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Determination of Organochlorines Pesticide Residues in Water Samples Using Liquid-Liquid Extraction Method

Ali SAMIL[1*], Erdal KUSVURAN[2]

Highlights:

- A rapid method was used for the detection of pesticide residues.
- Successful detection of pesticide residues.
- The method allows for determination at the levels required by low.

Keywords:

- Residue
- Analysis
- Pesticide
- Extraction

ABSTRACT:

In this study, chlorinated cyclic hydrocarbon pesticides were extracted from water using a solvent mixture (hexane: dichloromethane), and their content was determined by GC-MS equipped with electron ionization (EI) and selected ion monitoring (SIM) methods. Additionally, the validation parameters for the method used were established. The recovery ratios of the spike levels varied between 82.7% and 95.4%. *Heptachlor* had the lowest recovery value, 82.7%, at a concentration of 1.480 µg/L, while *Aldrin* had the highest recovery value, 95.4%, at 11.200 µg/L. A satisfactory linearity was found for each pesticide at the four varied spike levels during the extraction procedure. *Trans-Heptachlor* > *Heptachlor* > *trans-Chlordane* > *cis-Chlordane* was the order in which the recovery efficiency of pesticides containing chlorine cyclo rings declined. *Trans-Chlordane* > *trans-Heptachlor* >*Endosulfan* > *Dieldrin* > *Heptachlor* > *Aldrin* > *cis-Chlordane* was followed by a decline in the relevant value of pesticides having two or more cyclic rings for the seven pesticides that made up the entire analysis period in this experiment a sufficient differentiation was made in around 18 minutes.

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INTRODUCTION

The population significantly impacts food production, food consumption, and economic growth. In recent years there have been notable shifts in the birth rates and population trends of several nations and continents. While food production increases linearly, population numbers typically increase dramatically. More than 80 million people are added to the world's population annually. This condition led to several issues, including industrialization, a decline in agricultural lands as settlements grew, and a rise in worldwide environmental degradation. Between 1969 and 2015, the amount of agricultural land allotted per person declined from 0.33 to 0.19 hectares (Alexandratos et al., 2012). As a result, a mismatch is created between food production and population growth. When plant pests (insects, weeds, diseases, fungi, etc.) were considered, these scissors had already widened considerably. Since human does not want to share their meager food with them, they fight bugs to enhance production. Numerous studies have been done to boost production in current agricultural areas. These might be categorized as insect control, fertilizer, plant hormones, and genetic alteration (Bevan et al., 1983; Bock et al., 1984).

Pesticides are divided into several classes, such as benzoylureas, pyrethroids, carbamates, organophosphorus/organochlorine chemicals, sulfonyls, and triazines. Various instrumental devices and methods have to be used to determine their residues based on the chemical structure of pesticides. In an analysis method, physical properties (volatility, solubility) and chemical properties (acidic/basic, neutral, thermal stability, molecular size) are the main factors determining the analysis method. Researchers typically use liquid chromatography in combination with Ultra/Viole (Harshit et al.. 2017; Douglas et al., 2018) conductivity (Lawrence et al., 1976), microfluidic paper-based analytical device (Pengpumkiat et al., 2020) mass spectrometry (MS) (Wu et al., 2002; Ferrer et al., 2005) and tandem mass spectrometry (MS-MS) (Lehotay, 2005) detectors for the analysis of their residue.

The combination of a gas chromatograph (GC) with an electron capture detector (ECD), however (Brito et al., 2002; Rissato et al., 2004; Sereshti et al.,2022; Pellicer et al., 2022) Flame Photometric Detector (FPD) (Ahmadi et al., 2006) MS (Lehotay, 2005; Kusvuran et al., 2012) Nitrogen Phosphorus Detector (NPD) and MS-MS (Machado et al., 2017; Shabeer et al., 2018; Biswasa et al., 2019) and MS-MS detectors have been chosen for residue analysis of volatile, thermally stable, and small molecule structure pesticides. First, GC in combination with ECD, NPD, or FPD was frequently employed to determine the trace level residue of pesticides in diverse matrixes. The GC results, however, were unable to offer the required qualification. Additionally, MS (Lehotay, 2005; Kusvuran et al., 2012) and MS-MS (Biswasa et al., 2019) started favoring GC instead of pertinent detectors due to confirmation issues and many nations reducing their Maximum Residue Limits (MRL) lower levels. GC-MS is far superior to other GC detectors in many ways. Utilizing a selective ion monitoring technique during analysis allowed for the provision of both findings confirmations and the avoidance of interferences. At the same time, the evaluation of many pesticides with the same retention time has been simplified. In several pesticide analytical manuals, GC-MS analysis procedures were described (Thier et al., 1992).

The extraction process is a crucial element in the examination of pesticides. Researchers have used a wide range of organic solvents for extraction according to the type of pesticides and matrix. In recent years an analytical technique known as Quechers (Quick, Easy, Cheap, Effective, Rugged, and Safe) has become widely employed to measure the quantities of pesticide residue on matrices (Lehotay, 2005; Kusvuran et al., 2012; Machado et al., 2017). Although a helpful technique, the method's detection limit must be increased for several pesticides' MRL values. As a result, several extraction techniques are being used for the necessary pesticides. According to a 2008 study by Garcia-Reyes et al., the solid-phase extraction (SPE) method was used to extract pesticides from fruit-based soft drinks. The preferred solvent for removing pesticides from plants is ethyl acetate (Frenich et al., 2005). While some researchers extracted pesticides from apples using acetone (Grimalt et al., 2007).

This study aimed effectively extraction of cyclo hydrocarbon organochlorinated pesticides from water by using a solvent mixture (hexane:dichloromethane) and determination of their quantity of them by GC-MS equipped with Electron Ionization (EI) and Selective Ion Monitoring (SIM) method. In addition to validation, the method's parameters were also determined.

MATERIALS AND METHODS

All cyclo hydrocarbon organochlorinated pesticides utilized in this study were obtained from Sigma-Aldrich and applied directly. The following chemical compounds have been utilized in experimental experiments. Purchased from Merck were sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), dichloromethane, and hexane (Darmstadt. Germany). With a Brand Mark micropipette (0-100 µL), the spikes were injected into organic-free water. Pesticide studies were completed using an HP 5MS capillary column (30 m x 0.25 mm, Agilent) and a Gas Chromatography-Mass Spectrometry (GC-MS-QP 2010 Plus, Shimadzu, Japan). Pesticide residue extracts were concentrated using a rotary evaporator at 150 revolutions per minute at 40 °C.

Experimental Procedure

A separatory funnel containing 0.5 L of organic-free water was filled before adding stock standard pesticides solution to the water. The spikes were applied at the desired concentration levels with injection volumes ranging from 0 to 100 µL, and the separatory funnel's contents were forcefully agitated. Using 1.0 M H_2SO_4 and 1.0 M NaOH, the pH was roughly brought to a neutral value before being shaken forcefully. Then, 1 mL of saturated NaCl solution was poured into the separatory funnel before the pesticides were extracted using 60 mL of hexane-dichloromethane solvent mixture (1:1) (volume:volume) three times. The pesticide residue-containing extract was dried with anhydrous Na_2SO_4 and concentrated to 10 mL at 150 rpm at 40 °C. This process was carried out six times, with each spike level copied seven times. One microliter of the 10 mL extract was injected into the GC-MS using the GC-MS-Solution Software to determine the pesticide concentrations**.**

Pesticide analyses were completed using a Shimadzu GC-MS with an HP 5 MS capillary column (30 m x 0.25 mm). The GC oven was kept at 110 °C for 2 minutes before being raised to 280 °C at an 8 °C/min rate and held there for 1 minute. The temperatures of the injector, interface, and ion source were 280 °C, 280 °C, and 230 °C. The Electron Ionization (EI) and Selected Ion Monitoring (SIM) modes were used to quantify pesticides. Each pesticide was injected into the GC-MS (1 µL, 1 µg/L), and its fragmentation and quantitation ions were determined before SIM mode was used. To perform quantitative assessments of pesticides, standard solutions of each pesticide were produced in a hexane-dichloromethane mixture at concentrations ranging from 39 to 5000 µg/L. GC-MS evaluated them three times. The GC-MS response was used to draw the calibration graph of each pesticide against pesticide concentration, and Table 1 contains the regression coefficients for each pesticide. Equations from these graphs were used to compute the amounts of pesticides (Lehotay, 2005; Ahmadi et al., 2006; Kusvuran et al., 2012).

Table 1. For Pesticides Equations of Calibrations

No	Pesticides	Standart Range (µg/L)	Equ.	r^2
1	Heptachlor	5000-39	$C = 11.051 x10^{-3} A + 2.705$	0.998

2	Aldrin	$C = 5.013 \times 10^{-3} A + 1.524$	0.999
3	trans-Heptachlor	$C = 15.805 \times 10^{-3} A - 3.257$	0.999
4	cis-Chlordane	$C = 3.312 \times 10^{-3} A + 3.290$	0.999
5	α-Endosulfan	$C = 15.126 \times 10^{-3} A + 1.416$	1.000
6	trans-Chlordane	$C = 4.483 \times 10^{-3} A + 2.460$	0.999
7	Dieldrin	$C = 4.962 \times 10^{-3} A + 2.433$	0.999

*C: Concentration of pesticides, *A: Peak area of pesticides, *r^2: Regression coefficients.

RESULTS AND DISCUSSION

Verification of the Extraction Technique

In around 18 minutes, a good distinction was made. This analysis program was used for the entire investigation. The findings of seven distinct trials and their average recoveries are shown in Table 3 for seven different pesticide concentrations dependent on spike levels for water.

Table 2. The Ratios of Signal to Noise Corresponding to the Number of Pesticides

No	**Pesticides**	**r_t**	**Q_1**	**Concentration (µg/L)**	**S/N**	**Concentration Normalized (µg/L)**
1	Heptachlor	13.38	100	0.328	9.4	0.209
2	Aldrin	14.48	66	0.591	9.6	0.369
3	trans-Heptachlor	15.95	183	0.764	7.4	0.619
4	cis-Chlordane	16.61	373	0.424	8.3	0.307
5	α-Endosulfan	16.99	241	0.710	12.3	0.346
6	trans-Chlordane	17.12	373	0.458	7.6	0.362
7	Dieldrin	17.89	79	0.290	6.4	0.272

*rt: Retention time, *Q_1: Quantities ions of each pesticide, *S/N: Signal/Noise ratios corresponding to the number of pesticide amount.

When looking at the recovery ratios of the spike levels, Table 3 shows that the lowest and highest values, respectively, were 82.7% and 95.4%. The lowest recovery value was established to be 82.7% at a concentration of 1.480 µg/L for heptachlor, and the most significant recovery value was found to be 110.9% at a concentration of 16.000 µg/L for *Aldrin*. The recovery value for *Aldrin* is more significant than 100% because of the medium's reactions and impurities. α-*Endosulfan* and *trans-Heptachlor*, respectively, the recoveries of the two pesticides spiked at the identical lowest concentration level 0.800 µg/L were observed to be 0.710 and 0.764 µg/L. The relevant recovery was reported as 22.464 and 22.500 µg/L for the same order at the same highest concentration level, 25.610 µg/L. Similarly, at the lowest spike levels, 0.330 and 0.370 µg/L, the recoveries were determined as 0.290 and 0.329 µg/L for *Dieldrin* and *Heptachlor,* respectively. In contrast, at the highest spike levels, 10.560 and 11.840 µg/L were noted as 9.278 and 10.791 µg/L, corresponding to the same order. When the other spike levels were studied, the recovery was observed as 0.424 µg/L at 0.460 µg/L and as 12.743 µg/L at 14.720 µg/L for *cis-Chlordane*, respectively. The recovery of *trans-Chlordane* at 0.458 µg/L was carried out as 0.500 µg/L. The appropriate value was computed as 19.392 µg/L for *Aldrin* at a concentration of 22.400 µg/L. Besides, at 0.370 µg/L, spike level recovery of *heptachlor* was obtained as 0.329 µg/L. The 11.840 µg/L recovery value was determined at the spike level as 10.791 µg/L for *heptachlor*. When the lowest spike levels of *Heptachlo*r and *Dieldrin* were compared with the highest spike levels, it was seen that all other pesticides had better recovery values. However, *trans-Heptachlor* and *cis-Chlordane* were recovered at a lower rate Table 3. There was no significant difference between the pesticide α-Endosulfan's lowest and highest spike levels. The enrichment factors and recoveries relative to (Ago et al., 2023) ranged from 24 to 293% and 76-116%, respectively.

Limit of extraction method

Since the quantitative analysis of each pesticide depended on the Signal to Noise (S/N) ≥ 6 ratios, only one amount of ion was employed in this experiment. Table 2 displays S/N related to ion concentration and amount for each pesticide (Q1). Table 2 contains the normalized concentration that was discovered.

On the other hand, pesticides were added to organic-free water to determine the LOD values before it was removed. Table 4 displays the average recoveries with standard deviations obtained from seven independent investigations using the same level of continuous enrichment for each pesticide. Suppose the concentration of pesticide (C*Normalized*) matching with S/N≥ 6 is the detectable lowest concentration. In that case, LOD*Exp* can be derived using the standard deviations (σ) of the lowest concentration of pesticides, as given in Table 3.

Table 3 shows that when LODExp and LOD*Cal* were compared proportionally, significant differences ranging from 1 to 7 were found. It was observed that the ratios of LOD*Exp.* / LOD*Cal* was changed to a group of pesticides of *trans-Heptachlor, a-Endosulfan, trans-Chlordane*, and *Aldrin*. On the other hand, it was found that the relevant ratio increased for the pesticides *Dieldrin, cis-Chlordane*, and the last group, which included *heptachlor*.

Continuity of the extraction process averages of recoveries

This section examined the linearity of extraction techniques concerning recovery values for each spike in pesticide levels. The slope of obtained graphic for each pesticide plotted recovery percent versus spike pesticide levels represents average recovery (Raver) in the range of spike levels Table 3. Values for Raver in Table 3 changed from 84.1% to 91.6% for *cis-chlordane* and *trans-chlordane,* respectively. It was noted that the recovery rate for 7 out of the total pesticides was less than 90%. While the raver of one pesticide was above the recovery value of 100%, the rave of the remaining pesticides was higher than the relevant value. Using various extraction techniques, researchers have extracted pesticides from numerous matrixes, including vegetables (Frenich et al., 2005).

When their recovery results were compared to our results or pesticide recoveries from vegetables were compared to those from water, several pesticide recoveries from water were higher than those from vegetables. For instance, the values indicated as 83.8% - 91.0%, respectively, when the recovery outcomes of vegetables-water matrixes for *heptachlor* were compared. However, it was shown that a group of pesticides, including *Dieldrin* and *a-endosulfan,* recovered from the water at levels lower than those found in vegetables ranging from 87.9% to 109.3% and 87.8% to 109.5%, respectively.

Surprisingly the *Aldrin* recovery rate for each matrix was 87.1%. Another study that utilized the same matrix yielded nearly the same value when different pesticide solvent combinations were employed (Corcia et al., 1991). (Xiao et al., 2016) n-hexane was used instead of acetonitrile as the extraction solvent. A hydrophobic NaDES based on monoterpene thymol and myristyl alcohol in a 2:1 M ratio was prepared and used by (Sereshti et al.,2022) as the extraction phase. (Mao et al., 2011) developed a method for the determination of organophosphorus and pyrethroid pesticides in vegetables. Using quadrupole mass spectrometry (qMS) and high-resolution time-of-flight mass spectrometry (Hayward et al., 2009) reported the recovery of certain pesticides from ginseng *root* for three concentration levels (TOF).

Table 3. Liquid-Liquid Extraction Process Data

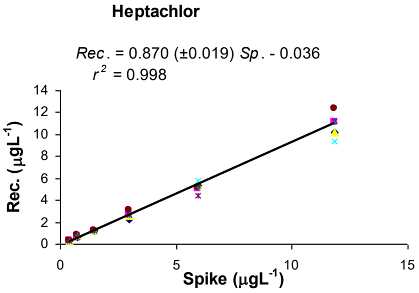
No	Pesticides	Spike µg/L	R_{Aver} µg/L	R_{Aver} %	STD %	*LOD_{Cal} µg/L*	*LOD_{Exp} µg/L*
1	Heptachlor	0.370	0.329	88.8	6.2	0.070	0.248
		0.740	0.691	93.4	11.0		
		1.480	1.224	82.7	3.9		
		2.960	2.668	90.1	8.5		
		5.920	5.193	87.7	7.7		
		11.840	10.791	91.1	8.9		
2	Aldrin	0.700	0.591	84.4	4.1	0.037	0.414
		1.400	1.158	82.7	3.9		
		2.800	2.524	90.1	8.5		
		5.600	4.912	87.7	7.7		
		11.200	10.208	91.1	8.9		
		22.400	19.392	86.6	10.9		
3	trans-Heptachlor	0.800	0.764	95.4	4.0	0.038	0.693
		1.601	1.436	89.7	10.6		
		3.201	2.899	90.6	6.9		
		6.403	6.028	94.1	11.5		
		12.805	10.994	85.9	12.0		
		25.610	22.500	87.9	6.6		
4	cis-Chlordane	0.460	0.424	92.1	4.6	0.042	0.349
		0.920	0.761	82.7	3.9		
		1.840	1.659	90.1	8.5		
		3.680	3.228	87.7	7.7		
		7.360	6.708	91.1	8.9		
		14.720	12.743	86.6	10.9		
5	α-Endosulfan	0.800	0.710	88.8	4.5	0.029	0.393
		1.601	1.507	94.1	11.5		
		3.201	2.803	87.6	11.6		
		6.403	5.543	86.6	10.9		
		12.805	11.488	89.7	10.6		
		25.610	22.464	87.7	7.7		
6	trans-Chlordane	0.500	0.458	91.7	4.4	0.033	0.410
		1.000	0.827	82.7	3.9		
		2.000	1.854	92.7	9.2		
		4.000	3.623	90.6	6.9		
		8.000	7.017	87.7	7.7		
		16.000	14.057	87.9	6.6		
7	Dieldrin	0.330	0.290	88.0	5.5	0.039	0.317
		0.660	0.621	94.1	11.5		
		1.320	1.133	85.9	12.0		
		2.640	2.448	92.7	9.2		
		5.280	4.737	89.7	10.6		
		10.560	9.278	87.9	6.6		

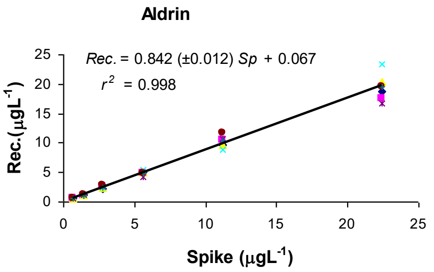
Recovering the extraction technique

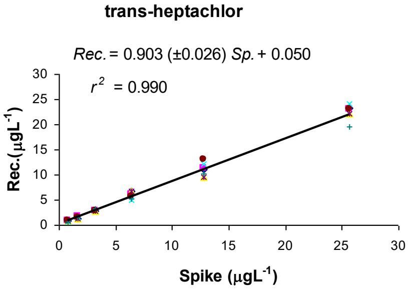
The recovery levels of pesticides between the lowest and highest spike levels were compared in this section. Table 2 displays these outcomes. The recovery percentage for pesticides was raised while the spike levels rose from the lowest to the most extraordinary. For the others, a different situation developed. The most considerable recovery improvement was when *trans-Heptachlor* levels increased by 76.4%.

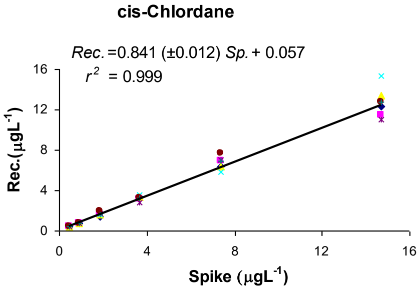
Along with these, the remaining pesticides improved by less than 10%. On the other hand, it was shown that the pesticide recovery data declined as spike levels rose. Less than 10% of these deteriorations were created.

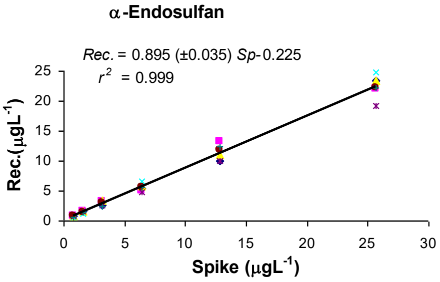
Table 4. Graphs of recovery values of pesticides

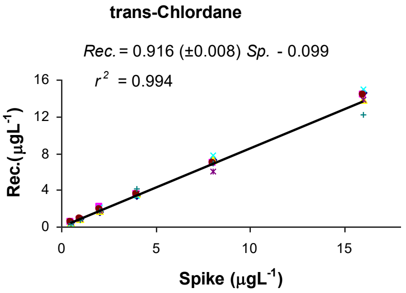


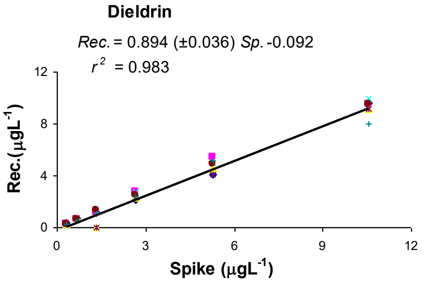












CONCLUSION

For the seven pesticides that made up the entire analytic period in this experiment, a sufficient differentiation was made in around 18 minutes. The recovery ratios for the spike levels fluctuated between 82.7% and 93.4%. For *Heptachlor*, the lowest recovery value was 82.7% at 1.480 µg/L. The most significant recovery value was calculated to be as 91.1% at 11.200 µg/L for *Aldrin*. The extraction efficiency of the pesticide group composed of a cyclohexane ring was decreased in the order of *trans-Heptachlor* > *Heptachlor* > *trans-Chlordane* > *cis-Chlordane*. The efficiency of pesticides formed from two or more cyclic rings was determined in order of *trans-Chlordane* > *trans-Heptachlor* > *a-Endosulfan* > *Dieldrin* > *Heptachlor* > *Aldrin* > *cis-Chlordane*.

Conflict of Interest

The article authors declare that there is no conflict of interest between them**.**

Author's Contributions

The authors declare that they have contributed equally to the article**.**

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