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Solid-phase extraction clean-up of soil and sediment extracts for the determination of various types of pollutants in a single run ☆

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Abstract

A new sample clean-up procedure based on solid-phase extraction (SPE) sorbents was proposed for the determination of pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in soils and sediments. The main purpose of the research was to find a combination of sorbents for the SPE method that would permit the determination of many types of analytes (polycyclic aromatic hydrocarbons, polychlorinated biphenyls, N-, P- and Cl-containing pesticides) in a single run. Elution profiles for both the analytes and the interfering components were determined for several types of SPE sorbents (alumina, silica and surface-modified silica) and combinations of them. The efficiency of the clean-up method developed was evaluated using real soil samples.

Keywords: Solid-phase extraction; Soil; Sediments; Environmental analysis; Pesticides; Polycyclic aromatic hydrocarbons; Polychlorinated biphenyls; Lipids

1. Introduction

Sample preparation prior to the determination of many environmental pollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) or organic pesticides in soil and sediments usually consists of many steps because of the complexity of the matrix. Extraction of the analytes and extract clean-up are the most critical steps in the analytical procedure when it comes to complete recovery of the target substances. The relatively new extraction technique of pressurized liquid extraction (PLE; Dionex trade name ASE for accelerated solvent extraction) is very useful in routine analysis of organic pollutants in environmental samples. The main problem with PLE and other liquid extraction techniques is low selectivity towards the analytes. During the extraction step many interfering components are co-extracted from soil and sediment samples together with target analytes;

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examples include lipids, sulphur, pigments, or cholesterol and its derivatives [1].

The main aim of the clean-up stage is to remove substances that could interfere with the final determination and quantitation of target analytes. Removal of interfering substances can be accomplished in many different ways. For example, copper is often used as the medium retaining sulphur [2–4]. Numerous other techniques are described in the literature [5,6].

Solid-phase extraction (SPE), introduced in the 1970s, is still the dominant method for soil and sediment extracts purification [7,8]. A large number of sorbents are used for the isolation of organic compounds from the extract solutions. They include alumina, Florisil, ion-exchange resins, silica gel and many silica-based sorbents (e.g. octadecyl bonded silica, octyl bonded silica, phenyl bonded silica, cyanopropyl bonded silica, diol bonded silica, etc.). Silica gel is the most polar sorbent available. It is very useful for extract clean-up in the determination of non-polar compounds. Elution with hexane, heptane, benzene–hexane mixtures or stepwise elution using hexane and dichloromethane were described in the literature. Silica gel was used among others in the determination of PAHs in atmospheric particulate samples [9], inorganic and organic pollutants in pine tree barks [10], PAHs in soil [11], PCBs in soil [12], organochlorine pesticides in animal tissue extracts [13] and soil [14].

Alumina (Al_2O_3) is somewhat similar to silica because of its very polar character. The primary retention mechanisms for alumina are based on Lewis acid/base, polar and ion-exchange interactions [15]. Use of alumina in sample preparation procedures for the determination of different analytes in complicated matrices, including PCBs in milk, blood [16], soil or mussel samples [17] or polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in soil samples [18,19], is widely described in the literature.

Florisil is a magnesia-loaded silica gel. Due to its extremely polar character, this sorbent is ideal for the isolation of non-polar analytes. Examples include determination of PCBs in biota samples [20], sewage sludge-amended soil [2] and marine sediments [21]; determination of PAHs in atmospheric particulate samples [22]; determination of butyltin and phenyltin compounds in mussel samples [23], or PCBs, PAHs, DDD/DDE/DDT and hexachlorocyclohexane (HCH) isomers in soil [24].

Octadecyl bonded silica (C_{18}) is the most hydrophobic silica-based sorbent available. C_{18} is a very popular SPE sorbent due to its strong retentive character for non-polar compounds. There are many examples of C_{18} use in analytical procedures, including the determination of organophosphorus pesticides in meat and fatty matrices, vegetable oils, butterfat and soil [25–27] or PAHs and PCBs in animal tissue and liver oil [28]. Certain other modified silica sorbents are used for sediment or soil extract clean-up [29–31] prior to the determination of specific target analytes.

The aim of this work was to evaluate the suitability of various sorbents and sorbent combinations for the clean-up of PLE extracts before the final determination of a wide range of analytes, including PAHs, PCBs, as well as N-, P- and Cl-containing pesticides in a single run.

2. Experimental

2.1. Samples

Sediment and soil samples were used in the investigations. Sediment samples collected at different locations from the Odra River bed were transported to the laboratory and stored in a refrigerator. After lyophilization, the samples were sieved (mesh size 0.43 mm) at room temperature. Several samples taken from various locations were mixed together, creating a composite sample for the analysis.

Soil samples were collected from one location on a lawn situated close to the Gdańsk University of Technology. The soil was dried at 40 °C and sieved similarly to the sediment samples.

2.2. Chemicals

Dichloromethane (DCM) and acetonitrile (MeCN) were of pesticide residue grade from Merck (Darmstadt, Germany). All SPE 500 mg cartridges used in this study were obtained from Supelco (Poznań, Poland) or Accubond, J&W Scientific (Folsom, CA, USA). Deionized water was produced with a Milli-Q

Table 1
Analytes used in the study

PAHs	PCBs	Pesticides
Naphthalene; acenaphthylene; acenaphthene; fluorene; phenanthrene; anthracene; pyrene; benz[*a*]anthracene; chrysene; benzo[*b*]fluoranthene; benzo[*k*]fluoranthene, benzo[*a*]pyrene; indeno[1,2,3-*cd*]pyrene; dibenz[*a,h*]anthracene; benzo[*ghi*]perylene	PCB 28 PCB 52 PCB 101 PCB 138 PCB 153 PCB 180	α-Lindane; simazine; atrazine; propazine; terbuthylazine; δ-lindane; γ-lindane, chlorpyrifos, aldrin, disulfoton; parathion methyl; guthion, methoxychlor, bromophos; malathion; chlorophenvinphos, fenchlorphos; fenitrothion; endrin; aldrin *p,p′*-DDE; *p,p′*-DDD; *o,p′*-DDT *o,p′*-DDD; *o,p′*-DDE; *p,p′*-DDT

purification system (Millipore, Milford, MA, USA). Anhydrous sodium sulphate was supplied by POCh (Gliwice, Poland) and treated at 140 °C for 24 h before using. 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.

2.3. Preparation of standard solutions

Standard solutions were diluted from the stock solutions with dichloromethane. Standard mixtures of pesticides were obtained from Supelco (Poznań, Poland), PCBs from Restek (Bellefonte, PA, USA) and PAHs from AccuStandard (New Haven, CT, USA). The concentration of each component in the pesticide solution was about 1 μg/ml; in the PCB solution it was about 0.5 μg/ml, and in the PAH solution about 4 μg/ml. The analytes are listed in Table 1. The internal standard (triphenyl phosphate) used in our work was supplied by Sigma–Aldrich (Poznań, Poland) and diluted in dichloromethane to a concentration of 1.030 μg/ml.

2.4. Research strategy

The first step in our investigations was the evaluation of well known and widely used sorbents, silica and alumina, for the clean-up of extracts prior to the analysis of various compounds in a single run.

After choosing the SPE conditions for the separation of the analytes from lipids, we determined the elution profiles for a wider group of analytes (standard solutions) and matrix components (extracts of real sediment samples) using several different sorbents and sorbent combinations (see Table 2).

Finally, after qualitative (GC–MS full scan mode) and quantitative (GC–MS-SIM mode) analysis of

Table 2
Sorbents and sorbent combinations used in the study

Sorbents and sorbent combinations	Symbol
Octadecyl bonded silica	C_{18}
Phenyl bonded silica	Ph
Aminopropyl bonded silica	NH_2
Diol bonded silica	Diol
Alumina	Al
Activated carbon + alumina	EnviCarb + Al
Cyano bonded silica + alumina	CN + Al
Octadecyl bonded silica + alumina	C_{18} + Al
Aminopropyl bonded silica + alumina	NH_2 + Al
Phenyl bonded silica + alumina	Ph + Al
Diol bonded silica + alumina	Diol + Al
Diol bonded silica + octadecyl bonded silica + alumina	Diol + C_{18} + Al
Phenyl bonded silica + octadecyl bonded silica + alumina	Ph + C_{18} + Al

sediment extracts (cleaned-up using different sorbents), a combination of three cartridges, Ph–C_{18}–Al, was chosen as the best of the tested. The final clean-up procedure efficiency was confirmed by recovery experiments using PLE extracts achieved from spiked soil samples.

2.5. Elution profiles of standard solutions

2.5.1. Basic studies with silica and alumina

Six compounds of various polarity were chosen for the basic experiments with silica and alumina beds: *p,p′*-DDT, γ-lindane, methoxychlor, atrazine, chlorophenvinphos and malathion.

A standard solution (1 ml) containing each compound at 0.80 μg/ml was deposited on top of a pre-conditioned SPE column. The analytes were then eluted with 14 fractions (ca. 2.1 ml each) of *n*-hexane–DCM mixture. Different proportions of the two solvents in the mixture were tested: 100% hexane, 20% DCM in hexane, 40% DCM in hexane, 60% DCM in hexane, 80% DCM in hexane and 100% DCM. For complete removal of the analytes from the sorbent, an additional 10 ml of DCM was passed through the bed. Each eluted fraction was analysed by GC–MS.

2.5.2. Elution profiles of lipids

To determine the elution profile of lipids, one representative compound, palmitic acid, was chosen. The conditions of the SPE procedure were the same as described above, except for the final determination. Detection of the acid in the fractions collected was performed using TLC plates and dichlorofluorescein as the detection reagent.

2.5.3. Evaluation of the final SPE conditions

As a result of experiments described in Sections 2.5.1 and 2.5.2, final SPE conditions were proposed and tested as follows. A mixture of standard solutions (75 μl of the pesticide solution, 50 μl of the PCB solution, 20 μl of the PAH solution and 75 μl of the triphenyl phosphate solution) was transferred to the top of an SPE column or column combination (see Table 2), pre-conditioned with acetonitrile. Ten fractions of 2 ml each were collected and analysed using GC–MS.

2.6. Fractionation of real sediment extracts

Evaluation of the fractionation efficiency for real sediment extracts was performed. At this research stage, several SPE sorbents and sorbent combinations including Al, C_{18} + Al, Ph + Al, Diol + Al and NH_2 + Al were used for fractionation of the sediment extracts. The sediment sample (5 g) was weighted into a glass vial and sonicated for 30 min with 15 ml of dichloromethane in an ultrasonic bath (UM4-Unitra, Olsztyn, Poland). Extracts were transferred into glass flasks by careful decantation. The residue was subsequently washed three times with 2 ml of pure dichloromethane and these volumes were combined with the extract. The final extract was concentrated to 0.5 ml using a rotary evaporator and evaporated to dryness under a gentle stream of nitrogen. The residue was dissolved in 1 ml of acetonitrile and fractionated using an SPE cartridge (or a cartridge combination). Copper (for sulphur removal) and anhydrous sodium sulphate (0.5 g) were added to the top of each sorbent bed. Ten fractions of 2 ml each were collected and analysed with GC–MS in full scan mode.

2.7. Final evaluation of the entire analytical procedure

As a result of the experiments described in Sections 2.5 and 2.6, two SPE sorbent combinations were proposed: Ph + C_{18} + Al and Diol + C_{18} + Al. A third combination, CN + Al, was chosen after theoretical studies. Six samples with standard addition and three without standard addition were analysed in order to evaluate the entire analytical procedure. Spiked soil samples were prepared by adding standard solutions of the analytes to 5 g of soil (75 μl of the pesticide solution, 50 μl of the PCB solution and 20 μl of the PAH solution). Internal standard (triphenyl phosphate) was added to each sample (75 μl). This gives the following concentrations in the soil sample: pesticides and internal standard—15 ng/g, PCB—7.5 ng/g and PAH—60 ng/g. The sample was then extracted with acetonitrile–methanol (9:1, v/v). The operating conditions of the Dionex ASE 200

extraction system were as follows: heating for 5 min, static extraction for 5 min at a pressure of 2000 p.s.i. (14 MPa) and oven temperature of 150 °C. The extract was purged from the sample cell using pressurised nitrogen purge at 150 p.s.i. (1 MPa) for 1 min. The extracts collected into suitable vials were then quantitatively transferred into glass flasks and concentrated to 0.5 ml using the rotary evaporator. The concentrated extracts were then subject to the clean-up procedure, i.e. they were transferred to the top of the SPE column combination. The upper column (containing alumina) was packed manually with copper and anhydrous sodium sulphate (0.5 g). Analytes were eluted using acetonitrile. One fraction of 6 ml was collected and analysed by GC–MS-SIM.

2.8. Final analysis

Each fraction collected in the experiments described above was evaporated to dryness under a gentle stream of nitrogen. The residue was dissolved in 0.5 ml dichloromethane before the analysis by GC–MS.

The GC–MS analysis was performed using an HP 5890 Series II gas chromatograph equipped with an HP 7673 autosampler and an HP 5972 mass-selective detector (Hewlett-Packard, CA, USA). The capillary column used was Rtx-5MS, 30 m × 0.25 mm × 0.25 μm, from Restek (Bellefonte, PA, USA). The split–splitless injector was operated in pulsed pressure splitless mode as follows: initial pressure 0.3 MPa (50 p.s.i.) for 1.05 min, decreased at 0.7 MPa/min (99 p.s.i./min) to 0.03 MPa (5 p.s.i.), followed by constant flow. The purge valve was opened after 1.5 min. Gooseneck splitless glass sleeve (liner) was used. The injection volume was 5 μl. The temperatures of the GC system were the following: injection temperature 240 °C; transfer line temperature 280 °C; oven temperature program: 50 °C (1.5 min)–30 °C/min–180 °C–10 °C/min–275 °C (15 min). For qualitative analysis, the MS detector was operated in full scan mode (50–500 u). For quantitative analysis, the MS detector was operated in the SIM mode. For each of the analysed substances, two characteristic ions were monitored during the analysis as described previously [32]. In order to achieve the best response from the GC–MS system, an overpotential of 400 V was applied.

3. Results and discussion

3.1. Basic studies with silica and alumina sorbents

Elution profiles of selected organochlorine, organonitrogen and organophosphorus pesticides were determined for silica and alumina SPE columns using hexane, dichloromethane and their mixtures for analyte elution. The pesticides could be divided into two groups according to their retention volumes:

(1) Organochlorine pesticides, with generally small retention volumes. γ-Lindane, *p,p′*-DDT and methoxychlor were eluted in the first fractions of hexane and hexane–DCM mixtures. In this group of compounds, methoxychlor was retained the strongest and could not be eluted with hexane.

(2) N,P-containing pesticides, which eluted later (i.e. were retained stronger by the column). Atrazine, malathion and chlorophenvinphos could not be eluted using hexane—they could be eluted only with mixtures containing more DCM.

These results can be explained by the polarity and solubility of the pesticides. In both cases, either the retention volumes or the peak widths of the pesticides decreased when the elution solvent strength increased (more DCM in the elution mixture). The results obtained for organochlorine pesticides were similar to those published previously by many researchers [33–39] who used partially deactivated silica or alumina beds.

In commercially packed SPE columns, it is not possible to control the activity of the sorbent bed (normally, the activated sorbent bed is deactivated by addition of water). Another way of deactivation was also described in the literature [36]. We evaluated a mixture of methanol in benzene as the conditioning/deactivating mixture, but it had almost no effect on elution profiles of the pesticides. Because of this, in all further experiments, solvents dried with silica gel (∅ = 3–6 mm) were used exclusively.

3.2. Elution profiles of lipids

Elution profile for palmitic acid as a compound representative for lipids was determined. With alumina, the acid was eluted in the first 3 fractions when using hexane–DCM mixtures. The acid was not eluted with hexane until the 14th fraction (30

Table 3
Elution profiles for palmitic acid using hexane–DCM (fraction 15 and subsequent: DCM) as the eluents

Eluent	Fraction number																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Hexane															■	■	■	■	■	
20% DCM											■	■	■	■	■	■	■			
40% DCM		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■				
60% DCM	■	■	■	■	■	■	■	■	■	■	■	■	■	■						

ml). The results obtained for silica are presented in Table 3.

The results of both experiments (determination of elution profiles of pesticides and palmitic acid) indicate that neither of the two sorbents can be used to completely separate the two groups of substances (Table 4). The best results for both sorbents could be achieved with hexane as the eluent. In this case, γ-lindane, *p,p′*-DDT (fractions 4–6 and 2–3, respectively, for SiO_2; fractions 1–11 and 0–2 for alumina) and partially methoxychlor (fractions 14–16 for SiO_2 and 13–15 for alumina) could be separated from palmitic acid (fractions 15–19 for SiO_2 and 15–16 for alumina). The N, P-containing pesticides (fractions 15–16 for both sorbents) co-eluted with the acid because stronger solvents had to be used to elute these compounds from the sorbents. Fractions 15 and later were eluted with dichloromethane. In general, the number of compounds coeluting with palmitic acid increased with increasing strength of the elution solvent.

3.3. Use of acetonitrile as the SPE eluent

Acetonitrile is a solvent that almost does not dissolve lipids, but dissolves easily a wide range of pesticides, therefore it was chosen as the eluent for the clean-up of the extracts. Elution profiles for pesticides, PCBs and PAHs were very similar to each other. These compounds were almost not retained by the sorbents and eluted in the first fractions. Palmitic acid was not eluted until 30 ml of the solvent passed through the sorbent under these conditions. This SPE setup can be used for one step extract clean-up in the analysis of a wide range of compounds. Selected

Table 4
Elution profiles for pesticides and palmitic acid using hexane as the eluent (fraction 15 and subsequent: DCM) for (a) silica and (b) alumina sorbent beds

Analyte	Fraction number																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Eluted from SiO_2																				
Palmitic acid															■	■	■	■	■	
γ-Lindane			■	■	■	■														
Methoxychlor														■	■	■				
p,p′-DDT	■	■																		
Atrazine															■	■				
Malathion															■	■				
Chlorophenvinphos															■	■				
Eluted from Al_2O_3																				
Palmitic acid															■	■				
γ-Lindane	■	■	■	■	■	■	■	■	■	■	■									
Methoxychlor													■	■	■					
p,p′-DDT	■	■																		
Atrazine															■	■				
Malathion															■	■				
Chlorophenvinphos															■	■				

results of such experiments performed for pesticides and PCBs were already presented [40].

3.4. Fractionation of standard solutions using different sorbents and sorbent combinations

The effectiveness of the clean-up step was evaluated for different sorbents and sorbent combinations using a standard solution of pesticides, PCBs and PAHs. For most of the sorbents and sorbent combinations, recoveries between 70 and 120% were achieved. In the case of phenyl-, amino- and diol-modified silicas (used separately), most of the analytes were usually eluted in the first fractions, whereas in the case of C_{18}, the analytes were mainly eluted in the first (most of the pesticides) or first and second fractions (PCBs and PAHs).

For the sorbent combinations, when two or three cartridges were used, the analytes were eluted mainly in the second and third fractions. The elution volume was strongly related to the dead volume, which increased when additional SPE cartridges were used. For all of the beds used in the experiments, weak retention of the analytes could be explained by high elution strength of acetonitrile and weak interactions of the analytes with the sorbents. An example of elution profiles of some of the analytes determined for a combination of three cartridges (Ph + C_{18} + Al) is presented in Table 5.

Consistently low recoveries were observed throughout all experiments for low-molecular-mass PAHs (including naphthalene, acenaphthylene, acenaphthene and fluorene). The phenomenon was probably related to the solvent exchange step, a critical point in the analytical procedure. Some analytes, e.g. benzo[*k*]fluoranthene and benzo[*b*]-fluoranthene, were not separated in some cases in the analysis of real samples by GC–MS. Consequently, the results obtained for these substances in the analysis of standard mixtures were also presented (calculated) as a sum.

Graphitized carbon sorbents are highly efficient in the removal of pigments from food extracts, as described in many papers [16,31]. Elution profiles for many analytes were described. Low recoveries (in our research work $\ll 50\%$) of such non-polar compounds as PCBs and PAHs made this type of sorbents useless. Most likely, the elution strength of acetonitrile is too low to efficiently remove these analytes from the sorbent. Some papers recommend that elution should always be stepwise for carbon-based sorbents, with several eluents and/or their mixtures used in succession [16,30].

3.5. Identification of matrix components

Identification of the chemical constitution of the matrix (sediment samples) and specification of the usage range of several SPE cartridges for the clean-up stage were performed. Each fraction of the USB (ultrasonic bath extraction) extracts collected from the clean-up step performed using different sorbents/sorbent combinations (including Al, C_{18} + Al, Ph + Al, Diol + Al, NH_2 + Al) was analysed by GC–MS in full scan mode. The substances were identified with the help of Wiley 275 mass spectral library.

The results obtained for various sorbents were comparable. Compounds identified in fractions 1–6 included *n*-alkanes (C_8–C_{14}), cycloalkanes, furane derivatives (e.g. dibenzofurane), phthalates, PAHs and their derivatives, and many others. Phthalates including dibutyl phthalate, diisooctyl phthalate and bis(2-ethylhexyl)phthalate were detected in all eight fractions collected after the clean up using the sorbents tested. These compounds originated most likely from the plastic cartridges and other plastic components (e.g. pipette tips or vial caps) that came in contact with the extracts.

Two chromatograms of the second fraction eluted from the C_{18} + Al and the Al sorbents were compared (see Fig. 1). Only one of the tested cartridge combinations, C_{18} + Al, retained cholesterol and its derivatives (retention times 21–30 min). These compounds were present in fractions 7 and 8, so the elution volume was about 16 ml. Under the same conditions, the analytes were eluted much earlier. Separation of cholesterol, its derivatives and other interfering substances from the analytes was the result of C_{18} usage.

Fig. 2 presents the chromatograms of the first fractions obtained using the Ph + Al, C_{18} + Al and Diol + Al sorbent combinations. For the first and the third combination, practically only the phthalates and the PAHs were present, which means that Ph and Diol sorbents can retain a wide spectrum of interfering substances. The analytes were eluted from the

Table 5
Elution profiles for the Ph + C_{18} + Al sorbent combination

Analyte	Recovery (%) Fraction number				
	1	2	3	4	5
α-Lindane	0	58	24	0	0
Simazine	0	2	46	50	0
Atrazine	0	8	42	0	0
Propazine	0	37	6	0	0
Terbuthylazine	0	31	82	0	0
β-Lindane	0	44	12	0	0
Disulfoton	0	37	36	0	0
δ-Lindane	0	36	19	0	1
Parathion methyl	2	84	10	6	4
Fenchlorphos	0	33	26	0	1
Fenitrothion	3	5	26	0	1
Malathion	0	39	9	0	0
Chlorpyrifos	0	40	28	0	1
Aldrin	0	7	40	0	0
Bromophos	0	36	26	0	0
o,p′-DDE	0	23	48	0	0
p,p′-DDE	0	23	52	0	0
o,p′-DDD	0	57	27	0	0
p,p′-DDD + *o,p′*-DDT	0	46	32	0	0
p,p′-DDT	0	31	47	0	0
PCB 28	2	14	49	0	0
PCB 52	0	24	51	0	0
PCB 101	0	5	69	1	0
PCB 153	0	0	83	1	0
Naphthalene	0	0	0	0	0
Acenaphthylene	0	2	5	0	0
Acenaphthene	0	2	13	0	0
Fluorene	0	16	23	0	0
Phenanthrene	0	26	41	0	0
Anthracene	0	28	47	0	0
Pyrene	0	9	77	1	0
Benzo[*a*]anthracene	0	0	80	1	0
Chrysene	0	1	94	2	0
Benzo[*b*]fluoranthene + benzo[*k*]fluoranthene	0	0	98	4	0
Benzo[*a*]pyrene	0	0	100	8	0
Indeno(1,2,3-*cd*)pyrene + dibenz[*a,h*]anthracene	0	1	79	27	0
Benzo[*ghi*]perylene	0	1	50	54	0

same SPE cartridges also in the first fraction during standard solution tests. This may have a significant impact on the final separation of analytes including pesticides, PCBs or PAHs from interfering substances in the clean-up of real sediment and/or soil samples. Of particular importance is the elimination of substances that are not separated from analytes such as α-lindane, atrazine, aldrin, PCB 28, PCB 52 and PCB 101, characterized by short retention times during the GC–MS separation.

3.6. Final clean-up method development

As a result of experiments described in Section 3.5, two sorbent combinations were chosen as the most effective: Ph + C_{18} + Al and Diol + C_{18} + Al. Another combination, CN + Al, was selected based on theoretical studies. Clean-up efficiency was evaluated for these sorbent combinations using real soil samples.

In spite of the satisfactory results obtained in the

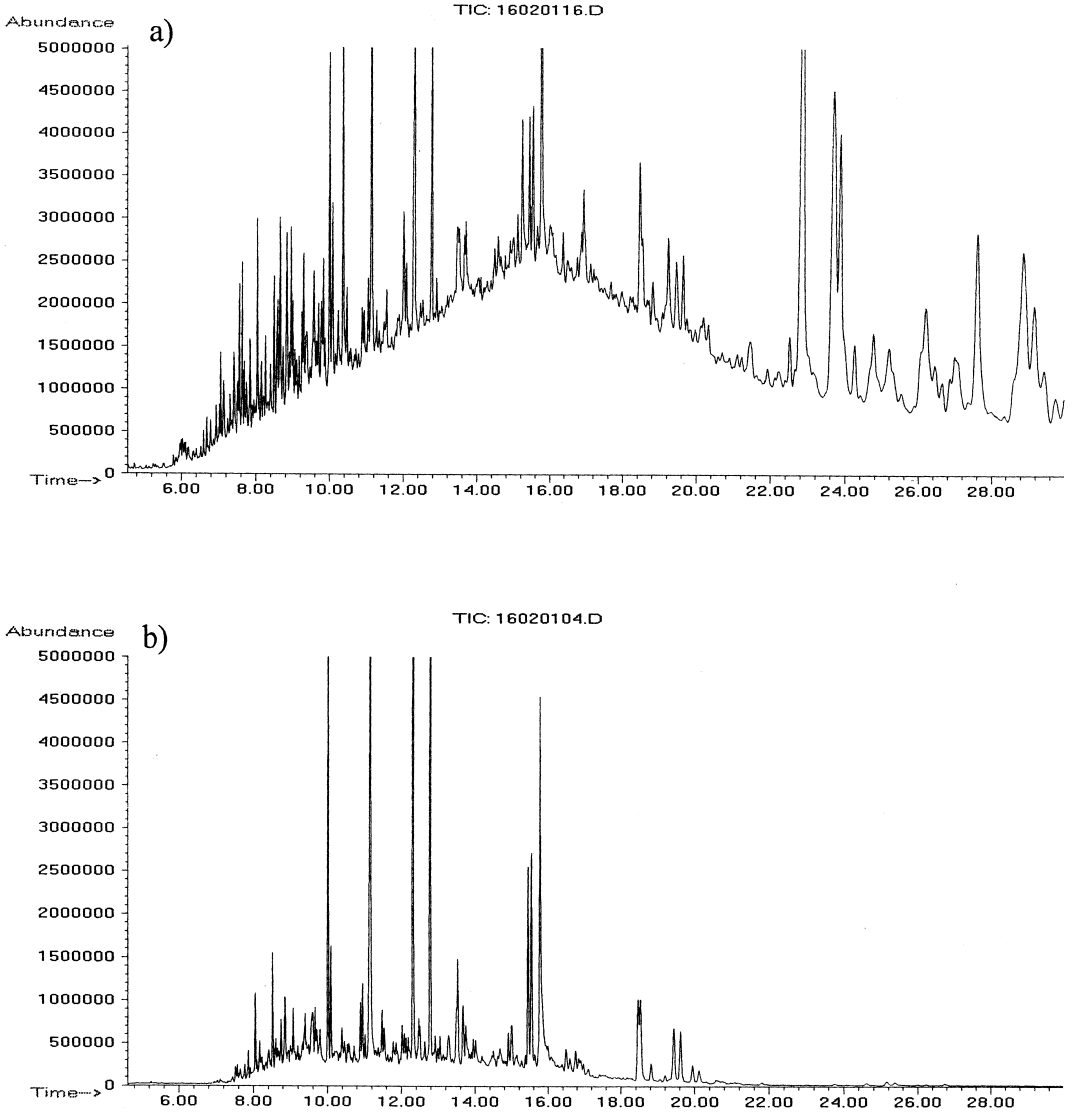

Fig. 1. Chromatograms of the second fraction of sediment extract obtained after clean-up using (a) Al, and (b) C_{18} + Al. Retention time of cholesterol and its derivatives: 21–30 min. Time scale in min.

preliminary experiments with the Diol + C_{18} + Al combination, final recovery experiments demonstrated limited usefulness of this combination in the analysis of real samples. A number of analytes, including lindanes, triazines and some PAHs, are not separated from matrix components. This is illustrated in Fig. 3, which presents a chromatogram of PCB 52 obtained for soil extracts cleaned-up using the Diol + C_{18} + Al combination. PCB 52 could be identified easily in the extract with standard addition (Fig. 3a), as confirmed by the relative intensity of the two qualifier ions (marked with black arrows). Positive identification of the analyte was not possible for the native extract (Fig. 3b) because the suspected analyte peak eluted too close to the large matrix peak.

The results of recovery experiments performed for selected pesticides, PCBs and PAHs in real soil samples using Ph + C_{18} + Al and CN + Al sorbent

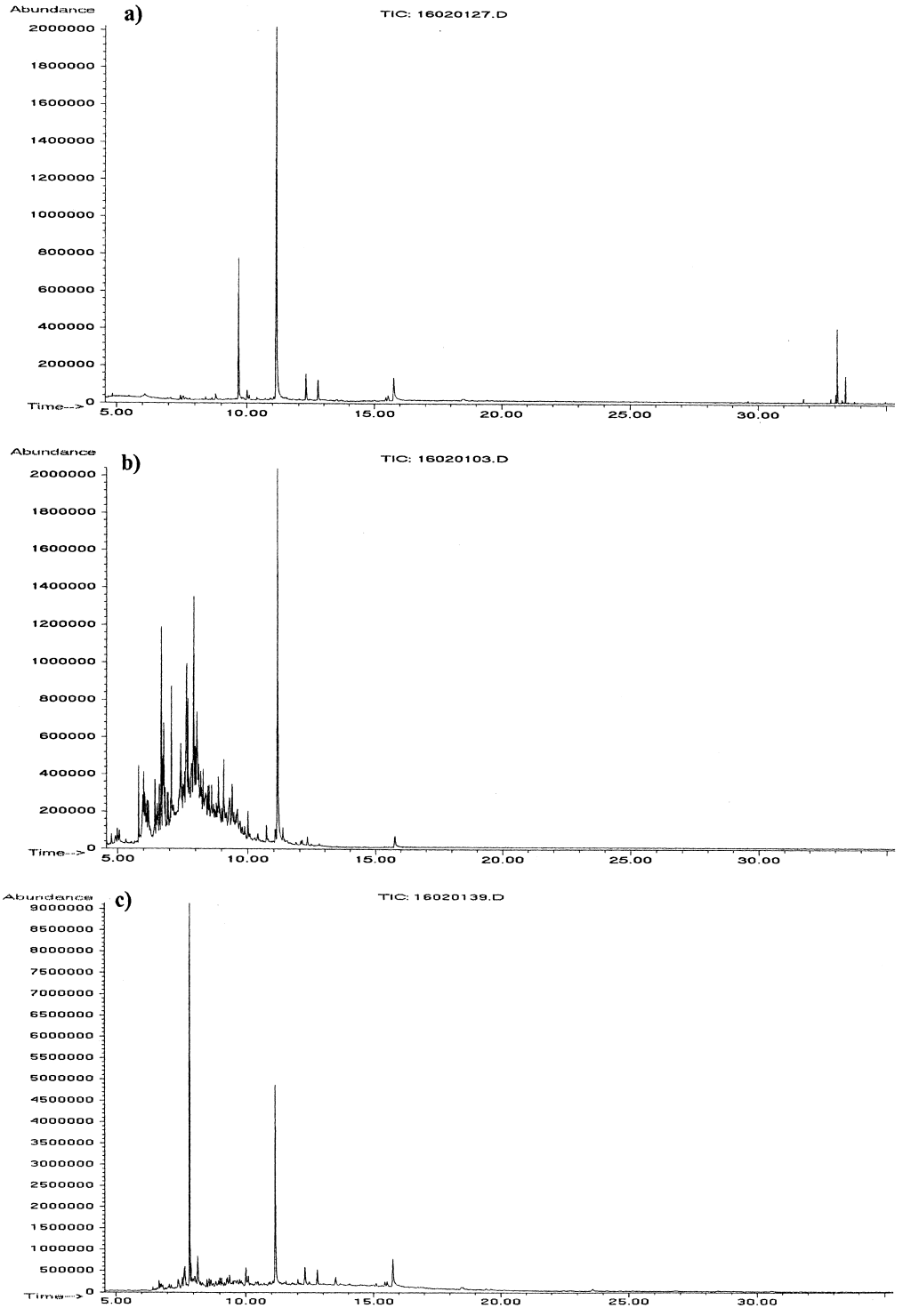

Fig. 2. Chromatograms of the first fraction of the sediment extract obtained after clean-up using different sorbent combinations: (a) Ph + Al; (b) C_{18} + Al; (c) Diol + Al. Time scale in min.

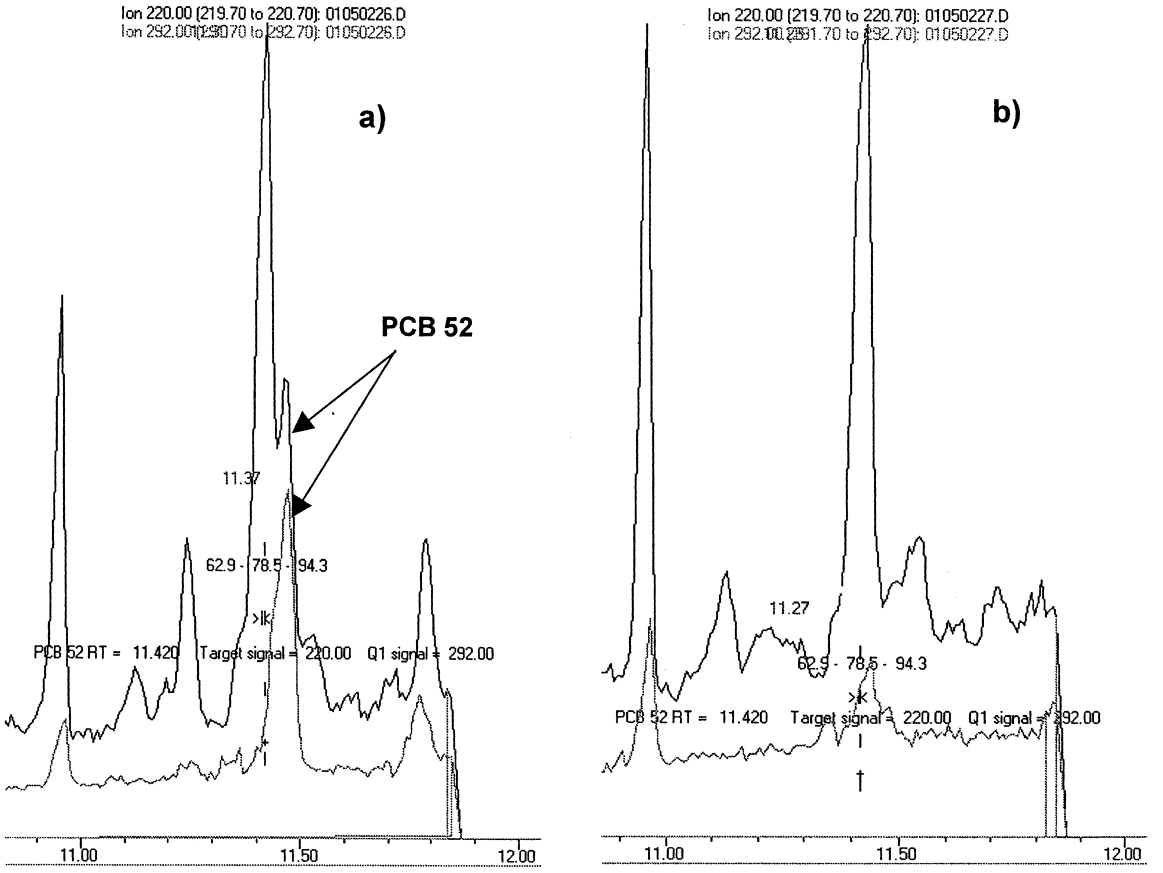

Fig. 3. Chromatograms of PCB 52 obtained for soil extracts pre-cleaned using Al + Diol + C_{18}. (a) Sample with standard addition, (b) Native sample extract. Time scale in min.

combinations are presented in Tables 6 and 7, respectively. For the Ph + C_{18} + Al combination, recoveries for most of the analytes ranged from 50 to 116%. In some cases the recoveries were considerably higher than 100%, for example for lindane, phenanthrene and benzo[*a*]anthracene. Coelution of some analytes, including *p,p′*-DDD + *o,p′*-DDT and indeno[1,2,3-*cd*]pyrene + dibenz[*a,h*]anthracene, were observed in two cases. A similar effect was also observed for the CN + Al combination. Moreover, the recoveries for some higher-molecular-mass PAHs, including fluoranthene, pyrene, benzo[*a*]anthracene, chrysene and benzo[*b*]fluoranthene, were abnormally high (about 150%) because of strong coelution with matrix components. This made positive identification and reliable quantitation of these analytes practically impossible. Relative standard deviations of the results were generally lower for the Ph + C_{18} + Al combination compared to the CN + Al combination.

3.7. Final procedure

The final procedure for soil and sediment sample preparation prior to the determination of selected pesticides, PCBs and PAHs using the SPE clean-up method developed was as follows: 5 g of the sample was placed into extraction cell. After the standard addition the cell was closed and shaken with the contents. Then the PLE with the MeCN–MeOH (9:1, v/v) mixture was performed (150 °C, 2000 p.s.i., i.e. 14 MPa). The extract was concentrated to 0.5 ml and transferred into the top of SPE column (Ph + C_{18} + Al, Cu, Na_2SO_4). The solvent of the collected

Table 6
Results for the clean-up using the Ph + C18 + Al sorbent combination

Analyte	Recovery [%]	RSD [%]
α-lindane	130	9
simazine	62	9
atrazine	71	6
propazine	85	9
terbuthylazine	56	6
disulfoton	82	9
δ-lindane	111	12
parathion methyl	95	10
malathion	96	16
chlorpyrifos	116	4
aldrin	63	6
bromophos	90	10
o,p'-DDE	70	5
p,p'-DDE	93	5
endrin	74	8
p,p'-DDD + o,p'-DDT	84	15
p,p'-DDT	66	4
PCB 28	89	12
PCB 52	52	8
PCB 101	41	20
naphthalene	42	9
acenaphthylene	77	7
acenaphthene	63	5
fluorene	67	4
phenanthrene	124	9
fluoranthene + pyrene	110	10
benzo(a)anthracene	131	17
chrysene	57	10
benzo(b)fluoranthene	45	13
indeno(1,2,3-c,d)pyrene + dibenz(a,h)anthracene	109	12
benzo(g,h,i)perylene	51	15

fraction was exchanged into dichloromethane for the final GC–MS analysis.

4. Conclusions

The well-known and widely used silica and alumina sorbents are not suitable for extract clean-up prior to the final determination of analytes ranging widely in polarity. Good efficiency can be achieved only for non-polar compounds using non-polar eluents. Only in this case is it possible to separate the analytes from lipids. Neither silica nor alumina should be used for extract clean-up in a single step when analysing compounds of various polarity. Experiments described previously [40] indicated that alumina and acetonitrile SPE system allowed clean-up of extracts prior to the analysis of compounds of different polarities by separating them from lipids. Acetonitrile eluted a wide range of analytes from various sorbent beds (Ph, NH_2, Diol, C_{18}) in the first 1–2 fractions. The results of basic fractionation experiments for standard solutions and real sediment extracts enabled the selection of the most suitable SPE combination for selected analytes or the whole group of the analysed compounds. A combination of alumina and additional sorbent beds efficiently removed matrix components that would coelute with the analytes during the final GC–MS analysis. The Ph + C_{18} + Al sorbent combination seems to be one of the most useful for extract clean-up prior to the analysis of pesticides, PCBs and PAHs. Additional

Table 7
Results for the clean-up using CN + Al sorbent combination

Analyte	Recovery (%)	RSD (%)
α-Lindane	122	6
Simazine	62	14
Atrazine	73	5
Propazine	61	12
Terbuthylazine	62	5
γ-Lindane	115	14
δ-Lindane	85	36
Fenchlorphos	89	8
Fenitrothion	101	16
Malathion	109	14
Chlorpyrifos	122	17
Aldrin	97	16
Bromophos	82	15
o,p′-DDE	92	9
p,p′-DDE	101	21
o,p′-DDD	111	17
Endrin	120	13
p,p′-DDD + *o,p′*-DDT	158	41
p,p′-DDT	117	7
PCB 28	68	23
PCB 52	90	10
PCB 101	83	9
PCB 138	113	6
PCB 153	100	26
PCB 180	127	8
Guthion	53	40
Naphthalene	27	17
Acenaphthylene	80	17
Acenaphthene	93	1
Fluorene	99	17
Phenanthrene	197	11
Anthracene	89	12
Benzo[*k*]fluoranthene	91	11
Benzo[*a*]pyrene	57	9
Indeno(1,2,3-*cd*)pyrene	54	4
Dibenz[*a,h*]anthracene	18	24
Benzo[*ghi*]perylene	37	19

experiments to validate the entire analytical procedure will be the subject of a future publication.

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