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Development of the QuEChERS Extraction Method for the Determination of Polychlorinated Biphenyls (Aroclor 1254) in Soil Samples by Using GC-MS

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Abstract: Polychlorinated biphenyls (PCBs) have been found in soil, which has typically been the result of industrial pollution in the past two decades. Although they are banned, PCBs can still be found in soils and other environmental media. For this reason, it is critical to develop an analytical method that can reliably identify and monitor their sources. This study describes a gas chromatography with mass spectrometry (GC-MS) technique, which was used to detect PCBs in soil samples by using a fast extraction method. Using the QuEChERS (quick, easy, cheap, effective, rugged, and safe) method, PCBs were more effectively extracted from soil. Different related parameters, such as time of shaking and centrifuging, type of solvent, and clean-up adsorbents, were compared and optimized. As the extraction solvent, acetonitrile/water produced the best results, and as the dispersive solid-phase extraction sorbent, diatomaceous earth produced the best results. Procedures allowed recovery values between 95.3% and 103.2%. A limit of detection of 1.9 μg/kg was determined with relative standard deviations (n = 3) of 2.1–4.0% for intra-day assays and 3.6–5.8% for inter-day assays. It was demonstrated that the method was simple, sensitive, efficient, and environmentally friendly when applied to soil samples. To our knowledge, an integrated approach based on QuEChERS for the determination of Aroclor 1254 in soil has not been published before. It is believed that this approach will eliminate the significant challenge of sample extraction in GC-MS processing, which was considered to be a procedural challenge in previous analyses.

Keywords: polychlorinated biphenyls (PCBs); quick; easy; cheap; effective; rugged; safe (QuEChERS); (GC-MS); sample preparation; extraction methods; soil environmental

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1. Introduction

Polychlorinated biphenyls (PCBs) are chemical compounds formed artificially by replacing hydrogen atoms within biphenyl molecules with chlorine atoms, classifying them as a persistent organic pollutant. A total of 209 possible PCB congeners exist due to different commercial names for PCBs, accumulating and posing an environmental hazard [1–3]. Despite the banning of using and/or producing PCBs, they are still widely spread in environmental media, including in agricultural soil [4].

Aroclor 1254 is one type of PCB that has attracted researchers in recent years. A product with dozens of highly chlorinated congeners, it has been widely used for numerous open and closed industrial applications due to its chemical and thermal stabilities [5–7]. Therefore, the possibility of exposing people to Aroclor 1254 has increased greatly in different ways, such as through dietary intake, dermal contact, or inhalation, which negatively affect the human body and cause serious conditions including neurotoxicity, dermatological disorders, and lung problems. Thus, the detection of Aroclor 1254 in the environment has become very important and requires a sensitive analytical method [8,9].

Gas chromatography is most commonly used to detect polychlorinated biphenyls usually in conjunction with an electron capture detector or mass spectrometry [10,11]. Some of the features of these techniques are accuracy, reliability, and sensitivity [12]. Isolating PCBs from the soil matrix is a crucial step in GC-MS. The PCB analysis has been carried out using a wide range of extraction techniques, such as chemical methods—involving soxhlet extraction [13–15], liquid–liquid extraction [16,17], and solid-phase extraction [18,19]—or physical ones, involving ultrasonic extraction [20], microwave-assisted extraction [21], supercritical fluid extraction [22], and pressurized fluid extraction [23].

Despite their own advantages, these methods suffer from hazardous solvents, and sample preparation is expensive and time-consuming; therefore, Anastassiades et al. introduced a quick, easy, cheap, effective, rugged, and safe method, known as QuEChERS, as an alternative means of extraction [24].

The method involves acetonitrile extraction, followed by salt addition and dispersive solid-phase extraction (d-SPE) cleanup. According to this alternative method, organic solvents are minimized, which was rarely discussed in the literature review [25]. PCBs have been removed from a variety of matrixes, including fish tissue [26–28], mussels [29], meat [30], and honey [31], and isolated by QuEChERS. Although different optimizations were discussed in the soil sample [32], further modification is required, including combinations of solvents, sorbents, or salts, considering volume, type, and ratio, which mostly depends on the analyte and the matrix.

Through the use of the QuEChERS method combined with GC-MS, this study aimed to develop and validate an inexpensive and reliable method of analyzing PCBs in soil. The QuEChERS method was examined for PCB extraction from six soil samples by examining the effect of water, solvent types, solvent volume, time of shaking, centrifuge time, speed, and types of sorbents used. To demonstrate the efficiency and accuracy of the methodology, blank samples spiked with standards were used to evaluate the precision and accuracy of the method.

2. Experiment

2.1. Instrumentation and Conditions for GC-MS

The GC-MS instrument used for the analysis of PCBs was an Agilent 6890/5973, which consisted of an Agilent 6890N GC equipped with an inert mass selective detector 5973. A capillary column HP-5MS [5%-phenyl)-methylpolysiloxane] Agilent J&W GC column, with a dimension of 0.25 mm ID × 30 m and a 0.25 µm film coating thickness, was used for the separation of PCB congeners. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min and a pressure of 18 psi. The injector was kept at a constant pressure and temperature of 250 °C. The oven temperature was programmed as follows: it was initially set at 70 °C and held for two minutes, then increased to 180 °C at a rate of 25 °C/min, then increased to 200 °C at a rate of 3 °C/min, then increased to 280 °C at a rate of 8 °C/min, and held for 13 min. The injector and detector temperatures were both set at 280 °C. The injection volume was 5 µL in the splitless mode. The ionization voltage was 70 eV, and the solvent delay was set to 6 min. Detection of the compounds was performed in full scan mode with a scan range of 50 to 500 mass to charge ratios (*m/z*). The total run time was 36.07 min. The MS transfer line temperature was 280 °C, and the ion source temperature was 250 °C.

2.2. Chemicals and Instruments

The following were all obtained from Sigma (Dublin, Ireland): an Aroclor 1254 stock solution at a concentration of 200 µg/mL in methanol; a surrogate solution of a mixture in acetone containing 200 µg/mL of decachlorobiphenyl (deca-CB) and of tetrachloro-m-xylene (TCMX); anhydrous $MgSO_4$ powder; sodium chloride NaCl powder; diatomaceous earth; clean soil; acetonitrile; hexane; acetone; ethyl acetate; methanol. The reagents and solvents used in the experiments were generally of an analytical grade or higher. Ultrapure deionized water, with a resistivity of 18.2 MΩ·cm, was obtained from a Milli-Q system (Millipore, Molsheim, France). We used a QuEChERS Original Method extraction kit (5 g samples), 50/pk. The kit contents were as follows: 4 g $MgSO_4$, 1 g NaCl with 50 mL tubes, and a QuEChERS dispersive clean-up kit (PSA, C18, $MgSO_4$); these were purchased from Agilent Technologies Ireland Limited (Cork, Ireland). We also used a centrifuge (Heraeus Megafuge 16, Thermo Fisher, Bremen, Germany), analog vortex mixer (VWR Mixer Mini Vortex, Missouri CT, USA), ultrasonic Branson 5510 cleaner (Branson Ultrasonics Corporation, Brookfield, CT, USA), suitable hoods, glassware, volumetric flasks, pipettes, cylinders, beakers, vials, tubes for soil sample extraction, and filter paper for soil sample filtration.

2.3. Standard and Sample Solution Preparation

A six-point calibration curve was employed for the quantitative analysis. Standard solutions of Aroclor 1254 were prepared at levels of 0.32, 0.65, 1.25, 2.5, 5, and 10 ng/mL by diluting 200 µg/mL Aroclor 1254 stock solutions with methanol. Surrogate standard solutions for Deca-CB and TCMX were prepared at a concentration of 5 ng/mL via dilution with acetone from a 200 µg/mL stock solution. To assess extraction recovery, a surrogate standard was added, and the standards and working solutions were stored at 4 °C. For the recovery experiment, the soil used in this work (about 100 g) was purchased from Sigma. The soil samples were stored at room temperature 25 °C in dark-colored glass bottles. The physicochemical properties of the soil were as follows: The soil texture was sandy; pH = 6.2; organic matter at levels of 0.1%. Afterwards, soil samples were spiked with PCBs standards at 10 µg/kg and 5 µg/kg. To obtain a homogeneous sample, a mechanical stirring apparatus was used. After that, to allow the solvent to evaporate, the samples were left in a ventilated area for eight hours. The standards are thought to bind the soil samples similarly to natural processes. For accurate recovery results, it is critical to use suitable extraction methods and solvents to avoid soil interference. The soil was pretreated to remove the interfering compounds. Additionally, the potential contamination sources were controlled and evaluated throughout the process to obtain better recovery.

To calculate the recovery, a chromatogram with characteristic peak areas and retention times, or a "fingerprint" pattern, was produced by a single PCB mixture of Aroclor 1254. In this study, an Aroclor 1254 mixture containing tetra-CB, *m/z* 292; hexa-CB, *m/z* 360; hepta-CB, *m/z* 394; penta-CB, *m/z* 326 with peak areas of penta-chlorinated biphenyls (penta-CBs) were selected and used to construct the calibration models for the quantification of Aroclor 1254, because penta-CBs are one of the major PCBs in Aroclor 1254 (48% weight). The areas of selected peaks in the sample were compared to the same areas in a standard PCB mixture, which was the method utilized.

Phase separation is a process in which a mixture is divided into two or more distinct phases, usually due to the presence of a separating agent. Salt is a commonly used separating agent, and its addition can induce phase separation. However, it is important to note that the effectiveness of the extraction system can also be influenced by the amount of salt used. In a recent study, the same amount of magnesium sulfate ($MgSO_4$) has been used as in a previous study to induce phase separation [24]. Magnesium sulfate ($MgSO_4$) is often used as a drying agent to remove water from the organic phase and improve the efficiency of the extraction process. In addition to $MgSO_4$, NaCl can also be employed to minimize the effects of polar interference. This can be particularly useful when analyzing samples that contain high levels of polar compounds, as these compounds can interfere with the extraction process and lead to inaccurate results. Therefore, careful consideration of the type and amount of separating agents used is crucial for the success of any extraction process.

2.4. Extraction and Clean-Up Procedure

Extraction was performed according to the QuEChERS method described by Anastassiades, Michelangelo Lehotay, Steven J. (2003) [24]. Approximately 5 g of soil samples were weighed into a 50 mL centrifuge tube and mixed with 15 mL of acetonitrile/water (75%: 25%, *v/v*) or hexane/water (75%: 25%, *v/v*) in a QuEChERS tube, followed by vortex homogenization for 4 min. Then, the tube containing samples was ultrasonically treated for 20 min. After that, 4 g of $MgSO_4$ and 1 g of NaCl were added. After vortexing the mixture for 4 min, the extract was centrifuged at 4500 rpm for 10 min to remove the upper layer. Approximately 6 mL of the organic layer extract was transferred into a clean-up tube containing 900 mg $MgSO_4$ and 150 mg of sorbent mix (PSA/C18) or diatomaceous earth. After 4 min of vortex homogenization, the tubes were centrifuged for 10 min at 4500 rpm. Approximately 1.5 milliliters of the upper layer were filtered before being transferred to GC vials for a GC-MS analysis, and 50 µL of deca-CB and TCMX internal standards were added the modified QuEChERS extraction method is shown in Figure 1. The blank samples (soils without PCBs) were treated the same way, but without the PCB standard solution. The experiments were replicated three times.

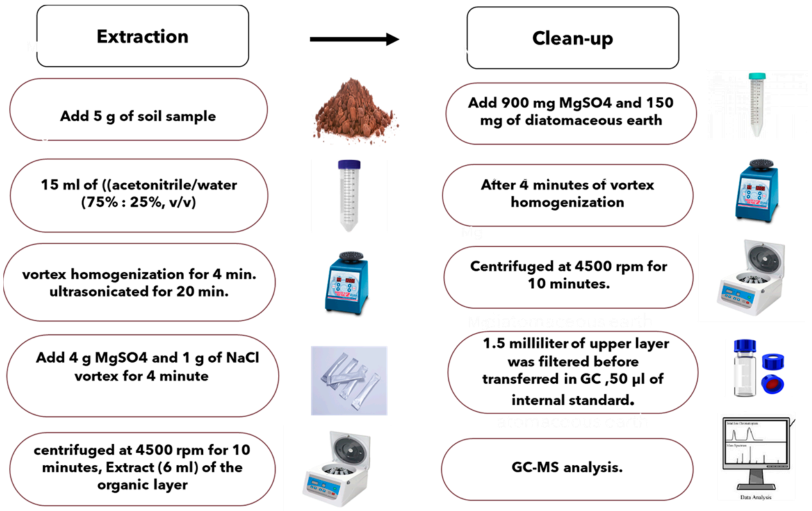

Figure 1. Schematic illustration of the modified QuEChERS extraction method.

2.5. Method Validation

The analytical parameters used to validate the method for analyzing PCBs include linearity, limit of detection (LOD), limit of quantification (LOQ), relative standard deviation (RSD), and recovery. The linearity of the relationship between concentration and peak area was determined by analyzing standard PCB solutions. Calibration curves used 6 standard solutions in the concentration range of 0.32–10 ng/mL for Aroclor 1254 in triplicate. LOD and LOQ were calculated using the formulas LOD = 3.3 SD of intercept/slope and LOQ = 10 SD of intercept/slope. Precision was evaluated by measuring the inter-day and intra-day variability at two concentration levels within the linearity range, with three replicates on the same day or on three different days. Recovery was assessed by performing a study at two concentration levels within the linearity range to evaluate the accuracy of the GC-MS method. The results of these analytical parameters are presented in the results section of the study.

3. Results and Discussion

3.1. Optimization of Extraction Solvent Conditions

For the purpose of this study, Aroclor 1254 was selected to be analyzed in soil samples. QuEChERS has been utilized in several studies to measure a variety of pollutants, including pesticides in soil samples [32,33], aromatic organochlorines [34], veterinary products, and pharmaceuticals [35,36]. In spite of this, the method has not been extensively used in the extraction of Aroclor 1254 from soil. The QuEChERS method should be optimized in order to obtain the best recovery. Several related parameters, including water effect, solvent effect, and solvent volume effect, were optimized.

A traditional QuEChERS extraction was performed with samples containing a high moisture content. Additionally, the QuEChERS method has been modified [37–39]. Humidity is an important factor when preparing soil samples [40,41]. It was necessary to add ultrapure water to soil samples in order to ensure moisture content and to improve the recovery of PCBs from soil samples. To achieve high extraction efficiency, different amounts of water (3, 5, 7, and 10 mL) were tested. According to the results, maximum peak intensity and maximum recovery were achieved with 5 and 7 mL of water; as the amount of water increases, peak intensity decreases (see Figure 2a). For the additional experiment we utilized 5 mL.

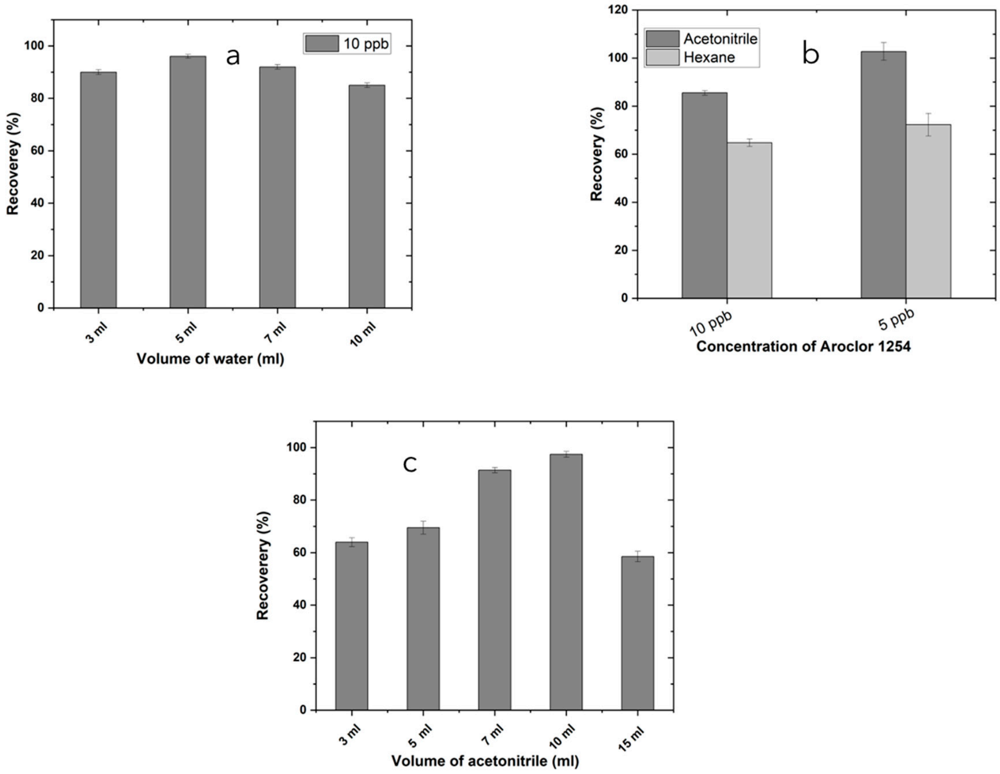

Figure 2. (**a**) The effect of water addition on extraction efficiency for the target Aroclor 1254 at 10 ng/mL; (**b**) the effect of acetonitrile and hexane as extraction solvents for the target Aroclor 1254 at 5 ng/mL and 10 ng/mL (n = 3); (**c**) the effects of different solvent volumes for the target Aroclor 1254 at 10 ng/mL (n = 3).

Extraction efficiency is highly dependent on the solvent used for extraction. In addition, the solvent must be less costly, compatible with analytical instruments, and eco-friendly [42]. To determine the most suitable solvent for the extraction of PCBs from soil samples, two different solvents were used: acetonitrile and hexane in combination with water. The original QuEChERS method used acetonitrile as the extract solvent, as did many other studies involving QuEChERS procedures [24]. Therefore, this solvent was chosen for use in the present study as one of the solvents, while hexane was chosen as the other solvent since it is commonly used to extract PCBs from soil [43], although it is less eco-friendly. As shown in Figure 2b, recovery rates of PCBs in the acetonitrile extraction were 85.53–102.72%, showing better efficiency, the production of cleaner extracts, and overall higher recoveries for PCBs than the hexane extraction. In this study, acetonitrile was found to be the most suitable extraction solvent, as it extracts a lower amount of the matrix, which is consistent with the findings of the previous study [31,44].

Furthermore, the volume of solvent used is critical for effective recovery, and there should be enough solvent to allow the sample to be fully immersed and interact with the analyte. Various amounts of acetonitrile, including 3, 5, 7, 10, and 15 mL were tested, and it was found that 10 mL of acetonitrile yielded the highest peak intensity and recovery, as depicted in Figure 2c. Acetonitrile is considered to be a more selective solvent and produces a cleaner chromatogram compared to most other solvents used in the QuEChERS technique [45]. When compared to other solvents utilized in QuEChERS, ACN separates from water more effectively in the presence of salts, producing good phase separation, which inhibits polar matrix interaction [46].

3.2. Optimization of Physical Extraction Condition

In this study, the effects of shaking time, centrifuge time, and speed were optimized and discussed. Several methods, including laboratory shakers, manual shakers, and vortexes, have been commonly used to extract targets from the soil. However, due to the strong binding characteristics of the soil, manual shaking for one minute, which was sufficient for the analysis of pesticides in fruits and vegetables according to the original QuEChERS method, resulted in lower recovery rates in this study. [24,47,48]. To compare the efficacy of manual shaking and vortex extraction, various extraction times ranging from 1 to 6 min were evaluated. The results showed that the recovery obtained with vortex extraction was higher than that obtained with manual shaking. Additionally, it was found that increasing the intensity of shaking was beneficial in breaking the strong interactions between analytes and matrix, resulting in improved extraction. Based on these findings, vortex extraction was selected as the preferred method of extraction for the targets from soil in this study. As shown in Figure 3a, the optimal extraction time for the removal of target PCBs from soil was found to be 4 min, and extending the extraction time beyond this did not improve recovery rate.

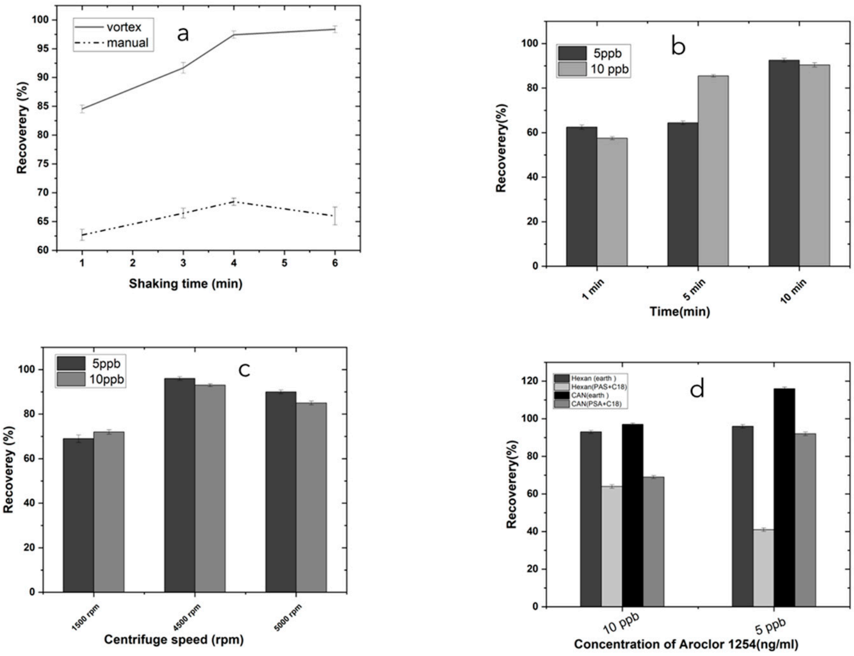

Figure 3. (**a**) Effect of shaking: 4 min, 15 mL of acetonitrile/water (75%:25%, *v/v*), 5 g of soil, 4 g $MgSO_4$, 1 NaCl. (**b**) Effect of centrifuge time: 4500 rpm, 15 mL of acetonitrile/water (75%:25%, *v/v*), 5 g of soil, 4 g $MgSO_4$, 1 NaCl. (**c**) Effect of speed: 10 min, 15 mL of acetonitrile/water (75%:25%, *v/v*), 5 g of soil, 4 g $MgSO_4$, 1 NaCl. (**d**) Comparison of recovery rates for different sorbents in the QuEChERS extraction method (n = 3). The conditions for the experiment were: 5 g of soil, 15 mL of acetonitrile/water (75%:25%, *v/v*), 4 g of $MgSO_4$, 1 g of NaCl, 4500 rpm.

There was a significant effect on centrifugation time and rate. In addition, different extraction times (1, 5, and 10 min) and rates (1500, 4500, and 5000 rpm) were investigated for 5 and 10 ng/mL concentration levels for PCB extraction. The results shown in Figure 3b indicate that excellent recovery of PCBs was achieved at 10 min, which was chosen as the optimal centrifugation time. A centrifuge of 4500 rpm was found to be sufficient to obtain good recovery of PCBs (Figure 3c). Using a centrifuge facilitates increased contact between the solvent and the soil sample, which improves dissolution of the analyte [49,50] and reduces the extraction time.

As part of the preparation of complex matrixes such as soil, a clean-up step was necessary in order to reduce interference, improve quantification, and avoid disturbing the signal on the chromatographic system [51]. In addition to traditional sorbents used in the clean-up step of QuEChERS extraction from soil samples, C18 and PSA, diatomaceous earth was also used as alternative sorbents [52,53]; they were less expensive and more eco-friendly than the traditional ones, but have not been extensively investigated in d-SPE [52]. As shown in Figure 3d, the sorbent has different effects on recovery and selectivity, and to achieve a satisfactory level of purification and recovery of PCBs, the effects of sorbent types were evaluated. The PSA retains a wide range of polar substances, including sugars, organic acids, and fatty acids. In addition, the nonpolar adsorbent, C18, retains trace amounts of nonpolar co-extractives and is capable of removing long chain fatty compounds and sterols from the extract. When PSA is used in conjunction with C18, additional lipids and sterols can be removed [53]. Diatomaceous earth consists of natural silica (SiO_2 nH_2O), with traces of metal oxides of specific structures, and its proposed use is as a simple alternative material and an environmentally-friendly natural sorbent [54]. The use of diatomaceous earth improved phase separation during QuEChERS extraction. Calculations of the differences between spiked and blank soil samples were used to determine recovery rates.

3.3. Method Validation

Under optimized extraction and clean-up conditions, we studied analytical parameters such as selectivity, linearity, LOD, LOQ, precision, and recovery. In order to evaluate the selectivity of the method, a blank sample was extracted by the optimized QuEChERS method, and positive samples were confirmed by GC-MS (Figure 4A). This confirms that the method has good selectivity, as no peaks interfered with analyte retention time. A standard calibration curve (Figure 4B) has been prepared using concentrations ranging from 0.31 to 10 ng/mL (0.31, 0.65, 1.25, 2.5, 5, 10 ng/mL) of Aroclor 1254 with a coefficient of determination R^2 of 0.9933; the linear regression equation fit is shown as (Y = 38,098 (x) − 26,023). The limit of detection (LOD) and limit of quantification (LOQ) were calculated based on three and ten times the standard deviation, respectively. The LOD value was 1.9 ng/mL and the LOQ value was 5.7 ng/mL, which indicated good sensitivity of this method.

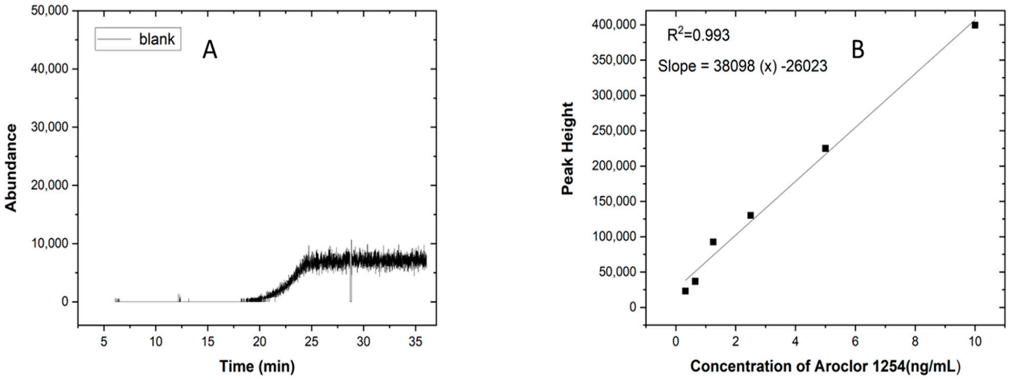

Figure 4. (**A**) GC analysis for the blank sample. (**B**) GC-MS calibration curve for standard Aroclor 1254.

3.4. Analysis of Aroclor 1254 in Spiked Soil Samples (Recovery and Precision)

The validation of a method is crucial to ensure that the results obtained are accurate and reliable. In the case of analyzing Aroclor 1254 in soil samples, sample spikes were used to improve the validation of the method. Two different levels of Aroclor 1254 standard solution were spiked into the soil samples at 5 and 10 µg/kg levels. The spiked samples were run in triplicate to evaluate the precision and repeatability of the assay. The RSD% was used to determine the precision, which was evaluated using two parameters: intra-day (repeatability) and inter-day precision. Repeatability was assessed by analyzing three replicates of soil samples spiked at two levels (5 and 10 µg/kg) on the same day, while inter-day precision was determined by analyzing samples on three different days over a period of two weeks.

The results of the analysis showed that the recovery of Aroclor 1254 from soil samples ranged from 95.3% to 103.2%, indicating the accuracy of the method. The RSD for inter-day precision ranged from 3.6% to 5.8%, while that for intra-day precision ranged from 2.1% to 4%, indicating the repeatability of the method. The developed modified QuEChERS method was compared with other recent studies in the literature, as demonstrated in Table 1. The present work shows great recovery value due to the use of different extraction solvents, which has a significant impact on the level of PCBs extraction from soil. Additionally, the comparison for blank (in black) and soil sample (in red) for 10 µg/kg and 5 µg/kg concentrations are presented in Figure 5, which further supports the accuracy and reliability of the modified QuEChERS and GC-MS methods for analyzing Aroclor 1254 in soil samples. These findings are important for environmental studies and risk assessments, as accurate analysis of pollutants in soil is necessary for identifying potential risks and implementing effective mitigation strategies.

Table 1. Comparison of the present study with other studies. For the present work recovery and RSD was included at different Aroclor 1254 concentrations in soil samples (n = 3).

Sample	Extraction	Added (µg/kg)	Intra-Day (RSD%)	Inter-Day (RSD%)	Recovery (%)	Reference
Water	acetonitrile	8 (µg/L)	≥15%	-	90–95%	[54]
Shrimp	water/MeCN *	1, 5, 10	>20%	-	70–115%	[55]
Sedimen	water/Ace/Hex * or wter/Ace/DCM *	50	≥15%	-	76–131%	[56]
Soil	Water/acetonitrile	5	4	5.8	103.2%	Present work
Soil	water/acetonitrile	10	2.1	3.6	95.3%	Present work

* MeCN (Acetonitrile), Ace (Acetone), Hex (Hexane), DCM (Dichloromethane).

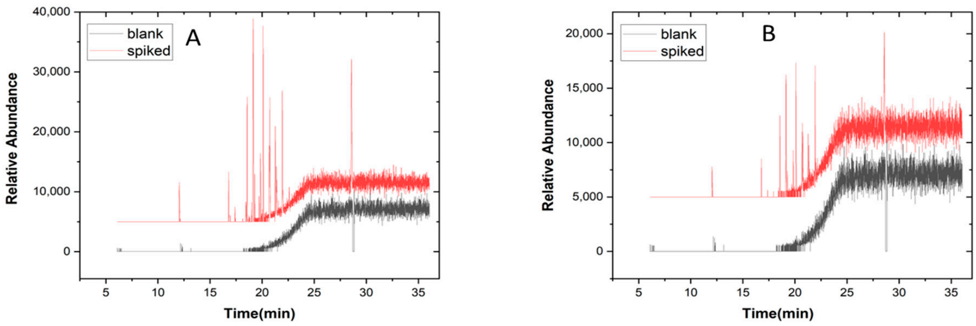

Figure 5. (**A**) GC/MS Total ion chromatogram of Aroclor 1254 (red line) and the blank (black line) for 10 µg /kg soil sample after QuEChERS extraction. (**B**) GC/MS Total ion chromatogram of Aroclor 1254 (red line) and the blank (black line) for 5 µg /kg soil sample after QuEChERS extraction.

4. Conclusions

In this study, we have utilized a modified QuEChERS method, combined with GC-MS analysis, to analyze Aroclor 1254 in soil samples. This novel method has several advantages over traditional techniques, including its simplicity, cost-effectiveness, eco-friendliness, and minimal solvent extraction. We have modified the sample pretreatment procedure by incorporating vortex shaking, a mixed solvent (either acetonitrile/water or hexane/water), and three adsorbents (PSA, C18, and diatomaceous earth) for the cleaning process. We have found that the best results were obtained when water/acetonitrile and diatomaceous earth were used. The method demonstrated excellent accuracy, linearity, LOD, LOQ, intra-day precision, and inter-day precision. Specifically, the recovery was in the range of 95.3–103.2%, correlation coefficients were higher than 0.98, the limit of detection (LOD) was 1.9 μg/kg, and the limit of quantification (LOQ) was 5.7 μg/kg, intra-day precision varied between 2.1% and 4%, and inter-day precision was between 3.6% and 5.8%.

This optimized method offers several advantages over traditional techniques, including a reduction in overall analysis time, an avoidance of the use of large levels of non-eco-friendly solvents, increased sensitivity, rapid results, and a reduction in the consumption of organic reagents. Compared to other common extraction methods, this streamlined procedure offers an efficient and effective technique for monitoring PCBs in the environment. Moreover, this technique has the potential to be applied to a wider range of sample types and applications, making it an even more valuable tool for environmental monitoring. Overall, the study provides a significant contribution to the field of analytical chemistry and environmental science, demonstrating a novel and effective method for analyzing Aroclor 1254 in soil samples.

Author Contributions: S.A.: writing—original draft; T.B.: writing—review and editing; H.A.: validation and investigation; I.A.: validation and investigation; A.H.: supervision; E.M.: supervision. All authors have read and agreed to the published version of the manuscript.

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