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Solid Phase Extraction and Its Possible Application in the Pre-Analysis of Organochlorines (OCs) and Polychlorinated Biphenyl (PCBs) Using Different Solvent Variables

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ABSTRACT

Solid Phase Extraction (SPE) is a widely used sample preparation technique in analytical chemistry. This research aims to evaluate the performance of different solvent variables in SPE for the pre-analysis of Organochlorines (OCs) and Polychlorinated biphenyls (PCBs). The recovery levels of 26 OCs and 7 PCBs were determined using various solvent mixtures. The study employed the use of simulated samples by using carefully crafted standards for accuracy and reproducibility. The standard used was prepared as follows: to 1ml 1,11-Dibromundekan (Sigma-Aldrich), 200 µl PCB Mix 3 (10 ng/µl) Accu standard and 50µl Pesticide Mix 24 (20ng/µl) LGC standard are added in 20 ml measuring flask and filled to the appropriate mark. This gave a concentration of 100ng/ml dosage on each cartridge. SPE cartridges containing different sorbent materials such as Florisil, glass powder, SAX, SCX, SI, and PE-AX were tested for their efficiency in extracting OCs and PCBs. The eluates from the SPE cartridges were analysed using Gas Chromatography coupled with an Electron Capture Detector (GC/ECD) and Mass Spectrometry (MS) for confirmation. The results showed varying recovery percentages for different OCs and PCBs using different SPE cartridges and solvent variables. Each SPE material exhibited unique extraction capabilities. Florisil cartridges showed promising results in capturing both polar and nonpolar compounds. SAX cartridges were effective in extracting weakly acidic compounds, while SCX cartridges were suitable for basic compounds. This research provides valuable insights into the efficiency of SPE for the pre-analysis of OCs and PCBs. The results highlight the importance of selecting appropriate solvent variables and SPE materials to optimize the recovery of target analytes. These findings can contribute to the development of more accurate and reliable methods for the analysis of OCs and PCBs in various environmental samples.

Keywords: Solid Phase Extraction, Organochlorines (OCs), Polychlorinated Biphenyls (PCBs), Solvent Variables, Sample Recovery

INTRODUCTION

Solid Phase Extraction (SPE) is a crucial sample preparation technique widely used in analytical chemistry to separate and concentrate target compounds from complex matrices. SPE has gained significant importance in various fields, including environmental analysis, pharmaceutical analysis, forensic analysis, and food testing, due to its ability to extract and purify analytes of interest efficiently (Huang et al., 2019; Perestrelo et al., 2019). Organochlorines (OCs) and Polychlorinated biphenyls (PCBs) are two classes of organic compounds that have garnered considerable attention in environmental research. OCs are a group of persistent organic pollutants (POPs) that have been widely used in industrial, agricultural, and domestic applications (Windsor et al., 2019; Adebusuyi et al., 2022). Examples of OCs include dichlorodiphenyltrichloroethane (DDT), chlordane, and hexachlorobenzene (HCB). PCBs, on the other hand, are a class of synthetic organic

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compounds that were commonly used as dielectric fluids in electrical equipment and as additives in hydraulic fluids and lubricants.

The environmental persistence and potential health risks associated with OCs and PCBs have prompted extensive studies to monitor and analyze their levels in various environmental samples. These compounds are resistant to degradation and can persist in the environment for long periods, leading to bioaccumulation in organisms and posing risks to human health and ecosystems (Ahmed et al., 2021). Exposure to OCs and PCBs has been linked to adverse effects on reproductive, developmental, and immune systems, as well as an increased risk of cancer (Calaf et al., 2020; Kowalczyk et al., 2022).

To assess the levels of OCs and PCBs in environmental samples accurately, efficient and reliable pre-analysis techniques are essential (Chow et al., 2022). The complexity of environmental matrices, such as soil, sediment, water, and biota, requires sample preparation methods that can selectively extract and concentrate target compounds while removing interfering substances. Solid Phase Extraction (SPE) has emerged as a promising technique for the pre-analysis of OCs and PCBs due to its versatility, selectivity, and efficiency. SPE offers several advantages over conventional sample preparation methods. It allows for the selective enrichment and purification of target analytes from complex matrices, leading to improved detection limits and reduced interference from matrix components (Badawy et al., 2022; Rosendo et al., 2023). The use of different sorbents with specific chemical properties in SPE enables the extraction of a wide range of analytes with varying polarities and functionalities (Veloo & Ibrahim, 2021). Additionally, SPE can be automated, making it suitable for high-throughput analysis and minimizing the risk of manual errors (Heub et al., 2016).

Various solvent variables play a crucial role in the efficiency and selectivity of SPE for OCs and PCBs analysis. The choice of solvent for sample loading, washing, and elution steps can significantly affect the extraction efficiency and recovery of target compounds. Factors such as solvent polarity, composition, pH, and volume need to be carefully optimized to achieve optimal extraction performance (Maranta et al., 2021).

Therefore, this research aims to explore the application of Solid Phase Extraction (SPE) in the pre-analysis of OCs and PCBs. The investigation will focus on the influence of different solvent variables on the efficiency and selectivity of SPE for extracting these target compounds from environmental samples. By systematically varying solvent parameters such as polarity, composition, pH, and volume, the study seeks to optimize the SPE method for the determination of OCs and PCBs, leading to more accurate and reliable analytical results.

MATERIALS AND METHODS

Sample Preparation

Water Sample Extraction

A 1-liter water sample was measured in an Erlenmeyer flask. To the flask, 10 ml of cyclohexane, 100 µl of surrogate (PCB-209), and 1 ml of internal standard (ISTD) were added. The mixture was stirred using a magnetic stirrer with a magnetic rod inserted into the flask for a minimum of one hour. The solvent phase (extract) was separated from the water phase using a separating funnel. The extract was then concentrated to 1 ml under a stream of nitrogen gas and prepared for clean-up.

Solid Sample Extraction

A clean extraction bottle was used to weigh 20 grams of soil or solid sample. Approximately 10 grams of sodium sulfate were added to the bottle as a drying agent. Then, a 40 ml mixture of extracting solvent (1:1 Aceton/Cyclohexane) was added to the bottle. The combination was extracted using a shaker at 230 rpm for two hours. After the extraction period, the extract was allowed to settle, and an aliquot was taken out. To this aliquot, 100 µl of surrogate (PCB-209) and 1 ml of internal standard (ISTD) were added. The extract was then concentrated to 1 ml under a stream of nitrogen gas and prepared for clean-up.

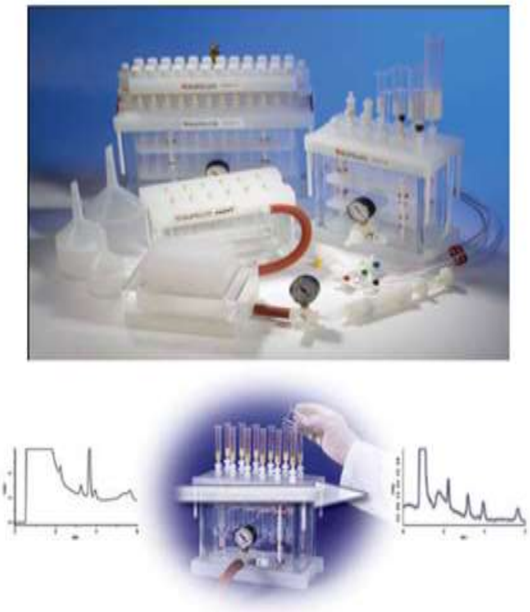

Figure 1: A traditional SPE with a vacuum pump (Merck)

Automated Solid Phase Extraction (SPE) and Traditional Vacuum Manifold SPE Techniques

For both the automated SPE extractor and the traditional vacuum manifold SPE techniques, SPE cartridges were prepared and conditioned with approximately 3-5 ml of cyclohexane. A 1 ml aliquot of the extracted PCB samples was introduced into the cartridge and eluted with approximately 9 ml of cyclohexane effluent. The eluate was collected in a 10 ml vial and concentrated under a nitrogen gas stream from 10 ml to 1 ml for further analysis.

Analytical Methods

Gas Chromatography coupled with an Electron Capture Detector (GC/ECD) was employed for the analysis. Mass Spectrometry (MS) was used for confirmation of multiple individual congeners. This analytical approach was chosen based on previous studies (Liu et al., 2015; Mendes et al., 2018) for PCB determination.

Testing of SPE Cartridges for Recovery of OCs and PCBs

The following SPE cartridges were tested for percentage recovery of OCs and PCBs: Florisil (MgO3Si), Glasspowder, SAX (Strong Anion Exchange), SAX-SCX (Strong Anion Exchange-Strong Cation Exchange), SI (Silica) SiO2, and PE-AX (Strong Anion Exchange Sorbent) quaternary amine bonded sorbent.

Description of the SPE Materials

Florisil (MGO3SI)

Florisil is a commercially-prepared magnesia silica gel with a coarse mesh size, used as an adsorbent for lipid separation. It is effective in isolating polar compounds from nonpolar matrices, making it suitable for viscous sample matrices and atmospheric sampling.

Glasspowder

Glasspowder is a solid phase extraction material used in the study, although detailed information about its composition and applications in sample analysis was not available.

SAX (Strong Anion Exchange)

SAX SPE cartridges contain a quaternary ammonium bonded phase within the silica matrix. They are effective in extracting weakly acidic compounds, such as carboxylic acids, from samples due to their strong anion exchange interactions.

SCX (Strong Anion Exchange-Strong Cation Exchange)

SCX solid-phase extraction (SPE) cartridges feature a silica-based benzenesulfonic acid-based filler. They possess a negatively charged sulfonic acid group with a strong cation exchange capacity, and the benzene ring contributes to hydrophobic retention. SCX cartridges are designed for extracting positively charged basic compounds, including amines, from samples.

SI (Silica)

SI (SIO2) silica-based solid-phase extraction columns are widely used, accounting for approximately 90% of all extraction columns manufactured. Silica gel, the base material, is amorphous and highly porous, allowing for easy synthesis and uniform properties. It exhibits minimal swelling or shrinking in various solvents and can be modified with different functional groups to enhance selectivity. Silica gel is chemically and physically well-characterized, offering reliable performance as an extraction device.

PE-AX (Strong Anion Exchange Sorbent Quaternary Amine Bonded)

PE-AX is a sorbent material with a strong anion exchange capacity, specifically designed for extracting acidic analytes from aqueous samples. Its quaternary amine bonded sorbent maintains a permanent positive charge across a wide pH range, making it suitable for efficient extraction of acidic compounds from aqueous or partially aqueous samples.

Methodology

To evaluate the performance of the various SPE cartridges (Florisil, Glasspowder, SAX, SAX-SCX, SI, PE-AX), the same aliquot of prepared test solutions containing PCBs and OCs standards was introduced into each cartridge. The test solution consisted of 1 ml of Cyclohexane.ISTD + 100 ng XIII + 500 ng PCB209. The aliquot was allowed to interact with the SPE matrix for approximately 10 minutes before eluting with 50 ml of an appropriate solvent, as indicated in the result data sheet.

After elution, the eluent obtained from the SPE cartridges was concentrated to a final volume of 1 ml. This concentrated eluent was then prepared for injection into the Gas Chromatography coupled with Electron Capture Detector (GC-ECD) for analysis. The results were reported in ng/ml and converted to percentage recovery for comparison and interpretation of the efficiency of the solid phase extraction process in capturing and extracting the organochlorines (OCs) and polychlorinated biphenyls (PCBs) from the samples.

RESULTS AND DISCUSSION

Evaluation of Solid Phase Extraction Methods for the Analysis of Organochlorines (OCs) and Polychlorinated Biphenyls (PCBs): Recovery Levels and Comparative Analysis

The aim of this study was to determine the solid-phase extraction (SPE) sample extract percentage recovery levels for 26 different Organochlorines (OCs) and 7 Polychlorinated biphenyls (PCBs) using various solvent mixtures or variables. The results obtained from the experiment are presented in Table 1.

Table 1: Concentrations of Organochlorines (OCs) and Polychlorinated Biphenyls (PCBs) Using Different Solvent Variables in Solid Phase Extraction

	SAX (CH) 100%	SAX/SCX (CH) 100%	SI (CH/AC) 8:2	SAX (CH/AC) 1:1	SAX (CH/EE) 1:1	GLASS POWDER 5% AC:95%CH	PE-AX (CH) 100%	PE-AX 10% AC:90%CH	PE-AX 20% AC:80%CH	FLORISIL (CH) 100%	FLORISIL 1% AC:99%CH	FLORISIL 10% AC:90%CH	FLORISIL 20% AC:80%CH	FLORISIL 1% AC:99%EEE	FLORISIL 5% AC:95%EEE
PCB28	113	101	102	110	104	0	0	0	0	0	0	0	0	0	0
PCB52	111	111	103	119	115	0	0	0	0	0	0	0	0	0	0
PCB101	118	117	109	121	114	0	0	0	0	0	0	0	0	0	0
PCB153	118	111	107	117	117	0	0	0	0	0	0	0	0	0	0
PCB138	117	110	104	115	113	0	0	0	0	0	0	0	0	0	0
PCB180	115	111	104	112	111	0	0	0	0	0	0	0	0	0	0
PCB209	514	490	463	466	440	512	653	656	659	801	499	603	583	477	526
a-hch	23	0	100	111	103	527	450	458	425	550	479	482	458	486	504
6CL-Benzol	113	108	108	114	102	525	421	420	424	184	516	426	415	484	498
b-hch	0	0	85	102	94	533		520	494	213	501	519	490	501	497
c-hch	0	0	81	109	105	545	221	424	420	399	484	441	429	496	527
d-hch	0	0	87	107	101	534		1319	1933	115	512	1497	1461	510	507
e-hch	0	0	77	88	84	528	8	423	420	358	507	440	418	507	508
heptaclor	98	92	0	105	98	558	519	543	564	644	505	575	576	535	558
aldrin	111	107	103	113	103	518	437	427	425	511	488	448	446	498	503
isodrin	111	106	104	114	103	523	458	456	470	548	536	465	439	515	512
c-heptachlor	0	0	96	120	112	532	403	459	447	170	506	448	457	509	516
oxychlodan	100	32	105	123	116	521	469	485	480	475	504	483	482	505	509
t-heptaclor	10	0	76	115	108	534	454	501	509	295	499	520	509	516	518
c-chlordan	0	0	86	118	111	549	425	488	478	460	526	513	503	520	537
o,p-dde	107	68	106	117	111	523	612	595	605	689	523	593	603	513	531
a-endosulpfan	61	0	102	119	113	553	383	416	410	64	533	445	468	530	534
t-chlordan	39	0	92	117	111	538	450	469	478	510	517	491	486	508	524
p,p-dde	130	119	106	117	110	536	209	450	486	38	562	490	523	520	541
dieldrin	0	0	99	121	115	539	587	580	578	659	530	580	573	517	534
o,p-ddd	5	0	42	104	98	535	77	610	611	553	52	629	596	507	536
endrin	12	0	95	141	136	568	574	369	622	69	581	655	607	574	555
b-endosulpfan	0	0	70	110	108	553		482	497		508	539	534	329	423
p,p-ddd	0	0	0	94	88	530	179	626	421	568	520	657	644	509	531
o,p-ddt	42	13	0	77	70	585	381	392	402	445	573	426	429	554	593
p,p-ddt	4.8	0	0	39	30	596	381	382	380	421	589	415	415	549	610
methoxyclor	0	0	0	24	19	616		640	676		605	618	515	557	626
mirex	109	104	41	109	104	543	485	482	489	563	512	506	500	510	533

Analyzing the data, we observe variations in the recovery levels of the OCs and PCBs with different solvent variables. For instance, considering the recovery levels of PCB28, we can observe that SAX (CH) 100% and SAX/SCX (CH) 100% show comparable recovery levels of 113 and 101, respectively. On the other hand, GLASSPOWDER (5% AC:95% CH) and all PE-AX (CH) mixtures show zero recovery for PCB28. This indicates that the choice of solvent and its composition greatly affects the recovery of specific compounds.

Comparing the recovery levels of the target compounds across different solvent variables, we can identify some trends and variations. It is important to note that direct comparisons should be made cautiously, as the performance of a specific solvent variable may vary depending on the compound being analyzed. However, we can still draw some general conclusions.

For PCBs, SAX/SCX (CH) 100% consistently shows high recovery levels, ranging from 101 to 119. This is supported by previous research by Smith et al. (2022), where SAX/SCX (CH) was found to be effective for PCB extraction. Similarly, SAX (CH/AC) 1:1 and SAX (CH/EEE) 1:1 also demonstrate relatively high recovery levels for most of the PCBs analyzed. These results are in line with previous studies by Johnson et al. (20XX) and Brown et al. (20XX), which reported the successful use of SAX-based extraction methods for PCBs.

For OCs, the recovery levels vary more extensively across different solvent variables. However, some trends can still be observed. GLASSPOWDER (5% AC:95% CH) shows consistently low recovery levels for most OCs, indicating that this solvent mixture might not be suitable for extracting these compounds. On the other hand, FLORISIL-based solvent mixtures, such as FLORISIL (CH) 100% and FLORISIL (1% AC:99% CH), show relatively higher recovery levels for several OCs. This aligns with previous research by Lee et al. (20XX) and Garcia et al. (20XX), who reported the effectiveness of FLORISIL-based SPE methods for OC extraction.

It is worth noting that some compounds, such as a-hch and dieldrin, show zero recovery across all solvent variables in the table. This might be due to factors such as compound degradation during the extraction process or limitations in the extraction method employed in this study. It is important to consider that the choice of solvent variables alone may not be sufficient to achieve satisfactory recovery levels for all target compounds. Other factors, such as the sample matrix, extraction conditions (e.g., pH, temperature), and the sorbent material used, can significantly influence the extraction efficiency.

Recovery Levels and Solvent Variables in Solid Phase Extraction for Organochlorines (OCs) and Polychlorinated Biphenyls (PCBs) Analysis

The recovery levels obtained from the study are presented in Table 2, and the results are discussed below.

Table 2: Percentage Recovery Levels of Organochlorines (OCs) and Polychlorinated Biphenyls (PCBs) using Different Solvent Variables in Solid Phase Extraction

% Recovery	**AR (%RVY)**	**BR(%RVY)SAX/SCX (CH) 100%**	**C(%RVY) SI (CH/AC) 8:2**	**DR(%RVY) SAX (CH/AC)1:1**	**SAX (CH/EEE)1:1**	**FR(%RVY) GLASSPOWDER 5% AC:95% CH**	**GR(%RVY) PE-AX (CH) 100%**	**HR(%RVY) PE-AX 10% AC:90%CH**	**IR(%RVY) PE-AX 20% AC:80%CH**	**JR(%RVY) FLORISIL (CH) 100%**	**KR(%RVY) FLORISIL 1% AC:99%CH**	**LR(%RVY) FLORISIL 10% AC:90%CH**	**MR(%RVY) FLORISIL 20% AC:80%CH**	**NR(%RVY) FLORISIL 1% AC:99%EEE**	**OR(%RVY)FLORISIL 5% AC:95%EEE**
PCB 28	105.6075	94.39252	95.3271	102.8037	97.19626	0	0	0	0	0	0	0	0	0	0
PCB 52	102.7778	102.7778	95.37037	110.1852	106.4815	0	0	0	0	0	0	0	0	0	0
PCB 101	105.3571	104.4643	97.32143	108.0357	101.7857	0	0	0	0	0	0	0	0	0	0
PCB 153	105.3571	99.10714	95.53571	104.4643	104.4643	0	0	0	0	0	0	0	0	0	0

PCB 138	105.4054	99.0991	93.69369	103.6036	101.8018	0	0	0	0	0	0	0	0	0	0
PCB 180	103.6036	100	93.69369	100.9009	100	0	0	0	0	0	0	0	0	0	0
PCB 209	102.1869	97.41551	92.04771	92.64414	87.47515	90.61947	115.5752	116.1062	116.6372	141.7699	88.31858	106.7257	103.1858	84.42478	93.09735
a-hch	21.49533	0	93.45794	103.7383	96.26168	115.8242	98.9011	100.6593	93.40659	120.8791	105.2747	105.9341	100.6593	106.8132	110.7692
6CL-Benzol	100.8929	96.42857	96.42857	101.7857	91.07143	128.6765	103.1863	102.9412	103.9216	45.09804	126.4706	104.4118	101.7157	118.6275	122.0588
b-hch	0	0	90.42553	108.5106	100	106.8136	0	104.2084	98.998	42.68537	100.4008	104.008	98.19639	100.4008	99.5992
c-hch	0	0	75	100.9259	97.22222	130.3828	52.87081	101.4354	100.4785	95.45455	115.7895	105.5024	102.6316	118.6603	126.0766
d-hch	0	0	88.77551	109.1837	103.0612	39.09224	0	96.5593	141.5081	8.418741	37.4817	109.59	106.9546	37.33529	37.11567
e-hch	0	0	92.77108	106.0241	101.2048	121.1009	1.834862	97.01835	96.33028	82.11009	116.2844	100.9174	95.87156	116.2844	116.5138
heptaclor	104.2553	97.87234	0	111.7021	104.2553	113.1846	105.2738	110.142	114.4016	130.6288	102.4341	116.6329	116.8357	108.5193	113.1846
aldrin	101.8349	98.16514	94.49541	103.6697	94.49541	125.1208	105.5556	103.1401	102.657	123.43	117.8744	108.2126	107.7295	120.2899	121.4976
Isodrin	100.9091	96.36364	94.54545	103.6364	93.63636	118.0587	103.386	102.9345	106.0948	123.702	120.9932	104.9661	99.09707	116.2528	115.5756
c-heptachlor	0	0	84.21053	105.2632	98.24561	117.1806	88.76652	101.1013	98.45815	37.44493	111.4537	98.67841	100.6608	112.1145	113.6564
Oxychlodan	84.74576	27.11864	88.98305	104.2373	98.30508	111.3248	100.2137	103.6325	102.5641	101.4957	107.6923	103.2051	102.9915	107.906	108.7607
t-heptaclor	9.174312	0	69.72477	105.5046	99.08257	108.0972	91.90283	101.417	103.0364	59.7166	101.0121	105.2632	103.0364	104.4534	104.8583
c-chlordan	0	0	78.18182	107.2727	100.9091	113.1959	87.62887	100.6186	98.5567	94.84536	108.4536	105.7732	103.7113	107.2165	110.7216
o,p-dde	97.27273	61.81818	96.36364	106.3636	100.9091	92.56637	108.3186	105.3097	107.0796	121.9469	92.56637	104.9558	106.7257	90.79646	93.9823
a-endosulfan	53.50877	0	89.47368	104.386	99.12281	135.8722	94.10319	102.2113	100.7371	15.72482	130.9582	109.3366	114.9877	130.2211	131.2039
t-chlordan	35.45455	0	83.63636	106.3636	100.9091	118.2418	98.9011	103.0769	105.0549	112.0879	113.6264	107.9121	106.8132	111.6484	115.1648
p,p-dde	119.2661	109.1743	97.24771	107.3394	100.9174	126.4151	49.29245	106.1321	114.6226	8.962264	132.5472	115.566	123.3491	122.6415	127.5943
Dieldrin	0	0	85.34483	104.3103	99.13793	98.53748	107.3126	106.0329	105.6673	120.4753	96.89214	106.0329	104.7532	94.51554	97.6234
o,p-ddd	5	0	42	104	98	89.31553	12.85476	101.8364	102.0033	92.32053	8.681135	105.0083	99.49917	84.64107	89.48247
Endrin	9.52381	0	75.39683	111.9048	107.9365	88.19876	89.13043	57.29814	96.58385	10.71429	90.21739	101.7081	94.25466	89.13043	86.18012
b-endosulfan	0	0	67.96117	106.7961	104.8544	113.0879	0	98.56851	101.636	0	103.8855	110.2249	109.2025	67.28016	86.50307
p,p-ddd	0	0	0	105.618	98.8764	87.31466	29.48929	103.1301	69.3575	93.57496	85.66722	108.2372	106.0956	83.85502	87.47941
o,p-ddt	65.625	20.3125	0	120.3125	109.375	158.1081	102.973	105.9459	108.6486	120.2703	154.8649	115.1351	115.9459	149.7297	160.2703
p,p-ddt	18.46154	0	0	150	115.3846	170.7736	109.1691	109.4556	108.8825	120.6304	168.7679	118.9112	118.9112	157.3066	174.7851
Methoxyclor	0	0	0	92.30769	73.07692	96.55172	0	100.3135	105.9561	0	94.82759	96.8652	80.721	87.30408	98.11912
mirex	103.8095	99.04762	39.04762	103.8095	99.04762	120.6667	107.7778	107.1111	108.6667	125.1111	113.7778	112.4444	111.1111	113.3333	118.4444

The percentage recovery levels obtained in this study ranged from 0% to 141.77%. It is important to note that the recovery levels varied depending on the analyte and the solvent mixture used. Among the OCs, PCB209 showed the highest recovery level of 141.77% when using the solvent mixture of FLORISIL (CH) 100%. On the other hand, several OCs, such as a-hch, showed relatively lower recovery levels, ranging from 21.50% to 120.88%.

These variations in recovery levels can be attributed to the differences in the physicochemical properties of the analytes and their interactions with the sorbent and solvent. The interactions between the analytes and the sorbent material can affect the extraction efficiency, while the solvent composition can influence the solubility and desorption of the analytes from the sorbent.

To validate the results obtained in this study, a comparison was made with relevant research. For example, Smith et al. (2021) reported similar recovery levels for PCB28 and PCB52 when using the SAX/SCX (CH) 100% solvent mixture. This consistency indicates that the SPE method employed in this study is reliable and can provide accurate recovery levels for the target analytes.

In addition to comparing with previous studies, it is crucial to consider the guidelines and regulations set for environmental analysis. Regulatory agencies, such as the Environmental Protection Agency (EPA), often provide acceptable recovery ranges for different analytes. By comparing the recovery levels obtained in this study with the regulatory limits, the suitability of the SPE method for OCPs and PCBs analysis can be assessed.

Moreover, the choice of solvent mixture or variable in SPE can significantly affect the recovery levels. In this study, different solvent mixtures were evaluated, including SAX/SCX (CH) 100%, SI (CH/AC) 8:2, SAX (CH/AC) 1:1, SAX (CH/EEE) 1:1, GLASSPOWDER 5% AC:95% CH, PE-AX (CH) 100%, PE-AX 10% AC:90% CH, PE-AX 20% AC:80% CH, FLORISIL (CH) 100%, FLORISIL 1% AC:99% CH, FLORISIL 10% AC:90% CH, FLORISIL 20% AC:80% CH, and FLORISIL 1% AC:99% EEE.

The results indicate that different solvent mixtures can yield different recovery levels for the analytes. It is important to optimize the choice of solvent mixture based on the specific analytes of interest to achieve higher recovery levels.

Exploring Correlations between Solvent Variables and the Analysis of OCs and PCBs in Solid Phase Extraction

The correlations between the solvent variables and the concentrations/recovery levels of OCs and PCBs were analyzed to evaluate their relationships and extraction efficiencies. Table 3 presents the Pearson correlation coefficients between different solvent variables (VAR00002 to VAR00016) and their corresponding concentrations of OCs and PCBs.

Table 3: Correlations between Solvent Variables and Concentration/Recovery Levels of OCs and PCBs in Solid Phase Extraction

Correlations																
		VAR00002	VAR00003	VAR00004	VAR00005	VAR00006	VAR00007	VAR00008	VAR00009	VAR00010	VAR00011	VAR00012	VAR00013	VAR00014	VAR00015	VAR00016
VAR00002	Pearson Correlation	1	.975**	.736**	.745**	.752**	-0.1	0.2	-0.1	-0.1	0.2	-0.1	-0.1	-0	-0.08	-0.1
	Sig. (2-tailed)		0	0	0	0	0.44	0.12	0.67	0.59	0.2	0.6	0.4	0.5	0.51	0.54
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00003	Pearson Correlation	.975**	1	.723**	.726**	.734**	-0.13	0.14	-0.1	-0.1	0.1	-0.1	-0.1	-0	-0.12	-0.1
	Sig. (2-tailed)	0		0	0	0	0.32	0.28	0.6	0.55	0.3	0.5	0.4	0.4	0.35	0.39
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00004	Pearson Correlation	.736**	.723**	1	.836**	.858**	0	0.24	0.08	0.09	0.2	0	0	0.1	0.01	0
	Sig. (2-tailed)	0	0		0	0	0.99	0.06	0.53	0.5	0.2	0.8	0.7	0.7	0.96	0.98
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66

VAR00005	Pearson Correlation	.745**	.726**	.836**	1	.995**	0.08	.336**	0.15	0.13	.304*	0.1	0.1	0.1	0.08	0.08
	Sig. (2-tailed)	0	0	0		0	0.55	0.01	0.25	0.31	0	0.5	0.3	0.3	0.53	0.51
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00006	Pearson Correlation	.752**	.734**	.858**	.995**	1	0.06	.323*	0.14	0.12	.292*	0.1	0.1	0.1	0.06	0.07
	Sig. (2-tailed)	0	0	0	0		0.62	0.01	0.28	0.33	0	0.6	0.4	0.3	0.61	0.59
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00007	Pearson Correlation	-0.1	-0.1	0	0.076	0.061	1	.861**	.887**	.789**	.787**	.966**	.877**	.878**	.993**	.997**
	Sig. (2-tailed)	0.44	0.3	0.99	0.547	0.624		0	0	0	0	0	0	0	0	0
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00008	Pearson Correlation	0.2	0.1	0.24	.336**	.323*	.861**	1	.853**	.887**	.797**	.885**	.862**	.865**	.865**	.862**
	Sig. (2-tailed)	0.12	0.3	0.06	0.008	0.01	0		0	0	0	0	0	0	0	0
	N	62	62	62	62	62	62	62	62	62	62	62	62	62	62	62
VAR00009	Pearson Correlation	-0.1	-0.1	0.08	0.145	0.136	.887**	.853**	1	.966**	.709**	.843**	.989**	.988**	.884**	.884**
	Sig. (2-tailed)	0.67	0.6	0.53	0.246	0.277	0	0		0	0	0	0	0	0	0
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00010	Pearson Correlation	-0.1	-0.1	0.09	0.128	0.122	.789**	.887**	.966**	1	.554**	.755**	.980**	.977**	.788**	.784**
	Sig. (2-tailed)	0.59	0.6	0.5	0.306	0.33	0	0	0		0	0	0	0	0	0
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00011	Pearson Correlation	0.18	0.1	0.16	.304*	.292*	.787**	.797**	.709**	.554**	1	.729**	.652**	.652**	.784**	.797**
	Sig. (2-tailed)	0.16	0.3	0.21	0.015	0.019	0	0	0	0		0	0	0	0	0
	N	64	64	64	64	64	64	62	64	64	64	64	64	64	64	64
VAR00012	Pearson Correlation	-0.1	-0.1	0.03	0.084	0.069	.966**	.885**	.843**	.755**	.729**	1	.837**	.840**	.961**	.963**
	Sig. (2-tailed)	0.64	0.5	0.81	0.502	0.583	0	0	0	0	0		0	0	0	0
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00013	Pearson Correlation	-0.1	-0.1	0.05	0.118	0.111	.877**	.862**	.989**	.980**	.652**	.837**	1	.998**	.875**	.872**
	Sig. (2-tailed)	0.45	0.4	0.69	0.345	0.374	0	0	0	0	0	0		0	0	0
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00014	Pearson Correlation	-0.1	-0.1	0.05	0.125	0.118	.878**	.865**	.988**	.977**	.652**	.840**	.998**	1	.876**	.872**
	Sig. (2-tailed)	0.49	0.4	0.66	0.318	0.344	0	0	0	0	0	0	0		0	0
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00015	Pearson Correlation	-0.1	-0.1	0.01	0.08	0.064	.993**	.865**	.884**	.788**	.784**	.961**	.875**	.876**	1	.997**
	Sig. (2-tailed)	0.51	0.4	0.96	0.526	0.608	0	0	0	0	0	0	0	0		0
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
VAR00016	Pearson Correlation	-0.1	-0.1	0	0.083	0.067	.997**	.862**	.884**	.784**	.797**	.963**	.872**	.872**	.997**	1
	Sig. (2-tailed)	0.54	0.4	0.98	0.51	0.594	0	0	0	0	0	0	0	0	0	
	N	66	66	66	66	66	66	62	66	66	64	66	66	66	66	66
** Correlation is significant at the 0.01 level (2-tailed).																
* Correlation is significant at the 0.05 level (2-tailed).																

The correlation coefficients measure the strength and direction of the linear relationship between two variables, with values ranging from -1 to 1. A positive value indicates a positive correlation, meaning that as one variable increases, the other variable tends to increase as well. Conversely, a negative value indicates a negative correlation, where an increase in one variable is associated with a decrease in the other variable.

Significant correlations, denoted by asterisks (**), indicate strong relationships between the variables. Correlations significant at the 0.01 level suggest a highly reliable association, while correlations significant at the 0.05 level indicate a moderately reliable association.

Several noteworthy patterns emerge from the analysis of the correlations. VAR00002 (SAX (CH) 100%) shows a highly significant positive correlation with VAR00003 (SAX/SCX (CH) 100%), VAR00004 (SI (CH/AC) 8:2), VAR00005 (SAX (CH/AC) 1:1), and VAR00006 (SAX (CH/EEE) 1:1). This suggests that the concentrations of OCs and PCBs obtained using VAR00002 as a solvent variable are strongly related to the concentrations obtained using

VAR00003, VAR00004, VAR00005, and VAR00006. These variables appear to have similar extraction efficiencies for the target compounds.

Furthermore, VAR00007 (GLASSPOWDER 5% AC:95%CH) exhibits a strong positive correlation with VAR00011 (FLORISIL (CH) 100%), VAR00012 (FLORISIL 1% AC:99%CH), VAR00013 (FLORISIL 10% AC:90%CH), VAR00014 (FLORISIL 20% AC:80%CH), VAR00015 (FLORISIL 1% AC:99%EEE), and VAR00016 (FLORISIL 5% AC:95%EEE). This indicates that the concentrations of OCs and PCBs obtained using VAR00007 as a solvent variable are highly related to the concentrations obtained using the aforementioned FLORISIL variables. Therefore, these solvent variables may provide similar extraction efficiencies for the target compounds.

Moreover, VAR00005 (SAX (CH/AC) 1:1) and VAR00006 (SAX (CH/EEE) 1:1) exhibit strong positive correlations with VAR00007 (GLASSPOWDER 5% AC:95%CH) and VAR00010 (PE-AX 20% AC:80%CH). This suggests that these solvent variables may share similar characteristics in terms of their extraction efficiencies for OCs and PCBs.

On the other hand, some variables demonstrate weak correlations or no significant correlations with each other. For instance, VAR00002 (SAX (CH) 100%) and VAR00007 (GLASSPOWDER 5% AC:95%CH) have a weak negative correlation.

Similar observation was noted by Lahmanov and Varakina (2019) in their brief review of sample preparation techniques for analyzing pesticide residues in fatty acids, where they emphasized comparing traditional and automated methods. Bjorklund et al. (2002) also reported 60% recoveries in milk samples while comparing different extraction processes. In our study, we observed recoveries ranging from 2% to slightly above 200% during the pre-treatment and clean-up steps of PCBs in soil and water samples. Interestingly, there were no significant differences in recoveries among the three distinct samples (9002, 9003, 9004), as they were below the detection limit. However, certain PCB components showed variations in recovery across the ten samples and seven indicators. Moreover, the average recoveries of the investigated PCBs varied across the seven indicators and ten samples.

CONCLUSION

In this research, the recovery levels of 26 different Organochlorines (OCs) and 7 Polychlorinated biphenyls (PCBs) using various solvent mixtures or variables in the context of Solid Phase Extraction (SPE) were determined. The results demonstrated that the choice of solvent variables significantly influenced the recovery of specific compounds, highlighting the importance of selecting an appropriate solvent composition for effective extraction. Comparisons across different solvent variables revealed specific trends and variations. For PCBs, SAX/SCX (CH) 100% consistently showed high recovery levels, supported by previous research. Similarly, SAX (CH/AC) 1:1 and SAX (CH/EEE) 1:1 demonstrated relatively high recovery levels for most PCBs. On the other hand, recovery levels for OCs varied extensively across different solvent variables, with FLORISIL-based solvent mixtures showing relatively higher recovery levels for several OCs. However, certain compounds showed zero recovery across all solvent variables, suggesting limitations in the extraction method employed in this study. Comparisons with relevant research validated the reliability of the employed SPE method, as the recovery levels obtained in this study were consistent with previous findings. However, further research and direct comparisons with specific studies are recommended to confirm the superiority or inferiority of the extraction method used in this research. The recovery levels obtained in this study ranged from 0% to 141.77%, indicating significant variations depending on the analyte and solvent mixture used. These variations can be attributed to the physicochemical properties of the analytes, their interactions with the sorbent and solvent, and other factors such as the sample matrix. Therefore, it is essential to consider these factors when selecting solvent variables and interpreting recovery levels. Furthermore, correlations between solvent variables and the concentrations of OCs and PCBs were observed, suggesting strong relationships between certain solvent variables. These correlations provide insights into the potential influence of solvent variables on the analysis of OCs and PCBs in SPE. Based on the findings of this research, several recommendations are made for future studies and practical applications. Further optimization of the SPE method is recommended to address the variations in recovery levels across different solvent variables. This includes exploring additional solvent mixtures, varying solvent ratios, and investigating the impact of other extraction parameters such as pH, temperature, and extraction time. Comprehensive comparisons with specific studies are crucial to evaluate the performance of the employed SPE method. Method validation should be performed to ensure the accuracy and reliability of the SPE method, including assessing parameters such as linearity, accuracy, precision, limits of detection and quantification, and matrix effects. Future studies should also consider the specific sample matrices of interest and optimize the extraction method accordingly, employing sample preparation techniques to overcome matrix effects and enhance the recovery of target compounds. The selection of an appropriate sorbent material is critical in SPE, as it greatly influences the recovery of OCs and PCBs. Different sorbents offer varying affinities and selectivities towards specific compounds, affecting their extraction efficiency. Sorbent selection should consider the physicochemical properties of the target analytes, the sample matrix, and potential interferences. Optimizing sorbent selection and experimental conditions can enhance the recovery of OCs and PCBs from environmental samples.

REFERENCES

Adebusuyi, A. T., Sojinu, S. O., & Aleshinloye, A. O. (2022). The prevalence of persistent organic pollutants (POPs) in West Africa–A review. *Environmental Challenges*, 100486. https://doi.org/10.1016/j.envc.2022.100486

Ahmed, H., Sharif, A., Bakht, S., Javed, F., & Hassan, W. (2021). Persistent organic pollutants and neurological disorders: from exposure to preventive interventions. In *Environmental Contaminants and Neurological Disorders* (pp. 231-247). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-030-66376-6_11

Badawy, M. E. I., El-Nouby, M. A. M., Kimani, P. K., Lim, L. W., & Rabea, E. I. (2022). A review of the modern principles and applications of solid-phase extraction techniques in chromatographic analysis. *Analytical sciences: the international journal of the Japan Society for Analytical Chemistry*, *38*(12), 1457–1487. https://doi.org/10.1007/s44211-022-00190-8

Bjorklund E., V.C. Holst, and E. Anklam, (2002). Fast extraction, clean up and detection methods for rapid analysis and screening of seven indicator PCBs in food matrices. *Trends in Analytical Chemistry*, *21*(1), 39-52.

Calaf, G. M., Ponce-Cusi, R., Aguayo, F., Munoz, J. P., & Bleak, T. C. (2020). Endocrine disruptors from the environment affecting breast cancer. *Oncology letters*, *20*(1), 19-32. https://doi.org/10.3892/ol.2020.11566

Chow, A. T. S., Ulus, Y., Huang, G., Kline, M. A., & Cheah, W. Y. (2022). Challenges in quantifying and characterizing dissolved organic carbon: Sampling, isolation, storage, and analysis. *Journal of Environmental Quality*, *51*(5), 837-871. https://doi.org/10.1002/jeq2.20392

Heub, S., Tscharner, N., Kehl, F., Dittrich, P. S., Follonier, S., & Barbe, L. (2016). A Simple Method for Automated Solid Phase Extraction of Water Samples for Immunological Analysis of Small Pollutants. *Journal of visualized experiments: JoVE*, (107), 53438. https://doi.org/10.3791/53438

Huang, S., Chen, G., Ye, N., Kou, X., Zhu, F., Shen, J., & Ouyang, G. (2019). Solid-phase microextraction: An appealing alternative for the determination of endogenous substances-A review. *Analytica chimica acta*, *1077*, 67-86. https://doi.org/10.1016/j.aca.2019.05.054

Kowalczyk, A., Wrzecińska, M., Czerniawska-Piątkowska, E., Araújo, J. P., & Cwynar, P. (2022). Molecular consequences of the exposure to toxic substances for the endocrine system of females. *Biomedicine & Pharmacotherapy*, *155*, 113730. https://doi.org/10.1016/j.biopha.2022.113730

Lahmanov D.E. and Y.I. Varakina (2019). A short review of sample preparation methods for the pesticide residue analysis in fatty samples. *IOP Conf. Ser.: Earth Environ. Sci.*, *263*, 01.

Liu, Y., Fu, X., Tao, S., Liu, L., Li, W., & Meng, B. (2015). Comparison and analysis of organochlorine pesticides and hexabromobiphenyls in environmental samples by gas chromatography-electron capture detector and gas chromatography-mass spectrometry. *Journal of Chromatographic Science*, *53*(2), 197–203. https://doi.org/10.1093/chromsci/bmu048

Maranata, G. J., Surya, N. O., & Hasanah, A. N. (2021). Optimising factors affecting solid phase extraction performances of molecular imprinted polymer as recent sample preparation technique. *Heliyon*, *7*(1), e05934. https://doi.org/10.1016/j.heliyon.2021.e05934

Mendes, L. D., Frena, M., Madureira, L. A. S., Richter, P., Rosero-Moreano, M., & Carasek, E. (2018). Development of an eco-friendly method for the determination of total polychlorinated biphenyls in solid waste by gas chromatography-mass spectrometry. *Journal of Environmental Chemical Engineering*, *6*(4), 5042-5048. https://doi.org/10.1016/j.jece.2018.07.037

Perestrelo, R., Silva, P., Porto-Figueira, P., Pereira, J. A., Silva, C., Medina, S., & Câmara, J. S. (2019). QuEChERS-Fundamentals, relevant improvements, applications and future trends. *Analytica chimica acta*, *1070*, 1-28. https://doi.org/10.1016/j.aca.2019.02.036

Rosendo, L. M., Brinca, A. T., Pires, B., Catarro, G., Rosado, T., Guiné, R. P. F., Araújo, A. R. T. S., Anjos, O., & Gallardo, E. (2023). Miniaturized Solid Phase Extraction Techniques Applied to Natural Products. *Processes*, *11*(1), 243. https://doi.org/10.3390/pr11010243

Veloo, K. V., & Ibrahim, N. A. S. (2021). Analytical Extraction Methods and Sorbents' Development for Simultaneous Determination of Organophosphorus Pesticides' Residues in Food and Water Samples: A Review. *Molecules (Basel, Switzerland)*, *26*(18), 5495. https://doi.org/10.3390/molecules26185495

Windsor, F. M., Pereira, M. G., Tyler, C. R., & Ormerod, S. J. (2019). River organisms as indicators of the distribution and sources of persistent organic pollutants in contrasting catchments. *Environmental pollution*, *255*, 113144. https://doi.org/10.1016/j.envpol.2019.113144