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Comparison of pressurised liquid extraction with Soxhlet extraction for the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from fly ash and environmental matrices[1]

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Abstract

Dynamic high-pressure solvent extraction is a new, rapid and solvent-saving extraction technique for performing pressurised liquid extractions. The technique uses conventional solvent or mixtures of solvents for the extraction of solid material under elevated temperature and pressure. A continuous flow of fresh solvent during the extraction provides for a high extraction efficiency, short extraction times and low solvent consumption. The extraction device and the optimisation of the extraction procedure shall be described. For demonstrating the applicability of this technique, polychlorinated dibenzodioxins and -furans were extracted from different matrices which include fly ash, filter dust, and soil. Soxhlet extractions were performed as a reference method. The comparative results show that dynamic high-pressure solvent extraction provides extraction efficiencies equal to, or even higher, than Soxhlet.

Keywords: Extraction methods; Pressurized liquid extraction; Dynamic high-pressure solvent extraction; Soil; Environmental analysis; Polychlorinated dibenzodioxins; Polychlorinated dibenzofurans

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are well known environmental pollutants of high toxic potential. Chemical analysis of these compounds is a complicated, time-consuming and expensive process. Besides sampling, this includes the extraction of the matrix, a multi-stage clean-up of the extracts and analysis by GC–MS or GC–high-resolution (HR) MS. To reduce costs, optimisation and automation of the sample preparation procedure is of considerable interest.

Conventional extraction methods, for example Soxhlet extraction, are often time-consuming and require large amounts of organic solvents. With the demand for reducing the solvent waste, faster analyses, and increased productivity, alternative extraction techniques are being developed. Supercritical fluid extraction (SFE) and pressurised liquid extraction techniques – e.g. accelerated solvent extraction, ASE or enhanced solvent extraction, ESE – which both involve the use of elevated extraction pressure and temperatures are examples of such alternative techniques.

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In SFE the use of pure CO_2 is desirable, since no organic solvent is required. Bowadt, et al. [1] and Heemken et al. [2] showed that quantitative recoveries of polychlorinated biphenyls (PCBs) may be obtained with pure CO_2. In contrast, SFE of certain polycyclic aromatic hydrocarbons (PAHs), pesticides, and PCDDs and PCDFs typically requires modifiers such as methanol [3–5].

Additionally, extraction yields in SFE are often matrix-dependent.

Pressurised liquid extraction (PLE) uses conventional solvents or mixtures of solvents [6]. Hence, PLE may be applied to a wide range of analytes (e.g. PAHs, PCBs, pesticides) in varying solid matrices which includes the extraction of PCDDs and PCDFs from fly ash and sediments [7–9]. These previous applications were performed using a commercial ASE instrument that required short static extraction times (5–15 min) and performed a semi-automated extraction of samples in sequential order.

In this paper, a new type of a PLE instrument is presented, which provides a continuous dynamic extraction of solid material at high pressure and temperature and permits extraction of up to five samples in parallel. As a result, sample preparation time and solvent consumption are reduced. This improvement is possible due to a combination of several temperature- and pressure-dependent processes: Increased diffusion rates, increased solubility of the analytes, decreased viscosity of the solvents, reduced matrix/analyte interactions, and the possibility to reach matrix pores by high pressure [10].

In contrast to the other extraction techniques, which applies only a short post-extraction dynamic rinse following the static extraction, dynamic high-pressure solvent extraction (DHPSE)[2] continuously uses fresh solvent under elevated temperatures and pressures. According to Fick's law of diffusion, mass transfer rates are thus accelerated. Hence, extraction efficiencies should be improved and extraction times reduced.

The present paper reports the results of the application of DHPSE on fly ash from municipal waste incinerators, dust samples from metal mills and soil samples. The data are compared with Soxhlet extraction as a reference method.

[2] DHPSE is the registered name of the utility model (Register no. DE 397 02 865 U) of the extraction device.

2. Experimental

2.1. Chemicals and samples

The solvents used (*n*-hexane, toluene, dichloromethane, methanol) were obtained from Merck, Germany (Suprasolv quality), the isotopic labelled PCDD and PCDF standards for quantification from Promochem.

The following samples were used for the experiments: (i) fly ash from several municipal waste incinerators (MWIs), (ii) particles from a dust collector of metal mills, and (iii) soil sample from an industrial area.

2.1.1. Sample pre-treatment

The samples were pulverised and homogenised in an analytical grinding mill. In addition, some of the fly ash samples were treated for 15–30 min with dilute hydrochloric acid (10%, w/w), and subjected to neutral washing and freeze drying before the extraction procedure.

2.2. Extraction conditions

2.2.1. Soxhlet

Aliquots of fly ash samples (1 g), particles from dust collectors (1 g) or dry soil (20 g) were extracted with 150 ml toluene for 24 h. Prior to the extraction, internal standards for the quantification of PCDDs and PCDFs were added to the sample.

2.2.2. DHPSE

2.2.2.1. Description of the DHPSE extraction device

In Fig. 1, the device is represented schematically. For the extraction, samples are introduced into pressure-stable stainless-steel extraction cells (built in the laboratory, 27 cm×11 mm I.D., 19 mm O.D.). The cells are closed by screw caps with adapters for finger-tight HPLC fittings. Depending on the amount of the sample, cell volumes of 5, 10, 15, 20 and 25 ml can be set by using various stainless-steel inserts. The five extraction cells are integrated in an oven

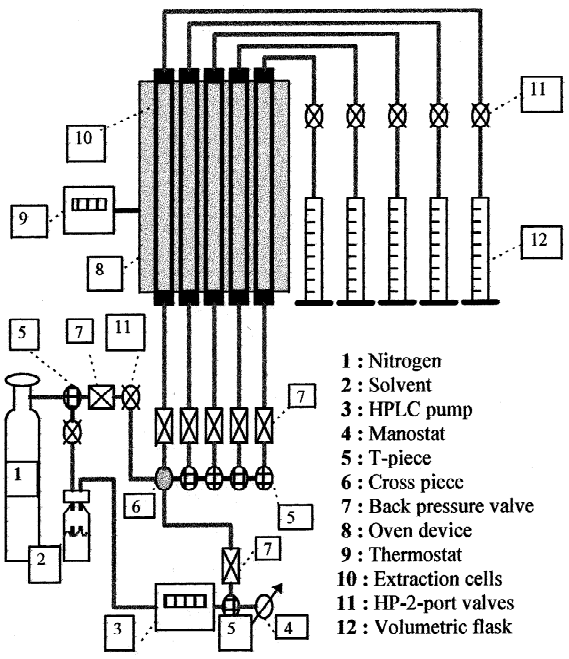

Fig. 1. Schematic representation of the DHPSE device.

device (Fig. 1, Nos. 8 and 10). Maximum temperatures of 200°C are practicable. Pure solvents or mixtures of solvents are fed in continuously by an HPLC pump (Latek, Germany, flow-rate of max. 10 ml/min) which is also responsible for building up the pressure (max. pressure 400 MPa) in the extraction cells. Pressure and temperature are kept constant automatically via a manostat and a temperature controller (Fig. 1, Nos. 4 and 9). Operating pressure usually ranges between 15 and 20 MPa, commonly a solvent flow of 1 ml/min through the extraction cells is used. The extraction of the individual cells can be controlled separately through utilisation of high-pressure variable valves (Fig. 1, No. 11). Hence, 1–5 cells may be extracted in parallel. If the valves are closed after flooding of the sample with solvent, implementation of static extraction experiments is possible. After the extraction is completed, the residual solvents may be removed from the cells by pressurised nitrogen.

The DHPSE device is ready for use after a few minutes for rinsing the lines and valves with pure solvents.

2.2.2.2. Preparation of the extraction cells

The extraction cells are filled with (in the direction of solvent flow): (i) a stainless steel insert (depending on the volume of the sample); (ii) silanised glass wool; (iii) sample and internal standards; (iv) inert material, e.g. pre-extracted quartz sand; and (v) silanised glass wool.

Following the extraction, the cells are rinsed with pure solvents. Additionally the extraction cells are cleaned in a Soxhlet apparatus for 6 h. If there are extraction cells in spare, these cells can be prepared during the extraction of the other five cells. In that way, extractions can be performed more or less in a row.

2.3. Clean-up procedure for the extracts

The procedure was accomplished according to the VDI method 3499. The volume of the extracts is reduced to 1 ml with a closed cell concentrator (TurboVap 500, Zymark, Germany). For the clean-up, an automatic medium-pressure liquid chromatography system (PARC-system, details in [11]) is used. The system works with a two-stage column clean-up using a combination of two columns: A mixed silica gel–$AgNO_3$/silica gel–H_2SO_4 column for precipitation and/or oxidation of interfering compounds [12 mm I.D., 2 g silica gel, 10 g silica gel, 44% (w/w) sulphuric acid, 63–200 mesh, active 60A, ICN Biomedicals, Germany] and an alumina column [12 mm I.D., 15 g alumina B super I, ICN Biomedicals] for fractionation into chlorobenzenes, PCBs and PCDDs and PCDFs. Following the fractionation the solvent is reduced to 30–50 μl using a closed cell concentrator and a gentle stream of dry nitrogen. Finally, the recovery standard is added to the sample.

2.4. GC–MS determination of PCDDs and PCDFs

The extracts were analyzed with a gas chromatograph (Hewlett-Packard 5890) equipped with either a mass-selective detector (HP MSD 5971) or a high-resolution mass spectrometer (VG Autospec). Separation was performed on two fused-silica capillary columns: a non-polar 30 m×0.25 mm I.D. column, coated with 0.25 μm DB5 (Supelco), used with the mass-selective detector and for isomer-specific detection a polar 60 m×0.25 mm I.D. column, coated

with 0.25 μm SP2331 (Supelco), used with the VG Autospec.

The GC oven temperature programs were as follows: Extracts in isooctane: 105°C for 3 min, increased at 10°/min to 200°C, increased at 5°/min to 300°C, and then 5 min isothermal; extracts in tetradecane: 200°C for 3 min, increased at 5°/min to 250°C, and then 25 min isothermal.

The extracts were injected splitless at 305°C injector temperature, using injection volumes of 1 μl and 60 s splitless time. The transferline was kept at 310°C.

The mass spectrometers were operated in the single-ion monitoring mode. The two most abundant ion masses of each isotopic chlorine cluster of PCDDs and PCDFs and their ^{13}C-labelled congeners were selected. Analysis with the HR-MS system were performed at a resolution of at least 10 000.

2.5. Quantification

Quantification was done using the isotope dilution technique. Prior to extraction, all samples were spiked with $^{13}C_{12}$-labelled PCDD/PCDF standards: 2,3,7,8-TCDD/F, 1,2,3,7,8-PCDD/F, 1,2,3,6,7,8-HxCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,4,6,7,8-HCDD/F, OCDD/F (25 μl at 0.12 ng/μl each for HR-MS and 2.8 ng/μl each for MS). Total recoveries were checked by adding $^{13}C_6$-labelled 1,2,3,4-TCDD (25 μl at 0.11 ng/μl for HR-MS and 2.8 ng/μl for MS) to the extracts following the last concentration step.

3. Results and discussion

In initial experiments, the kinetics of extraction was investigated under the following conditions: Solvent toluene, flow-rate 1 ml/min, temperature 150°C, pressure 15 MPa, cell volume 5 ml, fly ash sample A. Fractions of 10 ml were taken during the extraction, and cleaned up and analyzed separately. Fig. 2 gives the mean values of the 5-fold extraction experiments. As can be seen, most of the analytes are extracted in the first 30 ml of solvent. The reproducibility of the extraction is presented in Table 1. Soxhlet extraction was performed as a reference method. The reproducibility for both extraction techniques is comparable, but the extraction efficiency for DHPSE is significantly higher.

Starting from these results, the extraction conditions for fly ash were optimised in the following experiments. Since solvent mixtures do not disturb the subsequent clean-up procedure, different mixtures of toluene–methanol were used for the DHPSE. In combination with a raised temperature (200°C), extraction efficiencies could be improved by the use of a mixture of toluene–methanol (3:1, v/v). Thus, the volumes can be reduced to 30 ml. Although these operating conditions work well for most fly ashes, it should be kept in mind that an adaptation of the extraction procedure to each matrix used is recommended.

A comparison of Soxhlet extraction and DHPSE was made with these new conditions. Columns 2 and 3 of Table 2 give a summary of the results obtained for the extraction of untreated fly ash B of a municipal waste incinerator. Extraction yields of DHPSE exceed those of Soxhlet extraction for all PCDDs and PCDFs.

Apart from the total concentrations of PCDD and PCDF, the pattern of the individual isomers is important for the interpretation of the toxicity of a sample. This is accomplished by calculation of the international toxicological equivalent factors (I-TEF) on the basis of the individual concentrations of the 17 isomeric/congeneric dibenzodioxins and -furans with chlorine substitution in 2,3,7,8 positions.

As an example, Fig. 3 shows a mass chromatogram of the hexachlorinated dibenzofurans of the above samples. The relevant 2,3,7,8-congeners are marked in the chromatogram. When DHPSE is compared to Soxhlet extraction, it is confirmed by the pattern of the isomers that no discrimination occurs and the relative composition of the sample is not deteriorated by the type of extraction.

Generally, the concentration of PCDDs and PCDFs determined by DHPSE exceeds that of Soxhlet extraction. To exclude the possibility of increased concentrations due to the formation of dibenzodioxins and furans (from chlorophenols for example) during the extraction process, additional experiments were performed. A Soxhlet pre-extracted fly ash and a thermally treated fly ash were spiked with possible PCDD and PCDF precursors (chlorinated phenols and benzenes, PCBs) present in

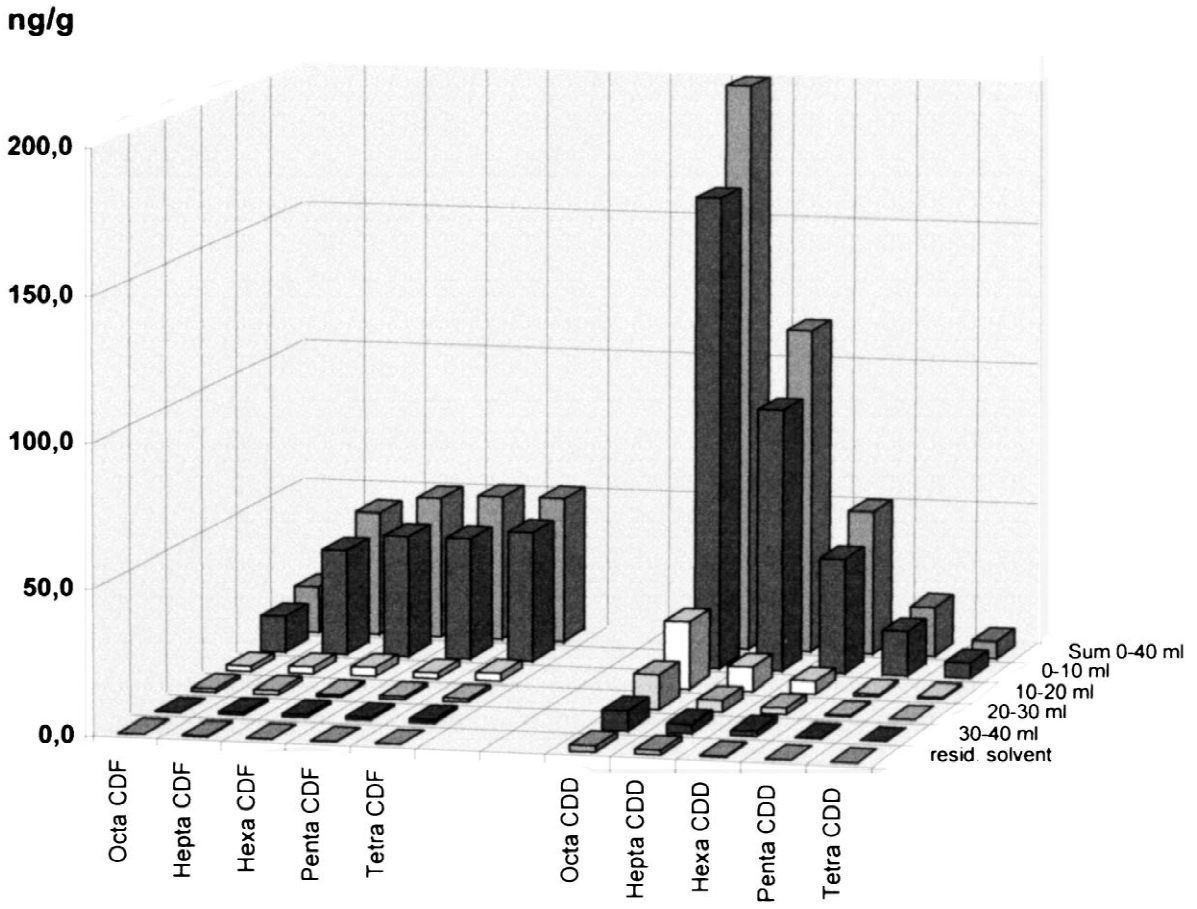

Fig. 2. Concentrations of PCDDs and PCDFs on untreated fly ash A as a function of the solvent volume (resid. solvent: residue of solvent in the extraction cell and solvent lines).

Table 1
Reproducibility of the extraction ($n=5$) for Soxhlet and DHPSE (fly ash A from a MWI without acid pre-treatment)

	Soxhlet		DHPSE	
	Mean sum	S.D. (%)	Mean sum (0–40 ml)	S.D. (%)
(ng/g)				
Tetra-CDD	4.5	7.1	6.1	6.7
Penta-CDD	14.7	10.4	17.5	2.3
Hexa-CDD	42	4.9	50.5	5.6
Hepta-CDD	72.5	4.6	114.2	6.5
Octa-CDD	154.5	5.5	217.1	7.0
Sum-PCDDs	288	5.1	405.3	6.2
Tetra-CDF	35.4	4.3	54.7	4.4
Penta-CDF	36.2	12.1	47.5	3.4
Hexa-CDF	42.6	5	49.9	5.7
Hepta-CDF	28.2	6.6	44.0	7.2
Octa-CDF	11.4	3.6	16.4	7.6
Sum-PCDFs	153.6	6	212.5	5.9

Table 2
Determination of PCDD/F on fly ash B (MWI) depending on the extraction and sample preparation technique ($n=2$)

Fly ash B, 1 g (MWI)	Soxhlet, untreated, toluene, 24 h (ng/g)	DHPSE, untreated, 30 ml, toluene–methanol (ng/g)	DHPSE, acid-treated, 30 ml, toluene–methanol (ng/g)	Soxhlet, acid-treated, toluene, 24 h (ng/g)	DHPSE, untreated, 30 ml, toluene–acetic acid (ng/g)
2,3,7,8-Tetra-CDD	0.19	0.25	0.25	0.26	0.28
1,2,3,7,8-Penta-CDD	1.3	2.0	2.2	2.1	2.7
1,2,3,4,7,8-Hexa-CDD	1.4	1.9	2.1	2.0	2.6
1,2,3,6,7,8-Hexa-CDD	2.9	4.2	4.6	4.5	5.0
1,2,3,7,8,9-Hexa-CDD	2.0	3.0	2.9	3.0	3.7
1,2,3,4,6,7,8-Hepta-CDD	42.7	59.7	68.3	67.6	71.0
Octa-CDD	144.0	158.0	172.0	175.0	154.0
2,3,7,8-Tetra-CDF	0.7	1.9	2.0	2.0	1.8
1,2,3,7,8-Penta-CDF+					
1,2,3,4,8-Penta-CDF	2.4	3.3	3.8	3.9	3.8
2,3,4,7,8-Penta-CDF	2.6	3.0	3.0	3.1	2.8
1,2,3,4,7,8-Hexa-CDF+					
1,2,3,4,7,9-Hexa-CDF	3.4	4.6	4.9	5.0	4.9
1,2,3,6,7,8-Hexa-CDF	3.6	4.8	5.1	5.3	5.3
1,2,3,7,8,9-Hexa-CDF	0.3	0.6	0.5	0.6	0.8
2,3,4,6,7,8-Hexa-CDF	4.2	5.3	5.9	5.9	5.2
1,2,3,4,6,7,8-Hepta-CDF	17.5	23.0	26.4	27.0	26.0
1,2,3,4,7,8,9-Hepta-CDF	1.4	1.8	2.1	2.2	2.1
Octa-CDF	12.4	16.1	18.7	19.2	17.5
I-TEF:	**4.9**	**6.5**	**7.0**	**7.0**	**7.3**
Sum Tetra-CDD	4.6	6.3	6.6	6.7	6.8
Sum Penta-CDD	16.2	25.8	31.6	27.9	34.7
Sum Hexa-CDDs	29.8	42.8	47.5	47.3	53.6
Sum Hepta-CDD	83.4	109.0	123.0	122.0	135.0
Octa-CDD	144.0	158.0	172.0	175.0	154.0
Sum PCDDs	**278.0**	**341.9**	**380.7**	**378.9**	**384.1**
Sum Tetra-CDF	25.7	34.1	37.3	39.2	34.1
Sum Penta-CDFs	31.2	39.0	42.1	44.3	41.7
Sum Hexa-CDFs	31.0	40.8	43.5	44.8	42.9
Sum Hepta-CDFs	24.5	31.9	36.5	37.6	35.8
Octa-CDF	12.4	16.1	18.7	19.2	17.5
Sum PCDFs	**124.8**	**161.9**	**178.1**	**185.1**	**172.0**

the samples and extracted as usual with DHPSE. In no case, a formation of dibenzodioxins and furans was observed. Hence, application of the new method seems to improve the extraction efficiency as compared to Soxhlet extraction without altering the sample composition.

It is well known that acid pre-treatment of fly ash before extraction increases the amount of dioxins and furans in most cases [12,13]. Columns 4 and 5 of Table 2 shows the results of the two extraction techniques for the same fly ash, but with an acid pre-treatment. If the pre-processed samples are extracted, the results for both techniques are comparable within the margins of error. Even the results of DHPSE for untreated fly ash are only slightly lower for most components. Hence, the application of DHPSE allows to reach, at least in part, analytes which are enclosed in the matrix. As mentioned above, this effect is probably induced by the high pressure, which makes it easier for solvent molecules to reach matrix pores.

In column 6 of Table 2, the results for DHPSE using another solvent mixture (toluene–glacial acetic acid 95:5, v/v) are presented. Richter et al. [10]

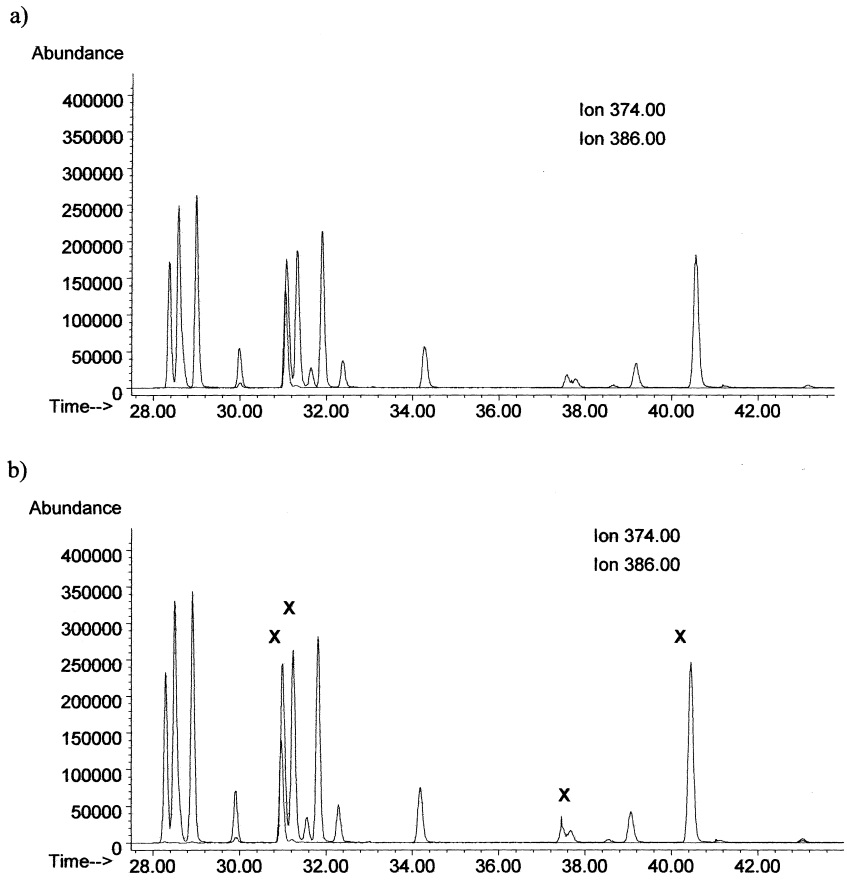

Fig. 3. Comparison of mass chromatograms (HRMS-selected ion monitoring mode) of hexachlorinated dibenzofurans of extracts (fly ash B) using: (a) Soxhlet extraction; (b) DHPSE (X: 2,3,7,8-substituted congeners).

suggested this mixture for ASE processes in order to avoid the acid pre-treatment step. Using this mixture for the extraction of the above fly ash with DHPSE, inconsistent results were obtained. Most of the dioxins were extracted more efficiently except for OCDD, whereas in most cases the furan concentrations were slightly lower than the results for the acid pre-treated fly ash.

To check these results, DHPSE was applied to another fly ash difficult to extract. Samples with and without acid treatment were studied and compared to the results achieved with Soxhlet extraction. In addition, the 'online' acid pre-treatment with a mixture of toluene/glacial acetic acid/methanol was performed. The results of this series of experiments are summarised in Table 3.

The extraction yields for Soxhlet extraction of the untreated fly ash are extremely low (<40%) as compared to the results for Soxhlet extraction of the acid pre-treated fly ash. In contrast, DHPSE provides even for the untreated fly ash higher extraction efficiencies than Soxhlet extraction of the pre-treated sample. Hence, the assumption that DHPSE can improve the extraction of analytes enclosed in the matrix is confirmed.

The results of the 'online acid treatment' do not agree with the results of the first experiment. In case of this fly ash, the furans were extracted more efficiently, whereas the concentrations of the dioxins were slightly lower as compared to the DHPSE of the untreated fly ash with toluene–methanol. Hence, the application of a mixture of toluene–methanol–acetic acid instead of the acid pre-treatment is questionable. Glacial acetic acid seems to have less

Table 3
Comparison of DHPSE and Soxhlet extraction of fly ash C

Fly ash C, 1 g (MWI)	Soxhlet, untreated, toluene, 24 h, $n=3$		Soxhlet, acid-treated, toluene, 24 h, $n=3$		DHPSE, untreated, toluene–methanol, $n=3$		DHPSE, untreated, toluene–methanol–acetic acid, $n=2$	
	(ng/g)	S.D. (%)	(ng/g)	S.D. (%)	(ng/g)	S.D. (%)	(ng/g)	S.D. (%)
2,3,7,8-Tetra-CDD	0.03	17.6	0.05	10.1	0.09	13.3	0.05	33.3
1,2,3,7,8-Penta-CDD	0.21	7.7	0.50	3.7	1.04	2.8	0.60	4.2
1,2,3,4,7,8-Hexa-CDD	0.25	5.0	0.54	6.0	1.08	3.7	0.88	2.9
1,2,3,6,7,8-Hexa CDD	1.32	14.1	4.16	0.7	5.88	1.8	5.02	3.5
1,2,3,7,8,9-Hexa-CDD	0.53	9.3	1.52	3.3	2.60	2.7	2.23	3.8
1,2,3,4,6,7,8-Hepta-CDD	11.7	9.8	35.9	2.5	39.50	4.3	25.30	2.4
Octa-CDD	29.9	17.0	74.9	5.8	77.6	7.3	75.75	3.2
2,3,7,8-Tetra-CDF	0.06	13.6	0.26	2.4	0.20	5.0	0.34	11.8
1,2,3,7,8- + 1,2,3,4,8-Penta-CDF	0.51	13.6	1.32	1.9	1.50	3.5	1.90	20.5
2,3,4,7,8-Penta-CDF	0.40	10.1	1.31	3.7	1.21	3.5	3.15	1.4
1,2,3,4,7,8- + 1,2,3,4,7,9-Hexa-CDF	0.92	11.6	2.18	3.2	2.41	3.8	3.49	4.4
1,2,3,6,7.8-Hexa-CDF	1.06	10.7	2.56	0.7	2.82	3.5	4.33	3.9
1,2,3,7,8,9-Hexa-CDF	0.22	14.2	0.61	1.3	0.67	5.9	1.53	6.2
2,3,4,6,7,8-Hexa-CDF	1.29	12.4	2.91	1.0	3.20	3.3	5.46	5.2
1,2,3,4,6,7,8-Hepta-CDF	6.29	28.1	8.59	3.5	15.37	5.1	7.70	19.6
1,2,3,4,7,8,9-Hepta-CDF	1.40	34.9	1.80	3.2	3.51	2.8	2.12	7.8
Octa-CDF	6.12	10.9	10.9	5.5	10.87	5.6	10.30	4.9
I-TEF	**1.15**	**8.9**	**2.87**	**1.75**	**3.86**	**3.2**	**4.77**	**2.1**
Sum Tetra-CDD	1.1	3.9	3.2	1.5	5.5	2.5	3.8	2.6
Sum Penta-CDD	4.5	5.0	16.0	2.2	23.4	3.0	18.0	0.3
Sum Hexa-CDDs	12.0	12.2	36.8	2.2	53.2	1.4	46.2	3.6
Sum Hepta-CDD	20.5	10.0	62.9	2.5	71.8	6.2	45.4	4.2
Sum Octa-CDD	29.9	17.0	74.9	5.8	77.6	7.3	75.8	3.2
Sum PCDDs	**68.0**	**9.1**	**193.8**	**3.4**	**231.5**	**4.9**	**189.0**	**3.2**
Sum Tetra-CDF	2.5	13.2	9.1	0.9	8.9	4.7	11.7	0.9
Sum Penta-CDFs	5.0	7.3	14.9	1.6	15.6	3.2	31.0	2.3
Sum Hexa-CDFs	8.0	10.9	19.0	0.7	21.2	3.0	33.7	4.5
Sum Hepta-CDFs	10.8	30.4	14.4	2.9	26.4	5.5	14.4	16.4
Sum Octa-CDF	6.1	10.9	10.9	5.5	10.9	5.6	10.3	4.9
Sum PCDFs	**32.4**	**15.2**	**68.3**	**2.1**	**83.0**	**4.0**	**101.1**	**3.7**

the role of an acidic compound, but rather of a polar solvent.

The results for the three fly ashes prove that it is necessary to evaluate the extraction conditions for each matrix. It is strongly recommended to compare the results of the new extraction technique with Soxhlet extraction of a acid pre-treated fly ash before using this method for routine analysis. Nevertheless, for screening of unknown samples DHPSE may be employed without a time-consuming pre-treatment in order to obtain an idea of the expected concentrations.

Another question arises: To what extent do differences exist between static and dynamic extraction. Filter dust (1 g each) from an aluminium recycling process was extracted in three different ways: Soxhlet extraction (24 h, toluene), static extraction applying 1–3 static extraction cycles (conditions per cycle: Static extraction for 10 min at 200°C and 15 MPa with toluene–methanol 3:1, v/v) and DHPSE (con-

ditions: 50 ml toluene–methanol 3:1, v/v at a flow-rate of 1 ml/min, 200°C, 15 MPa). The results are summarised in Fig. 4.

Especially the toxicologically relevant tetra-chlorinated dioxins and furans are extracted more efficiently by DHPSE in comparison to the other techniques.

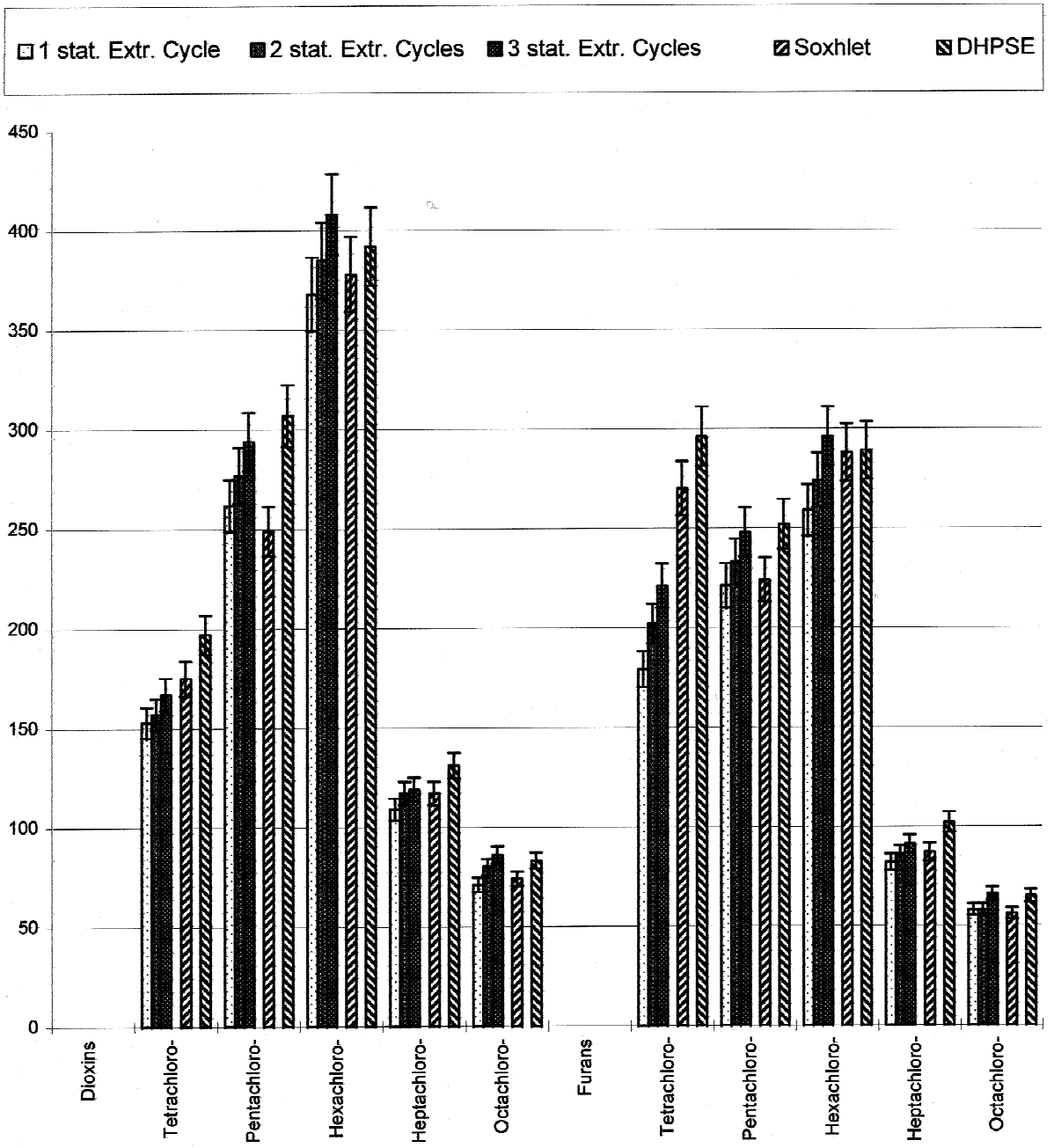

Fig. 4. Comparison of Soxhlet extraction, static extraction (1–3 static extraction cycles) and DHPSE of filter dust from a metal-working industry (in ng/g, error bars represent the mean standard deviation, $n=3$).

As expected static extraction requires several extraction cycles to achieve satisfying extraction results. The experiments confirm that DHPSE can compete with the other extraction techniques. The method provides at least results comparable to other techniques, the extraction efficiency is often even better.

Another matrix examined was a soil sample. The dry sample was extracted with Soxhlet extraction and DHPSE. For DHPSE again a mixture of toluene–methanol (3:1) was applied. The results are summarised in Table 4.

Tetra- to heptachlorinated dioxins yielded comparable results, whereas octa-chloro-dibenzodioxin and furans in general were extracted more efficiently by DHPSE. Due to this effect, the calculated I-TEF values for DHPSE are about 15% higher than the results from Soxhlet.

4. Conclusion

DHPSE is an appropriate method for the extraction of PCDDs and PCDFs from solid samples. The extraction yields are at least comparable to the results obtained from conventional Soxhlet extrac-

Table 4
PCDDs and PCDFs in a soil sample using Soxhlet extraction and DHPSE ($n=2$)

Dry soil (20 g)	DHPSE, toluene–methanol, 50 ml		Soxhlet, toluene, 24 h	
	(ng/kg)	S.D. (%)	(ng/kg)	S.D. (%)
2,3,7,8-Tetra-CDD	2.3	6.1	2.3	9.4
1,2,3,7,8-Penta-CDD	11.6	0.6	10.8	3.9
1,2,3,4,7,8-Hexa-CDD	10.5	10.1	10.7	4.6
1,2,3,6,7,8-Hexa-CDD	22.6	0.3	21.3	3.3
1,2,3,7,8,9-Hexa-CDD	15.0	1.9	15.6	1.8
1.2,3,4,6,7,8-Hepta-CDD	201.0	4.2	207.5	1.0
Octa-CDD	495.5	1.6	443.5	2.7
2,3,7,8-Tetra-CDF	57,4	7.4	46.7	6.8
1,2,3,7,8-Penta-CDF+				
1,2,3,4,8-Penta-CDF	131.5	1.6	128.0	5.5
2,3,4,7,8-Penta-CDF	59.6	2.4	44.2	2.7
1,2,3,4,7,8-Hexa-CDF+				
1,2,3,4,7,9-Hexa-CDF	239.0	1.8	224.0	1.9
1,2,3,6,7,8-Hexa-CDF	123.5	1.7	110.5	0.6
1,2,3,7,8,9-Hexa-CDF	19.0	0.4	16.6	10.7
2,3,4,6,7,8-Hexa-CDF	86.3	1.7	79.5	3.4
1,2,3,4,6,7,8-Hepta-CDF	575.5	10.2	515.5	1.5
1,2,3,4,7,8,9-Hepta-CDF	99.8	4.3	95.5	11.1
Octa-CDF	999.0	2.0	957.5	2.3
I-TEF:	**115.5**	**1.8**	**99.5**	**2.1**
Sum Tetra-CDD	114.5	0.6	120.0	0.0
Sum Penta-CDD	211.5	0.3	206.0	0.0
Sum Hexa-CDDs	266.5	3.4	267.5	2.9
Sum Hepta-CDD	363.0	3.1	373.0	0.8
Octa-CDD	495.5	1.6	443.5	2.7
Sum PCDDs	**1451.0**	**2.0**	**1410.0**	**1.6**
Sum Tetra-CDF	627.0	2.0	530.5	0.1
Sum Penta-CDFs	767.5	0.3	707.5	3.5
Sum Hexa-CDFs	1073.5	0.1	1019.5	3.0
Sum Hepta-CDFs	911.5	6.1	855.0	3.3
Octa-CDF	999.0	2.0	957.5	2.3
Sum PCDFs	**4523.5**	**1.6**	**4229.5**	**1.4**

tions. Whereas Soxhlet extractions require 100–500 ml of solvent per sample and 8–24 h of extraction time, DHPSE takes only 10–50 ml solvents in 10–40 min extraction time. A DHPSE device may be realised at low costs and is easily adaptable to routine analysis applications. The possibility to apply a wide range of solvents, mixtures of solvents or solvent gradients for the extraction offers a large potential for the future.

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