 GFF 和 PUF 装入 ASE 萃取池中, 萃取条件为 100 $^{\circ}\text{C}$ 、1500 psi, 以丙酮为萃取溶剂进行两次循环提取. 根据美国 EPA 1613B 的方法萃取液经过浓缩过硅胶柱后用 HRGC/HRMS 检测. 样品的回收率在 32.9%—124% 和 25.3%—150% 之间, 符合 1613B 的要求. 2017 年该课题组采用与上述相同的 ASE 条件, 样品的前处理基于 EPA 1613B 方法, 结合气相色谱/三重四极杆质谱 (GC-MS/MS) 对北京周边的大气样品进行分析. 样品的加标回收率在 43%—103% 之间, 大气中二噁英的毒性当量 (TEQ) 平均值为 $0.10 \text{ pg}\cdot\text{m}^{-3}$ WHO-TEQ₂₀₀₅^[38]. 该检测方法

具有灵敏度高、重现性好、成本低等特点,有较好的推广性.

1.4 飞灰中二噁英的提取

目前,高效地检测飞灰中的二噁英仍然存在一定的难度,由于飞灰本身结构的复杂性,加大了二噁英提取的难度.为提高飞灰中二噁英组分的提取效率,需要预先用 HCl 对飞灰进行消解,并且选择合适的压力、温度等提取条件. Windal 等^[60]采用超临界流体萃取法(SFE)和加速溶剂萃取法(ASE)分别提取飞灰中二噁英并与索氏提取法进行对比.萃取前用 $1 \text{ mol} \cdot \text{L}^{-1}$ 的 HCl(8 mL)对飞灰消解 2 h. SFE 过程是将用 HCl 消解的粉煤灰与海沙混合,然后放入萃取池(10 mL)中.萃取器温度设定为 $150 \text{ }^\circ\text{C}$,压力设定为 400 bar.在萃取之前,将甲苯添加到样品池中,并在 30 min 动态萃取之前进行 1 h 或 3 h 的静态萃取. ASE 过程是将提取的甲苯收集在小瓶中,预填充 10 mL 甲苯. ASE 的萃取温度设定为 $150 \text{ }^\circ\text{C}$,压力设定为 50 bar,动态萃取为 1 h 或 2 h.结果表明,索氏提取对于低碳含量的粉煤灰中二噁英组分的提取效率较高,但对于高碳含量的粉煤灰中二噁英组分提取效率较低.与索氏提取相比 SFE 对基质的纯净程度要求更高一些, SFE 对于纯净程度高的基质样品中二噁英的提取效果更好. ASE 可以在 $80 \text{ }^\circ\text{C}$ 下 2 h 内获得与索氏提取相似的回收率.将温度提高到 $150 \text{ }^\circ\text{C}$, ASE 的回收率为 110%—160%.对于提取飞灰中的二噁英来说, ASE 可达到与索氏提取法相当的回收率,并且提取时间缩短了 20 倍,效率更高.

2 生物基质中二噁英的提取 (Extraction of dioxins from biological matrix)

2.1 海洋生物组织中二噁英的提取

对于鱼组织等复杂的生物基质中二噁英的提取,通常的方法是先提取再通过净化柱净化两步完成样品前处理. Subedi 等^[61]分析鱼组织中的二噁英时,将氧化铝、硅藻土和石墨化碳黑(carbopack)、Florisil 和硅胶等净化材料与鱼肉组织一起加入到萃取池中(如图 2),鱼组织置于萃取池顶部. ASE 过程中提取溶剂提取鱼组织中的二噁英的同时,净化材料吸附鱼肉基体中的干扰物,从而实现了提取和净化一步完成.提取条件是用 1:1(V/V)的二氯甲烷:正己烷(1个循环)提取样品,然后再利用甲苯(1个循环)提取.每个样品的萃取条件为 $100 \text{ }^\circ\text{C}$ 、1500 psi、1个循环、5 min 静态提取时间、吹扫 290 s 和 75% 的溶剂冲洗量.该方法能将鱼组织中的 PCDD/Fs 和 PCBs 在萃取池中通过两次不同条件的萃取分离出来,并且 PCDD/Fs 的回收率高,可达到 85%.该方法将加速溶剂萃取与净化同时进行,提取过程自动操作,压缩了实验步骤,减少了样品前处理时间,提高了样品分析的效率.

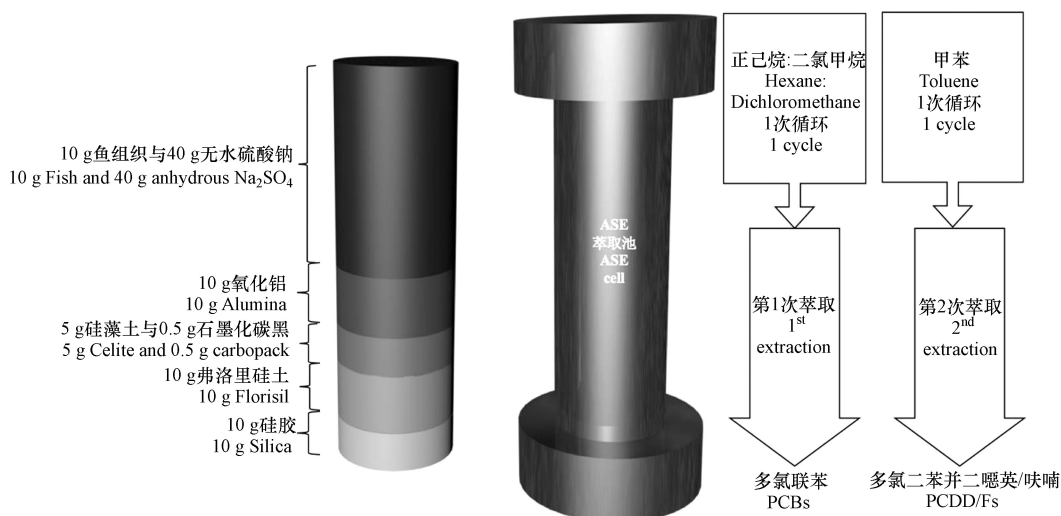


图 2 加速溶剂萃取鱼肉组织中二噁英类物质的示意图^[61]

Fig.2 Schematic diagram of ASE for polychlorodibenzo-p-dioxins, polychlorodibenzofurans, and polychlorobiphenyls in fish tissue^[61]

2.2 人体血浆中二噁英的提取

长期接触二噁英会对人体造成严重危害,特别是会干扰内分泌系统的正常工作.为了分析血液中的二噁英浓度水平, Zhang 等^[62]将采集到的血浆与硅藻土混合加入到 ASE 系统中,以 $120 \text{ }^\circ\text{C}$ 为萃取温

度, 正己烷/二氯甲烷/丙酮(45:45:10, *V/V*)为萃取溶剂, 提取时间为 5 min 进行 3 个循环, 萃取液经无水硫酸钠除水后过硅胶柱净化, 采用 GC-HRMS 检测. 二噁英的加标回收率在 36%—108% 之间. Todaka 等^[63]采集患有 Yusho 病的病人血浆经过 15 h 的冷冻干燥后放置在 ASE 系统中用压力为 2000 psi, 温度为 120 °C, 提取时间为 10 min, 吹扫 180 s, 提取溶剂为丙酮和正己烷的混合溶液(1:3, *V/V*), 进行 2 次循环, 提取液过硅胶柱除脂, 采用 HRGC/HRMS 检测. 结果显示病人血液中二噁英含量比正常人含量高 3.5 倍. 该方法耗时短、灵敏度高, 对于血浆二噁英的检测具有较好的实用性.

2.3 树皮中二噁英的提取

Clarkson 等^[6]对英格兰北部城市的树皮进行采样, 将树皮研磨碎, 用 ASE 提取树皮中的二噁英. 在 150 °C, 1500 psi 下, 用甲苯静态提取 8 min 进行 3 次循环, 萃取液经过硅胶柱净化, 结合 GC-MS/MS 检测. 该法的回收率在 70%—95% 之间. 说明该法对于树皮等固体样品的提取也能快速高效, 对于草本植物中二噁英的检测具有参考性, 可以更好地了解环境中二噁英的来源、分布、迁移等环境行为.

3 食品基质中二噁英的提取 (Extraction of dioxins from food matrix)

3.1 食物中二噁英的提取

食物样品中含有大量的脂肪组织, 用 ASE 提取时脂肪组织与目标物同时萃取出来, 对后续检测存在干扰, 所以需要萃取液进行再处理才能用于分析. Lorenzi 等^[91]将牛奶与硅藻土混合后加入到 ASE 系统中, 用甲苯在 135 °C 和 1500 psi 的条件下进行两次循环萃取, 萃取液用重量分析法确定脂肪含量, 以得到 ASE 的萃取效率, 结果表明 ASE 的回收率能达到美国 EPA 1613B 的要求. Wiberg 等^[65]将鱼肉、鸡肉和猪肉组织等处理后装到 ASE 的萃取池(100 mL)中, 用硫酸钠填补萃取池中的空隙, 在 100 °C, 提取时间为 5 min, 以庚烷为萃取溶剂进行两个循环, 对萃取液浓缩后过硅胶柱净化, 利用 GC-HRMS 检测. 结果测得样品中二噁英的回收率在 81%—97% 之间, 比传统食物样品中二噁英的提取节省了时间和溶剂的消耗.

3.2 饲料中二噁英的提取

Bernsmann 等^[51]将索氏提取法与 ASE 对草、面粉等粗饲料和其它类别饲料中二噁英的提取作了比较. 将饲料样品放入 ASE 的萃取池(100 mL)中, 同时在池中加入硅胶, 提取温度为 120 °C, 压力为 1500 psi, 萃取液过硅胶柱净化, 结合 HRGC/HRMS 检测. 结果表明, 在 ASE 萃取池中高压、高温的环境下硅胶的脂肪保留能力较低, 饲料原料的脂肪含量低于 5% 才能用该法提取二噁英. 由于粗饲料中蜡的含量较高, 高温高压下会溶解, 导致 ASE 不适于粗饲料中二噁英的提取. 目前提取粗饲料中的二噁英可以用振荡提取的方式^[92], 回收率在 80.6%—93.5% 之间, 能满足要求. 但是其它类别的饲料中 ASE 与索氏提取法的总 WHO-TEQ 分别为 0.48 $\text{pg}\cdot\text{g}^{-1}$ 和 0.50 $\text{pg}\cdot\text{g}^{-1}$, 提取回收率在 63%—102% 之间. 在其它类别饲料样品中二噁英的提取, ASE 的结果与索氏提取并无差别, 而且节省了提取时间和溶剂的消耗, 是更优的提取手段.

3.3 添加剂中二噁英的提取

Kleinhenz 等^[64]检测了腌制猪肉等肉类食物香料中二噁英的含量. 将处理好的香料加入 ASE 系统中, 正己烷作为萃取溶剂, 在 100 °C 和 100 bar 下, 静态提取时间为 10 min 进行两次循环, 萃取液过硅胶柱净化, 结合 GC-HRMS 检测. 结果测得香料中二噁英的检出限低于 0.03 ng WHO-PCDD/PCDF-TEQ/kg, 定量限低于 0.10 ng WHO-PCDD/PCDF-TEQ/kg, 回收率在 82.6%—105.6% 之间. 该法检测香料中二噁英含量时, 可以降低 HRGC/HRMS 的检出限, 并且得到较高回收率.

4 其它基质中二噁英的提取 (Extraction of dioxins from other matrix)

我国对于固体废弃物的处理以填埋为主, 因此固废中二噁英含量的检测十分重要. 周全法课题组^[66-67]对废线路板中的二噁英含量进行检测, 并比对了 ASE 与索氏提取法. 将粉碎处理后的废线路板粉末加入 ASE 萃取池(34 mL)中, 萃取温度为 190 °C, 压力为 1500 psi, 60 mL 甲苯为萃取溶剂, 加热和静态萃取时间分别为 9 min 和 10 min, 进行 3 次循环. 而索氏提取法则用 300 mL 甲苯提取 16 h 以上. 两个方法的萃取液均过硅胶柱净化, 结合 HRGC-HRMS 检测. 结果测得 ASE 和索氏提取法的回收率分

别为 54.3%—113.0% 和 28.3%—77.7%，满足国标要求。两种方法相比，ASE 的回收率更高，说明高温高压对该样品的萃取效率和渗透性的准确性更高，尽管 ASE 的平均相对偏差值略差于索氏提取法，但是均在国标要求的范围内。所以对于废线路板类的复杂样品中二噁英的提取，ASE 缩短提取时间并节省有机溶剂的消耗，且回收率更优异，能为以后此类样品中二噁英的检测建立快速高效的分析方法提供参考。

5 结论与展望 (Conclusion and prospect)

目前，加速溶剂萃取技术提取二噁英的应用已经遍及公共安全、地质勘探、环境检测、食品卫生、生物制药等领域，加速溶剂萃取技术在二噁英检测的样品前处理过程中体现出了明显的优势和巨大的应用潜力。对于绝大多数固体样品基质中的二噁英，均可以用 ASE 对二噁英进行提取，并且提取的回收率能够满足要求。与传统的索氏提取方法相比，ASE 萃取时间大大减少。另一方面，加速溶剂萃取仪器具有高通量的优点，可降低样品前处理过程的内在成本（包括：时间、溶剂、人工、实验室空间等）。在 ASE 应用研究中，值得关注的是，加速溶剂萃取池中可同时加入净化材料，既萃取二噁英的同时也进行了净化，避免了萃取溶液要过净化柱的步骤，将提取和净化两个步骤合二为一，大大缩短了样品前处理时间，而且也减少了有机溶剂的使用。但是，加速溶剂萃取池体内壁大多为不锈钢材料，对于酸碱性样品的提取还存在一定局限性，今后在加速溶剂萃取仪器池体制作方面应当适当考虑对含酸、碱性基质的样品的适用性，以便使该技术得到更广泛的应用。

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