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DEVELOPMENT OF A METHOD FOR THE ISOMER-SPECIFIC DETERMINATION OF PCDDs/PCDFs IN LEACHATE-OIL EXTRACTS OF A WASTE LANDFILL

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Abstract

A clean-up procedure for the isomer-specific analysis of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in oil extracts from water leachate of a hazardous waste landfill is described. Sample pretreatment was performed by ultrasonics or by ultrasonics and subsequent refluxing with toluene. The clean-up procedure consists of four basic steps:

1. Chromatography on Alumina B-Super I (macro-column)
2. Chromatography on silica gel combined with silica gel/44 % conc. H_2SO_4.
3. Flash chromatography on Bio-Beads S-X3.
4. Separation of 2,3,7,8-tetra-CDD and final sample purification on Alumina B-Super I (micro-column).

Except for 2,3,7,8-tetra-CDF, all the 2,3,7,8-substituted PCDDs/PCDFs could be detected. Among the 2,3,7,8-tetra-to hexa-CDDs/CDFs, 2,3,7,8-TCDD was by far the most abundant isomer, determined at a mean concentration of 70,5 ppb. Industrial wastes from 2,4,5-trichlorophenol production are assumed to be the main source for this high concentration. From the isomer-specific analysis of the hepta-CDFs, pentachlorophenol can be considered as source of the higher chlorinated PCDDs/PCDFs.

ENTWICKLUNG EINER METHODE ZUR ISOMERENSPEZIFISCHEN BESTIMMUNG VON PCDD/PCDF IN SICKERWASSERÖLEXTRAKTEN EINER MÜLLDEPONIE

Zusammenfassung

Ein Aufreinigungsverfahren für die isomerenspezifische Bestimmung von polychlorierten Dibenzodioxinen (PCDD) und polychlorierten Dibenzofuranen (PCDF) in Sickerwasserölextrakten einer Sondermülldeponie wird beschrieben. Nach einer Vorbehandlung mit Ultraschall bzw. Ultraschall mit anschließender Toluolextraktion wurden die Proben einem vierstufigen Clean-up unterzogen:

1. Chromatographie an basischem Aluminiumoxid (Makrosäule)
2. Chromatographie an Kieselgel und Kieselgel/44% konz. H_2SO_4.
3. Flash Chromatographie an Bio-Beads S-X3.
4. Abtrennung von 2,3,7,8-Tetra-CDD und Endaufreinigung an basischem Aluminiumoxid (Mikrosäule).

Bis auf 2,3,7,8-Tetra-CDF wurden alle 2,3,7,8-substituierten PCDD/PCDF in den Proben gefunden. Die Analyse der Tetra-, Penta- und Hexachlorisomeren ergab die höchsten Werte für 2,3,7,8-TCDD (70,5 ppb). Es kann angenommen werden, daß Industrieabfälle aus der 2,4,5-Trichlorphenolproduktion für die hohen 2,3,7,8-TCDD-Werte verantwortlich sind. Nach isomerenspezifischer Analyse der Heptachlordibenzofurane kann eindeutig Pentachlorphenol als Quelle der höherchlorierten PCDD/PCDF betrachtet werden.

CONTENTS

1. INTRODUCTION

Since 2,3,7,8-TCDD was detected in leachates of the landfill Georgswerder/Hamburg in 1983 (1), the isomer-specific determination of PCDD and PCDF in different samples of hazardous waste landfills has been the subject of much concern in recent years: they were detected in water and oil leachates (2-4), in bottom sediments (4) and in PCB oil (5). But there are no reports on PCDD/PCDF determination in oil extracts from water leachates, nor do the reports of oil leachates include any description of the sample pretreatment and clean-up.

This paper describes a method for the isomer-specific determination of PCDD/PCDF in oil extracts from water leachates of a waste landfill. The development of the method was based on a clean-up procedure described for the PCDD/PCDF analysis in motor oil, used oil and recycled oil (6). Each clean-up step was tested separately with a PCDD standard mixture and optimized by sample application with respect to the complexity of the material. The efficiency of the clean-up enabled an unambiguous identification and quantification of all the PCDDs/PCDFs in the leachate-oil extracts, even of those ranging in sub-ppb levels. From the isomer distribution pattern, clues for PCDD/PCDF sources are possible.

2. EXPERIMENTAL

2.1 MATERIALS

ICN Alumina B-Super I and ICN Silica (63-200 active, 60 A) were obtained from ICN Biomedicals (Eschwege), Bio-Beads S-X3 from Bio-Rad (München). All solvents (nanograde) as well as the unlabelled and C13-labelled PCDDs/PCDFs were supplied by Promochem (Wesel).

For impregnation of the silica gel with sulfuric acid, 11,2 g of silica gel were transferred in a 150 ml round bottom flask. A quantity of 8,8 g of conc. H_2SO_4 was added dropwise and the reaction mixture shakened thoroughly for 5-10 min.

2.2 GC/ECD ANALYSES

The gas chromatographic analyses (GC) were performed on a Sichromat 1 gas chromatograph (Siemens) with an electron capture detector (ECD) under the following conditions: 30 m DB 5 fused silica capillary column (0,25 mm i. d.); carrier gas hydrogen, at 2 ml/min; column temperature 105 ^{o}C for 3 min, then programmed at 12 ^{o}C/min to 200 ^{o}C and at 5 ^{o}/min to 280 ^{o}C; sample size 1 µl at splitless injection; injector block temperature 295 ^{o}C, detector temperature about 300 ^{o}C.

2.3 GC/MS ANALYSES

For the gas chromatographic-mass spectrometric analyses (GC/MS), a mass selective detector, Mod. 5970 (Hewlett-Packard) directly coupled with a Mod. 5890 gas chromatograph (Hewlett-Packard) was used. The GC conditions were as follows: on column injection on an uncoated precolumn (4 m length) coupled to a 40 m SP 2331 fused silica capillary column (0,25 mm i. d.); column temperature 105 ^{o}C for 3 min then programmed at 15 ^{o}C/min to 200 ^{o}C and 5 ^{o}C/min to 250 ^{o}C. Sample size 1-2 µl, carrier gas helium at a pressure of 0,8 bar. The mass selective detector was operated in the multi-ion

detection mode (dwell time per mass 80 ms).

The following ions were monitored for the C13-labelled PCCDs: M^+, $(M+2)^+$ for 2,3,7,8-tetra-CDD; $(M+2)^+$, $(M+4)^+$ for the penta-to hepta-CDDs; $(M+2)^+$, $(M+6)^+$ for octa-CDD.

The PCDDs were analyzed via the following selected ions: M^+, $(M+2)^+$ for the tetra-CDDs; M^+, $(M+4)^+$ for the penta-CDDs; $(M+2)^+$, $(M+4)^+$ for the hexa- to octa-CDDs.
The tetra-to hepta-CDFs were monitored via their $(M+2)^+$-, $(M+4)^+$ -ions, octa-CDF via $(M+4)^+$, $(M+6)^+$.

The intensities of the M^+-,$(M+2)^+$-,$(M+4)^+$,$(M+6)^+$-ions are defined via the natural isotopic ratio of ^{35}Cl : ^{37}Cl = 3 : 1. They correspond to the number of chlorines, thus being most characteristic for each congener group. The ratios of the M^+-Peaks (Table I) and the respective $(M+2)^+$, $(M+4)^+$-peaks were determined for all the PCDDs/PCDFs analyzed within the leachate-oil extracts. The mass ratios were considered to be correct at relative deviations of about 10% (see chapter 2.4).

Table I: M+ - values (m/z) of tetra- to octa- CDDs/CDFs

	Tetra-	Penta-	Hexa-	Hepta-	Octa-
PCDDs	320	354	388	422	456
PCDFs	304	338	372	406	440

2.4 IDENTIFICATION, QUANTIFICATION, EVALUATION OF THE RECOVERIES

2.4.1 PROCEDURE FOR THE DEVELOPMENT OF THE METHOD

Identification of the PCDDs in the fractions obtained from the corresponding clean-up steps (2.6 a-d) was achieved by GC/ECD analysis of the untreated standard mixture (2.6) and of each reference compound separately.

Recoveries were calculated for each PCDD by the ratio of the PCDD concentrations obtained from GC-analysis of the standard mixture without clean-up and after one clean-up step, according to:

$$R = 100 \times \frac{x_2}{x_1}$$

R = percentage recovery
x_1 = concentration (peak area) of the PCDD without clean-up
x_2 = concentration (peak area) of the PCDD after the corresponding clean-up step

2.4.2 PROCEDURE FOR THE APPLICATION OF THE METHOD

Identification of the PCDDs/PCDFs analyzed in the samples (2.5) was achieved as follows: a purified extract of fly ash was analyzed by GC/MS under the conditions as described in 2.3. The PCDDs and PCDFs of the fly ash were identified by their retention times derived from the data reported by Buser and Rappe (10,11). Additionally, the isotopic mass ratio of the ions monitored for the respective compounds (2.3) was controled. By comparison of the retention data obtained from the fly ash and obtained from the sample, identification of the PCDDs/PCDFs within the leachate-oil extracts was carried out, followed by additional control of the respective mass ratios.
Quantification of the PCDD/PCDF was achieved via the C13-labelled internal standards (2.7) assuming an equal response of isomers of the same congener group.

Recoveries were evaluated for 2,3,7,8-tetra-CDD by addition of a definite amount of $^{13}C_6$-1,2,3,4-TCDD directly before GC/MS analysis; the percentage recovery was calculated via the ratio of the concentrations of $^{13}C_6$-1,2,3,4-TCDD and $^{13}C_{12}$-2,3,7,8-TCDD, as described above.

2.5 SAMPLES

The oil extracts of the leachates (extraction ratio of 1:500, oil:water) were stored in the landfill in 500-liter-barrels. Samples were taken from the upper part of the barrels containing the liquid oil and from the bottom layer.

2.6 DEVELOPMENT OF THE METHOD

Each clean-up step was tested with a standard mixture of the following PCDDs in concentrations of 0,7-2 ng/µl, dissolved in toluene: 1,2,3,4-tetra-CDD, 2,3,7,8-tetra-CDD, 1,2,3,7,8-penta-CDD, 1,2,3,6,7,8-hexa-CDD, 1,2,3,7,8,9-hexa-CDD, 1,2,3,4,7,8-hexa-CDD, 1,2,3,4,6,7,8-hepta-CDD and octa-CDD.

2.6.1 CLEAN-UP STEP ON ALUMINA B-SUPER I (MACRO-COLUMN)

An amount of 10 µl of the standard mixture described above was dissolved in 10 ml of benzene and applied to a column (1,5 x 25 cm) of 20 g Alumina B-Super I and 10 g of Na_2SO_4, prewashed with 400 ml of hexane.

A quantity of 60 ml of benzene (fraction 1) and 120 ml of hexane/dichloromethane, 98:2 (fraction 2) were passed through the column. The PCDDs and PCDFs were eluted with 100 ml of hexane/dichloromethane, 1:1 (fraction 3). Fractions 1-3 were concentrated to about 3 ml on a rotary evaporator (40 °C, 40 mbar) and evaporated to dryness by a stream of nitrogen. The residue was redissolved in 400 µl of toluene and each fraction was analyzed by GC/ECD.

Fractions 1-2 were analyzed to secure that no PCDD was eluted with benzene and with hexane/dichloromethane (98:2). Within fraction 3, all PCDDs of the standard mixture were detected, with recoveries determined at 90-100% (Fig. 1).
To test the reproducibility of this clean-up step, triplicate analyses were performed. The recovery values for the corresponding isomers of the three workups were determined at deviations between 5-15%.

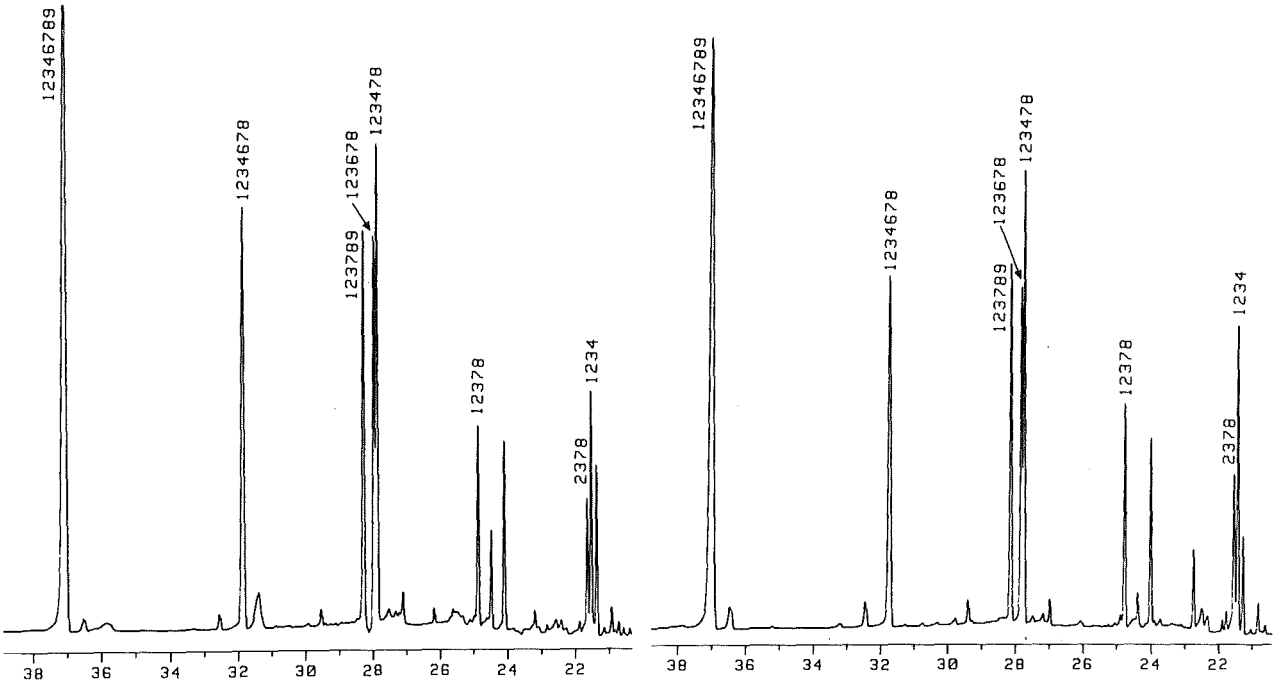

Fig. 1 Gas chromatograms of the PCDD standard mixture (on the left) and of the standard mixture after the application on Alumina B-Super I (on the right)

2.6.2 CLEAN-UP STEP ON SILICA GEL COMBINED WITH SILICA GEL/44% CONC. H_2SO_4

A quantity of 10 µl of the standard mixture was dissolved in 10 ml of hexane. The solution was applied to a column (1,5 x 32 cm), filled from bottom to top with 10 g of silica gel, 20 g of silica gel combined with silica gel/44% conc. H_2SO_4 and 10 g of Na_2SO_4 (7), prewashed with 400 ml of hexane. The column was eluted with a total amount of 150 ml of hexane, fractionated into seven subfractions S 1-S 7, each of 20 ml and one subsequent subfraction S 8 of 10 ml. The subfractions S 1-S 8 were concentrated as described for (2.6.1) and analyzed by GC/ECD.

Within fraction S 1, small amounts of 2,3,7,8-tetra-CDD and 1,2,3,7,8-penta-CDD are eluted. All PCDDs are detected in subfractions S 2 and S 3, with maximal elution in S 2. Within the subsequent subfractions S 4 and S 5, only traces of the PCDDs are observed, and no PCDDs are detected in the fractions S 6-S 8. Triplicate analyses under the conditions as described above, but without the fractionation of the eluate confirmed this elution behaviour of the PCDDs with recoveries determined at 90-100% (Fig. 2).

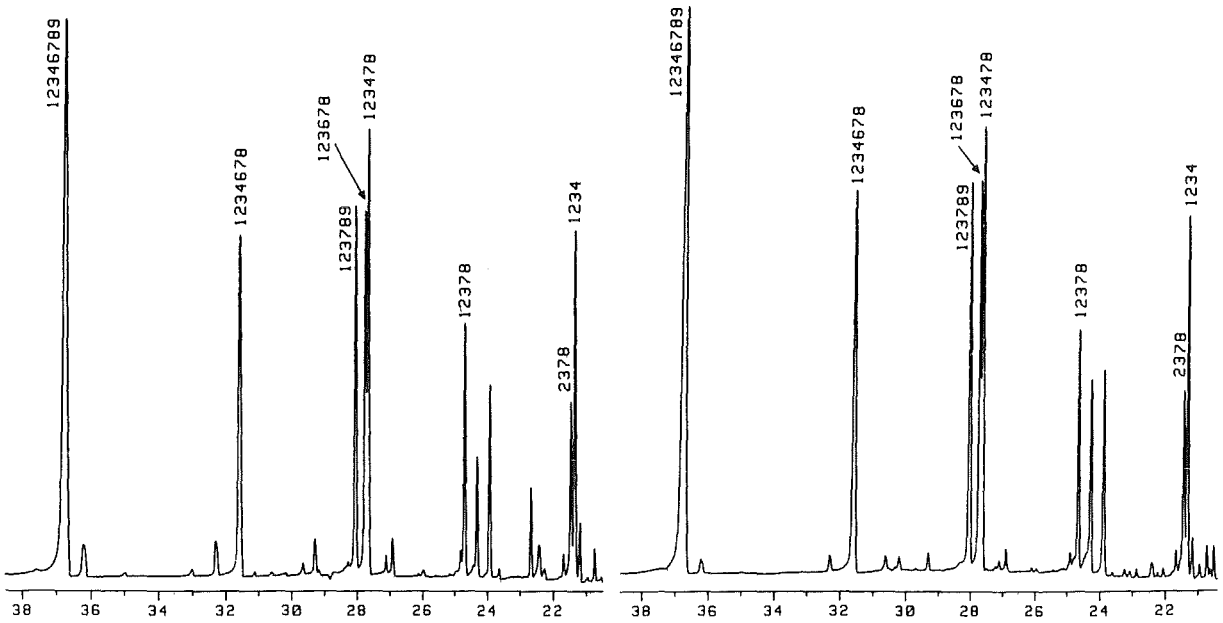

Fig. 2 Gas chromatograms of the PCDD standard mixture (on the left) and of the standard mixture after the application on silica gel combined with silica gel /44% conc. H_2SO_4 (on the right)

2.6.3 CLEAN-UP STEP ON BIO-BEADS S-X3

After swelling with cyclohexane/ethylacetate 1:1 (48 hrs), Bio-Beads S-X3 was filled in a column (3,5 x 15 cm), equipped with a glass frit (0,1-0,2 mm pore size) and topped with a kit for performing flash chromatography (Fig. 3). An amount of 10 µl of the standard mixture was dissolved in 2-5 ml of hexane and applied to the column, equilibrated with 400 ml of cyclohexane/ ethylacetate (1:1). First 80 ml of cyclohexane/ ethylacetate (1:1) were passed through the column, followed by six 20 ml-portions of the same solvent mixture. Each eluate was collected separately. Standard application and elution were performed by flash chromatography (8) using nitrogen pressure (10 ml N_2/min, 3 bar). The eluates were concentrated as described for (2.6.1) and analyzed by GC/ECD. The PCDDs were eluted between 120-180 ml, with the maximum at 140-160 ml (Fig.4).

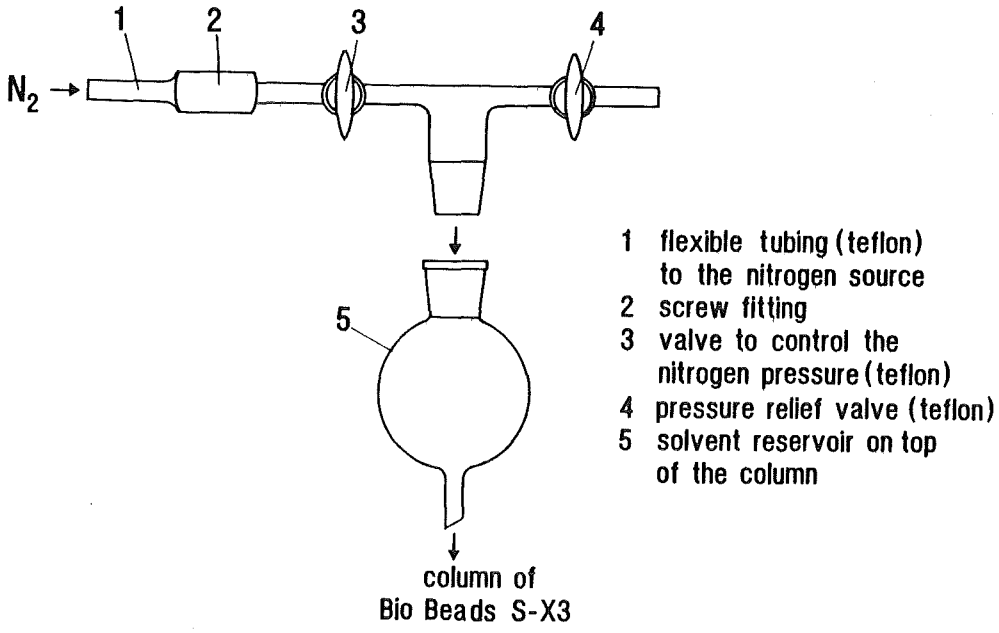

Fig. 3 Kit for performing flash chromatography

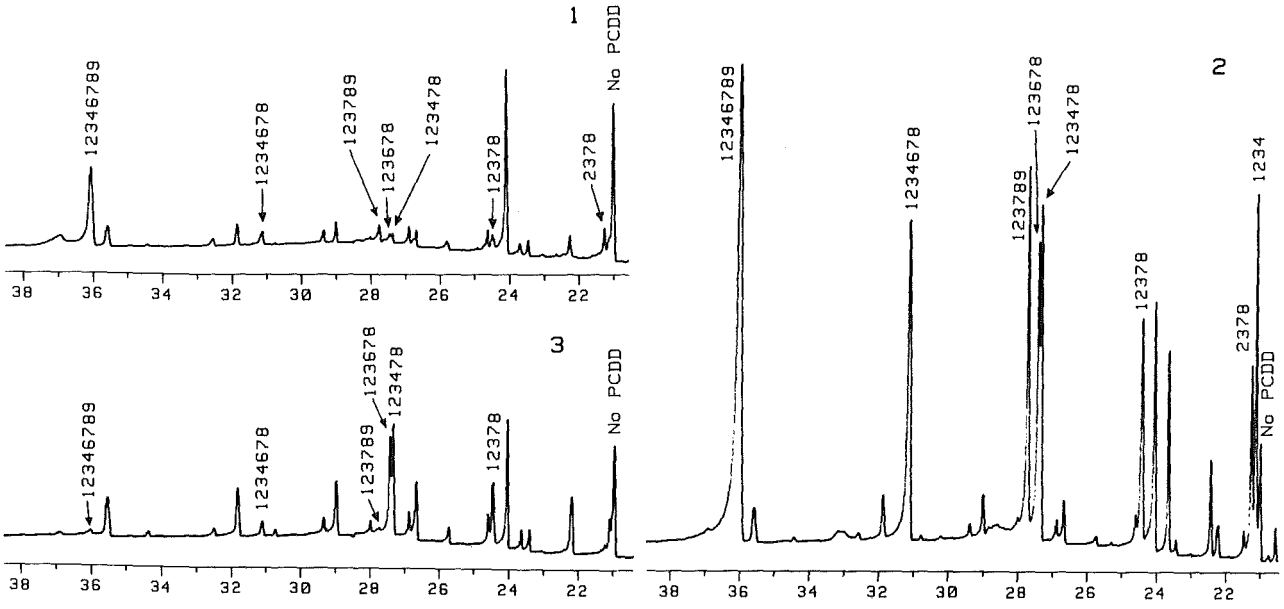

Fig. 4 Gas chromatograms of the PCDD standard mixture after application on Bio-Beads S-X3, eluted with cyclohexane/ethylacetate (1:1). 120-140 ml fraction (1), 140-160 ml fraction (2) and 160-180 ml fraction (3).

2.6.4 CLEAN-UP STEP ON ALUMINA B-SUPER I (MICRO-COLUMN) - SELECTIVE ANALYSIS OF 2,3,7,8-TETRA-CDD

The clean-up step was developed for the separation and selective analysis of 2,3,7,8-tetra-CDD, based on the findings of HAGENMAIER and coworkers (9). The elution behaviour of the PCDDs, especially of 2,3,7,8-TCDD was investigated under the following conditions:

(a) An amount of 10 µl of the standard mixture, dissolved in 5 ml of benzene, was applied on a column (1,0 x 15 cm) filled with 5 g of Alumina B-Super I and 3 g of Na_2SO_4, prewashed with 100 ml of hexane. The column was eluted with 60 ml of hexane/dichloromethane (80:20), followed by two 10 ml-portions of the same solvent mixture. The eluates were concentrated as described for (2.6.1) and analyzed by GC. Within the first eluate, all the PCDDs of the standard mixture including 2,3,7,8-TCDD were detected at recoveries of 80-100% (Fig. 5). No PCDDs were observed within the 10 ml-fractions.

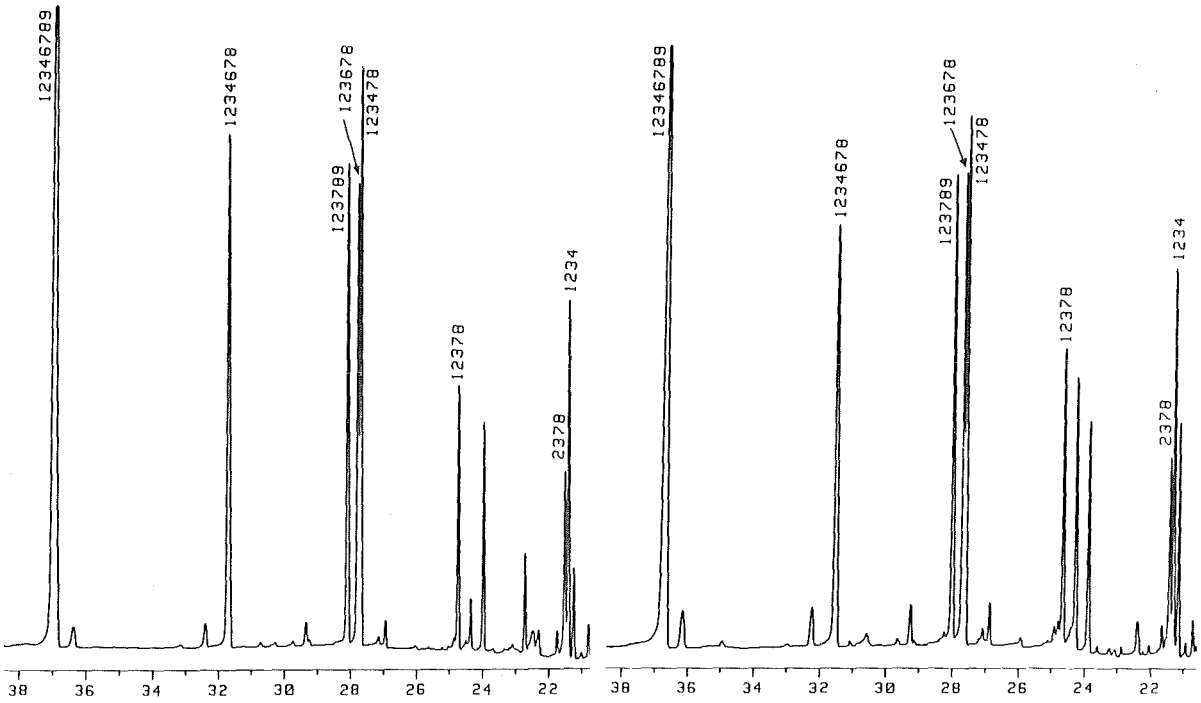

Fig. 5 Gas chromatograms of the PCDD standard mixture (on the left) and of the first eluate hexane/dichloromethane 80:20, obtained from the micro Alumina-column (on the right)

(b) In order to achieve a selective separation of 2,3,7,8-TCDD from all the other PCDD/PCDF, the procedure described above was modified as follows: the column was eluted first with 40 ml of hexane/dichloromethane 80:20 (F 1), then with 20 ml of hexane/ dichloromethane (70:30), fractionated into two equal subfractions (F 2, F 3). Within F 1, all the PCDDs of the standard mixture except for 2,3,7,8-TCDD were detected. Within subfraction 2, only traces of 2,3,7,8 - TCDD, together with residual amounts of 1,2,3,7,8-penta-CDD and 1,2,3,7,8,9 hexa-CDD are observed, whereas considerable amounts of octa-CDD are eluted. Within F 3, maximal elution of 2,3,7,8-TCDD in the presence of small amounts of octa-CDD is performed (Fig. 6).

The recoveries for the PCDDs in F 1 were between 90-100%, except for octa-CDD, determined at about 70%. The recovery for 2,3,7,8 - tetra-CDD in F 3 was at about 75%.

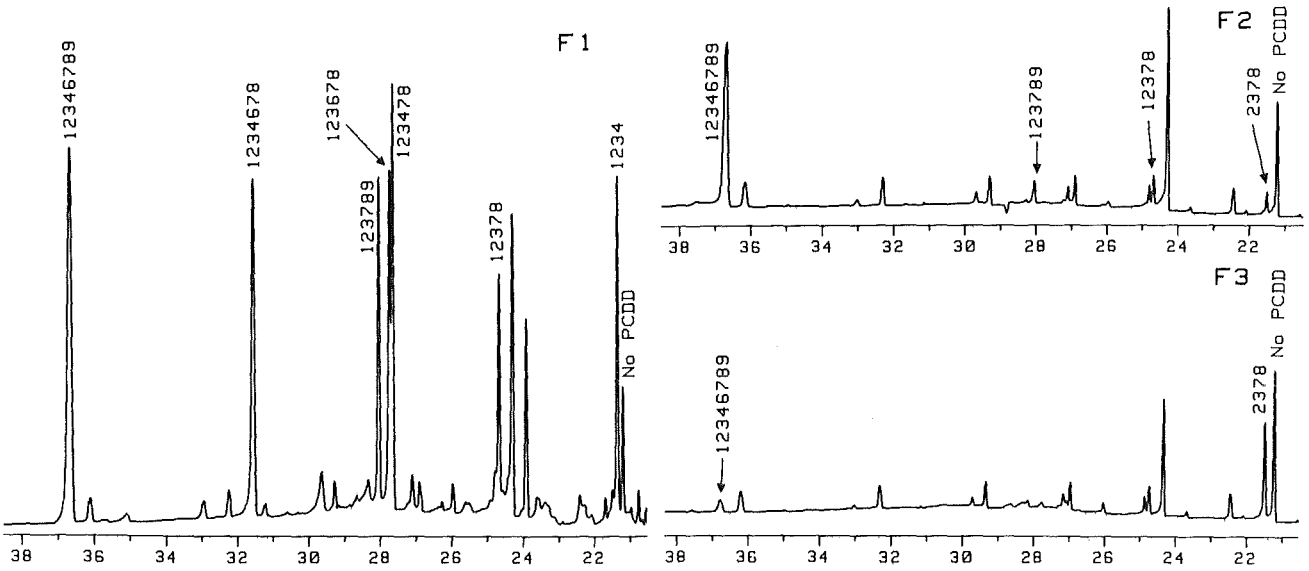

Fig. 6 Gas chromatograms from refined fractionation on the micro-Alumina column (2.6.4,b): 40 ml-fraction of hexane/dichloromethane, 80:20 (F 1), 10 ml-fractions of hexane/dichloromethane, 70:30 (F 2, F 3)

(c) In order to improve the recoveries for octa-CDD and for 2,3,7,8-TCDD, the following modifications were applied to the procedure of (b): instead of 40 ml hexane/dichloromethane (80:20), 50 ml were passed through the column to elute all PCDDs except 2,3,7,8-TCDD. Then 30 ml of hexane/dichloromethane (70:30), fractionated into three equal subfractions were used to elute the 2,3,7,8-TCDD from the column. The recoveries of the PCDDs within the first 50 ml-eluate were between 90-100%, including octa-CDD. 2,3,7,8 Tetra-CDD elutes within the first 10 ml-fractions, the last fraction only containing traces of the isomer (Fig. 7).

To secure the selectivity of the procedure, triplicate analyses by applying the procedure of (c) without subfractionation of the 2,3,7,8-TCDD fraction were performed. The recoveries for 2,3,7,8-TCDD were between 80-85%.

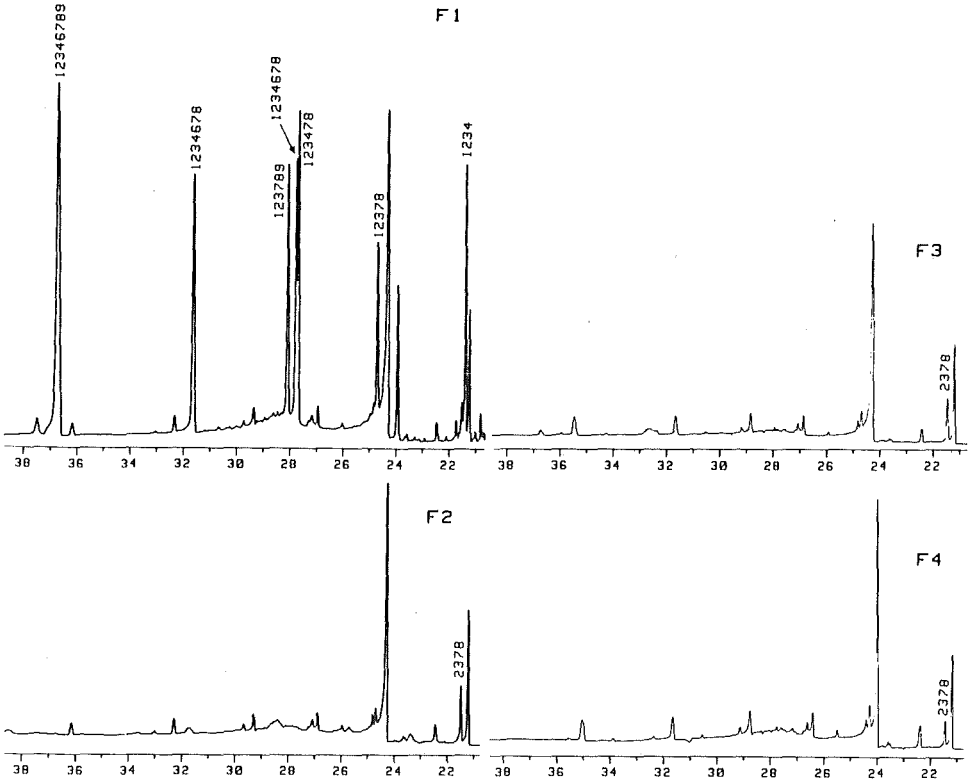

Fig. 7 Gas chromatograms from refined fractionation on the micro-Alumina column (2.6.4,c). 50 ml-fraction of hexane/dichloromethane, 80:20 (F 1). 10 ml-fractions of hexane/dichlormethane, 70:30 (F 2-F 4)

2.7 SAMPLE PRETREATMENT AND EXTRACTION

1. A quantity of 50 g of the liquid oil extract (2.5) was homogenized in an ultrasonic bath for 15 min (stock material 1). For each analysis, an amount of 2 g of stock material 1 was dissolved in 10 ml of benzene. Then the following C13-labelled PCDDs were added: 2,3,7,8-tetra-CDD (25 ng), 1,2,3,7,8-penta-CDD (25 ng), 1,2,3,6,7,8-hexa-CDD (50 ng), 1,2,3,4,6,7,8-hepta-CDD (50 ng) and octa-CDD (80 ng).

2. An amount of 200 g of the sample taken from the bottom layer (2.5) was homogenized with an ultrasonic probe (Branson Sonic Company) at 60 ^{o}C for 3 hrs (stock material 2). 3 g of stock material 2 were transferred to 300 ml of toluene. After addition of the

same C13-labelled PCDDs as described above, the mixture was refluxed for 24 hrs and filtered. The filtrate was concentrated to about 3 ml and dissolved in 10 ml of benzene.

2.8 APPLICATION OF THE METHOD

The fractionation scheme of the clean-up for the PCDD/PCDF determination in leachate-oil extracts is shown in Fig. 8. The application of the whole clean-up to the leachate-oil extracts required modifications concerning only few details. To sum up the clean-up steps (2.6 a-d) and to render their application more distinct, the sample clean-up is described at full length.

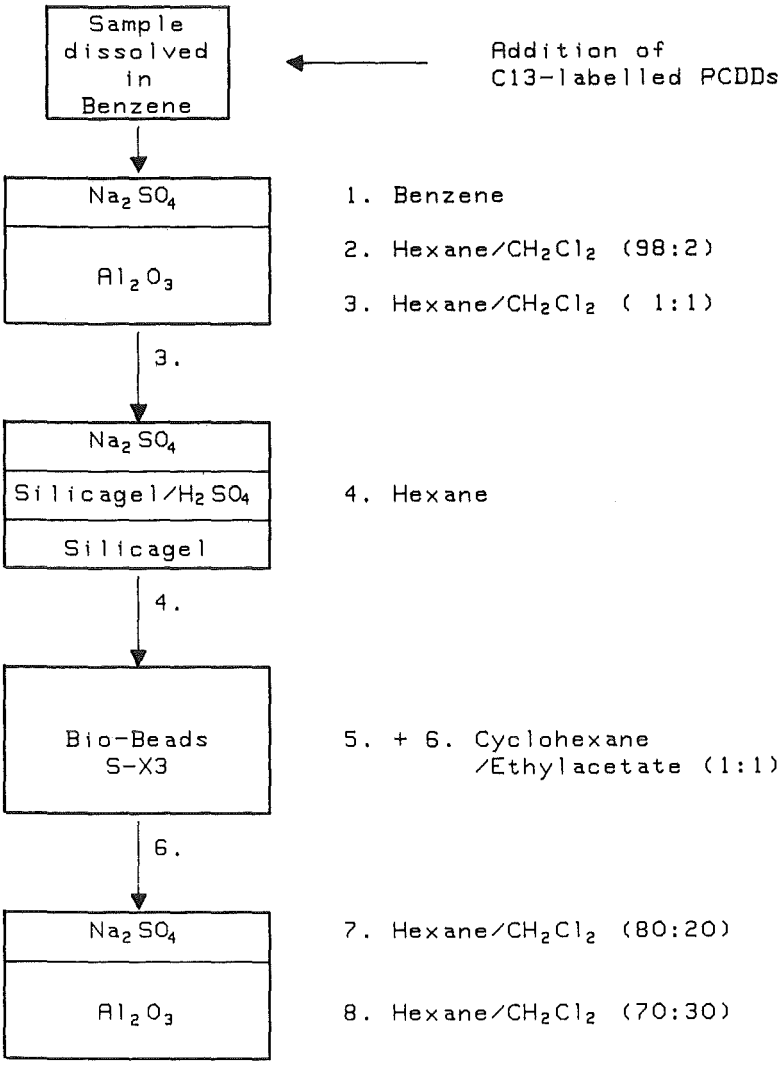

Fig. 8 Fractionation scheme of the clean-up for PCDD/PCDF analysis of leachate-oil extracts

The pretreated samples of stock material 1 and 2 were processed as follows:
Each sample was applied to a column (1,5 x 25 cm) of 20 g Alumina B-Super I and 10 g of Na_2SO_4, prewashed with 400 ml of hexane. After sample application, 60 ml of benzene and 400 ml (instead of 120 ml, 2.6.1) of hexane/dichloromethane (98:2) were passed through the column. 400 ml of hexane/dichloromethane (98:2) were used to enable complete removal of the polychlorinated biphenyls (PCBs) from the sample material. The PCDDs/PCDFs were eluted with 100 ml of hexane/dichloromethane (1:1). This eluate was concentrated to about 10 ml on the rotary evaporator at 40 ^{o}C (40 mbar).

The concentrated eluate was applied to a column (1,5 x 32 cm) filled from bottom to top with 10 g of silica gel, 20 g of silica gel/44% conc. H_2SO_4 and 10 g of Na_2SO_4, prewashed with 150 ml of hexane. The PCDDs and PCDFs were eluted with 150 ml of hexane. The fraction was concentrated to about 2 ml.

The concentrate was chromatographed on a column (3,5 x 15 cm) of Bio-Beads S-X3, equilibrated with 400 ml of cyclohexane/ ethylacetate (1:1). First 120 ml of cyclohexane /ethylacetate (1:1) were passed through the column, the PCDDs and PCDFs were eluted subsequently with 60 ml of the same solvent mixture. Sample application and elution were performed by flash chromatography under the conditions described (2.6.3). The PCDDs and PCDFs containing fraction was concentrated to about 2 ml and the solvent mixture completely removed by a stream of nitrogen.

The residue was redissolved in 5 ml of benzene and applied on a micro-column of Alumina B-Super I (2.6.4). First 50 ml of hexane/dichloromethane (80:20) were passed through the column, the eluate containing all the PCDDs and PCDFs except 2,3,7,8-tetra-CDD, which was eluted subsequently with 30 ml of hexane/dichloromethane. Recoveries were determined by addition of $^{13}C_6$-1,2,3,4-tetra-CDD (25 ng). Both fractions were concentrated to about 20 µl and analyzed by GC/MS.

To exclude the loss of single isomers other than those corresponding to the C13-labelled internal standards, a purified extract of fly ash was processed by the clean-up and analyzed by GC/MS after

each step. The same isomer distribution pattern was observed for treated and untreated extract.

The recoveries for 2,3,7,8-tetra-CDD, evaluated via $^{13}C_6$-1,2,3,4-tetra-CDD were between 60 and 80%.

3. RESULTS AND DISCUSSION

In Tables II-IV, the PCDD/PCDF contents of three samples (sample N_o A,B,C) from stock material 1 are listed with their mean value x and standard deviation s. Except for 2,3,7,8-tetra-CDF, which could not be detected at a detection limit of 0,02 ppb (with a signal to noise ratio of 3:1) all the other 2,3,7,8-substituted PCDDs (Table II) and PCDFs (Table III) were found. Among the tetra-CDDs, 2,3,7,8-TCDD was by far the most abundant isomer, determined at a mean concentration of 70,5 ppb. Fig. 9 shows the mass fragmentograms obtained from the 2,3,7,8-TCDD fraction. At m/z 320, only 2,3,7,8-TCDD elutes, together with the C13-labelled internal standard, monitored at m/z 332. The 2,3,7,8-TCDD in the PCDD/PCDF fraction (m/z 320, Fig. 10) corresponds only to 3-4% of its total amount.

The 2,3,7,8-substituted penta- to hepta-CDDs are determined at levels ranging significantly below the 2,3,7,8-TCDD concentration (Table (II). The concentrations of the 2,3,7,8-penta- to octa-CDDs are increased with increasing number of chlorines, the concentra-

Table II: Concentrations (ng/g) of 2,3,7,8,-substituted PCDDs in samples A,B,C from the liquid oil extract.

Compound	A	B	C	$\bar{X}$	S
2,3,7,8- Tetra- CDD	71,9	69,6	69,9	70,5	1,2
1,2,3,7,8- Penta- CDD	2,9	2,6	2,8	2,8	0,1
1,2,3,4,7,8- Hexa- CDD	2,0	2,0	2,2	2,1	0,1
1,2,3,6,7,8- Hexa- CDD	8,3	8,9	8,7	8,6	0,3
1,2,3,7,8,9- Hexa- CDD	11,4	11,2	9,6	10,7	0,9
1,2,3,4,6,7,8- Hepta- CDD	35,2	42,1	44,2	40,5	4,7
Octa- CDD	90,2	116,0	117,3	107,8	15,2

tion of octa-CDD even predominating over the 2,3,7,8-TCDD concentration. In Fig. 10, the mass fragmentograms of the tetra- to octa-CDDs obtained from the PCDD/PCDF fraction of the liquid oil extract (stock material 1) are shown. Within the penta-CDDs (m/z 354), 1,2,3,7,8- and 1,2,3,7,9-penta-CDD are significantly enhanced over all the other isomers, ranging in sub-ppb levels mainly. Within the hexa-CDDs (m/z 390), the 2,3,7,8-substituted isomers are not so pronounced. The early eluting peaks of 1,2,4,6,7,9- /1,2,4,6,8,9-/ 1,2,3,4,6,8-hexa-CDD and of 1,2,3,6,7,9- /1,2,3,6,8,9-hexa-CDD are dominating; but altogether, the concentration levels of the hexa-isomers do not differ as significantly as observed within the penta-CDDs. The same holds true for the hepta-isomers, with the 2,3,7,8-substituted hepta-CDD

Table III: Concentrations (ng/g) of 2,3,7,8-substituted PCDFs in samples A,B,C from the liquid oil extract.

Compound	A	B	C	$\bar{X}$	S
2,3,7,8- Tetra- CDF	n.d.	n.d.	n.d.	-	-
1,2,3,7,8- Penta- CDF[a]	0,59	0,46	0,52	0,52	0,06
2,3,4,7,8- Penta- CDF	0,35	0,28	0,46	0,36	0,09
1,2,3,4,7,8- Hexa- CDF[b]	3,9	3,5	3,7	3,7	0,2
1,2,3,6,7,8- Hexa- CDF	3,5	3,8	4,6	3,9	0,5
1,2,3,7,8,9- Hexa- CDF	0,67	0,72	0,64	0,68	0,04
2,3,4,6,7,8- Hexa- CDF	0,94	1,1	1,1	1,0	0,09
1,2,3,4,6,7,8- Hepta- CDF	5,2	7,3	5,3	5,9	1,1
1,2,3,4,7,8,9- Hepta- CDF	0,76	0,71	0,79	0,75	0,04
Octa- CDF	30,4	50,3	36,2	38,9	10,2

[a]not separated from 12348- penta- CDF [b]not separated from 123479- hexa- CDF
n.d.= not detected

being slightly elevated.

Fig. 11 shows the mass fragmentograms of the PCDFs obtained from the PCDD/PCDF fraction.The 2,3,7,8-substituted PCDFs (Table III) detected in the liquid oil extracts are characterized by concentration levels ranging mainly in sub-ppb- and low-ppb levels, except for octa-CDF at a mean concentration of 38,9 ppb. Other than the PCDDs, the distribution of the PCDF isomers within the corresponding congener groups do not show any predominance of the 2,3,7,8-substituted congeners. For the hepta-CDFs, this distribution pattern becomes most important with respect to possible PCDD/PCDF sources: a pattern is obtained, as described generally for pentachlorophenol and Na-pentachlorophenolate: 1,2,3,4,6,8,9-hepta-CDF is the most abundant isomer and predominates over 1,2,3,4,6,7,8-hepta-CDF, the other isomers ranging in sub-ppb levels. In fly ash samples, the 1,2,3,4,6,7,8-congener is by far the most abundant isomer of all the other hepta-CDFs.

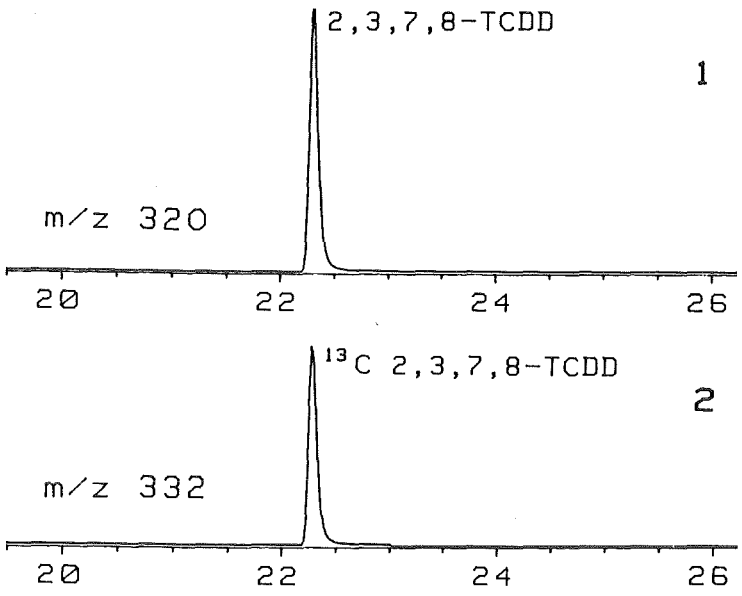

Fig. 9 Mass fragmentograms at m/z 320 (1) and m/z 332(2) from the 2,3,7,8-TCDD fraction of the liquid oil extract

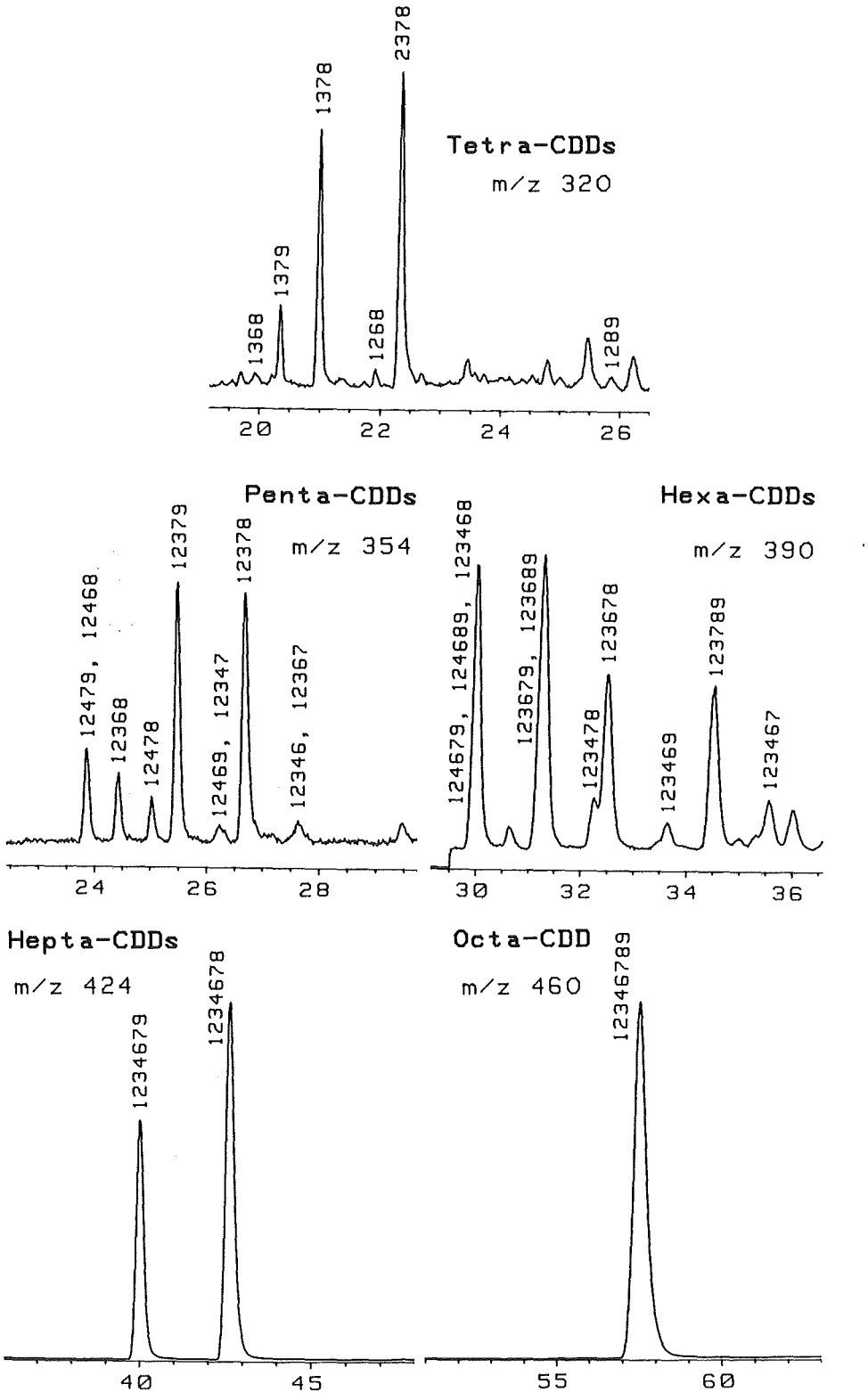

Fig. 10 Mass fragmentograms of the tetra-to octa-CDDs obtained from the PCDD/PCDF fraction of the liquid oil extract.

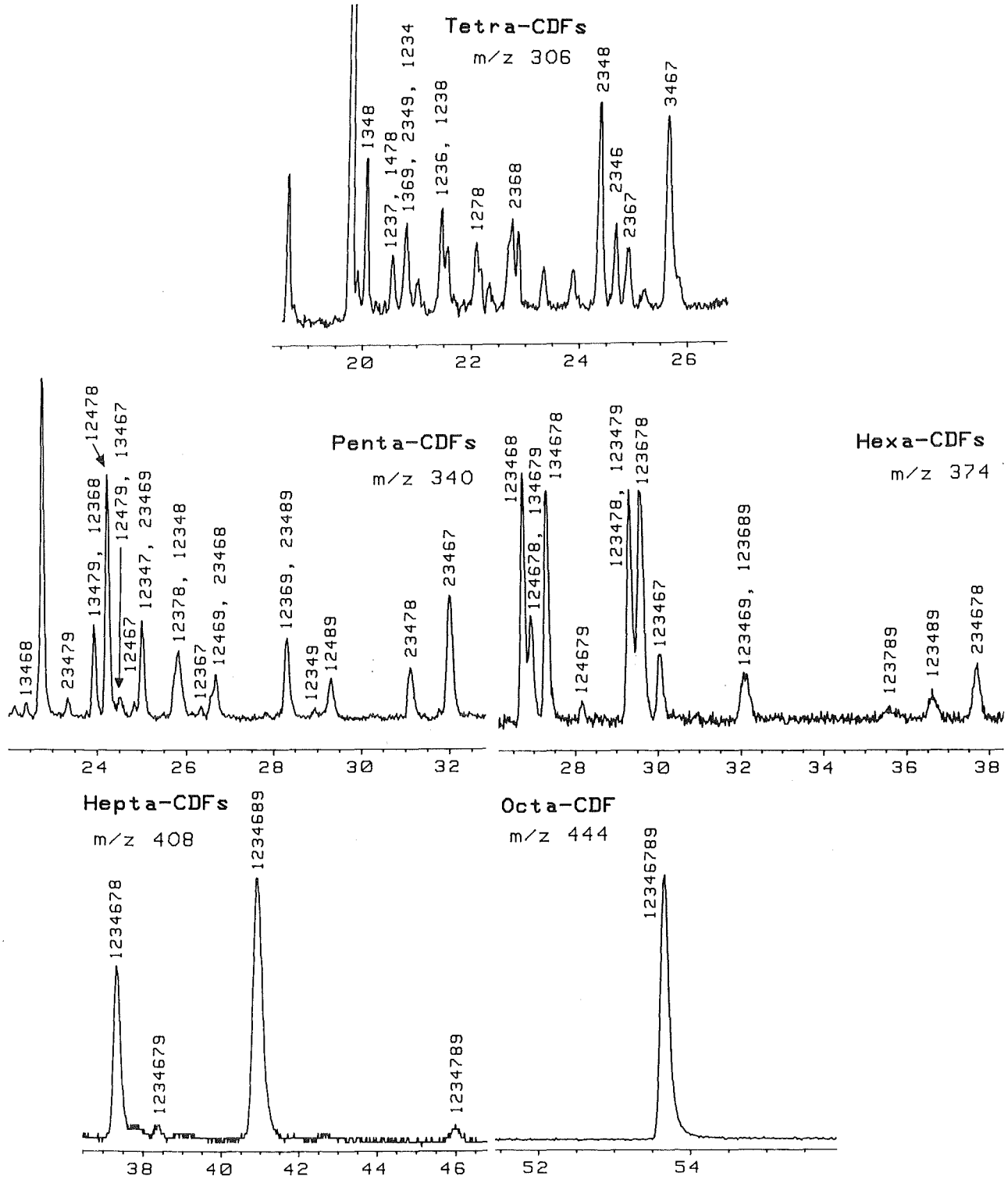

Fig. 11 Mass fragmentograms of the tetra-to octa-CDFs obtained from the PCDD/PCDF fraction of the liquid oil extract.

Table IV lists the total PCDDs/PCDFs of each congener group. At the Cl_4-level, the PCDDs are much more abundant than the PCDFs, induced by the prevalence of 2,3,7,8-TCDD. At the Cl_6-, Cl_7- and Cl_8-levels, the PCDDs predominate as well, but to a minor extent.

With respect to the PCDD/PCDF sources, informations can be obtained by the concentration ratio of the PCDF at the Cl_4- and Cl_8-levels: in fly ash samples, the total tetra-CDF predominates by far over the octa-CDF concentration, whereas in pentachlorophenol, octa-CDF is determined at the most abundant concentration level. Within the leachate-oil extracts, a concentration pattern is received indicating pentachlorophenol as a possible source of the higher chlorinated PCDD/PCDF.

Table IV: Total PCDD/PCDF content (ng/g) of the Cl_4- Cl_8 congener groups in samples A,B,C from the liquid oil extract.

Compounds	A	B	C	$\bar{X}$	S
Tetra- CDDs	75,7	71,6	73,7	73,6	2,0
Penta- CDDs	9,1	8,1	8,6	8,6	0,5
Hexa- CDDs	55,7	57,8	49,8	54,4	4,1
Hepta- CDDs	53,3	65,3	64,1	60,9	6,6
Octa- CDD	90,2	116,0	117,3	107,8	15,2
total- PCDDs	284,0	318,8	313,5	305,4	18,7
Tetra- CDFs	6,8	6,6	6,1	6,5	0,4
Penta- CDFs	6,6	5,4	5,1	5,7	0,8
Hexa- CDFs	23,0	21,7	20,0	21,6	1,5
Hepta- CDFs	14,0	15,4	14,1	14,5	0,8
Octa- CDF	30,4	50,3	36,2	38,9	10,2
total- PCDFs	80,8	99,4	81,5	87,2	10,5

In Tables V and VI, the quantitative results for the sample taken from the bottom layer (stock material 2) are summarized. As expected, the PCDD/PCDF amounts are significantly lower than the concentrations obtained from the liquid oil extract.
Concerning the question of possible sources for the PCDDs/PCDFs found in the samples analyzed, the following can be assumed: the extremely high concentration of 2,3,7,8-TCDD is generated by industrial wastes from 2,4,5-trichlorophenol production deposited in the landfill. From the distribution pattern of the hepta-CDFs, pentachlorophenol and Na-pentachlorophenolate are considered as possible sources for the higher chlorinated PCDDs/PCDFs.

Table V: Concentrations (ng/g) of 2,3,7,8- substituted PCDFs in the bottom layer of the oil extract.

PCDDs		PCDFs	
2,3,7,8- Tetra- CDD	28,7	2,3,7,8- Tetra- CDF	n.d.
1,2,3,7,8- Penta- CDD	1,6	1,2,3,7,8- Penta- CDF	0,14
1,2,3,4,7,8- Hexa- CDD	1,2	2,3,4,7,8- Penta- CDF	0,40
1,2,3,6,7,8- Hexa- CDD	3,6	1,2,3,4,7,8- Hexa- CDF	1,6
1,2,3,7,8,9- Hexa- CDD	1,4	1,2,3,6,7,8- Hexa- CDF	2,0
1,2,3,4,6,7,8- Hepta- CDD	17,4	1,2,3,7,8,9- Hexa- CDF	0,15
Octa- CDD	42,9	2,3,4,6,7,8- Hexa- CDF	0,27
		1,2,3,4,6,7,8- Hepta- CDF	4,6
		1,2,3,4,7,8,9- Hepta- CDF	0,06
		Octa- CDF	15,6

n.d.= not detected

Table VI: Total PCDD/PCDF content (ng/g) of the Cl_4- Cl_8 congener groups in the bottom layer of the oil extract.

PCDDs		PCDFs	
Tetra- CDDs	30,4	Tetra- CDFs	2,9
Penta- CDDs	5,5	Penta- CDFs	3,4
Hexa- CDDs	25,0	Hexa- CDFs	8,2
Hepta- CDDs	32,9	Hepta- CDFs	7,8
Octa- CDD	42,9	Octa- CDF	15,6
total PCDDs	136,7	total PCDFs	37,9

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