Talanta 101 (2012) 504–509

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Optimization of matrix solid phase dispersion coupled with gas chromatography electron capture detection for determination of chlorinated pesticides in soil

Amir Salemi [a,*], Elham Shafiei [b], Maryam Vosough [c]

[a] Environmental Sciences Research Institute (ESRI), Shahid Beheshti University, G.C., Evin, Tehran 1983963113, Iran
[b] Department of Chemistry, Ardabil Payamenoor University, Motahhari Ave., Ardabil, Iran
[c] Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran

ARTICLE INFO

Article history:
Received 24 June 2012
Received in revised form
3 October 2012
Accepted 4 October 2012
Available online 12 October 2012

Keywords:
Box–Behnken design
Chlorinated pesticides
Gas chromatography
Matrix solid phase dispersion
Soil

ABSTRACT

A fast, simple and efficient technique based on matrix solid phase dispersion has been presented for extraction and clean-up of some chlorinated pesticides and derivative products; α-BHC, β-BHC, γ-BHC, δ-BHC, heptachlor, aldrin, dieldrin, endrin, endosulfan 1, endosulfan 2, 4,4′-DDT, 4,4′-DDE, 4,4′-DDD, heptachlor epoxide, endrin aldehyde, endosulfan sulfate. Box–Behnken response surface methodology was employed for optimization of the extraction efficiency. As the optimized procedure, 0.5 g of dried and sieved soil samples were mixed with 2.0 g of 10% C18 in silica (w/w) as dispersant and after transferring into the extraction tube they were extracted with 8 mL of dichloromethane-*n*-hexane (1:1, v/v). Gas chromatography with electron capture detector was used for selective and sensitive determination of the analytes. Recoveries for the extraction of the proposed analytes were calculated and were satisfying (more than 75%), except for endrin aldehyde (59%) and endosulfan sulfate (62%). Also the method was linear over the calibration range ($R^2 > 0.991$) and the quantitative results were reasonably reproducible and sensitive (LODs ranged between 0.3 and 1.8 ng g^{-1}).

1. Introduction

Organochlorine pesticides are amongst the mostly concerned and studied pollutants of environmental media and due to their stability in the biogeochemical processes, most of them are classified as persistent organic pollutants (POPs). Despite public warnings and even banning rules against their application, organochlorine pesticides and their degradation products widely exist in the environment and their presence has been revealed in a variety of environmental media, such as vegetation [1], water [2], air [3] soil [4], fish [5], food products [6], etc.

Due to the presence of one or more chlorine atoms in their chemical structure, electron capture detector (ECD) could be a suitable choice for the sensitive and relatively selective detection of organochlorine pesticides after gas chromatographic separation [7–9]. However, mass spectrometry, has also been employed for detection purpose to benefit from its unique capabilities in qualitative and quantitative analysis at ultra-trace concentration levels, especially when multi-residue analysis was intended [10–12].

A wide variety of extraction techniques has been employed as the main step in the sample preparation procedure for the analysis of organochlorine pesticides in soil media. For example, solid phase extraction, SPE [13], gas purge micro-syringe extraction, GP-MSE [14], pressurized liquid extraction, PLE [15], QuEChERS extraction [16] and headspace ionic liquid-based microdrop liquid-phase micro-extraction, LPME [17] are amongst the techniques that could be mentioned from the recent reports.

Matrix solid phase dispersion introduced by Barker et al. in 1989 [18], integrates extraction and clean up procedures and helps the analyst by reducing time and labor through omitting some steps such as separating the extracting phase from the sample (filtration and centrifugation) and moisture removing from the final sample. This way the risk of analyte loss is also minimized and accuracy and precision of the entire method is enhanced. The proficiency and applicability of MSPD in the extraction of different analytes in various solid and semi-solid samples has been concisely reviewed by Kristenson et al. [19]. Amongst the newer reports, Pena et al. successfully optimized MSPD for extraction of polycyclic aromatic hydrocarbons (PAHs) followed by high performance liquid chromatography with fluorescence detection and showed that this technique was comparable with microwave assisted extraction from the viewpoint of extraction yield [20]. Similar comparative study on MSPD and

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[*] Corresponding author. Tel.: +98 21 22431971; fax: +98 21 22431972.
E-mail addresses: amirsalemi@gmail.com (A. Salemi), Niyayesh_elsh@yahoo.com (E. Shafiei), vosough@ccerci.ac.ir (M. Vosough).

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http://dx.doi.org/10.1016/j.talanta.2012.10.009

microwave assisted extraction was carried to find the more suitable extraction technique for the analysis of endocrine disrupting alkylphenols and parabens in the soil samples [21]. The authors showed that MSPD was less affected by the variation of soil type and remained relatively unchanged at the optimum efficiency level and hence was selected as the superior method for the extraction of real soil samples from different locations in Spain. Although, various analytes, even of the same family of compounds, need different conditions to be extracted efficiently and on the other hand sample clean-up is also performed simultaneously during the extraction, MSPD cannot be considered as a selective technique. To improve this aspect, Wang et al. [22] employed molecularly imprinted polymer (MIP) for the selective extraction of chloramphenicol from soil. However, they showed that due to ion suppression, sensitivity declined significantly, when compared with C18 instead of MIP, as the dispersing material. Another improvement in MSPD has been reported using graphene for dispersing the sample [23] and the authors showed that amongst the tested materials (C18, florisil, carbon nanotubes and graphene), due to its large surface area, graphene could yield better extraction recoveries for polybrominated diphenyl ethers and their analogs. MSPD has also been combined with dispersive liquid–liquid micro-extraction to achieve better sensitivity and more purification for the analysis of selected pyrethroids in soil samples [24].

As a three level design to fit response surfaces, Box–Behnken Design (BBD) was proposed by Box and Behnken in 1960 [25]. In fact, BBD is a combination of factorial and incomplete block design, in which the vertices of the design cube are empty and therefore extreme conditions are avoided. This design has been evaluated and explained from theoretical and applicability aspects by Ryan [26] and today the number of reports on its application is growing in the literature as an efficient approach in the optimization of the extraction and the analysis procedures [27–30].

Considering the mentioned statements, the main objective of the present work was to evaluate and optimize the efficiency of MSPD extraction technique in conjunction with GC-ECD for simultaneous determination of organochlorine pesticides and some of their degradation products in soil media. For this purpose a Box–Behnken design was implemented to study effect of the most important factors; the extracting solvent, the type of the dispersing material and its weight ratio to the soil sample. The optimized technique showed satisfying analytical performance characteristics also robustness against the change in soil matrix properties.

2. Materials and methods

2.1. Reagents and chemicals

Standard analytes were purchased from Supelco (USA) as a mixed solution of organochlorine pesticides and degradation products in toluene-*n*-hexane (50:50, v/v), consisting of α-BHC, β-BHC, γ-BHC, δ-BHC, heptachlor, aldrin, dieldrin, endrin, endosulfan 1, endosulfan 2, 4,4′-DDT, 4,4′-DDE, 4,4′-DDD, heptachlor epoxide, endrin aldehyde, endosulfan sulfate. The concentration of the analytes ranged from 10.10 to 62.24 $\mu g\ mL^{-1}$ in the stock standard solution from which working standards were prepared. All solvents (*n*-hexane, methanol, dichloromethane (DCM) and acetone, all of analytical reagent grade or higher), anhydrous sodium sulfate, Lichrolut C18 (70-230 mesh) and silica gel 60 were obtained from Merck (Germany) and 1-bromo-2-nitrobenzene (injection standard) was purchased from Sigma-Aldrich (USA).

2.2. Chromatographic analysis

An Agilent 7890 A GC equipped with spilt/splitless injector and electron capture detector (μECD) was used for the chromatographic procedures. 1 μL of the analytes solution (extracted or standard) was injected into the gas chromatograph under the splitless mode (250°C) which was held for 0.5 min before turning into split mode (100:1). Flow rate of helium as the carrier gas was remained constant at 1.0 $mL\ min^{-1}$ during the chromatographic run and separation was performed on a HP5-MS capillary column (30 m, 0.25 mm i.d. and 0.25 μm film thickness). The column oven temperature was initiated at 80 °C and held for 2 min, raised to 200 °C (15 $°C\ min^{-1}$), then to 240 °C at 3 $°C\ min^{-1}$ (held for 1 min) and finally ramped 20 $°C\ min^{-1}$ to 280 °C (5 min), resulting in a run time of about 33 min. Detector temperature was set at 320 °C and nitrogen was used as make-up gas at 30 $ml\ min^{-1}$. Data collection and processing was carried out using Chemstation software which was as well as other chromatography apparatus from Agilent Technologies Inc. (USA).

2.3. Sample preparation and extraction procedure

Soil sample was collected from a garden in which no chlorinated pesticide had been used during the last 15 years and was used in the method development procedure. The most important physico–chemical properties of the soil was as follows: pH = 7.95 (in water), air dried moisture = 8.06%, organic carbon content = 2.71% and conductivity = 2.12 $dS\ m^{-1}$ at 25 °C. Another sample was gathered from a forest for the purpose of studying the effect of sample properties on the analytical performance characteristics of the method. The values of the above mentioned physico–chemical properties for the second soil sample were 6.20, 7.44%, 2.89% and 0.97 $dS\ m^{-1}$ at 25 °C. The sample was dried at room temperature, sieved (sized less than 2 mm) and then kept in airtight amber glass containers at 2 to 4 °C and was used for spiking or blank analysis. During the study, this sample showed to contain no detectable analyte and be practically blank regarding the proposed chlorinated pesticides, degradation products and injection standard. To prepare a spiked sample, predetermined volume of working standard, diluted in acetone, was added to the proper weight of the soil, the slurry was mixed for 1 h and then spread on the glass plates and was permitted to dry overnight. The final spiked sample was gathered in airtight amber glass and kept refrigerated.

Predetermined and precisely weighed amounts of blank or spiked soil sample (0.5 g), dispersing material and clean-up sorbent were transferred into a mortar, mixed for 1 min using a pestle and transferred into a polymeric extraction tube which contained 1 g of sodium sulfate. The contents of the tube were packed by mild pressure using a glass rod and then covered by a frit. Appropriate volume of the extraction solvent was added gradually to the tube, permitted to flow by gravity and collected in glass tube. The gathered solution was dried by a gentle stream of nitrogen and the residue was reconstructed in 0.5 mL of *n*-hexane (containing 50 $ng\ mL^{-1}$ of 1-bromo-2-nitrobenzene as injection standard to correct the injected volume) and transferred into the amber glass vials.

2.4. Design of experiments

Table 1 demonstrates the standard and randomized run order of the experiments as well as coded and real levels of the studied factors according to the employed Box–Behnken design. All the procedures dealing with the response surface methodology were carried out using Design-Expert, version 7.1.6 from Stat-Ease (USA).

3. Results and discussion

3.1. Selection of the factors

Reviewing the published reports on the use of MSPD for soil samples, revealed that eluting solvent type and volume, dispersing material as well as the ratio of its weight to that of sample and presence and amount of clean-up sorbent have been the most frequently studied significant factors in the optimization of MSPD procedure. The flow rate of the eluting solvent through the cartridge could also be added to the list. Before starting the response surface methodology based on the all of the mentioned factors (i.e. 6–7 factors, which would lead to at least 54–62 experimental runs), some screening experiments were performed to reduce the number of factors and also to determine the experimental domain of the proposed design.

3.1.1. Solvents

Dichloromethane, *n*-hexane and their mixture in a variety of proportions, have been the solvents of choice in the extraction of chlorinated pesticides from soil or other solid samples. Preliminary experiments (data not included) showed that methanol was capable of performing such task, but the rate at which the solvent passed through the sample was extremely low, under the test conditions. So dichloromethane and *n*-hexane were selected for the further experiments. Also, as it was noted earlier in the experimental section, after evaporating the eluting solvent to dryness, samples were reconstructed in an adequate volume of solvent (containing injection standard).

Performing MSPD procedure using different volumes of eluting solvents (at 2, 5, 8, 11 and 15 ml) revealed that there was no significant improvement in the extracted amount of the analytes with more than 8 ml of both solvents (dichloromethane and *n*-hexane). So the volume of the extracting solvent was set to 8 ml for the rest of the analyses. Also to make the sample preparation easier, solvents were allowed to pass through the cartridges by gravity force. This resulted in a flow rate of approximately 0.4 to 0.5 ml min^{-1} (15 to 20 min).

3.1.2. Dispersing and clean up material

Silica gel is the most frequently used material as dispersant in the published MSPD reports, although alumina and C18 have been used for such purpose, too. Silica and alumina could also act as normal phase sorbents to clean up the sample while C18 has been reported to provide better dispersion of the sample and retaining the lipophilic contaminants of the sample [31]. The other main aspect of the dispersing and clean up materials is their amount or more precisely stated their weight ratio to the sample. This ratio has usually been set and studied between 1:1 and 4:1 and generally the higher the ratio, the higher the obtained extraction efficiencies . Taking into account the above mentioned points, the main factors and their studied levels were set as presented in Table 1.

Table 1
Box–Behnken Design matrix.

Run order		**Factors coded level**		
Standard	Random	A	B	C
1	2	−1	−1	0
2	7	+1	−1	0
3	10	−1	+1	0
4	12	+1	+1	0
5	15	−1	0	−1
6	6	+1	0	−1
7	13	−1	0	+1
8	3	+1	0	+1
9	1	0	−1	−1
10	9	0	+1	−1
11	8	0	−1	+1
12	14	0	+1	+1
13	11	0	0	0
14	4	0	0	0
15	5	0	0	0
Factor levels		**−1**	**0**	**+1**
Solvent composition (A; % v/v DCM)		0	50	100
Dispersant ratio (B; w/w) dispersant/soil		1:1	2.5:1	4:1
Dispersant composition (C; % silica)		0	50	100

3.2. Data handling

In order to simultaneously optimize the sample preparation procedure for sixteen analytes, a logical technique was needed for average responses of all analytes in a run out to a single figure. So, this average could possibly be the best representative of the entire group of the analytes and the optimization method could be easily applied on it to get the overall optimized experimental condition. It is worth noting that here no priority has been taken to account based on the different importance of individual analytes (e.g. their relative toxicity, abundance, persistency, etc.). The technique which has been used in this work was based on the concept of *desirability function* and was performed as follows: the maximum response of each analyte (peak area of the analyte after correction due to the injection standard) in the entire experimental runs of the design (set of 15 runs) was determined and all the responses of the same analyte were divided by that. In other words, the responses of the analytes were normalized based on their maximum obtained values and were brought to a single scale. Then, for each single run of experiment, geometrical average of the normalized analytes responses (set of 16 analytes) was calculated. This provided a matrix of 15 rows and 1 column, which then could be introduced into the optimization software as the response to be optimized. It is worth noting that extraction efficiency or recovery could be used instead of peak area values as were described above. However, since recovery values are obtained from dividing peak areas (which have been used here) by a constant figure (i.e. peak area of the analytes which were directly injected into the gas chromatograph and preferably at the same concentration level of the spiked and extracted soil samples), the final results of the optimization would be the same.

3.3. Box–Behnken design

Table 1 shows the details of the designed experiments. The resulting data was analyzed using Design-Expert software and the following characteristics of the model were obtained (based on ANOVA). The model was significant considering the *F*-value of 13.03 ($df=9$) and *p*-value of 0.0057. Also, the lack of fit of the model ($df=3$) relative to its pure error ($df=2$) showed a *F*-value of 3.65 and a *p*-value equal to 0.2224 and so was not significant. All three main effects; solvent composition (A), dispersant ratio (B) and dispersant composition (C), one interaction (BC) and two quadratic terms (A^2 and B^2) were significant and had *p*-value less than 0.05. The final equation describing the model in terms of coded values of the significant factor levels was; $\text{Response}=0.86+0.088\ A+0.15\ B-0.097\ C-0.13\ BC-0.22\ A^2-0.14\ B^2$, from which some conclusions could be drawn.

First, there was no significant interaction between solvent composition and solid sorbents parameters (B and C). In other words, performance of the selected solvents in extracting and eluting the analytes from soil was independent from composition

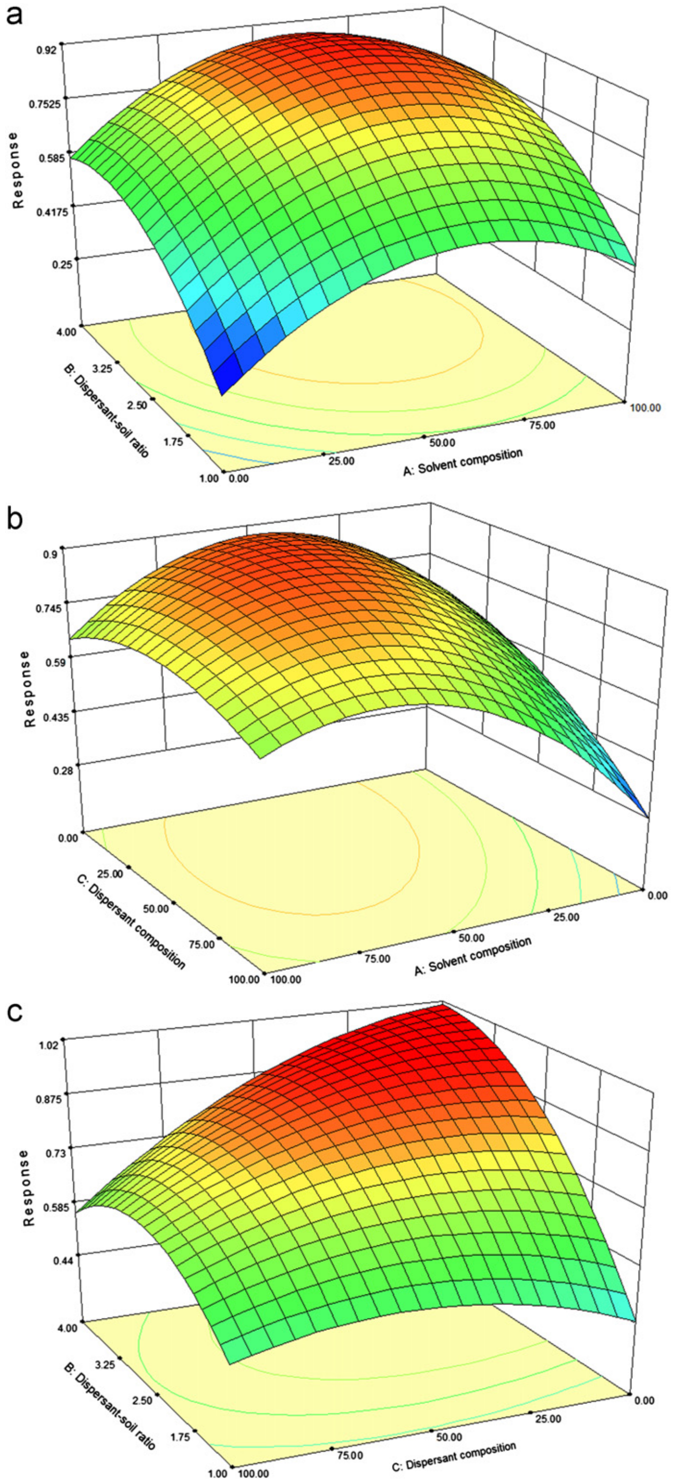

Fig. 1. Response surface for three possible pairs of the factors: (a) dispersant ratio and extracting solvent composition, (b) dispersant and extracting solvent composition and (c) dispersant ratio and its composition.

of the selected dispersing material or its weight ratio to the sample. But, composition of dispersing material and its weight ratio showed relatively strong interaction. In fact, as the model showed, when dispersant weight ratio to the soil sample was set at its minimum (1:1), C18 content of the material became nearly ineffectual. Otherwise stated, any deliberate composition of C18 and silica gel would produce approximately the same result. On the other hand, using the highest level of the factor B (4:1 ratio), caused a significant difference between C18 and silica gel, considering their contribution to the overall average response of the method for all 16 analytes.

As the second conclusion, the quadratic effect of the dispersing material ratio is as important as its linear term and in the case of solvent type, the numeric value of the quadratic term is approximately three times its linear effect. Such relationship between the response and factors would usually lead to significant curvature in the factor effects which cannot be handled by linear models, like a full or fractional factorial design. Therefore, selection of a response surface methodology, here Box–Behnken design, for studying the proposed technique was confirmed to be correct and appropriate.

The model properties, factor effects and also above mentioned statements, have been graphically demonstrated in Fig. 1a–c, as response surfaces of the model for each of three possible pair of factors. The presented graphs also contain the corresponding contour plot. The strong interaction between dispersing material composition and its weight ratio, BC, could be easily understood from considering any of two pairs of the opposite edges in the surface presented in Fig. 1c. This interaction can become more clear by comparing it with the response surfaces of AB and AC, which showed no statistically significant interaction, as can be seen in Fig. 1a and b, respectively.

3.4. *Optimum levels of factors*

According to the calculated model, there were several sets of factor levels which led to the maximum response value. Among these sets, the most desirable factor levels ranged as follows: 26–68% for the percentage of dichloromethane in the eluting solvent (most frequently 50–60%), 3.15–4 for the ratio of dispersant to sample of which most of the numbers were more than 3.7 and 0–29% for the percentage of C18 in the dispersant material while the dispersing material composition levels between 10 and 20% were dominant. So the 1:1 mixture of dichloromethane and *n*-hexane for the eluting solvent, the 4:1 ratio of the dispersant to the soil sample and 10% C18 in silica gel were chosen to provide the optimal extraction efficiency.

It is obvious that the above mentioned optimum conditions have been deduced for the (geometrical) average of analytes responses and hence may not result in the best performance when individual pesticides or any other selected set of analytes are considered. For instance 4,4′-DDT showed the optimum when eluted by 50% dichloromethane, dispersant to soil ratio was 2.5–4 and dispersant contained 50–60% of C18. Also, the optimum extraction condition for 4,4′-DDD was found to be similar to 4,4′-DDT except for dispersing material type which calculated to be 100% silica.

Another important point in this regard is that although the response surface of the overall signal showed strong curvature (Fig. 1), but some individual analytes demonstrated a planar response surface without any significant curvature (at 95% confidence level). α, β, γ and δ-BHC where among this group. This means that compromising the behavior of different chemical compounds through averaging their corresponding signal, although may lead the analyst to the approximately best solution, but chances are that the true chemical characteristics and behaviors of the analytes be neglected. So the scientific and fundamental interpretation of the relationship between overall optimum extraction condition and physico–chemical properties of the individual analytes would be groundless and misleading. As a matter of fact, the set of optimum factor levels could only be considered as a practical guidance and not an intrinsic phenomenon.

The last point about the experimental condition deals with the interaction of final solution composition and the chromatographic detector, ECD. As described in the experimental section (Section 2.3), after eluting the analytes from sample, the resulting solution was evaporated to dryness and then reconstructed. Pure *n*-hexane (plus injection standard) was utilized in this step, because presence of even few percents of chlorinated solvent in the final solution would lead to overloaded and broadened solvent peak, instability in the baseline in the first few minutes (upto 6–10 min) of the resulting chromatograms and also weak reproducibility of signals.

3.5. Figures of merit

Table 2 contains analytical characteristics that have been obtained by running the entire procedure of sample preparation and chromatographic analysis under the optimized set of conditions. As it is observed in the second column of the table, recovery of the extraction procedure ranged from 59.0% for endrin aldehyde upto 93.1% for aldrin. These values were calculated using the equation; Recovery %=A_{exp}/A_{cal} in which A_{exp} was the peak area of each analyte in the chromatogram of the extracted sample and A_{cal} was the calculated and ideally expected value (derived from direct injection of standard solution). Regarding the differences between the overall optimum experimental conditions and those of the individual analytes, it could be reasonable to expect that when the optimum conditions have been calculated and set based solely on the peak area of a single analyte or a small group of the selected analytes, higher recoveries would be achieved.

To study the effect of sample matrix characteristics on the recovery of the developed method, another soil sample which had been collected from a forest, was spiked and analyzed in an exactly similar procedure. The results showed no significant difference while all the individual analytes were taken to the account.

Table 2 also shows that the method was linear in the calibration range; 15 upto 750 ng g^{-1}, except for heptachlor and 4,4′-DDT for which the upper range of calibration curve was set at 600 ng g^{-1}. LODs of the entire optimized method ranged between 0.1 ng g^{-1} for 4,4′-DDT and 1.8 ng g^{-1} for endosulfan sulfate ($S/N=3$), that seemed promising regarding the small amount of sample needed for the procedure of the analysis.

Table 2
Performance parameters of the MSPD-GC-μECD.

	Recovery (%)[a]	LOD[b] (ng g^{-1})	LOQ[c] (ng g^{-1})	RSD (%)[d]	Linearity[e]
α-BHC	76.2	0.4	0.7	1.3	0.998
β-BHC	81.1	0.3	1.0	3.4	0.997
δ-BHC	77.9	0.6	2.0	2.8	0.993
γ-BHC	79.8	0.4	1.3	8.0	0.996
Heptachlor	80.0	0.2	0.7	5.3	0.997[f]
Aldrin	93.1	1.0	3.3	3.7	0.991
Heptachlor epoxide	91.6	0.4	1.3	8.0	0.996
Endosulfan 1	81.2	0.9	3.0	6.0	0.997
4,4′-DDE	79.5	0.5	1.7	6.2	0.991
Dieldrin	70.4	0.3	1.0	5.8	0.994
Endrin	80.7	0.9	3.0	4.4	0.992
4,4′-DDD	76.3	0.5	1.7	8.5	0.998
Endosulfan 2	68.3	0.5	1.7	6.6	0.994
4,4′-DDT	78.9	0.1	0.3	4.5	0.991[f]
Endrin aldehyde	59.0	1.1	3.7	5.8	0.991
Endosulfan sulfate	61.6	1.8	6.0	11.4	0.993

[a] Based on the average result of five replicate analyses on the soil samples spiked at the lowest concentration level of the calibration curve.

[b] $S/N=3$.

[c] $S/N=10$.

[d] Based on the results of five replicate analyses which carried out for recovery study.

[e] R^2 value of the calibration curves from 15 upto 750 ng g^{-1}.

[f] To prevent signal overloading, upper limit of calibration was set at 600 ng g^{-1}.

4. Conclusion

A simple, fast and inexpensive technique based on matrix solid phase dispersion was developed and optimized for the extraction of selected chlorinated pesticides and some important degradation products (total number of 16). A Box–Behnken response surface methodology was applied to investigate the optimized level of the most important factors of the extraction procedure, which were the composition of the dispersing material and its weight ratio to the soil sample and also the eluting solvent composition. The proposed method needed only 0.5 g of the dried soil sample (less than 2–3 g of the fresh and wet soil before drying and sieving, depending on its water content and particle size distribution), while the sensitivity of the method considered to be satisfying. It also required less than 10 mL of potentially toxic and environmentally harmful organic solvents, of which less than half was chlorinated. As an important factor in the environmental trace analysis in the soil media, no memory effect was observed. Reproducibility of the procedure, stated as relative standard deviation of five replicates ranged from 1.3 upto 11.4% at approximately 15 ng g^{-1} of concentration level.

Acknowledgments

The authors wish to gratefully acknowledge Dr. H. Liaghati, the former president of Environmental Sciences Research Institute of Shahid Beheshti University, for supporting the presented study. Research Council of Shahid Beheshti University is also appreciated.

The authors responsibly declare no financial, commercial or other conflict of interest.

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