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Solvent-based de-emulsification dispersive liquid–liquid microextraction combined with gas chromatography–mass spectrometry for determination of trace organochlorine pesticides in environmental water samples

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ABSTRACT

In this work, we propose solvent-based de-emulsification dispersive liquid–liquid microextraction (SD-DLLME) as a simple, rapid and efficient sample pretreatment technique for the extraction and preconcentration of organochlorine pesticides (OCPs) from environmental water samples. Separation and analysis of fifteen OCPs was carried out by gas chromatography–mass spectrometry (GC/MS). Parameters affecting the extraction efficiency were systematically investigated. The detection limits were in the range of 2–50 ng L^{-1} using selective ion monitoring (SIM). The precision of the proposed method, expressed as relative standard deviation, varied between 3.5 and 10.2% ($n = 5$). Results from the analysis of spiked environmental water samples at the low-ppb level met the acceptance criteria set by the EPA.

1. Introduction

Analysis of organochlorine pesticides (OCPs) is of great importance in environmental pollution sciences because these may cause adverse effects on human health and animals. Although the use of OCPs has been banned or restricted in industrialized countries (Stockholm Convention of Certain Persistent Organic Pollutants), these compounds are still detected in the environmental samples and in foodstuffs [1]. On this basis, there is an increasing demand to determine the OCPs residues in environmental samples [2].

Gas chromatography especially coupled to mass spectrometric detection has proved to be a powerful analytical tool for the analysis of pesticides in various matrixes offering high separation efficiency, low limits of detection and enhanced selectivity. However, due to the strict environmental legislation on pesticide residues and the demand for ultra-trace analysis, a preconcentration step is mandatory prior to measurement [3,4]. Typical pretreatment protocols involve extraction of the pesticide analytes from the usual aqueous matrixes to a phase that is compatible to GC (organic solvents, SPME fibers, etc.). On this basis, sample pretreatment techniques that are commonly used in environmental water analysis include the traditional liquid–liquid extraction [5], solid phase extraction (SPE) [6], single-drop microextraction (SDME) [7], solid phase microextraction (SPME) [8], headspace SPME (HS-SPME) [9] and hollow fiber liquid phase microextraction (HF-LPME) [10].

In 2006, a new member of the family of liquid phase microextraction techniques known as dispersive liquid–liquid microextraction (DLLME) – has been introduced by the research group of Assadi [11] and has been coupled to many analytical techniques including HPLC [12], GC [13] or atomic absorption spectroscopy (AAS) [14]. DLLME offers significant advantages including simplicity, easy handling, cost-effectiveness, rapidity, limited consumption of organic solvents, and high enrichment capabilities [15]. These features have attracted the interest of many research groups that over the last four years have presented interesting alternative approaches of the originally proposed scheme [16–21].

The basic common characteristic of the above-mentioned DLLME approaches is that phase separation is accomplished by a centrifugation step. This extra – time consuming – step can be avoided by the recently-introduced alternative of solvent-terminated DLLME (ST-DLLME) [22]. In solvent-terminated DLLME the extraction is terminating by the addition of a second portion of the disperser that acts as a de-emulsifier and promotes physical phase separation without centrifugation. From a terminology point of view we believe that "solvent-based de-emulsification" DLLME (SD-DLLME) would be a rather more informative term for this technique and we adopted this throughout this work.

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In the presented work we demonstrate the feasibility of the usage of SD-DLLME for the preconcentration and determination of OCPs at trace concentration levels using GC/MS. The exploitation of lighter-than-water extraction solvent (e.g. hexane, xylene, toluene) offers a simpler and more convenient protocol from a handling point of view without sacrificing sensitivity and efficiency. To the best of our knowledge our work is the second report of SD-DLLME in the international literature.

2. Experimental

2.1. Reagents and solutions

A mixture (1000 mg L^{-1}) of 15 organochlorine pesticides including etridiazole, chloroneb, propachlor, trifluralin, hexachlorobenzene, chlorothalonil, cyanazine, chlorpyrifos, DCPA (dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate), cis-chlordane, trans-chlordane, trans-nonachlor, chlorobenzilate, cis-permethrin, trans-permethrin in methyl tert-butyl ether were purchased from Accustandard (New Haven, CT, USA). Some properties of the OCPs are tabulated in Appendix A Table 1. 1-Bromo decahexane (ISTD), acetonitrile (ACN), methanol, *n*-hexane, acetone, sodium chloride, and phosphoric acid were provided by Merck (Darmstadt, Germany). Iso-octane, cyclohexane, toluene and *m*-xylene (all of purity >99%) were purchased from Sigma–Aldrich (Steinheim, Germany). Sudan III (technical grade, Sigma) was used as a colored hydrophobic compound for the measurement of the volume of the organic solvent. Ultrapure water (18 MΩ cm) was used throughout this work (Millipore Direct-Q UV, Millipore S.A.S., Molsheim, France).

A standard pesticides stock mixture (100 mg L^{-1}) was prepared in ACN and stored at −20 °C protected from the light. This solution was stable over a period of at least two months. Standard working aqueous solutions were prepared daily by dilutions of the stock.

2.2. Instrumentation

GC/MS analyses were performed on a 7890A gas chromatography (Agilent Technologies, Wallbronn, Germany) equipped with an electronically controlled split/splitless injection port and an inert 5975C mass selective detector with electron impact (EI) ionization chamber. Pesticides separation was carried out on a 30 m × 0.25 mm, 0.25 μm film thickness HP-5MS column (Agilent Technologies). The carrier gas was helium (purity 99.999%) at constant flow of 1.0 mL min^{-1}. The injector temperature was set at 250 °C while the injection of sample ($V_{inj.}$ 2 μL) was made in splitless mode (purge flow 30 mL min^{-1} for 1 min). The total GC/MS analysis time was 25.7 min with the oven programmed to hold 2 min at 100 °C, ramp to 150 °C at 20 °C min^{-1}, ramp to 225 °C at 7 °C min^{-1} and finally ramp to a final temperature of 280 °C at 10 °C min^{-1} and held for 3 min.

The mass selective detector (MSD) was operated in electron ionization mode at 70 eV. The source, quadrupole and transfer line temperatures were 230 °C, 150 °C and 285 °C, respectively. Detection was achieved in selected ion monitoring (SIM) mode with a solvent delay of 5 min. Full-scan MS data were acquired over the range of *m*/*z* 50–500 to obtain the fragmentation spectra of the analytes. The peak identification was carried out by matching retention times of standards (within ±0.02 min), base peak and the fragmentation pattern. Relative retention time and peak quantification were performed against to ISTD. The Enhanced ChemStation (G1710 EA, E.02.00.493) chromatographic management software (Agilent Technologies) was used for data acquisition. The retention times, target and qualifier ions, start times of SIM groups and data acquisition rates for pesticides are tabulated in Appendix A Table 2.

A 10 μL micro-syringe (FN 23/42/HP, Agilent Technologies) was used for sample injection. Glass tight syringes with volumes of 50, 100 and 1000 μL (Hamilton Company, Nevada, USA) were employed for measurements of the volumes of the extraction organic solvents and for the dispersive/de-emulsification processes.

2.3. SD-DLLME protocol

An aliquot of 10 mL of aqueous standard or sample was transferred in a 10 mL volumetric flask and kept under continues stirring at 200 rpm. An emulsion (water/ACN/*m*-xylene) was formed by rapid injection of a mixture containing 750 μL ACN (disperser) and 40 μL *m*-xylene under the surface of the aqueous phase (Appendix A Fig. 1A and B) promoting the extraction of the analytes into the fine *m*-xylene microdroplets. After 2 min a second 750 μL-portion of ACN (de-emulsifier) was injected into the solution to break down the emulsion (Appendix A Fig. 1C). Phase separation was achieved in less than 1 min (Appendix A Fig. 1D). A volume of 2 μL of the organic solvent were withdrawn by the micro-syringe and injected immediately into the GC inlet.

3. Results and discussion

The extraction efficiency in DLLME is affected by various parameters including: (i) the type and the volume of both extraction and disperser (and de-emulsifier in SD-DLLME) solvent, (ii) the ionic strength, (iii) the pH of the aqueous phase, (iv) the extraction time and (v) the agitation speed [22]. The above-mentioned parameters were carefully investigated using the "one-parameter-at-a-time" approach and aqueous standards of the analytes at the 20 μg L^{-1} mass concentration level. The extraction recovery (*ER*, %) and the enrichment factor (*EF*) were calculated by the well-known equations mentioned in [11].

In order to visualize the extraction procedure, preliminary experiments were carried using a hydrophobic red-colored compound (Sudan III) as microdroplets' marker. These experiments excluded the usage of typical Teflon-coated stirring bars, as large amount of the organic microdroplets were stack in the bar due the good affinity with the Teflon material. Such a behaviour would certainly lead to low pesticides recoveries and loss in precision. To overcome this potential problem, a glass-coated magnetic stirring bar was used throughout this study.

3.1. Investigation of the type and volume of the extraction solvent

The type of the extraction solvent is an essential parameter that usually affects the overall efficiency of a LPME procedure [23]. The extraction solvent has to meet the following general requirements: (i) low solubility in water, (ii) high extraction efficiency and (iii) good gas chromatographic behaviour. On the basis of simpler overall handling of the extraction procedure, low-density organic solvent were preferred in this study since they can be withdrawn directly from the extraction vial via a suitable micro-syringe. Solvents with different water-solubilities, namely iso-octane (d_{25} = 0.692 g mL^{-1}), *n*-hexane (d_{25} = 0.659 g mL^{-1}), cyclohexane (d_{25} = 0.779 g mL^{-1}), toluene (d_{25} = 0.865 g mL^{-1}), *m*-xylene (d_{25} = 0.868 g mL^{-1}) were examined.

The extraction efficiency of the above-mentioned solvents was investigated using standard aqueous solutions of the analytes at the 20 μg L^{-1} concentration level in all cases. ACN was employed as both disperser and de-emulsifier (500 + 500 μL). The initial volume of the extraction solvents were varied in the range of 57–70 μL

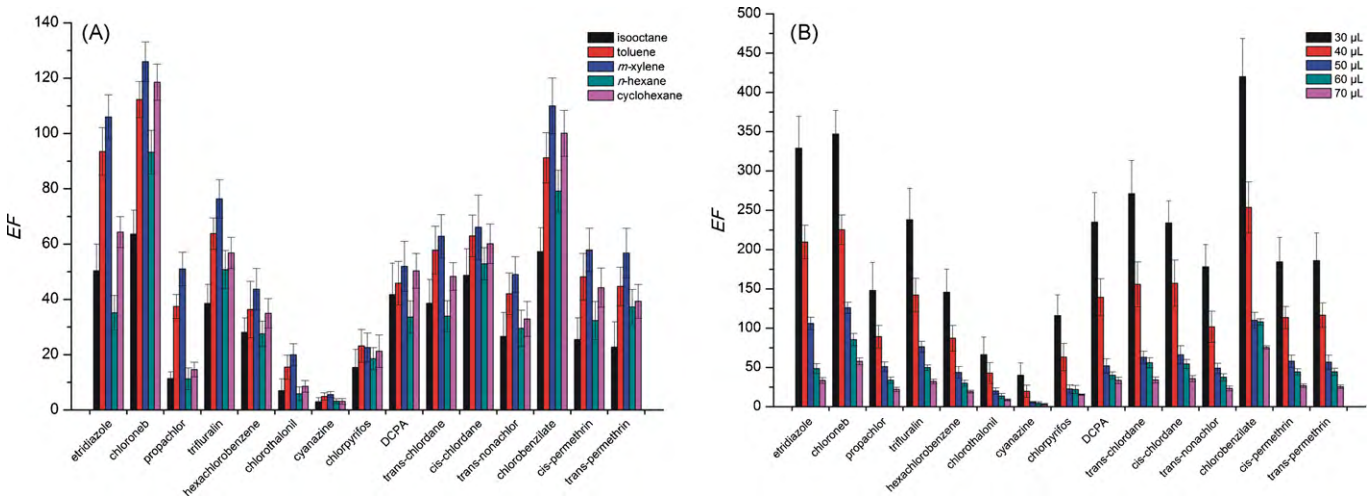

Fig. 1. Effect of the type of the organic solvent on the extraction efficiency (A) and the effect of the *m*-xylene volume on the enrichment factor (B). Experimental conditions: aqueous solution volume 10 mL (at 20 μg L^{-1}); disperser/terminating solvent, ACN (500 + 500) μL; stirring rate, 150 rpm ($n = 3$).

– depending on their solubility in the extraction system – in order to achieve a uniform final volume of the upper phase of 50 (±1.0) μL ($n = 3$). As it can be seen in Fig. 1A higher recoveries were generally achieved by using aromatic organic solvents (toluene, *m*-xylene) compared to non-aromatic ones. This behaviour can be attributed to unsuccessful de-emulsification process when non-aromatic organic solvents were employed. Additionally, since most of the analytes contain aromatic ring in their molecular structures (expect from chlordane and nonachlor), higher extraction yields can be expected in aromatic solvents. Finally, *m*-xylene was chosen as extraction solvent because it provides slightly higher recoveries of the analytes compared to toluene. Additionally, the selected solvent is significantly less toxic compared to other typical extraction solvents used in DLLME (Appendix A Table 3).

Another important parameter that influences the performance of the microextraction and the enrichment of the analytes is the volume of the organic solvent. A series of SD-DLLME experiments were carried out varying the *m*-xylene volume in the range of 30–70 μL and keeping the other experimental parameters constant. As can be seen from the experimental results of Fig. 1B, higher EF of the analytes in the range of 349–448 were achieved using 30 μL of extraction solvent. However, using this volume the precision was poor due to difficulties in the collection/withdrawal of reproducible and water-free portions of the *m*-xylene phase. A *m*-xylene volume of 40 μL was chosen for subsequent experiments as a compromise between the enrichment factor and the precision of the extraction procedure.

3.2. Investigation of type and volume of disperser/de-emulsifier solvent

The effectiveness of the emulsification/de-emulsification of oil-in-water emulsions is depended on the type of the disperser/terminating solvent [22,24]. In this work, three types of solvents that are commonly used in DLLME, namely ACN, methanol and acetone were studied. For simplicity reasons the same type of

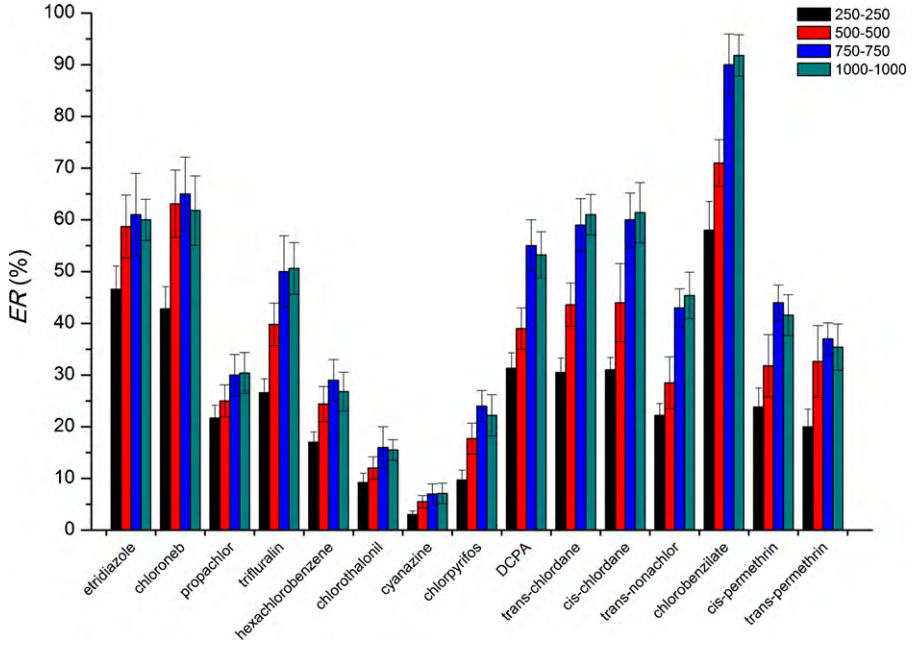

Fig. 2. Effect of the disperser/terminating volume on the extraction recovery. For experimental details see Section 3.2.

Table 1
Analytical figures of merit of the proposed SD-DLLME method.

Analytes	Linear dynamic range ($\mu g\,L^{-1}$)	r	Precision (RSD %)		LOD[a] ($ng\,L^{-1}$)	EF[b]
			Intra-day[c]	Between-day[d]		
Etridiazole	0.5–50	0.9990	4.3	5.6	24	216
Chloroneb	0.05–50	0.9996	4.9	6.3	6	232
Propachlor	0.5–50	0.9995	5.1	7.7	11	106
Trifluralin	0.1–50	0.9992	6.2	5.2	2	179
Hexachlorobenzene	0.05–50	0.9991	5.8	5.3	3	105
Chlorothalonil	0.2–50	0.9989	4.6	8.9	13	55
Cyanazine	1–50	0.9992	5.0	9.2	50	25
Chlorpyrifos	0.05–50	0.9990	3.8	6.8	9	84
DCPA	0.05–50	0.9988	3.5	8.4	2	195
trans-Chlordane	0.05–50	0.9993	4.3	7.3	4	212
cis-Chlordane	0.05–50	0.9989	3.7	5.1	3	215
trans-Nonachlor	0.05–50	0.9992	3.8	6.2	2	153
Chlorobenzilate	0.05–50	0.9991	3.7	9.7	9	319
cis-Permethrin	0.05–50	0.9990	7.1	10.2	6	158
trans-Permethrin	0.05–50	0.9993	4.3	6.2	2	132

[a] Limit of detection calculated at a three signal-to-noise ratio (S/N = 3).
[b] Enrichment factor.
[c] Calculated by five replicates ($n = 5$) at concentration level of 1 $\mu g\,L^{-1}$.
[d] Calculated by five consecutive days ($n = 5$).

organic solvent was used both as disperser and terminating solvent (500 + 500 μL). The results revealed that ACN provided 5–10% higher extraction recoveries in most of the pesticides compared to methanol and acetone. Based on these findings, ACN was adopted for subsequent experiments.

In order to investigate the effect of the volume of disperser/terminating solvent, the total ACN volume was varied between 500 and 2000 μL at equal disperser/terminating volumes (250 + 250 500 + 500, 750 + 750 and 1000 + 1000, μL + μL). Higher and generally constant extraction efficiency was achieved for total ACN volumes of higher than 1500 μL (750 + 750), obviously due to more efficient dispersing/terminating actions at higher ACN volumes (Fig. 2). A volume of ACN of 1500 μL (750 + 750) was finally chosen. Under the selected extraction conditions, the final volume of the *m*-xylene was 28 (±1) μL.

3.3. Investigation of other parameters

Other important parameters that were investigated were the pH, the ionic strength, the agitation rate and extraction time. A detailed discussion on the effect of these parameters can be found in the Appendix A. The selected values for further experiments were: (i) pH = 7.0, (ii) no salt addition, (iii) stirring rate of 200 rpm and (iv) 2 min extraction time.

3.4. Evaluation of method performance

Under the selected experimental conditions, the proposed SD-DLLME methodology was applied to a series of eight standard solutions at different concentration levels (0.05–50 $\mu g\,L^{-1}$). The concentration of the ISTD was 50 $\mu g\,L^{-1}$ in all cases. The linear dynamic ranges, the correlation coefficients (r), the LODs and the enrichment factors are summarized in Table 1. The repeatability of the proposed method, expressed as relative standard deviation (RSD), was determined by carrying out five independent extraction experiments at the 1 $\mu g\,L^{-1}$ concentration level and found to be in the range of 3.5 and 7.1%. The reproducibility was validated by performing three extractions during five consecutive days ($n = 5 \times 3$) at the same concentration level as mentioned above. The RSDs varied between 5.1 and 10.2%. The precision data for each analyte is also included in Table 1. The variation of the retention times was less than 0.5% during these experimental series. The limits of detection were calculated using the signal-to-noise ration (S/N) criteria in all cases (LOD = 3 S/N).

3.5. Analysis of real samples

Underground, mineral and natural water samples collected from different locations in Northern Greece were transferred into amber

Table 2
Accuracy (% recoveries) of the proposed SD-DLLME–GC/MS method in spiked water samples.

Pesticides	Underground water Spiked level ($\mu g\,L^{-1}$)			Tap water Spiked level ($\mu g\,L^{-1}$)			Mineral water Spiked level ($\mu g\,L^{-1}$)		
	0.5	1	2	0.5	1	2	0.5	1	2
Etridiazole	86(11)	95 (7)	112 (7)	92 (6)	110 (7)	107 (5)	97 (5)	99 (6)	107 (5)
Chloroneb	91(9)	93 (10)	86 (11)	89 (11)	91 (6)	106 (7)	96 (8)	104 (6)	106 (5)
Propachlor	92(7)	90 (14)	101 (14)	106 (7)	100 (13)	98 (5)	87 (6)	105 (6)	99 (7)
Trifluralin	88 (8)	89 (6)	99 (13)	115 (5)	101 (6)	94 (6)	90 (12)	98 (13)	92 (11)
Hexachlorobenzene	90 (12)	86 (9)	100 (7)	83 (13)	96 (9)	109 (7)	94 (11)	108 (8)	104 (6)
Chlorothalonil	94 (6)	103 (8)	97 (7)	87 (9)	93 (7)	104 (5)	101 (6)	91 (7)	107 (6)
Cyanazine	–	108 (6)	103 (4)	–	106 (11)	101 (4)	–	93 (10)	94 (5)
Chlorpyrifos	75 (9)	96 (13)	100 (8)	82 (9)	95 (8)	105 (5)	103 (7)	89 (5)	90 (11)
DCPA	103 (7)	97 (8)	102 (9)	89 (6)	104 (7)	96 (6)	101 (5)	106 (13)	111 (7)
trans-Chlordane	107 (6)	102 (8)	77 (8)	94 (7)	84 (7)	92 (4)	98 (5)	103 (10)	109 (7)
cis-Chlordane	96 (12)	101 (13)	86 (9)	97 (11)	87 (10)	103 (6)	100 (8)	90 (11)	94 (13)
trans-Nonachlor	91 (7)	94 (4)	89 (8)	103 (9)	82 (8)	99 (3)	89 (8)	96 (5)	98 (10)
Chlorobenzilate	96 (10)	98 (6)	86 (7)	113 (5)	106 (7)	102 (7)	107 (7)	104 (9)	96 (7)
cis-Permethrin	105 (6)	95 (12)	90 (6)	108 (6)	101 (5)	92 (6)	106 (5)	94 (6)	101 (8)
trans-Permethrin	98 (5)	101 (8)	82 (7)	94 (8)	92 (5)	98 (5)	104 (5)	97 (5)	113 (6)

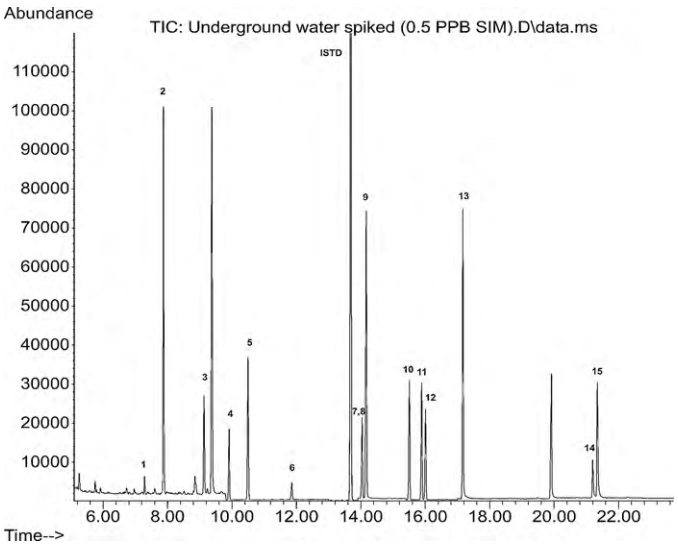

Fig. 3. GC/MS (SIM) chromatogram of organochlorine pesticides spiked at 500 ng L^{-1} in underground water sample after SD-DLLME. Peak identification: 1: etridiazole; 2: chloroneb; 3: propachlor; 4: trifluralin; 5: hexachlorobenzene; 6: chlorothalonil; 7: cyanazine; 8: chlorpyrifos; 9: DCPA; 10: trans-chlordane; 11: cis-chlordane; 12: trans-nonachlor; 13: chlorobenzilate; 14: cis-permethrin; 15: trans-permethrin.

glass containers and preserved according to EPA guidelines [25]. Tap water was allowed to run for at least 10 min prior to collection and analyzed immediately. Prior to analysis, all samples were filtered through 0.45 μm pore size membrane filters (Whatman®). Initial analysis confirmed that they were free of all target analytes.

The potential matrix effect of the real samples was evaluated by spiking them at three concentration levels (namely 0.5, 1.0 and 2.0 μg L^{-1}) and calculating the percent recoveries versus an aqueous calibration curve. It should be noted that according to EPA guidelines the acceptance criteria is $R \pm 30\%$ (namely 70–130%) [25]. The experimental findings are summarized in Table 2. The recovery data showed that no significant matrix-effect from the samples was observed for the pesticides tested. A representative chromatogram of the analysis of underground water sample after spiking is depicted in Fig. 3.

4. Conclusions

In the present work we demonstrated the usefulness and suitability of SD-DLLME in combination with GC/MS for the preconcentration and quantification of fifteen EPA 508 chlorinated pesticides in environmental water samples. SD-DLLME as sample preparation technique offers certain important advantages: (i) it is simple requiring no specific operation skills, (ii) it is cost effective employing typical laboratory equipment, (iii) high extraction efficiency and preconcentration are achieved in less than 2 min, (iv) the sample preparation time is further decreased by the fact that no centrifugation is required for phase separation and collection and (v) no toxic chlorinated solvents are used. Two disadvantages of our method can be pointed out: (i) the ability of collection of small extractant volumes (<30 μL) is dictated by the geometry of the extraction vessels and (ii) the use of larger amounts of the disperser compared to conventional DLLME might lead in certain cases on dissolution of the analytes.

The significant features of the proposed protocol are often missing from pretreatment techniques in recent GC methods for the determination of OCPs [26–32]. SDME and static-LPME require increased handling skills that might limit its applicability in routine basis [28,32]. HS-SPME is a solvent-less technique that offers high sensitivity but requires exhaustive extraction lasting 60 min [30]. FOD-LPME besides the long extraction time requires and extra icing step for solidification of the organic phase [31]. LLME-MMSPE and DHT-LPME involve rather complicated procedures, long extraction times and strict control of the experimental conditions [26,29]. Finally, conventional DLLME applied to the analysis of OCPs [27] is fast (0.5 min) and simple but utilizes a toxic extraction solvent (tetrachloroethylene) that is heavier than water and therefore an extra centrifugation step is needed for phase separation and collection. The main figures of merit of these methods can be found in Appendix A Table 4.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.07.065.

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