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Application of accelerated solvent extraction followed by gas chromatography, high-performance liquid chromatography and gas chromatography–mass spectrometry for the determination of polycyclic aromatic hydrocarbons, chlorinated pesticides and polychlorinated dibenzo-*p*-dioxins and dibenzofurans in solid wastes

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Abstract

Accelerated solvent extraction (ASE) is a new method for the extraction of organic compounds from soils, sludges and other wastes. Due to the elevated temperatures and pressures, the ASE is a time-saving procedure with low consumption of solvents. Applications of this procedure for the determination of chlorinated pesticides in contaminated soils, for the determination of polycyclic aromatic hydrocarbons in heap material, slurry from copper smelting (Theissenschlamm) and soils and for the determination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in a fly ash sample are given. Optimization of the procedure relating to extraction time, number of extractions and solvents is described. Comparisons with other extraction methods (Soxhlet extraction and automated Soxhlet extraction) are carried out. © 1997 Elsevier Science B.V.

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1. Introduction

In this paper, we report our first results with the accelerated solvent extraction (ASE), a new extraction procedure that uses organic solvents at high pressures and temperatures above the boiling point. With ASE extraction, a solid sample is placed in a cartridge and different solvents are used to extract the sample statically under elevated temperatures (50–200°C) and pressures (7–20 MPa) to increase the speed of the extraction process with low solvent consumption. ASE is equivalent to standard US Environmental Protection Agency (EPA) extraction methodology in terms of recovery and precision and is the proposed Method 3545 in Update III of the EPA SW-846 Methods [1,2]. Richter et al. [3] and Höfler et al. [4–6] gave first details about the effects caused by various parameters (temperature, pressure, volume of solvent used) on the performance of ASE and studied recoveries of total hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) from certified samples.

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This paper describes applications of the ASE 200 device from Dionex for the determination of contaminants in various environmental samples e.g. the determination of chlorinated pesticides from contaminated soils of the region Bitterfeld (eastern part of Germany), the determination of PAHs in heap material, Theisenschlamm and in soils from different sites and the determination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) from a fly ash sample.

A number of investigations were performed to optimize the procedure. The dependence of the extraction yield from the static extraction time and from the number of following extractions was studied, various solvents or solvent mixtures were investigated and in the case of PCDD/F extraction, a special sample pre-treatment was used to increase the ASE extraction yields. The results of these investigations are compared with those of Soxhlet extraction and automated Soxhlet extraction (Soxtec) taking into account the possible influence of different matrices.

2. Experimental

2.1. Sample information

The following samples were used for the investigations:

Two soil samples of the sites Keller and Spittel located in the floodplain of the stream Spittelgraben (this stream flows into the river Mulde and was used for several decades as a waste water channel of the chemical industry).

Two soil samples (Greppin near Bitterfeld, Saxony-Anhalt, Germany and Muldenaue from the floodplain of the river Mulde) polluted with heavy metals and organic contaminants.

A heap material from the copper shale mining of the Mansfeld region.

A scrubber dust slurry (so-called Theisen slurry or Theisenschlamm) generated as a by-product during extraction of copper from a mineralized black shale in Saxony–Anhalt.

A fly ash sample from a round robin test of the German Environmental Agency (Umweltbundesamt).Soils, heap material and Theisenschlamm were air dried, ground to a diameter ≤ 2 mm and homogenized.

2.2. Chemicals

The solvents used, acetone, hexane, dichloromethane, and toluene (quality: LiChrosolv) were obtained from Merck, acetonitrile (HPLC, Ultra Gradient Grade) and HPLC water were purchased from Baker. Chlorobenzene, HCH and DDX reference materials were obtained from Supelco, PCB reference materials from Riedel de Haen, PAH standard materials and the isotopic labelled PCDD/F reference materials from Promochem.

2.3. Accelerated solvent extraction

The extractions were carried out using a Dionex ASE 200 Accelerated Solvent Extractor with 11 ml, 22 ml or 33 ml stainless-steel extraction cells. Solvents were acetone–hexane (1:1, v/v), toluene, and dichloromethane–acetone (1:1, v/v).

In the case of acetone–hexane and dichloromethane–acetone, a system pressure of 10 MPa/14 MPa, an oven heat-up time of 5 min and an oven temperature of 100°C were chosen. The flush volume amounted to 60% of the extraction cell volume.

In the case of toluene as solvent the conditions were modified to a system pressure of 14 MPa, an oven heat-up time of 8 min and an oven temperature of 175°C/200°C. The optimization of the static extraction time is described in Sections 3.1–3.3

2.4. Conditions for the determination of chlorinated pesticides

The ASE extracts were concentrated to 1 ml and directly injected into the gas chromatograph. The gas chromatograph used was a HP 5890 II device (Hewlett–Packard) with electron-capture detection (ECD). For the experiments a 25-m×0.32-mm I.D. HP5 capillary column with a 0.52-μm film thickness was used. The carrier gas was hydrogen, the make-up gas was nitrogen. A split–splitless injector was used in the splitless mode and maintained at 250°C. The column temperature programme was as follows: initial temperature 80°C (held for 8 min), increased at 6 C°/min to 250°C and held at the final tempera-

ture for 8.5 min. The detector temperature was 250°C.

To ensure a reliable identification of the substances additional GC–MS analyses were carried out. The device used was a HP 5890 with MS equipped with a 30-m×0.25-mm HP5 capillary column (0.25-μm film thickness). The temperature programme was identical with that of the GC–ECD device.

2.5. Conditions for the PAH determination

For the PAH determination from the contaminated soils, a solvent exchange from toluene to acetonitrile was carried out. In these cases, no further procedures before HPLC analyses were performed. Prior to the PAH determination in heap material and in Theisenschlamm the samples were subjected to a solvent exchange (cyclohexane), ultrasonic treatment (5 min), a silica gel clean-up, and a final solvent exchange (acetonitrile). For HPLC analysis a Beckmann system 'Gold' equipped with a programmable fluorescence detector (Shimadzu RF-551) was used. The PAHs were separated on a Bakerbond PAH 16 Plus column (250×3-mm I.D.) with a pre-column at a column temperature of 25°C. Acetonitrile and water were used as the mobile phase at a flow-rate of 0.5 ml/min. The composition gradient of the mobile phase started with 50% acetonitrile and 50% water for 5 min, then the acetonitrile content was increased to 100% in 30 min with a linear gradient. This content was held constant for 10 min until the end of the analysis. For detection, the following excitation (ex) and emission (em) wavelength programme was used; naphthalene, acenaphthene, fluorene, and phenanthrene (λ_{ex} 275 nm, λ_{em} 350 nm), anthracene (λ_{ex} 375 nm, λ_{em} 425 nm), fluoranthene and pyrene (λ_{ex} 335 nm, λ_{em} 440 nm), benz[*a*]anthracene and chrysene (λ_{ex} 315 nm, λ_{em} 405 nm), benzo[*b*]-fluoranthene (λ_{ex} 330 nm, λ_{em} 420 nm), benzo[*k*]-fluoranthene and benzo[*a*]pyrene (λ_{ex} 375 nm, λ_{em} 460 nm), dibenz[*a,h*]anthracene and benzo-[*ghi*]perylene (λ_{ex} 345 nm, λ_{em} 420 nm) and indeno[1,2,3]pyrene (λ_{ex} 300 nm, λ_{em} 500 nm).

2.6. Conditions for the PCDD/F determination

For comparison purposes the fly ash sample was extracted with a conventional Soxhlet device (extraction time: 20 h) and with the ASE 200. The fly ash sample was processed with and without an acid pre-treatment step. In the case of pre-treatment prior to the extraction, the sample (1 g) was mixed with a sufficient amount of hydrochloric acid (10%, ca. 20 ml) and was shaken for 2 h. Then the fly ash was separated by filtration and washed until the filtrate became neutral. Afterwards the sample was air dried at ambient temperature. A quantifying mixture of ten $^{13}C_{12}$ isotopically labelled 2,3,7,8-PCDD/F-isomers was used as internal reference mixture.

The clean-up procedure entails a series of liquid chromatographic clean-up sequences, which include a carbon column, and a combination silica gel column containing basic alumina, acid modified and neutral silica gel and silver nitrate–silica gel.

Fly ash samples are strongly loaded with a great variety of organic matrix compounds. Remaining impurities can disturb the separation and decrease the sensitivity of the GC–MS procedure dramatically. To avoid such problems, an additional pre-cleaning step was chosen. A mixture of 44% sulfuric acid and 56% (w/w) silica was added to the sample extract in *n*-hexane. The mixture was refluxed for 30 min, the hexane was decanted and the residue was washed twice with heptane. Prior to injection into the gas chromatograph a [$^{13}C_6$]1,2,3,4-TCDD standard solution was added.

For the gas chromatographic separation of the PCDD/F, a non-polar and a polar capillary column were used. The non-polar column was 30-m×0.25-mm I.D. with a 0.20-μm film thickness of DB-5 (J&W Scientific). The temperature programme was initially 90°C for 2 min, increased at 50 C°/min to 125°C, at 2 C°/min to 230°C, then at 7 C°/min to 290°C and held isothermally for 30 min at 290°C. The polar column was 60-m×0.25-mm I.D. with a 0.10-μm film thickness of RTX-2330 (Restek Corporation). The temperature programme was as follows: initial temperature 90°C (held for 1 min), increased at 25 C°/min to 160°C, then at 3 C°/min to 230°C, held isothermally for 22 min, then increased at 5 C°/min to 260°C and held at the final temperature for 20 min. Helium at a linear velocity of 30 cm/s was used as the carrier gas. Samples were injected by use of a split/splitless injector. Using the polar column, a piece of phenyl–methyl

Table 1
Results of 3×5-min ASE extractions of contaminated soils with acetone–hexane (1:1)

	Soil KEL				Soil SPI			
	α-HCH (ng/g)	HCB (ng/g)	β-HCH (ng/g)	γ-HCH (ng/g)	α-HCH (ng/g)	HCB (ng/g)	β-HCH (ng/g)	γ-HCH (ng/g)
First extraction	440	1200	1051	3.5	3057	394	2216	15
Second extraction	11	51	20		120	41	71	
Third extraction	5	29	16		66	19	38	

deactivated guard column was connected to the front- and backend of the column for the connection with the injector (290°C) and the mass spectrometer source. The GC–MS interface was maintained at 275°C. The mass spectrometric detection was carried out on a Finnigan MAT 95 mass spectrometer. The instrument was operated at high resolution of approximately 10 000. Detection was performed by simultaneous recording of the two most abundant ions of the chlorine isotope cluster of molecular ions of the analytes and the internal standards.

3. Results and discussion

3.1. Determination of chlorinated pesticides

According to the requirements of the proposed Method 3545 in Update III of the EPA SW-846 Methods [2,7] the extraction of chlorinated pesticides should be performed with acetone–hexane (1:1, v/v) as solvent. A static extraction time of 5 min is also proposed.

To ensure that the accelerated solvent extraction of contaminated soils is carried out under optimum conditions first of all we used acetone–hexane as solvent and varied the number of the extractions. The results of these investigations with HCH-contaminated soils of the regions Keller (KEL) and Spittel (SPI) are given in Table 1.

The predominant part of the contaminants is extracted during the first extraction step. The yield of the second extraction is much lower but not neglectible and the yield of the third procedure is very low. The results of further investigations with static extraction times of 5 min, 10 min, and 15 min showed that the yields of the 10-min and the 15-min extractions were nearly the same and that the yields of a 10 min extraction were higher than those of a 5-min extraction but lower as the yields of two successive 5-min extractions. For that reason a static extraction time of 2×5 min was chosen for all further investigations of pesticide contaminated soils.

A comparison of ASE, Soxhlet, and Soxtec extraction was carried out using the same soils (KEL and SPI) and acetone–hexane as solvent. Results are given in Table 2. It is seen, that the differences between the concentrations of the main contaminants α-HCH, HCB, and β-HCH are very low and that a 2×5 min ASE is equivalent to a Soxtec extraction of 6 h or a Soxhlet extraction of 18 h.

To test the dependence of the extraction yields on the solvent used we performed the ASE of a HCH- and DDX-contaminated soil of the Bitterfeld region

Table 2
Comparison of ASE, Soxhlet and Soxtec extraction of contaminated soils of the regions Spittel (SPI) and Keller (KEL)

	Soil KEL			Soil SPI		
	Soxhlet 18 h c (ng/g)	Soxtec 6 h c (ng/g)	ASE 2×5 min c (ng/g)	Soxhlet 18 h c (ng/g)	Soxtec 6 h c (ng/g)	ASE 2×5 min c (ng/g)
α-HCH	412	431	439	3131	3760	3481
HCB	1198	1128	1197	865	793	835
β-HCH	992	1152	1106	2962	2655	2441

Table 3
Extraction yields of HCHs and DDX compounds using different solvents (soil GRE)

	Acetone–hexane		CH_2Cl_2–acetone		Toluene	
	c (μg/g)	R.S.D. (%)	c (μg/g)	R.S.D. (%)	c (μg/g)	R.S.D. (%)
α-HCH	0.90	12.1	0.91	13.6	1.33	11.6
β-HCH	4.55	10.1	4.77	14.2	4.10	15.8
γ-HCH	0.18	3.2	0.15	5.9	0.17	9.1
δ-HCH	0.34	4.4	0.28	6.9	0.23	7.4
p,p'-DDE	0.25	4.6	0.25	3.9	0.21	4.2
p,p'-DDD	0.49	4.8	0.38	6.8	0.39	3.2
p,p'-DDT	0.67	13.0	0.68	18.2	0.58	11.3

(Greppin, GRE) and a highly contaminated riverside soil (Muldenaue, MUL) with acetone–hexane (1:1, v/v), dichloromethane–acetone (1:1, v/v), and toluene. The mean concentration values of the main contaminants and relative standard deviations of 6 extractions for the three solvents used are given in Table 3 and Table 4.

The values for the soil GRE are comparable. Except α-HCH, the values of the toluene extraction are somewhat lower than those of the extraction with the other solvents. The relative standard deviations of the 6 independent extractions with following GC–ECD measurement lay between 3.2% and 18.2% and the best precision was generally obtained with a hexane–acetone extraction. Regarding the soil MUL we can see, that the efficiency of the three solvents especially for the predominant β-HCH is different (Table 4). The yields of the toluene extraction are the highest, those of the acetone–hexane extraction are lower and the dichloromethane–acetone extraction provides the lowest values. The standard deviations of the ASE-GC–ECD analyses of the Muldenaue soil are relatively low (3.1%–16.7%).

Generally, the 2×5-min acetone–hexane extraction is a suitable method for the determination of chlorinated pesticides from soils but in the case of difficult matrices and high concentrations of pollutants the use of toluene as solvent may be the best choice. Fig. 1 gives a comparison between GC–MS chromatogramms of acetone–hexane and toluene extraction of the soil MUL. The concentrations of nearly all compounds are higher if toluene is the solvent. A certain disadvantage are the higher levels of accompanying compounds (e.g. retention time range between 21.0–23.5 min).

3.2. Determination of PAHs

For the extraction of PAHs, the Method 3545 proposes dichloromethane–acetone (1:1, v/v) as solvent [2,8]. Höfler et al. [4] showed that acetone–hexane (1:1, v/v) is also a suitable extraction solvent. To find out the most favorable solvent we used the variation of the extraction solvents described in Section 3.1 not only for the determination of chlorinated pesticides of the soil samples GRE and MUL but also for the determination of PAHs. In these cases the HPLC with fluorescence detection

Table 4
Extraction yields of HCHs and DDX compounds using different solvents (soil MUL)

	Acetone–hexane		CH_2Cl_2–acetone		Toluene	
	c (μg/g)	R.S.D. (%)	c (μg/g)	R.S.D. (%)	c (μg/g)	R.S.D. (%)
α-HCH	3.72	4.7	3.05	7.1	4.19	5.0
β-HCH	222.76	10.7	137.92	9.3	363.00	6.6
γ-HCH	0.90	15.2	0.70	10.0	1.03	6.9
δ-HCH	2.60	6.6	2.27	5.1	2.91	5.6
p,p'-DDE	2.21	3.1	2.31	5.1	2.91	3.5
p,p'-DDD	2.92	4.8	1.92	5.9	2.67	5.9
p,p'-DDT	5.58	9.4	6.03	5.4	6.93	16.7

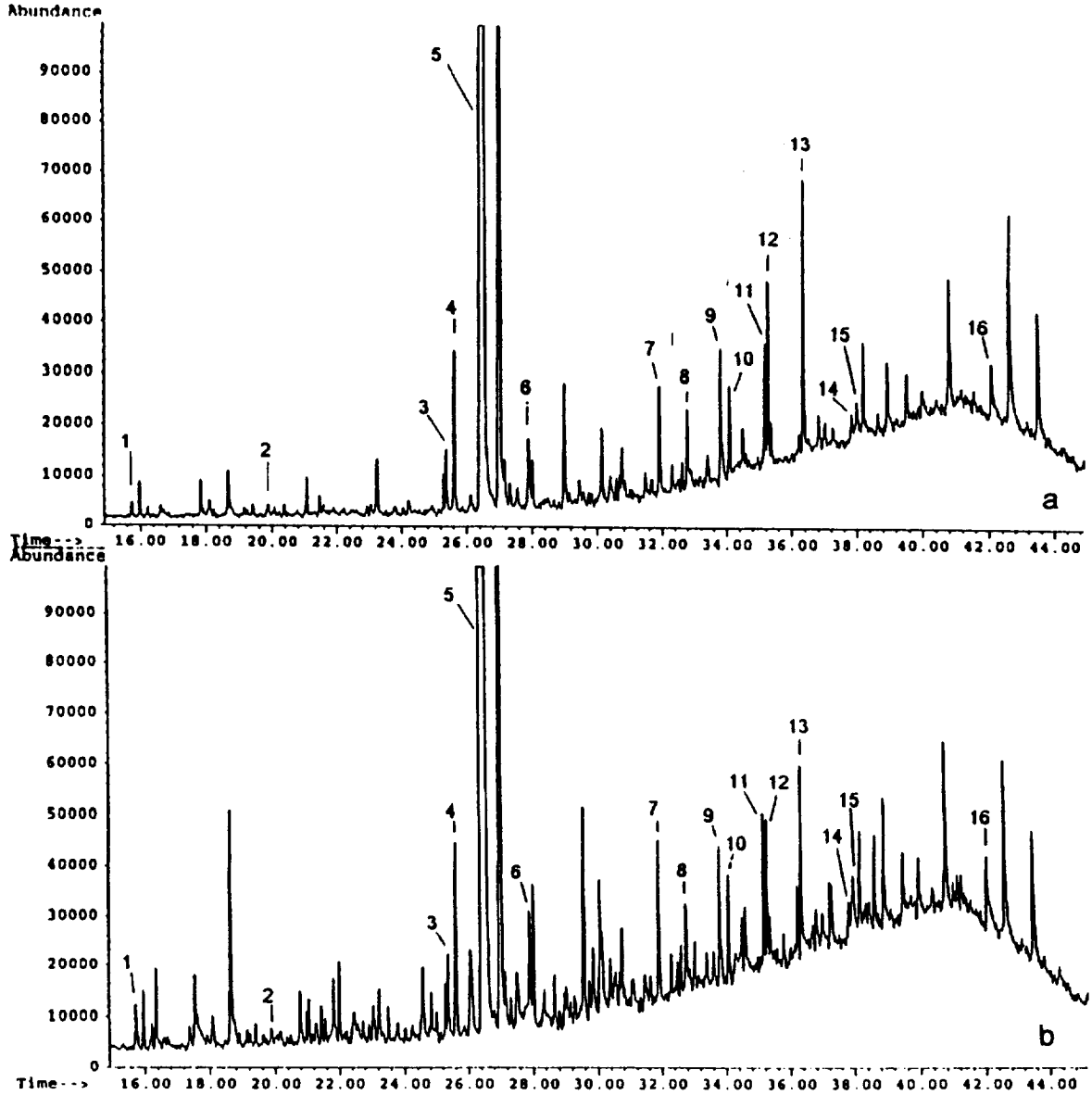

Fig. 1. GC–MSD chromatogramms of a contaminated soil using acetone–hexane (a) and toluene (b) as solvents. 1 = 2-methylnaphthalene; 2 = acenaphthylene; 3 = α-HCH; 4 = HCB; 5 = β-HCH; 6 = δ-HCH; 7 = fluoranthene; 8 = pyrene; 9 = *p,p'*-DDE; 10 = *o,p'*-DDD; 11 = *p,p'*-DDD; 12 = *o,p'*-DDT; 13 = *p,p'*-DDT; 14 = benz[*a*]anthracene; 15 = chrysene; 16 = benzo[*a*]pyrene.

was used for the analyses of the extracts. Table 5 shows the results for 12 of the 16 EPA–PAHs. It is seen, that the contaminated soil MUL has higher PAH concentrations compared with the soil GRE but independent of these differences, in both cases, toluene provides the highest extraction yields. Using dichloromethane–acetone the extraction yields decrease and with hexane–acetone as solvent somewhat lower yields are observed. For the extraction of PAHs from other matrices (pine-tree barks) we found the same dependences.

As a result of these investigations, we use toluene

Table 5
ASE extraction of PAHs with three different solvents (soils GRE and MUL)

	Soil GRE			Soil MUL		
	Acetone–hexane c (ng/g)	Acetone–CH_2Cl_2 c (ng/g)	Toluene c (ng/g)	Acetone–hexane c (ng/g)	Acetone–CH_2Cl_2 c (ng/g)	Toluene c (ng/g)
Phenanthrene	581	887	1240	868	946	1584
Anthracene	42	62	92	91	97	167
Fluoranthene	823	1042	1515	1394	1452	2016
Pyrene	488	583	813	925	920	1126
Benz[*a*]anthracene	193	257	418	371	485	626
Chrysene	245	313	603	558	590	906
Benzo[*b*]fluoranthene	301	393	670	670	741	1054
Benzo[*k*]fluoranthene	99	124	236	231	251	377
Benzo[*a*]pyrene	152	186	323	367	392	551
Dibenz[*a,h*]anthrac.	29	42	80	70	80	120
Benzo[*ghi*]perylene	111	147	283	264	278	449
Indeno[1,2,3]pyrene	138	203	452	329	383	652

as solvent for the ASE of PAHs from toxic wastes. Table 6 shows results of the analyses of heap material from the copper–shale mining (Mansfeld region). Soxhlet extraction (18 h) and ASE (2×5 min), in both cases with toluene, are compared. Except for phenanthrene and benz[*a*]anthracene the ASE provides higher extraction yields for the EPA–PAHs. Table 7 shows a typical result of the analyses of Theisenschlamm. Using ASE (2×5 min) with toluene, very high concentrations of PAHs were determined and the ASE is more effective than the Soxhlet extraction (18 h).

Table 6
Comparison between ASE and Solvent extraction of PAHs from heap material of the copper shale mining

	Soxhlet c (ng/g)	ASE c (ng/g)
Naphthalene	180	220
Acenaphthene	324	1058
Fluorene	12	12
Phenanthrene	3530	3051
Anthracene	86	106
Fluoranthene	3605	4368
Pyrene	2567	2761
Benz[*a*]anthracene	958	904
Chrysene	2242	2646
Benzo[*b*]fluoranthene	1672	2239
Benzo[*k*]fluoranthene	669	893
Benzo[*a*]pyrene	1028	1248
Dibenz[*a,h*]anthracene	105	131
Benzo[*ghi*]perylene	87	131
Indeno[1,2,3]pyrene	878	1158

3.3. Determination of PCDD/F

We have tested the ASE for the extraction of PCDD/F from a fly ash sample originating from an municipal incineration plant. Because no published results for the accelerated solvent extraction of

Table 7
Comparison between ASE and Soxhlet extraction of PAHs from Theisenschlamm

	Soxhlet c (μg/g)	ASE c (μg/g)
Naphthalene	n.q.	n.q.
Acenaphthene	1.1	1.5
Fluorene	16.1	23.6
Phenanthrene	173.4	209.1
Anthracene	31.0	38.8
Fluoranthene	61.8	76.1
Pyrene	92.8	120.2
Benz[*a*]anthracene	36.2	38.7
Chrysene	67.6	75.5
Benzo[*b*]fluoranthene	21.8	26.7
Benzo[*k*]fluoranthene	8.0	9.8
Benzo[*a*]pyrene	21.8	23.9
Dibenz[*a,h*]anthracene	0.9	1.2
Benzo[*ghi*]perylene	13.6	14.5
Ideno[1,2,3]pyrene	8.8	9.0

n.q. = not to quantify.

Table 8
PCDD/F homologue concentrations of a fly ash sample for ASE and Soxhlet extraction without pre-treatment step

	2×5-min ASE c (μg/kg)	2×10-min ASE c (μg/kg)	20-h Soxhlet c (μg/kg)
sum TCDD	7.6	9.2	9.6
sum PeCDD	18.7	22.3	23.9
sum HxCDD	56.3	60.6	72.5
sum HpCDD	107.4	125.0	178.8
OCDD	241.5	298.6	483.7
sum TCDF	38.4	45.9	43.2
sum PeCDF	55.0	61.2	78.0
sum HxCDF	45.7	52.4	70.9
sum HpCDF	38.5	46.0	67.4
OFDF	15.4	16.8	29.7

Table 9
PCDD/F concentrations of a fly ash sample for ASE and Soxhlet extraction with acid pre-treatment step

2×10-min ASE		Isomeres/homologues	20-h Soxhlet	
Concentration (μg/kg)	Toxic equiv. (μg iTE/kg)		Concentration (μg/kg)	Toxic equiv. (μg iTE/kg)
0.82	0.82	2,3,7,8-TCDD	0.64	0.64
4.91	2.46	1,2,3,7,8-PeCDD	3.93	1.97
7.34	0.73	1,2,3,4,7,8-HxCDD	5.42	0.54
19.07	1.91	1,2,3,6,7,8-HxCDD	14.69	1.47
13.46	1.35	1,2,3,7,8,9-HxCDD	14.79	1.48
248.87	2.49	1,2,3,4,6,7,8-HpCDD	171.21	1.71
1403.14	1.40	OCDD	979.28	0.98
20.71	2.07	2,3,7,8-TCDF	11.96	1.20
10.07	0.50	1,2,3,7,8-PeCDF	7.54	0.38
12.84	6.42	2,3,4,7,8-PeCDF	14.57	7.28
16.70	1.67	1,2,3,4,7,8-HxCDF	16.48	1.65
17.09	1.71	1,2,3,6,7,8-HxCDF	12.22	1.22
21.37	2.14	1,2,3,7,8,9-HxCDF	17.76	1.78
0.75	0.08	2,3,4,6,7,8-HxCDF	0.90	0.09
121.78	1.22	1,2,3,4,6,7,8-HpCDF	91.42	0.91
9.37	0.09	1,2,3,4,7,8,9-HpCDF	6.66	0.07
99.21	0.10	OCDF	69.97	0.07
28.48		sum TCDD	15.10	
73.02		sum PeCDD	49.64	
225.38		sum HxCDD	166.51	
479.42		sum HpCDD	330.18	
1403.14		OCDD	979.28	
120.01		sum TCDF	71.40	
190.21		sum PeCDF	122.38	
163.40		sum HxCDF	127.91	
163.83		sum HpCDF	121.44	
99.21		OCDF	69.97	
2946.09	27.16	total sum	2053.81	23.44

PCDD/F existed we compared all results with those of a 20-h Soxhlet extraction. With toluene as solvent, we used the highest possible working temperature of the ASE 200 device (200°C); extraction times of 2×5 min and 2×10 min were chosen. The analyses of the extracts (clean-up procedures see Section 2.6) were carried out with GC–MS. The homologue concentrations (the sum of all PCDD/F isomers of a homologue group of 4 to 8 Cl atoms) are given in Table 8. It is observed, that the ASE extraction yields increase with rising extraction times. Furthermore it is shown, that the extraction yields obtained with the ASE are much lower than those of Soxhlet extraction. The ASE/Soxhlet extraction yield ratio decreases with the degree of chlorination. For the tetrachlorodibenzodioxins this ratio was nearly 1 (2×10-min ASE extraction time) but for OCDD and OCDF it decreases to 0.6.

Höckel et al. [9] describe a special extraction procedure (18-h Soxhlet extraction with toluene, ethyleneglycol monoethyl ether and HCl) for fly ash samples and Höfler [10] recommended the application of a HCl pre-treatment. We used the procedure described in Section 2.6. to improve the extraction yields. In Table 9 the PCDD/F homologue and congener concentrations of the fly ash sample with acid pre-treatment step for Soxhlet and ASE extraction are listed. In these cases the ASE/Soxhlet extraction yield ratio of the 2,3,7,8-substituted congeners and of the homologues exceeds the value of 1. That means that under these conditions the ASE is more efficient than the Soxhlet extraction of 20 h.

With this application we worked out a procedure for the accelerated solvent extraction of fly ash samples only. An unmodified transfer to the extraction of PCDD/F from other matrices (e.g. sludge) is not possible. For such applications, in comparison with Soxhlet extraction, appropriate procedures must be developed.

4. Conclusions

ASE is a suitable method for the extraction of organic contaminants from toxic wastes. With careful optimization the extraction yields are comparable or even higher than those of a Soxhlet or Soxtec extraction.

For the ASE of chlorinated pesticides from contaminated soils acetone–hexane (1:1, v/v) as solvent and a static extraction time of 2×5 min are useful but in the case of extremely contaminated soils, toluene as solvent is more suitable.

Among the examined solvents [toluene, acetone–hexane (1:1), dichloromethane–acetone (1:1)] toluene provides the highest extraction yields of PAHs from contaminated soils, heap material or Theisenschlamm. An improved ASE extraction of PCDD/F from fly ash can be achieved by acid pre-treatment and use of toluene (2×10 min extraction time) as solvent.

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