

同位素稀释-高分辨气相色谱/高分辨质谱测定大气中有机氯农药

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摘要:建立了测定大气中 25 种有机氯农药 (OCPs) 的同位素稀释-高分辨气相色谱/高分辨质谱法 (ID-HRGC/HRMS)。样品用正己烷/二氯甲烷 (1:1, v/v) 进行加速溶剂萃取 (ASE)。通过柱洗脱实验、单柱和组合柱净化实验, 最终确定样品的净化方案为弗罗里硅土固相萃取柱和石墨化炭黑固相萃取柱组合净化。样品萃取液净化后进行 HRGC/HRMS 分析。采用平均相对响应因子 (RRF) 法对样品中目标物进行定量, 6 点校准溶液 RRF 的相对标准偏差 (RSD) 均 $\leq 20\%$ 。线性范围为 0.4 ~ 800 $\mu\text{g/L}$, 相关系数 R^2 均 > 0.992 。对空白样品依次进行 100 pg、400 pg 和 15 ng 水平下的加标试验, 各添加水平下 OCPs 测定值的 RSD 为 0.64% ~ 16%, 加标回收率为 67.2% ~ 135%。穿透试验表明, 滤膜+聚氨酯泡沫/聚氨酯泡沫作为吸附介质的的大体积主动大气采样器 (AAS) 在采集环境空气时, 五氯苯极易发生穿透, 有效采样模式待进一步研究。在上述采样模式下, 六氯苯的有效采样体积较小, 标准状态 (101.325 kPa, 273 K) 采样体积应 $\leq 30 \text{ m}^3$, 其他 OCPs 应 $\leq 1200 \text{ m}^3$ 。以上述体积计算, 25 种目标化合物的检出限为 0.002 ~ 0.7 pg/m^3 。对北京环境空气样品分析测定, 结果显示除反式-环氧七氯、异狄氏剂、顺式-九氯和 4,4'-滴滴滴在部分样品中未检出外, 其他 OCPs 均为 100% 检出; 六氯苯浓度在 514 ~ 563 pg/m^3 之间, 其他 OCPs 的浓度在 0.01 ~ 18.9 pg/m^3 之间, 替代标回收率为 33.9% ~ 155%。由于现有相关监测标准的仪器灵敏度较低、方法检出限较高, 已无法满足目前空气中痕量 OCPs 的测定需求, 因此亟待修订新的高灵敏度监测方法标准。该方法适用于目前大气中 OCPs 的超痕量水平分析, 为新标准的制订奠定基础, 也为国家履行相关国际公约提供有力技术指导。

关键词: 同位素稀释法; 高分辨气相色谱/高分辨质谱; 有机氯农药; 环境空气

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Determination of atmospheric organochlorine pesticides using isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry

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Abstract: A method for the determination of 25 organochlorine pesticides (OCPs) in the atmosphere using isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry (ID-HRGC/HRMS) was developed. Sample extraction was performed using an accelerated solvent extractor (ASE). The extraction parameters were as follows: the extraction solvent was 50% (v/v) hexane in dichloromethane, the extraction temperature was 100 °C, the static time was 8 min, the cell was rinsed with 60% cell volume using the aforementioned extraction solvent, the purging time was 180 s with N_2 gas, and the extraction proceeded through three cycles. The eluting solutions of common cartridges such as florisil, graphitized carbon black, alumina, and silica were determined via cartridge elution tests. Use of the aforementioned cartridges alone cannot remove the pigments in the air sample solution. Subsequently, all possible pairwise combinations of the four cartridges were used for sample

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cleaning, and only the combination of florisil and graphitized carbon black was found to completely remove the pigments. Thus, the combination of florisil and graphitized carbon black cartridges using 10 mL toluene for elution was determined as the final cleaning method in this study. A high-resolution mass spectrometer equipped with a gas chromatograph was used for quantification. A fused-silica capillary column (Rtx-CL Pesticides2, 30 m×0.25 mm×0.2 μm) was used to separate the target compounds. Injection was performed in the splitless mode at 250 °C. The flow rate of nitrogen gas was maintained constant at 1 mL/min. The oven temperature was 110 °C (1 min), 20 °C/min up to 210 °C, 1.5 °C/min up to 218 °C (1 min), and 2 °C/min up to 260 °C (1 min). HRMS was conducted at >8 000 resolution, the source temperature was 280 °C in the electron impact mode using ionization energy of 35 eV, and measurements were performed in the selective ion monitoring (SIM) mode. Twenty-five OCPs were identified by comparing their GC retention times with those of the corresponding labeled compounds, and the actual ion abundance ratios of two exact m/z values with the corresponding theoretical values. The 25 OCPs were quantified by average relative response factors (RRFs), and the relative standard deviations (RSDs) of the RRFs with six calibration solutions were no more than 20%. The linear range of this method was 0.4 to 800 μg/L, and the correlation coefficients (R^2) were higher than 0.992. To validate the method, clean materials (one quartz fiber filter (QFF) and two polyurethane foam (PUF) plugs) were spiked with 100 pg, 400 pg, and 15 ng native OCP standards, respectively; the RSDs of the 25 OCPs for each spiked level ranged from 0.64% to 16%. The spiking recoveries of the native OCPs ranged from 67.2% to 135%. Penetration experiments were conducted by sampling various volumes of air (15–1 000 m³) using a filter-PUF/PUF high-volume active sampler. The breakthrough volume was sampled when the amount of OCPs collected in the PUF of the non-sampling end reached 5% of the total amount collected by both PUFs. When a high-volume active sampler with filter-PUF/PUF was used as an adsorbent for sampling atmospheric OCPs, a serious breakthrough of pentachlorobenzene (PeCB) occurred. The effective sampling volume of hexachlorobenzene (HCB) was very low, and was no more than 30 m³ under the standard conditions (101.325 kPa, 273 K). The effective sampling volumes of other OCP compounds should be no more than 1 200 m³. This will necessitate the use of high-adsorption-capacity adsorbents such as the PUF-XAD (a styrene-divinylbenzene copolymer) sandwich used for sampling air PeCB and HCB. Calculation with the effective sampling volumes from the penetration experiment revealed that the limits of detection of the 25 OCPs were in the range of 0.002 to 0.7 pg/m³. Thus, the detection levels of OCPs in this study were reduced to at least 2% of the current monitoring standards. Analysis of air samples in Beijing showed that all the target compounds except for *trans*-heptachlor epoxide, endrin, *cis*-nonachlor and 4,4'-DDD were 100% detected in the air samples. The concentrations of HCB (in volumes of 15–30 m³) ranged from 514 to 563 pg/m³, while those of the other OCPs (in a volume of 600 m³) ranged from 0.01 to 18.9 pg/m³. The recoveries of surrogate standards in this sample analysis were in the range of 33.9% to 155%, which satisfied the requirements of EPA Method 1699. Because of the very high detection limits, the current related monitoring standards cannot meet the requirements of atmospheric OCP analysis, especially at the ultra-trace level. In addition, highly sensitive monitoring standard methods are urgently needed. This method is suitable for analyzing most atmospheric OCPs, even at the ultra-trace level. It also lays the foundation for a new standard method formulation and provides strong support for the implementation of relevant international conventions.

Key words: isotope dilution (ID); high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS); organochlorine pesticides; ambient air

持久性有机污染物(persistent organic pollutants, POPs)是一类具有高毒性、难生物降解,能在环境中长距离迁移和扩散、可生物富集并生物放大的化合物^[1,2],其在各种环境介质甚至动物和人体中普遍检出^[3-10],在生态安全和人类健康方面产生风险,目前已引起世界范围内的广泛关注。2001年联合国环境规划署(United Nations Environment Programme, UNEP)通过了《关于持久性有机污染物的斯德哥尔摩公约》(简称公约),以消除或限制 POPs 生产、使用及排放,目前公约已纳入 30 类化合物^[11]。

POPs 具有一定挥发性,可通过大气进行扩散和迁移,因此大气中 POPs 的赋存水平可直观地反映环境污染的现状,UNEP 全球 POPs 监测计划也将大气作为主要监测对象^[12]。有机氯农药(organochlorine pesticides, OCPs)目前在公约受控清单中已多达 17 种^[11],作为典型的 POPs,其大气监测分析方法的开发与优化对履约监测工作意义重大。目前相关的标准方法多为气相色谱-电子捕获检测(GC/ECD)^[13-18]和气相色谱/质谱(GC/MS)^[19-21]。这些方法的仪器分辨率较低,检出限较高,多在 $10^{-1} \sim 10^2 \text{ pg/m}^3$ ^[13-20],高于履约背景点大气中 OCPs 的浓度水平(一般为 $10^{-3} \sim 10^1 \text{ pg/m}^3$),不能满足背景点大气监测的需求^[22]。检出限的定义和计算方式多样,不利于方法间的比较^[16-18,23-26]。也有部分研究用到了气相色谱/串联质谱(GC/MS-MS)^[23-25]和气相色谱/高分辨质谱^[26,27]测定的方法,但是其净化方法较为简单,有待优化。同时,在大气 OCPs 采样方面,挥发性较强的 α -HCH (α -hexachlorocyclohexane) 和 HCB (hexachlorobenzene) 等化合物容易受环境温、湿度影响,在聚氨酯泡沫(PUF)上发生吸附穿透^[16,24,27,28],但很少有研究进行系统的穿透试验^[20,23-25],导致化合物实际污染水平被低估。

本研究采用同位素稀释-高分辨气相色谱/高分辨质谱法(ID-HRGC/HRMS)测定大气中的 OCPs,在借鉴已有的 ID-HRGC/HRMS 测定环境样品方法的基础上^[29-33],严格根据《环境监测分析方法标准制修订技术导则》(HJ 168-2010),从大气采样、样品净化、方法适用性等多方面进行方法开发,为我国大气中的 OCPs 检测标准制订奠定基础,同时为履约监测提供技术支持。

1 实验部分

1.1 仪器与试剂

7890A 气相色谱仪(美国 Agilent 公司); Autospec Premier 高分辨磁质谱仪(美国 Waters 公司);大气主动采样器(Echo Hivol,意大利 TCR TECORA 公司);加速溶剂萃取仪(ASE350,美国 Thermo 公司)。弗罗里硅土(1 g, 6 mL)和石墨化炭黑固相萃取柱(500 mg, 6 mL, Envi-carb)(美国 Supelco 公司),硅胶(1 g, 6 mL)以及氧化铝固相萃取柱(1 g, 6 mL)(美国 Sep-Pak 公司)。

丙酮、二氯甲烷和甲苯(美国 J. T. Baker 公司)、正己烷(德国 Merck 公司)和壬烷(德国 Alfa Aesar 公司)均为农残级。无水硫酸钠为分析纯,使用前于 $400 \text{ }^\circ\text{C}$ 下烘烤 4 h。OCPs 类校准溶液(ES 5464)、天然混合标准溶液(ES 5467)、替代标溶液(ES 5465)和进样内标溶液(EC 5350)均购于美国剑桥同位素实验室。

PUF(美国 Tisch 公司)直径 5.08 cm (2 英寸),高 5 cm,密度 0.025 g/cm^3 ,使用前用沸水烫洗后在温水中反复搓洗,沥干水分放入烘箱除水;之后用加速溶剂萃取(ASE)清洗,提取溶剂为正己烷/二氯甲烷(1:1, v/v),于 $100 \text{ }^\circ\text{C}$ 静态平衡 8 min,吹扫 180 s,循环 3 次,冲洗比例 60%;清洗完毕,置于真空干燥箱 $50 \text{ }^\circ\text{C}$ 加热 8 h,密封保存。石英纤维滤膜(QFF, Munktell 公司)直径 102 mm,使用前于 $600 \text{ }^\circ\text{C}$ 下烘烤 6 h,密封保存。

1.2 实验方法

1.2.1 样品采集

大流量主动采样器(active air samplers, AAS)放置于中国环境监测总站(北京)3 楼楼顶采样平台,以滤膜+PUF/PUF 模式采集大气中的 OCPs, 220 L/min 连续采样,采集约 600 m^3 大气样品。采样完毕,将滤膜和 PUF 用铝箔包裹密封,冷藏保存直至分析。

1.2.2 样品前处理

向滤膜和 PUF 中加入 1 ng 替代标,平衡 30 min 后 ASE 提取,提取方法与 PUF 清洗相同。将提取液旋蒸浓缩至 $1 \sim 2 \text{ mL}$,用弗罗里硅土小柱进行净化。预先用 5 mL 甲苯活化小柱,上样后用 10 mL 甲苯洗脱并接收流出液。流出液旋蒸至约 1 mL,再用石墨化炭黑小柱净化。事先用 5 mL 甲苯活化小柱,10 mL 甲苯洗脱。流出液旋蒸、氮吹浓

缩,溶剂置换为 20 μL 壬烷,加入 1 ng 进样内标,涡旋混匀后待测。

1.2.3 HRGC/HRMS 条件

色谱:进样口 250 $^{\circ}\text{C}$;载气为 1.0 mL/min 的高纯氦气;不分流进样,进样体积 1 μL ;中等极性色谱柱 Rtx-CL Pesticides2 (30 $\text{m} \times 0.25 \text{ mm} \times 0.2 \mu\text{m}$);升温程序:110 $^{\circ}\text{C}$ 保持 1 min; 20 $^{\circ}\text{C}/\text{min}$ 升温至 210 $^{\circ}\text{C}$; 1.5 $^{\circ}\text{C}/\text{min}$ 升温至 218 $^{\circ}\text{C}$,停留 1 min; 2 $^{\circ}\text{C}/\text{min}$ 升温至 260 $^{\circ}\text{C}$,停留 1 min。

质谱:离子源温度 280 $^{\circ}\text{C}$;电子能量 35 eV;捕获电流 650 μA ;检测器电压 350 V;动态分辨率 ≥ 8000 ;选择离子监测(SIM)模式,各 OCPs 特征离子的参数见表 1。

1.2.4 定性定量方法

在给出色谱/质谱条件下获得样品色谱/质谱峰,根据保留时间和特征离子丰度比进行定性,以平均相对响应因子(RRF)法进行定量。由校准溶液测定化合物的 RRF,并计算平均值。其中 23 种 OCPs 使用其各自的 ^{13}C 标记的替代标定量;反式-环氧七氯和顺式-氯丹分别采用 $^{13}\text{C}_{10}$ -顺式-环氧七氯和 $^{13}\text{C}_{10}$ -反式-氯丹定量;所有替代标的回收率采用

保留时间接近的进样内标定量。

2 结果与讨论

2.1 仪器条件的优化

比较 OCPs 分析常用的色谱柱 DB-5MS、DB-35 与专用柱 Rtx-CL Pesticides2 对 25 种 OCPs 的分离效果,发现 Rtx-CL Pesticides2 效果最优(见图 1),且该柱对 25 种 OCPs 的仪器检出限低至其他色谱柱的 5%~50%,因此选择 Rtx-CL Pesticides2 作为分析色谱柱。

2.2 净化方法优化

2.2.1 柱洗脱条件选择

调研发现,弗罗里硅土、活性炭、氧化铝以及硅胶等常用于 OCPs 的净化(见附表 1,详见 <http://www.chrom-China.com/>)。其中弗罗里硅土可以将 OCPs 与脂肪族、芳香族以及含氮化合物等干扰物相分离,石墨化炭黑能有效去除色素和甾醇类等非极性干扰物,硅胶、氧化铝可以去除有机磷酸酯和氯酚类的污染^[34]。丙酮、二氯甲烷、甲苯、正己烷以及不同比例混合溶剂常用作上述净化柱的洗脱溶剂。

表 1 高分辨气相色谱/高分辨质谱测定 OCPs 的参数

Table 1 HRGC/HRMS parameters of organochlorine pesticides (OCPs) determination

No.	Compound	Retention time/min	Characteristic ion m1 (m/z)	Characteristic ion m2 (m/z)	m1/m2	
					Ratio	Tolerance/%
Target/surrogate standard						
1	hexachlorobenzene (HCB, 六氯苯)	6.85	283.8102	285.8073	1.24	± 25
	$^{13}\text{C}_6$ -HCB	6.85	289.8303	291.8273	1.24	± 25
2	α -hexachlorocyclohexane (α -HCH, α -六六六)	7.10	180.9379	182.9349	1.04	± 25
	$^{13}\text{C}_6$ - α -HCH	7.08	186.9580	188.9550	1.04	± 25
3	γ -HCH (γ -六六六)	7.69	180.9379	182.9349	1.04	± 25
	$^{13}\text{C}_6$ - γ -HCH	7.69	186.9580	188.9550	1.04	± 25
4	β -HCH (β -六六六)	7.84	180.9379	182.9347	1.04	± 25
	$^{13}\text{C}_6$ - β -HCH	7.84	186.9580	188.9550	1.04	± 25
5	δ -HCH (δ -六六六)	8.42	180.9379	182.9349	1.04	± 25
	$^{13}\text{C}_6$ - δ -HCH	8.42	186.9580	188.9550	1.04	± 25
6	heptachlor (七氯)	8.53	271.8102	273.8072	1.24	± 25
	$^{13}\text{C}_{10}$ -heptachlor	8.53	276.8269	278.8240	1.24	± 25
7	aldrin (艾氏剂)	9.26	262.8570	264.8541	1.55	± 25
	$^{13}\text{C}_{12}$ -aldrin	9.25	269.8804	271.8775	1.55	± 25
8	oxychlordane (氧化氯丹)	10.53	386.8053	388.8024	1.05	± 25
	$^{13}\text{C}_{10}$ -oxychlordane	10.51	396.8387	398.8358	1.05	± 25
9	cis-heptachlor epoxide (顺式-环氧七氯)	10.80	352.8442	354.8413	1.24	± 25
	$^{13}\text{C}_{10}$ -cis-heptachlor epoxide	10.78	362.8777	364.8748	1.24	± 25
10	trans-heptachlor epoxide (反式-环氧七氯)	10.86	352.8442	354.8413	1.24	± 25
	$^{13}\text{C}_{10}$ -trans-heptachlor epoxide	10.78	362.8777	364.8748	1.24	± 25
11	trans-chlordane (反式-氯丹)	11.39	372.8260	374.8231	1.05	± 25
	$^{13}\text{C}_{10}$ -trans-chlordane	11.38	382.8595	384.8565	1.05	± 25

表 1 (续)
Table 1 (Continued)

No.	Compound	Retention time/min	Characteristic ion m1 (<i>m/z</i>)	Characteristic ion m2 (<i>m/z</i>)	m1/m2	
					Ratio	Tolerance/%
12	2,4'-DDE (2,4'-滴滴伊)	11.46	246.0003	247.9975	1.56	±25
	¹³ C ₁₂ -2,4'-DDE	11.46	258.0405	260.0376	1.56	±25
13	<i>trans</i> -nonachlor (反式-九氯)	11.70	406.7870	408.7841	0.89	±25
	¹³ C ₁₀ - <i>trans</i> -nonachlor	11.70	416.8205	418.8175	0.89	±25
14	<i>cis</i> -chlordane (顺式-氯丹)	11.89	372.8260	374.8231	1.05	±25
	¹³ C ₁₀ - <i>trans</i> -chlordane	11.38	382.8595	384.8565	1.05	±25
15	endosulfan- I (硫丹- I)	12.06	240.9145	242.9116	0.75	±25
	¹³ C ₉ -endosulfan-I	12.06	248.9414	250.9384	0.75	±25
16	4,4'-DDE (4,4'-滴滴伊)	12.63	246.0003	247.9975	1.56	±25
	¹³ C ₁₂ -4,4'-DDE	12.61	258.0405	260.0376	1.56	±25
17	dieldrin (狄氏剂)	13.12	262.8570	264.8541	1.55	±25
	¹³ C ₁₂ -dieldrin	13.09	269.8804	271.8775	1.55	±25
18	2,4'-DDD (2,4'-滴滴滴)	13.43	235.0081	237.0053	1.56	±25
	¹³ C ₁₂ -2,4'-DDD	13.43	247.0483	249.0454	1.56	±25
19	endrin (异狄氏剂)	14.38	262.8570	264.8541	1.55	±25
	¹³ C ₁₂ -endrin	14.36	269.8804	271.8775	1.55	±25
20	2,4'-DDT (2,4'-滴滴涕)	14.76	235.0081	237.0053	1.55	±25
	¹³ C ₁₂ -2,4'-DDT	14.76	247.0483	249.0454	1.55	±25
21	<i>cis</i> -nonachlor (顺式-九氯)	14.84	406.7870	408.7841	0.89	±25
	¹³ C ₁₀ - <i>cis</i> -nonachlor	14.82	416.8205	418.8175	0.89	±25
22	4,4'-DDD (4,4'-滴滴滴)	15.18	235.0081	237.0053	1.56	±25
	¹³ C ₁₂ -4,4'-DDD	15.16	247.0483	249.0454	1.56	±25
23	endosulfan- II (硫丹- II)	15.37	240.9145	242.9116	0.75	±25
	¹³ C ₉ -endosulfan- II	15.35	248.9414	250.9384	0.75	±25
24	4,4'-DDT (4,4'-滴滴涕)	16.72	235.0081	237.0053	1.55	±25
	¹³ C ₁₂ -4,4'-DDT	16.70	247.0483	249.0454	1.55	±25
25	mirex (灭蚁灵)	21.10	271.8102	273.8072	1.24	±25
	¹³ C ₁₀ -mirex	21.07	276.8269	278.8240	1.24	±25
a	pentachlorobenzene (PeCB, 五氯苯)	5.61	249.8492	251.8463	1.55	±25
	¹³ C ₆ -PeCB	5.61	255.8693	257.8663	1.55	±25
Injection internal standard						
b	¹³ C ₁₂ -4,4'-DiCB (¹³ C ₁₂ -4,4'-二氯联苯)	7.60	234.0406	236.0376	1.56	±25
c	¹³ C ₁₂ -2,3',4',5-TetraCB (¹³ C ₁₂ -2,3',4',5-四氯联苯)	10.69	301.9626	303.9597	0.77	±25

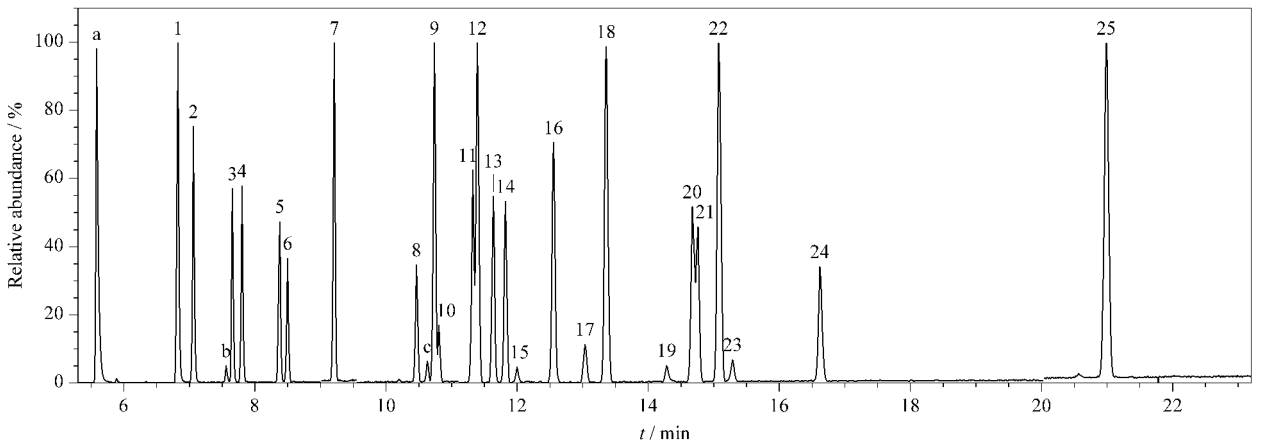


图 1 25 种 OCPs 的总离子流图

Fig. 1 Total ion current chromatogram of the 25 OCPs

OCPs: 800 μg/L standard solution. Peak Nos.: see Table 1.

将含 1 ng OCPs 替代标的溶液作为模拟样品,在净化小柱活化后进行上样和洗脱,考察了不同净化方法对应的替代标回收率(见表 2~表 5)。

佛罗里硅土小柱的洗脱结果(见表 2)表明,丙酮/正己烷(1:9, v/v)以及甲苯作洗脱溶剂时,洗脱效果均较好,且从追加 5 mL 洗脱溶剂的结果来看,10 mL 溶剂用量已足够。二氯甲烷/正己烷(2:8, v/v)对硫丹-I、狄氏剂、异狄氏剂和硫丹-II 的洗脱效果较差,追加的 10 mL 二氯甲烷/正己烷(3:7, v/v)虽能洗脱 50%~70% 的硫丹-I、狄氏剂和异狄氏剂,但硫丹-II 的回收率仅达 7%,洗脱效果仍不尽人意。整体而言 10 mL 甲苯的洗脱效果最突出,因此后续实验中此柱的洗脱溶剂定为 10 mL 甲苯。

石墨化炭黑小柱的洗脱结果(见表 3)表明,甲苯的洗脱效果较好,且 10 mL 用量已足够。丙酮/正己烷(1:1, v/v)和二氯甲烷/正己烷(1:1, v/v)不能有效地将六氯苯从柱上洗脱,故后续实验选择 10 mL 甲苯作为该柱的洗脱溶剂。

氧化铝小柱的洗脱结果(见表 4)表明,二氯甲

烷/正己烷(1:9, v/v)作洗脱溶剂时,六氯苯的回收率约为 30%, α -HCH 和 γ -HCH 的回收率约为 40%,其他均>50%。10 mL 正己烷作洗脱溶剂时,不能将硫丹-II 和 δ -HCH 从柱上洗脱,可能是正己烷极性太弱所致,而追加的 5 mL 二氯甲烷/正己烷(2:8, v/v)洗脱溶剂下 δ -HCH 和硫丹-II 的回收率高达 60%~80%。考虑到整体洗脱效果和简化操作,后续实验选择 15 mL 二氯甲烷/正己烷(1:9, v/v)作为氧化铝小柱的洗脱溶剂。

硅胶小柱的洗脱结果(见表 5)表明,二氯甲烷/正己烷(1:1, v/v)的洗脱效果较好,化合物回收率均在 46% 以上(五氯苯的回收率为 33%),且 10 mL 用量已足够。与氧化铝小柱相似,正己烷也不能有效地将硫丹-II 和 δ -HCH 从硅胶柱上洗脱,且 β -HCH 的回收率仅为 6%。追加 5 mL 二氯甲烷后,狄氏剂、异狄氏剂回收率增加, β -HCH、 δ -HCH 和硫丹-II 的回收率大大增加。考虑整体洗脱效果和简化操作,后续实验选择 10 mL 二氯甲烷/正己烷(1:1, v/v)作为此柱的洗脱溶剂。

表 2 佛罗里硅土小柱在不同溶剂洗脱下的替代标回收率

Table 2 Surrogate standard recoveries of florisol cartridge with different elution solvents

Compound	Recoveries/%							
	Acetone/hexane (1:9, v/v)		Toluene		Dichloromethane/hexane (2:8, v/v)			
	10 mL	Additional 5 mL	10 mL	Additional 5 mL	10 mL	Additional 5 mL	Additional 10 mL dichloromethane/hexane (3:7, v/v)	
¹³ C ₆ -PeCB	39	0	75	0	28	0		0
¹³ C ₆ -HCB	34	0	61	0	30	0		0
¹³ C ₆ - α -HCH	53	0	75	0	43	0		0
¹³ C ₆ - γ -HCH	57	0	70	0	46	0		0
¹³ C ₆ - β -HCH	58	0	53	0	52	0		0
¹³ C ₆ - δ -HCH	67	0	84	0	68	0		0
¹³ C ₁₀ -Heptachlor	56	0	60	0	45	0		0
¹³ C ₁₂ -Aldrin	59	0	84	0	49	0		0
¹³ C ₁₀ -Oxychlorane	60	0	83	0	55	0		0
¹³ C ₁₀ - <i>cis</i> -Heptachlor epoxide	65	0	78	0	51	5		1
¹³ C ₁₀ - <i>trans</i> -Chlordane	54	0	64	0	50	0		0
¹³ C ₁₂ -2,4'-DDE	77	0	98	0	73	0		0
¹³ C ₁₀ - <i>trans</i> -Nonachlor	49	0	47	0	47	0		0
¹³ C ₉ -Endosulfan-I	65	0	80	0	5	12		53
¹³ C ₁₂ -4,4'-DDE	78	0	92	0	75	0		0
¹³ C ₁₂ -Dieldrin	67	0	100	0	1	8		60
¹³ C ₁₂ -2,4'-DDD	89	0	91	0	89	0		0
¹³ C ₁₂ -Endrin	82	0	83	0	2	5		70
¹³ C ₁₂ -2,4'-DDT	91	0	61	0	88	0		0
¹³ C ₁₀ - <i>cis</i> -Nonachlor	56	0	41	0	54	0		0
¹³ C ₁₂ -4,4'-DDD	94	0	86	0	95	0		0
¹³ C ₉ -Endosulfan-II	70	0	79	0	0	0		7
¹³ C ₁₂ -4,4'-DDT	98	0	51	0	93	0		0
¹³ C ₁₀ -Mirex	80	0	76	0	77	0		0

表 3 石墨化炭黑小柱在不同溶剂洗脱下的替代标回收率

Table 3 Surrogate standard recoveries of graphitized carbon black cartridge with different elution solvents

Compound	Recoveries/%					
	Toluene		Acetone/hexane (1:1, v/v)		Dichloromethane/hexane (1:1, v/v)	
	10 mL	Additional 5 mL	10 mL	Additional 5 mL	10 mL	Additional 5 mL
¹³ C ₆ -PeCB	61	1	0	0	13	2
¹³ C ₆ -HCB	104	1	0	0	0	0
¹³ C ₆ -α-HCH	56	1	45	0	47	0
¹³ C ₆ -γ-HCH	55	1	54	0	52	1
¹³ C ₆ -β-HCH	49	1	66	0	61	1
¹³ C ₆ -δ-HCH	55	1	80	0	76	1
¹³ C ₁₀ -Heptachlor	83	1	62	0	59	1
¹³ C ₁₂ -Aldrin	83	1	63	0	62	0
¹³ C ₁₀ -Oxychlorane	102	1	75	0	79	1
¹³ C ₁₀ - <i>cis</i> -Heptachlorepoide	79	1	79	0	81	1
¹³ C ₁₀ - <i>trans</i> -Chlordane	113	1	77	0	79	1
¹³ C ₁₂ -2,4'-DDE	87	1	93	0	97	1
¹³ C ₁₀ - <i>trans</i> -Nonachlor	150	1	73	0	72	1
¹³ C ₉ -Endosulfan- I	67	1	84	0	91	1
¹³ C ₁₂ -4,4'-DDE	74	1	97	0	102	1
¹³ C ₁₂ -Dieldrin	80	1	86	0	94	1
¹³ C ₁₂ -2,4'-DDD	87	1	105	0	114	2
¹³ C ₁₂ -Endrin	79	0	103	0	102	1
¹³ C ₁₂ -2,4'-DDT	77	1	99	0	103	1
¹³ C ₁₀ - <i>cis</i> -Nonachlor	133	1	73	0	76	1
¹³ C ₁₂ -4,4'-DDD	81	1	110	0	119	2
¹³ C ₉ -Endosulfan- II	74	1	96	1	101	1
¹³ C ₁₂ -4,4'-DDT	80	1	108	0	110	1
¹³ C ₁₀ -Mirex	72	1	88	0	94	1

表 4 氧化铝小柱在不同溶剂洗脱下的替代标回收率

Table 4 Surrogate standard recoveries of alumina cartridge with different elution solvents

Compound	Recoveries/%			
	Dichloromethane/hexane (1:9, v/v)		Hexane	
	10 mL	Additional 5 mL	10 mL	Additional 5 mL dichloromethane/hexane (2:8, v/v)
¹³ C ₆ -PeCB	25	0	28	0
¹³ C ₆ -HCB	30	0	31	0
¹³ C ₆ -α-HCH	40	0	41	0
¹³ C ₆ -γ-HCH	42	0	43	0
¹³ C ₆ -β-HCH	50	0	35	12
¹³ C ₆ -δ-HCH	58	3	0	66
¹³ C ₁₀ -Heptachlor	50	0	48	0
¹³ C ₁₂ -Aldrin	56	0	56	0
¹³ C ₁₀ -Oxychlorane	62	0	56	0
¹³ C ₁₀ - <i>cis</i> -Heptachlor epoxide	65	0	61	0
¹³ C ₁₀ - <i>trans</i> -Chlordane	55	0	50	0
¹³ C ₁₂ -2,4'-DDE	78	0	71	0
¹³ C ₁₀ - <i>trans</i> -Nonachlor	51	0	45	0
¹³ C ₉ -Endosulfan- I	65	0	59	1
¹³ C ₁₂ -4,4'-DDE	82	0	73	0
¹³ C ₁₂ -Dieldrin	74	0	69	0
¹³ C ₁₂ -2,4'-DDD	93	0	84	0
¹³ C ₁₂ -Endrin	84	0	68	0
¹³ C ₁₂ -2,4'-DDT	97	0	85	0
¹³ C ₁₀ - <i>cis</i> -Nonachlor	60	0	53	0
¹³ C ₁₂ -4,4'-DDD	102	0	89	0
¹³ C ₉ -Endosulfan- II	55	14	1	71
¹³ C ₁₂ -4,4'-DDT	104	0	87	0
¹³ C ₁₀ -Mirex	83	0	75	0

表 5 硅胶小柱在不同溶剂洗脱下的替代标回收率
Table 5 Surrogate standard recoveries of silica cartridge with different elution solvents

Compound	Recoveries/%			
	Dichloromethane/hexane (1:1, v/v)		Hexane	
	10 mL	Additional 5 mL	10 mL	Additional 5 mL dichloromethane
¹³ C ₆ -PeCB	33	0	29	0
¹³ C ₆ -HCB	46	0	38	0
¹³ C ₆ -α-HCH	46	0	42	1
¹³ C ₆ -γ-HCH	43	0	47	1
¹³ C ₆ -β-HCH	50	1	6	60
¹³ C ₆ -δ-HCH	60	1	0	76
¹³ C ₁₀ -Heptachlor	62	0	55	0
¹³ C ₁₂ -Aldrin	65	0	60	0
¹³ C ₁₀ -Oxychlorane	70	0	74	1
¹³ C ₁₀ -cis-Heptachlor epoxide	69	1	49	28
¹³ C ₁₀ -trans-Chlordane	72	0	78	1
¹³ C ₁₂ -2,4'-DDE	79	1	86	1
¹³ C ₁₀ -trans-Nonachlor	67	1	74	1
¹³ C ₉ -Endosulfan- I	71	1	66	5
¹³ C ₁₂ -4,4'-DDE	80	1	91	0
¹³ C ₁₂ -Dieldrin	73	1	36	47
¹³ C ₁₂ -2,4'-DDD	84	1	94	1
¹³ C ₁₂ -Endrin	67	1	54	28
¹³ C ₁₂ -2,4'-DDT	84	0	90	0
¹³ C ₁₀ -cis-Nonachlor	67	1	63	14
¹³ C ₁₂ -4,4'-DDD	84	1	97	2
¹³ C ₉ -Endosulfan- II	73	1	0	76
¹³ C ₁₂ -4,4'-DDT	83	0	93	1
¹³ C ₁₀ -Mirex	71	0	85	0

2.2.2 单一填料柱净化

多个空气样品经过提取后,合并提取液,浓缩并定容至 10 mL,制备统一样品溶液。取 0.5 mL ($n=2$),加入 1 ng 替代标,混匀后分别用弗罗里硅土、石墨化炭黑、氧化铝和硅胶小柱进行净化,各净化柱均用上文中的较优洗脱溶液进行洗脱,将流出液收集后浓缩至 20 μL,结果发现浓缩液色素均较重,即单一净化柱不能有效去除样品溶液色素,为减少色素对仪器测样干扰,本文进一步研究了组合净化柱。

2.2.3 组合填料柱净化

将统一样品溶液分别进行组合净化,组合方式

及净化效果见表 6。弗罗里硅土小柱和石墨化炭黑小柱组合能够很好地去掉样品色素,减弱对目标物出峰的干扰,延长色谱柱寿命。进一步将经过弗罗里硅土小柱和石墨化炭黑小柱组合净化的大气样品溶液进行仪器测定,样品中 OCPs 的替代标回收率为 33.9%~155%。

2.3 方法适用性

2.3.1 穿透试验

AAS 因能通过采样泵加流量计精确控制大气采样量,而广泛应用于大气 OCPs 采样。AAS 吸附介质多为滤膜+PUF 模式,但是一些 OCPs 挥发性

表 6 组合固相萃取小柱对空气样品中 OCPs 的净化效果
Table 6 Cleaning effects of cartridge combination on OCPs in air samples

Cartridge combination	Elution solvent	Pigments remain
Silica→florisil	silica: 10 mL dichloromethane/hexane (1:1, v/v); florisil: 10 mL toluene	yes
Silica→graphitized carbon black	silica: 10 mL dichloromethane/hexane (1:1, v/v); graphitized carbon black: 10 mL toluene	yes
Silica→alumina	silica: 10 mL dichloromethane/hexane (1:1, v/v); alumina: 15 mL dichloromethane/hexane (1:9, v/v)	yes
Florisil→alumina	florisil: 10 mL toluene; alumina: 15 mL dichloromethane/hexane (1:9, v/v)	yes
Florisil→graphitized carbon black	florisil: 10 mL toluene; graphitized carbon black: 10 mL toluene	no
Alumina→graphitized carbon black	alumina: 15 mL dichloromethane/hexane (1:9, v/v); graphitized carbon black: 10 mL toluene	yes

较强,采样时容易在 PUF 上发生穿透,所以现场采样前应先确定有效采样体积。确定方式主要有以下两种^[14]:一种是穿透试验,即串联 2 块及以上 PUF 进行采样,计算下层 PUF 吸附目标物量相对上层 PUF 或总 PUF 的比值^[16,27,28];另一种是动态保留试验,即向 PUF 气体流入端加标,采样后计算加标回收率^[15,19,35]。其中穿透试验的方法在研究中更常见,但穿透标准不一,如穿透限值存在下层 PUF 占上层 PUF 的 33.3%^[28]或 50%^[27]、下层 PUF 占总 PUF 比值 5%^[36]等多种说法(见附表 1,详见 <http://www.chrom-China.com/>)。鉴于 PUF 对 HCB 和 α -HCH 的吸附容量极易受环境温、湿度影响^[16,27],本文采用穿透试验的方式,并选择定义下层 PUF 吸附目标物量占总 PUF 比值(简称“穿透比率”)5%即为穿透这一严格标准,以增强本次实验结果的指导意义。

2019 年 2 月,在中国环境监测总站(北京)3 楼楼顶进行穿透试验,以滤膜+PUF/PUF 模式,多台主动采样器同时采集不同体积的空气样品,各体积

采集 1 个平行样。采样结束后,分别测定两层 PUF 中 OCPs 的含量,计算下层 PUF 吸附的目标物占总 PUF 吸附量的比值,结果见表 7(采样体积已换算为标准状态(101.325 kPa, 273 K)对应的体积)。

由表 7 可见,样品中下层 PUF 吸附的五氯苯和六氯苯的量在总 PUF 中占比均较大。其中五氯苯在采样体积为 15 m³ 时,穿透比率也已超出 40%,即严重穿透;六氯苯在低于 50 m³ 时,穿透比率较低,其中在 15 m³ 时为 5%; α -六六六在 53 和 387 m³ 时,穿透比率为 13%,在采样体积 ≤ 677 m³ 时,穿透比率均 $< 5\%$,可能是期间天气变化较大所致;其他 OCPs 在采样体积为 607 m³ 时,整体而言穿透比率均在 5% 左右。

综上,五氯苯不适合滤膜+PUF/PUF 的采样模式,建议与 XAD(苯乙烯-二乙烯基苯共聚物)或 Tenax-TA(聚 2,6-二苯基对苯醌)等强吸附性能介质相结合。对于 α -HCH,采样时应尽量避开高湿度天气。在相似采样环境下安装单块 PUF,六氯苯的采样体积应 ≤ 15 m³,双块 PUF 时应 ≤ 30 m³。其他

表 7 穿透实验中下层 PUF 吸附目标物占总 PUF 吸附量的比值

Table 7 Ratio of OCPs adsorbed by the bottom polyurethane foam (PUF) to total PUFs during the breakthrough tests

Compound	Ratios at different sampling volumes/%											
	15 m ³	30 m ³	53 m ³	181 m ³	271 m ³	387 m ³	486 m ³	607 m ³	677 m ³	780 m ³	892 m ³	958 m ³
PeCB	43	48	53	49	53	51	59	58	50	41	36	35
HCB	5.0	25	37	45	43	49	24	30	41	55	61	59
α -HCH	N.D.	1.0	13	3.0	4.4	13	0.5	0.9	4.3	10	28	20
γ -HCH	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.1	1.3	6.8	0.8	2.8	3.4
β -HCH	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.1	3.5
δ -HCH	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.8	0.9
Heptachlor	5.0	N.D.	N.D.	N.D.	N.D.	N.D.	0.6	0.9	7.0	0.4	7.2	1.8
Aldrin	2.2	1.6	1.1	1.0	1.5	2.8	1.6	1.6	3.8	1.3	1.6	1.9
Oxychlorane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.4	4.3	3.6	3.5	2.0	2.5
<i>cis</i> -Heptachlor epoxide	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.4	2.3	2.2	2.1	1.2	1.5
<i>trans</i> -Heptachlor epoxide	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
<i>trans</i> -Chlordane	N.D.	1.5	1.5	3.4	2.7	2.0	4.2	4.4	5.3	2.5	1.4	2.5
2,4'-DDE	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.0	3.2	2.1	1.2	1.0	0.9
<i>trans</i> -Nonachlor	1.6	0.9	1.7	2.9	1.3	1.2	1.8	2.1	2.8	1.6	0.2	1.2
<i>cis</i> -Chlordane	N.D.	N.D.	N.D.	2.4	2.7	1.5	2.7	1.0	3.5	0.9	0.5	1.5
Endosulfan- I	1.7	0.6	N.D.	0.2	0.3	0.2	5.4	5.1	6.7	3.9	0.4	1.5
4,4'-DDE	N.D.	N.D.	N.D.	0.3	N.D.	0.2	1.6	1.4	1.7	0.3	0.2	0.2
Dieldrin	N.D.	N.D.	N.D.	3.4	3.7	2.1	2.9	2.4	2.8	5.4	1.2	2.7
2,4'-DDD	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	8.4	3.6	5.0
Endrin	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	8.4	7.5
2,4'-DDT	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.8	3.3	1.5	0.9	1.0
<i>cis</i> -Nonachlor	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
4,4'-DDD	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.7	6.7
Endosulfan- II	N.D.	9.5	N.D.	0.7	2.3	0.9	0.0	5.3	N.D.	N.D.	N.D.	N.D.
4,4'-DDT	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.4	1.0	1.3
Mirex	2.9	1.7	1.5	0.4	0.6	0.5	0.8	1.5	2.2	0.6	0.3	0.5

N.D.: not detected in the lower layer.

OCPs 采样体积为, 单块 PUF 应 $\leq 600 \text{ m}^3$, 双块 PUF 应 $\leq 1\,200 \text{ m}^3$ 。

2.3.2 平均相对响应因子、线性范围、相关系数和检出限

测定 0.4~800 $\mu\text{g/L}$ 的 OCPs 校准溶液, 计算目标物和替代标的平均相对响应因子, 其对应的 RSD $\leq 20\%$, 线性相关系数 (R^2) 均 > 0.992 , 详见表 8。按照 HJ 168 要求, 计算方法的检出限 (MDL): 按照样品分析的全流程重复测定 7 次空白试样, 测定结果以浓度表示, 其中六氯苯按采样体积 30 m^3 计算, 其他 24 种 OCPs 按 $1\,200 \text{ m}^3$ 计算, 得出测定结果的标准偏差 (S), MDL 为 $3.143S$, 对空白试验中未检出的目标物进行加标后测定, 判断各目标物 MDL 的合理性, 必要时调整加标量。六氯苯的 MDL 为 0.7 pg/m^3 , 其他 24 种 OCPs 的 MDL 为 $0.002 \sim 0.007 \text{ pg/m}^3$, 详见表 8。

2.3.3 精密度和回收率

向空白滤膜和 PUF 中加入低 (100 pg)、中 (400 pg)、高 (15 ng) 3 个水平的 OCPs 标准物质 ($n=6$), 按照实际样品处理流程进行提取、净化和仪器分析,

表 8 25 种 OCPs 的方法检出限、线性相关系数和加标回收率
Table 8 Method detection limits (MDL), liner correlation coefficients (R^2) and recoveries of the 25 OCPs

Compound	MDL/ (pg/m^3)	R^2	Recovery/ %
HCB	0.7	0.9986	90.2-125
α -HCH	0.006	0.9997	88.6-135
γ -HCH	0.007	0.9998	92.9-121
β -HCH	0.004	0.9999	97.8-117
δ -HCH	0.004	0.9999	92.0-110
Heptachlor	0.003	0.9994	77.6-102
Aldrin	0.006	1.0000	82.1-98.6
Oxychlorane	0.003	0.9996	81.4-124
<i>cis</i> -Heptachlor epoxide	0.002	0.9999	83.3-103
<i>trans</i> -Heptachlor epoxide	0.002	0.9969	70.9-104
<i>trans</i> -Chlordane	0.006	0.9994	76.8-120
2,4'-DDE	0.003	0.9999	76.0-102
<i>trans</i> -Nonachlor	0.003	0.9998	76.5-130
<i>cis</i> -Chlordane	0.004	0.9987	76.2-118
Endosulfan- I	0.004	0.9929	67.2-120
4,4'-DDE	0.004	0.9999	80.0-102
Dieldrin	0.003	0.9997	82.4-104
2,4'-DDD	0.003	0.9999	74.9-98.4
Endrin	0.003	0.9990	75.7-107
2,4'-DDT	0.003	0.9995	82.6-108
<i>cis</i> -Nonachlor	0.002	0.9993	75.9-130
4,4'-DDD	0.003	0.9998	84.8-98.2
Endosulfan- II	0.005	0.9973	81.5-115
4,4'-DDT	0.003	0.9990	82.2-99.3
Mirex	0.003	0.9999	85.6-101

计算同一加标水平下 OCPs 测定值的 RSD。3 个加标水平下, 测定值的 RSD 均在 0.64%~16% 之间, 加标回收率为 67.2%~135%, 详见表 8。

2.4 空气样品的测定结果

根据穿透情况, 采集 15~30 m^3 的空气样品, 测得六氯苯的浓度为 514~563 pg/m^3 。采集约 600 m^3 的空气样品, 测得除反式-环氧七氯、异狄氏剂、顺式-九氯和 4,4'-滴滴滴在部分样品中未检出外, 其他 OCPs 均为 100% 检出, 浓度为 0.01~18.9 pg/m^3 , 低于现有标准 HJ 900 的检出限 (0.03~0.07 ng/m^3), 所有样品的替代标回收率为 33.9%~155%。

3 结论

本文建立了弗罗里硅土小柱与石墨化炭黑小柱组合净化, 中等极性 Rtx-CL Pesticides2 色谱柱分离, 同位素稀释-HRGC-HRMS 分析大气 25 种 OCPs 的方法。空白样品进行低、中和高 3 个水平的加标试验, 测定结果的 RSD 为 0.64%~16%, 加标回收率为 67.2%~135%。实际样品分析中替代标的回收率为 33.9%~155%。穿透试验确定六氯苯的有效采样体积 (标态) 应 $\leq 30 \text{ m}^3$, 其他 24 种 OCPs 应 $\leq 1\,200 \text{ m}^3$ 。以上述体积计算, 方法的检出限为 0.002~0.7 pg/m^3 。该方法较系统、全面, 测定干扰因素较少, 回收率较好, 检出限能很好地满足当前大气中痕量 OCPs 的测定需求, 可用于履约监测以及大规模大气样品的调查。

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