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Journal of Chromatography A, 957 (2002) 59–67

JOURNAL OF CHROMATOGRAPHY A

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Some aspects of the analysis of environmental pollutants in sediments using pressurized liquid extraction and gas chromatography–mass spectrometry

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Abstract

Pressurized liquid extraction (PLE) is a fully automated extraction technique for isolation of analytes from solid samples. This technique combines elevated temperature and pressure of liquid solvents during the extraction process. In this study the efficiency of a PLE system for the isolation of wide range of analytes (polychlorinated biphenyls and organic pesticides from sediments under different pressure and temperature conditions) was investigated. The temperature 100 °C and pressure 6.9 MPa (1000 p.s.i.; 1 p.s.i.=6894.76 Pa) were found to be the most efficient from all investigated conditions. Using these PLE parameters, the average recoveries for most of the analytes were in the range 80–105% and relative standard deviation was usually under 15%. The conditions of determination of analytes in the extracts using GC–MS were established. Some problems occurring during the analysis of real samples, such as coelution of analytes, were established. The influence of internal standard addition on the final analysis results was determined. © 2002 Published by Elsevier Science B.V.

Keywords: Sediments; Pressurized liquid extraction; Extraction methods; Pesticides; Polychlorinated biphenyls

1. Introduction

Organic pesticides and polychlorinated biphenyls (PCBs) are contaminants which are widely distributed in all parts of the environment, including soil and sediments. Many studies have confirmed a high toxicity of these chemicals and proved their ability to generate carcinogenic and mutagenic changes in the human body [1–3]. This is the main reason why many research groups are working on new analytical procedures for the determination of pesticides and PCBs in different samples. A large number of different isolation procedures of these analytes from various matrices have been described in the literature [4–7].

Sample preparation usually consists of a number of stages (isolation, clean-up) because of the complicated matrix composition of a sediment sample. Pressurized liquid extraction (PLE; Dionex trade name ASE for accelerated solvent extraction; also known as pressurized fluid extraction [8–10], enhanced solvent extraction (ESE) [11], or high-pressure solvent extraction (HSPE) [12]) is a relatively new technique for isolation of analytes from a

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0021-9673/02/$ – see front matter
PII: S0021-9673(02)00287-X

variety of matrices. It requires less volume of solvent and is more rapid than existing techniques. An elevated temperature (50–200 °C) and pressure 3.4–20.7 MPa (500–3000 p.s.i.; 1 p.s.i.=6894.76 Pa) enhance solubilization and desorption of analytes from the matrix and accelerated the speed of the extraction process with very good recoveries of analytes in this stage of the procedure [9]. The first reports on PLE in scientific literature appeared in 1995, presenting the basic experimental set-up as well as extraction results for pesticides and herbicides in spiked soil and polynuclear aromatic hydrocarbons in urban dust [13–16]. Due to its high efficiency, PLE has been rapidly accepted by many laboratories and government agencies for routine sample preparation [17,18].

In many research works, PLE has been compared to other extraction techniques [12,19,20].

David and Seiber [12] concluded that, in general, despite the technical differences between PLE and Soxhlet extraction (as a bench technique), the recoveries obtained using PLE were in good agreement with Soxhlet data.

The PLE technique has many advantages over traditional techniques (Soxhlet or shake-flask extraction) such as a short time of extraction, low solvent consumption and additionally filtration of the extract [19,21]. On the other hand, the main problem with PLE is a low selectivity towards the analytes; during the extraction, many interferents are co-extracted, including lipids, pigments, cholesterols and others.

Many scientists have successfully used PLE for the isolation of different substances from soils or sediments, but they used extracts for analysis without a further clean-up [18]. This solution is possible, but samples of crude extracts result in the deterioration of a chromatographic column and can give many negative effects during the final analysis (e.g. matrix enhancement effect, coelution of analytes and interferences) [18,22].

Low concentration levels and physical and chemical properties of pesticides and PCBs are the main reasons why GC is the most often used technique during the final analysis of these substances. Different detection systems such as electron-capture detection (ECD), mass spectrometry (MS) or atomic emission detection (AED) can be connected to the GC systems.

Some problems with pesticide or PCB coelution during analysis using a conventional GC system with selective detectors have already been described [23]. Usually it is recommended to use a secondary GC column to confirm identifications made with the primary column [24]. One of the advantages of this approach is the use of detectors which give information about the structure of the analysed compounds (MS, AED), thus simplifying the analytical problem [25–27]. Another problem, low detection limit, was resolved using various techniques which allow an injection over 2 μl of the sample. Many researchers tried to lower the detection limit using the large volume injection technique [28] or pressure pulsed splitless injection [29].

In this work, we tried to accomplish these (PLE and GC) conditions and pointed out some of the problems which could occur during analysis.

2. Experimental

2.1. Chemicals

Dichloromethane (DCM) and acetonitrile (ACN) were of pesticide residue grade from Merck (Darmstadt, Germany). Alumina (Al_2O_3) solid-phase extraction (SPE) cartridges (500 mg) used in this study were obtained from Supelco (Poznań, Poland). Deionized water was produced with a Milli-Q purification system (Millipore, Milford, MA, USA). Anhydrous sodium sulphate was supplied by POCh and treated at 140 °C for 24 h before use. Copper was obtained from POCh and activated using HNO_3, then rinsed sequentially with Milli-Q purified water (until pH 7) and finally rinsed with acetonitrile. We used two mixed pesticide solutions. One consisted of organochlorine and nitrogen-containing pesticides; the second one contained only phosphorus pesticides. Standard solutions were prepared from the stock solutions—pesticides obtained from Supelco and PCBs from Restek (Bellefonte, PA, USA)—by dilution with dichloromethane. The concentration of each component in the pesticide solution was about 1 μg/ml and that of the PCB solution was about 0.5 μg/ml. The internal standards used in our work were supplied by Sigma–Aldrich (Poznań, Poland) and diluted in dichloromethane to suitable concentrations (in gaps): 2-nitro-*m*-xylene (1.025 μg/ml), 2-fluoro-

biphenyl (0.985 μg/ml), 2,4,5,6-tetrachloro-*m*-xylene (1.045 μg/ml), triphenyl phosphate (1.030 μg/ml), PCB 209 (0.588 μg/ml).

2.2. Sample preparation and pressurized liquid extraction

The outline of the sample preparation procedure is shown in Fig. 1.

2.2.1. Sediment samples

Sediment samples were collected at different points of the Odra's riverbed, transported to the laboratory and stored in a refrigerator. After lyophilization, sediments were sieved at room temperature (0.43 mm). Several samples which were taken from various locations were mixed creating a composite sample for the analysis.

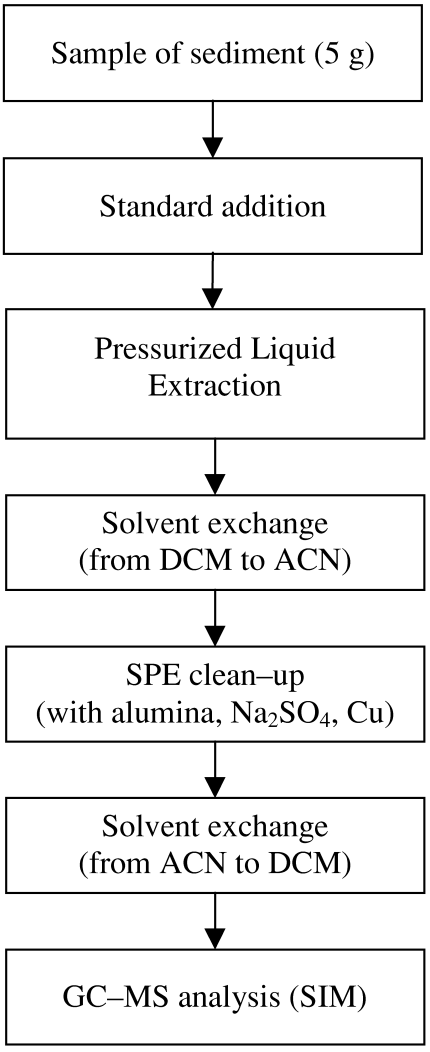

Fig. 1. The outline of the sample preparation procedure.

2.2.2. Standard addition

A sample of sediments (5 g) was weighed into a PLE extraction cell and standard solutions were added—50 μl of the PCB solution and 75 μl of each of the pesticide solutions. After natural evaporation of solvents, 2 g of anhydrous sodium sulphate was added into the cells, according to standard analytical procedure which is practiced even in the case of a certified reference soil (the soil samples must be absolutely dry during extraction) [9,10]. Before extraction, samples were mixed with the anhydrous sodium sulphate.

2.2.3. PLE

The sediment samples were extracted using a ASE 200 Accelerated Solvent Extractor (Dionex, Sunnyvale, CA, USA), equipped with 22-ml stainless steel extraction cells. To prevent clogging of the metal frit in the extraction cell, special PLE filters were placed at the exit of the cell. Extractions were done using DCM. The PLE conditions were optimised for the extraction of selected PCB congeners and pesticides. The first experimental step was the optimisation of static extraction temperature. This was done at three temperatures: 75, 100, 150 °C and at a constant pressure of 13.8 MPa (2000 p.s.i.). The experiments were repeated five times for spiked samples and one extraction was performed for an unspiked sample. The second experimental step was optimisation of a static extraction pressure (6.9, 13.8 and 20.7 MPa—1000, 2000 and 3000 p.s.i., respectively) at constant temperature which was previously selected. The oven heat-up time and the static period were the same (5 min). The extracts were purged from the sample cell using pressurized nitrogen (60 s, 1.0 MPa).

2.2.4. Post-extraction operations

Post-extraction operations were carried out according to the method described previously [30]. The extract was collected in a 40-ml glass cell and internal standards (75 μl of the mixture) were added, mixed and after that the extract was evaporated to

approximately 1.5 ml using a rotary evaporator. Then the evaporation was continued till dryness with a stream of nitrogen. The dried residue was dissolved in acetonitrile (2×0.5 ml) and transferred onto the top of an SPE cartridge containing activated copper (500 mg), dried anhydrous sodium sulphate (600 mg) and alumina (500 mg). The elution was conducted using acetonitrile. Only one fraction (the first 6 ml) was collected. This fraction was evaporated with a stream of nitrogen. The residue was dissolved in 1 ml of dichloromethane and analysed with the GC–MS system.

The recovery for each of the analysed compounds and for each of the samples was determined separately. The average recoveries and precision (measured as relative standard deviation) of the determination of pesticides and PCBs were determined by performing six analyses of the entire procedure. The entire procedure was repeated with six samples and with one blank sample.

2.3. Influence of internal standard addition on the final analysis results

In our work, we tried to use five internal standards: 2-nitro-*m*-xylene, 2-fluorobiphenyl, tetrachloro-*m*-xylene, triphenyl phosphate and PCB 209. They were added before the extraction step (see Section 2.2.2). For further experiments—according to the results achieved—only two of these standards were used (triphenyl phosphate and PCB 209). In these experiments, the optimum PLE conditions (as described in Section 2.2) were applied.

The main assumption was that the relation between the detector signal for analytes and for internal standards should be constant for all parallel samples. This way, the final results are independent of varying conditions during the analytical procedure and the precision of the method is improved. A 75-μl volume of each standard solution was added to the samples before the extraction.

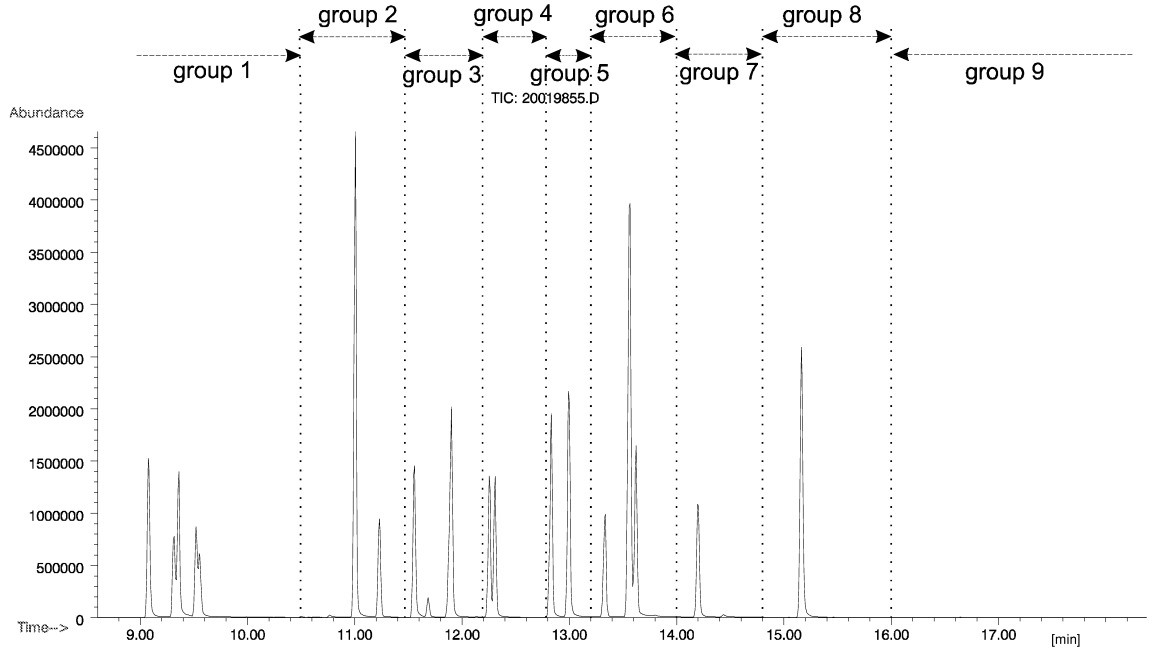

Fig. 2. Sample chromatogram of a pesticide mixture. SIM program: (*m*/*z* for each of the ion groups monitored: group 1—181, 219, 186, 203, 200, 215, 229, 214; group 2—256, 186, 173, 220, 293, 292, 125, 263; group 3—331, 329, 355, 353, 267, 323; group 4—359, 331, 246, 318, 326, 254; group 5—246, 318, 235, 165; group 6—236, 281, 235, 165, 326, 254, 360, 290; group 7—235, 165, 360, 290, 274; group 8—396, 324, 274; group 9—498, 214).

2.4. GC–MS analysis

GC–MS analysis was performed with a HP 5890 Series II gas chromatograph equipped with an HP 7673 autosampler and HP 5972 mass-selective detector (Hewlett-Packard, CA, USA). An Rtx-5MS capillary column, 30 m×0.25 mm, 0.25 μm from Restek, was used. Injector (split–splitless type) was operated in the pressure pulsed splitless mode as follows: initial pressure was 0.3 MPa (50 p.s.i.) for 1.05 min, then decreased at 0.7 MPa min^{-1} (99 p.s.i. min^{-1}) to 0.03 MPa (5 p.s.i.), then constant flow. The purge valve was opened after 1.5 min. The gooseneck splitless glass sleeve (liner) was used. The injection volume was 5 μl. The temperatures of the GC system were: injection temperature 240 °C; auxiliary temperature 280 °C; oven temperature program: 50 °C (1.5 min), 30 °C min^{-1} to 180 °C, 10 °C min^{-1} to 275 °C (15 min). The MS detector was operated in the selected ion monitoring (SIM) mode. For each of the substances analysed, two characteristic ions were monitored during the analysis (Fig. 2). In order to achieve the best response from the GC–MS set-up, the optimum over-potential (400 V) was used.

3. Results and discussion

3.1. GC–MS analysis

An example of a chromatogram of the pesticide mixture is shown in Fig. 2. The retention times and m/z values of quantitative (ion 1) and qualitative (ion 2) ions for each of the substance are presented in Table 1.

Almost all of the quantitation ions represent the most abundant ion for the analytes. Not each mass chromatogram was found to be noise-free. It was caused by coeluting analytes and matrix components, and the similarity of their mass spectra. One such case is the coelution of methoxychlor (one of the analytes) and chrysene (a polynuclear aromatic hydrocarbon which is usually present in the environment at high concentrations). During the clean-up stage applied in our experiments, these substances were not separated. In the case of significant differences in mass spectra of the analytes it is possible to resolve coeluted peaks. This condition is not fulfilled in this case: the mass spectra of methoxychlor and chrysene are shown in Fig. 3. The most abundant peak in the methoxychlor mass spectrum, 227, is also formed during chrysene fragmentation. Despite the low amount of this ion in the spectrum (compared to the main ion: 228), a high concentration of chrysene causes a high influence on methoxychlor's main ion. This made resolving of these peaks impossible and was the main reason why methoxychlor was not quantified.

A similar problem occurs when analysing *o,p′*-DDT and *p,p′*-DDD. They can be separated only when a new GC capillary column is used. During the analysis of real sample extracts, chromatographic resolution was found to deteriorate. In the chromatogram, they often form only one peak. Because of the similarity of *o,p′*-DDT and *p,p′*-DDD mass spectra

Table 1
Retention times and m/z values of quantitative (ion 1) and qualitative (ion 2) ions for the analytes

Compound	Retention time (min)	m/z	
		Ion 1	Ion 2
α-Lindane	9.45	181.00	218.95
Symazine	9.63	186.05	203.05
Atrazine	9.68	200.00	215.00
Propazine	9.71	214.15	229.20
Terbuthylazine	9.88	214.15	229.10
γ-Lindane	9.97	181.00	218.95
Malathion	11.36	173.15	125.00
Aldrin	11.76	262.90	292.95
Bromophos	11.96	330.95	329.00
Heptachlor epoxide	12.42	352.85	354.85
Chlorfenvinfos	12.26	267.00	323.00
Bromophos ethyl	12.65	358.95	330.85
o,p′-DDE	12.80	246.00	317.95
p,p′-DDE	13.35	246.00	317.95
p,p′-DDD	14.12	235.05	165.10
Endrin	13.96	262.90	280.90
o,p′-DDD	13.50	235.00	165.00
o,p′-DDT	14.17	235.00	165.00
p,p′-DDT	14.79	235.00	165.00
Methoxychlor	15.74	227.10	228.20
PCB 28	10.94	256.05	186.10
PCB 52	11.48	292.00	220.00
PCB 101	12.96	326.00	254.00
PCB 118	14.07	326.00	254.00
PCB 138	14.92	360.00	290.00
PCB 153	14.43	360.00	290.00
PCB 180	16.13	396.00	324.00
PCB 209	19.15	498.00	214.00

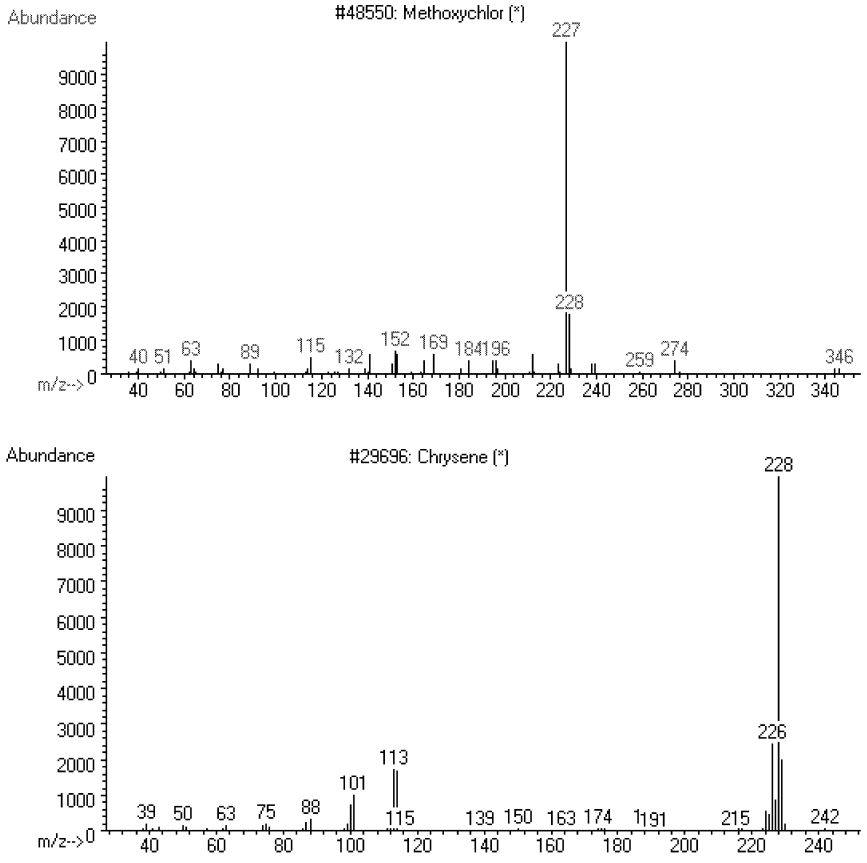

Fig. 3. Mass spectra of methoxychlor and chrysene.

and similar chromatographic behaviour, the two components are reported as a sum.

3.2. Detection limits

The limit of detection (LOD) was defined as the analyte concentration giving a peak height equivalent to the blank value plus three standard deviations for the blank value [31]. The limit of quantitation (LOQ) was defined as the analyte concentration giving a peak height equivalent to six times the observed noise of the chromatogram. The use of pressure pulsed splitless injection technique made it possible to inject 5 μl of sample into the GC column. Also, the other optimised GC–MS parameters resulted in improvement of instrument detection limits.

The results of LOQ determination are presented in Table 2. Low values of these detection limits make the developed procedure useful in trace analysis of sediment samples.

3.3. Relationships between recoveries and temperature of extraction

As a result of this work, the relationships between various temperatures (75, 100, 150 °C) and extraction efficiency were obtained. The pressure during the experiments was fixed at 13.8 MPa (2000 p.s.i.).

A comparison of the recoveries and RSDs obtained for these three temperatures indicates that the results obtained at 100 °C were the best. Our results confirmed (what has been demonstrated in many papers) that 100 °C is a suitable temperature for isolating PCBs and organic pesticides from solid environmental samples [9,32]. Thus the next experi-

Table 2
LOQs in the extract analysed by the GC–MS system

Compound	LOQ (ng/ml)
α-Lindane	4.0
Symazine	5.3
Atrazine	5.9
Propazine	6.0
Terbuthylazine	5.0
γ-Lindane	4.0
Malathion	4.0
Aldrin	5.0
Bromofos	5.8
Heptachlor epoxide	4.9
Chlorfenvinfos	4.6
Bromophos ethyl	5.8
o,p′-DDE	4.4
p,p′-DDE	3.9
p,p′-DDD	3.8
Endrin	5.7
o,p′-DDD	3.9
o,p′-DDT	4.4
p,p′-DDT	6.0
Methoxychlor	4.6
PCB 28	1.8
PCB 52	1.8
PCB 101	1.8
PCB 118	1.8
PCB 138	1.8
PCB 153	1.8
PCB 180	1.8
PCB 209	2.8

ments aimed at optimisation of pressure were carried out at 100 °C.

3.4. Relationship between recovery and pressure of the extraction

The relationship between the recoveries of the analytes and pressure of the extraction (6.9, 13.8 and 20.7 MPa—1000, 2000 and 3000 p.s.i., respectively) was established. The highest recoveries are obtained using a pressure of 6.9 MPa (1000 p.s.i.). Under these conditions, the RSDs have the lowest values. In both relationships (i.e. temperature and pressure), a decrease in the recovery when the temperature or pressure are increased can be explained as a result effect of analyte degradation. For some of the compounds, the recovery exceeds 100%. This may be caused by the coelution of unknown compounds with similar mass spectra. The recovery and RSDs under optimal conditions—100 °C and 6.9 MPa (1000 p.s.i.)—are presented in Fig. 4.

3.5. Influence of internal standard addition on the results of final determination

Three of the standards added: 2-nitro-*m*-xylene,

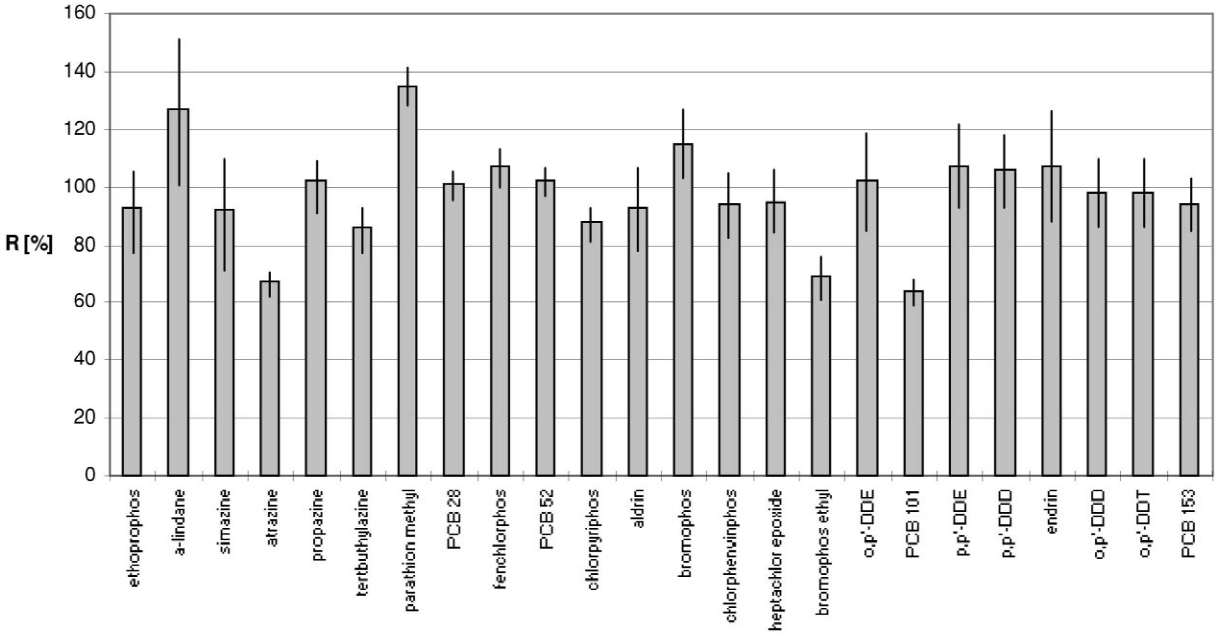

Fig. 4. The recovery of the analytes under optimal conditions—100 °C and 6.9 MPa (1000 p.s.i.). The vertical lines represent the errors.

2-fluorobiphenyl, tetrachloro-*m*-xylene were not detected in the analysed samples. Probably the main reason for these losses is the clean-up step (low solubility of these substances in acetonitrile, permanent adsorption on SPE sorbents) or solvent exchange (volatilisation). Only triphenyl phosphate and PCB 209 were used as internal standards.

Finally, the recoveries and RSDs were calculated for absolute areas of analytes (excluding internal standards) and relative areas of analytes (including internal standards). A comparison of all results is presented in Fig. 5.

As shown in Fig. 5 in most cases, the highest recoveries were achieved when internal standards (I.S.) were not included in the calculations, but in either case, all results were comparable.

The lowest RSD values (about 10%) were achieved for triphenyl phosphate as internal standard and for the absolute values (calculated excluding I.S.). When PCB 209 was used, the lowest precision was obtained. We observed a broadened peak near the expected retention time of PCB 209. This unknown compound made the proper qualitative and quantitative I.S. analysis impossible. We carried out the experiments using one type of soil and this phenomenon could occur only for this characteristic constitution of the matrix. However, for unknown types of soil samples it is advisable to use both internal standards.

4. Conclusions

The optimal conditions established in the experiments for the extraction of pesticides and PCBs are 100 °C and 6.9 MPa (1000 p.s.i.). Nevertheless, these conditions could vary for different (i.e. taken from another places) soil and sediment samples because of the difference in influence of matrix components on the extraction process. These matrix effects are hard to predict.

The GC–MS system allows to obtain reliable

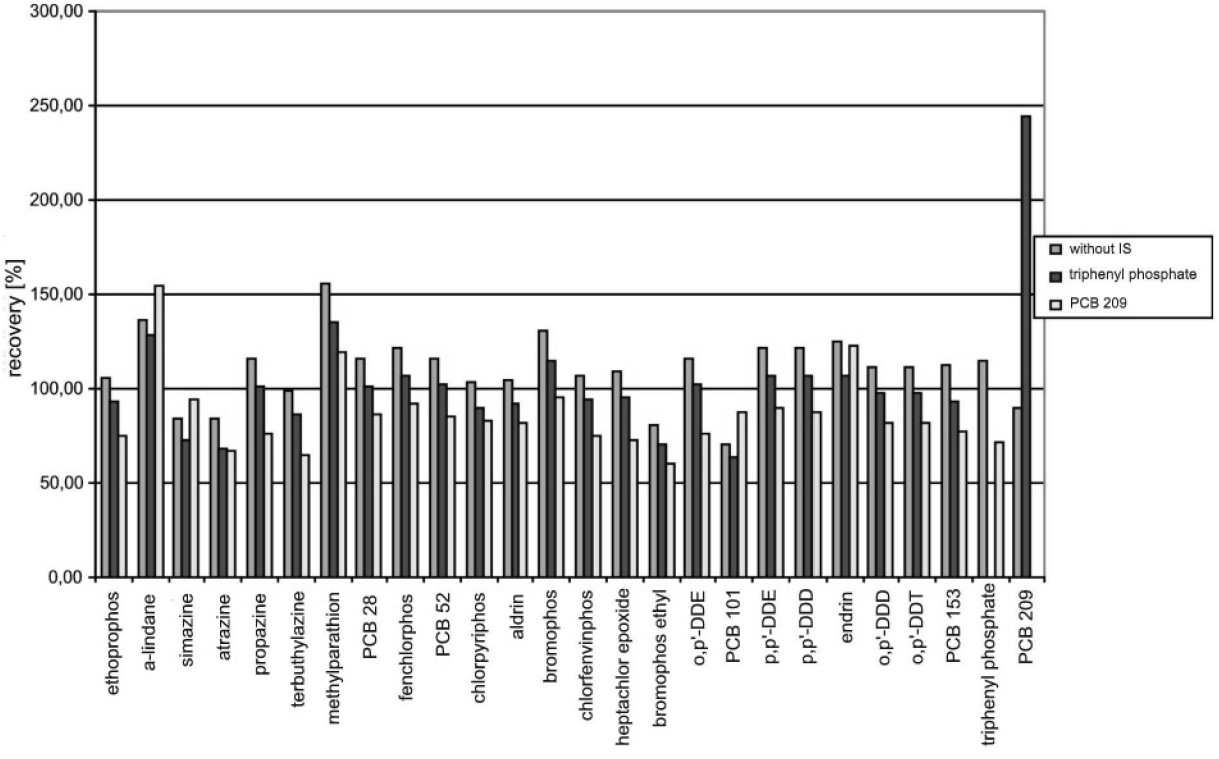

Fig. 5. Recoveries of the analytes with internal standard addition (triphenyl phosphate or PCB 209) and without internal standard addition.

results for almost all of the analysed compounds. For quality assurance of the entire procedure, the use of an internal standard (triphenyl phosphate or PCB 209) is recommended.

The recovery, LOD and RSDs of the developed procedure demonstrate its suitability for routine monitoring of pollutants in soil and sediments. The concentrations of the compounds added before the extraction were low enough to evaluate this method as a trace analytical method.

PLE allows a rapid and automatic extraction of many samples and it could be very useful for the laboratories which perform routine pollutant analysis in soils and sediments. We use this method to analyse pesticides, PCBs and polynuclear aromatic hydrocarbons in sediments and soil samples. Several hundred samples have already been analysed using the conditions described in this work.

Acknowledgements

The authors would like to thank Anna Pinkiewicz and Aleksandra Szymańska for their participation in carrying out the analyses. This work was partially realized in the framework of International Odra Project (IOP) and financially supported by the Polish–German Cooperation Foundation.

References

[1] W. Calmano, U. Forstner (Eds.), Sediments and Toxic Substances, Springer, Berlin, 1996, p. 51.
[2] R. Loos, S. Vollmuth, R. Niessner, Fresenius J. Anal. Chem. 357 (1997) 1081.
[3] M. Blanchard, M.J. Teil, A.M. Carru, D. Ollivon, B. Garban, A. Chesterikoff, M. Chevreuil, Arch. Environ. Contam. Toxicol. 37 (1999) 242.
[4] K.D. Wenzel, A. Hubert, M. Manz, L. Weissflog, W. Engewald, G. Schuurmann, Anal. Chem. 70 (1998) 4827.
[5] J.F. Focant, G. Eppe, C. Pirard, E. de Pauw, J. Chromatogr. A 925 (2001) 207.
[6] M. Krauss, W. Wickle, W. Zech, Environ. Sci. Technol. 34 (2000) 4335.
[7] P. Popp, P. Keil, M. Moder, A. Paschke, U. Thuss, J. Chromatogr. A 774 (1997) 203.
[8] B.E. Richter, L. Covino, LC–GC 18 (2000) 1068.
[9] E. Björklund, S. Bøwadt, T. Nilsson, L. Mathiasson, J. Chromatogr. A 836 (1999) 285.
[10] S. Lundstedt, B. van Bavel, P. Haglund, M. Tysklind, L. Öberg, J. Chromatogr. A 883 (2000) 151.
[11] A. Rübel, R. Bierl, Fresenius J. Anal. Chem. 364 (1999) 648.
[12] M.D. David, J.N. Seiber, Anal. Chem. 68 (1996) 3038.
[13] J.L. Ezzell, B.E. Richter, W.D. Felix, S.R. Black, J.E. Meikle, LC–GC 13 (1995) 390.
[14] F. Höfler, J.L. Ezzell, B.E. Richter, Labor Praxis 19 (3) (1995) 62.
[15] F. Höfler, J.L. Ezzell, B.E. Richter, Labor Praxis 19 (4) (1995) 58.
[16] F. Höfler, D. Jensen, J.L. Ezzell, D. Felix, B.E. Richter, GIT Chromatogr. 15 (1995) 68.
[17] US Environmental Protection Agency Method 3545, Accelerated Solvent Extraction, Test Methods for Evaluating Solid Waste, 3rd ed., Update III; EPA SW-846; US GPO, Washington, DC, July 1995.
[18] F.J. Schenck, S.J. Lehotay, J. Chromatogr. A 868 (2000) 51.
[19] N. Saim, J.R. Dean, M.P. Abdullah, Z. Zakaria, J. Chromatogr. A 791 (1997) 361.
[20] O. Heemken, N. Theobald, B.W. Wenclawiak, Anal. Chem. 69 (1997) 2171.
[21] H. Giergielewicz-Możajska, Ł. Dąbrowski, J. Namieśnik, Crit. Rev. Anal. Chem. 31 (2001) 149.
[22] Ł. Dąbrowski, H. Giergielewicz-Możajska, Ł. Górski, M. Biziuk, J. Namieśnik, B. Janicki, J. Sep. Sci., 25(5–6) (2002) 297.
[23] K. Ballshmiter, M. Zell, Fresenius Z. Anal. Chem. 302 (1980) 20.
[24] V.S. Ong, R.A. Hites, Environ. Sci. Technol. 29 (1995) 1259.
[25] I. Moret, R. Piazza, M. Benedetti, A. Gambaro, C. Barbante, P. Cescon, Chemosphere 43 (2001) 559.
[26] C. Sanchez-Brunete, R.A. Perez, E. Miguel, J.L. Tadeo, J. Chromatogr. A 823 (1998) 17.
[27] Ł. Dąbrowski, B. Truchanowicz, A. Żwir, M. Biziuk, J. Gaca, Adv. Chromatogr. Electrophoresis Relat. Separation Methods 1 (1998) 39.
[28] H.J. Stan, M. Linkerhägner, J. Chromatogr. A 727 (1996) 275.
[29] F.J. López, J. Beltran, M. Forcada, F. Hernández, J. Chromatogr. A 823 (1998) 25.
[30] Ł Dąbrowski, B. Truchanowicz, A. Żwir, M. Biziuk, J. Gaca, Adv. Chromatogr. Electrophoresis Relat. Separation Methods 1 (1998) 39.
[31] K. Dancer, E. Than, D. Molch, Systematischer Überblick, Geest and Portig, Leipzig, 1976, p. 51.
[32] P. Popp, P. Keil, M. Moder, A. Paschke, U. Thuss, J. Chromatogr. A 774 (1997) 203.