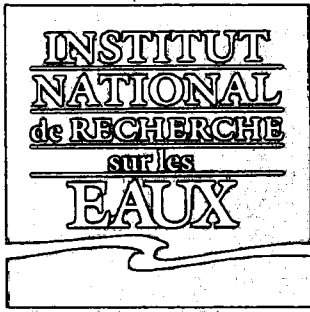
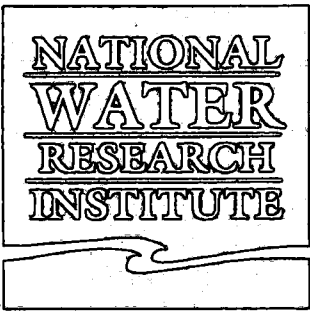
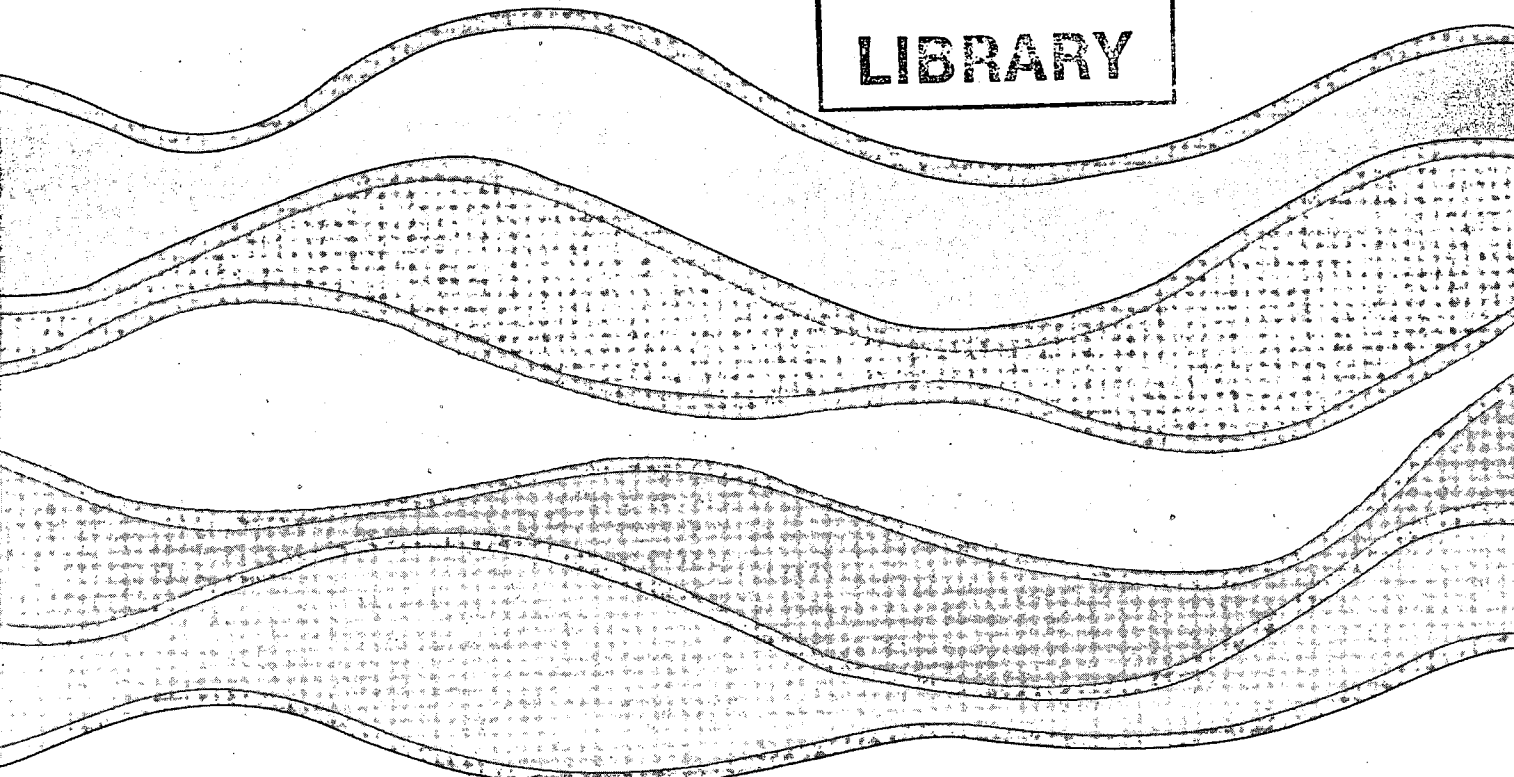


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**THE ANALYSIS OF CHLORINATED  
DIBENZOFURANS IN MUNICIPAL FLY ASH:  
SUPERCRITICAL FLUID EXTRACTION VS  
SOXHLET**  
**F.I. Onuska, K.A. Terry and R.J. Wilkinson**  
**NWRI Contribution No. 92-15**

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**THE ANALYSIS OF CHLORINATED DIBENZOFURANS IN MUNICIPAL  
FLY ASH: SUPERCRITICAL FLUID EXTRACTION VS SOXHLET**

**F.I. Onuska, K.A. Terry and R.J. Wilkinson**

**Research and Applications Branch  
National Water Research Institute  
Burlington, Ontario L7R 4A6**

**NWRI Contribution No. 92-15**

## **MANAGEMENT PERSPECTIVE**

This report describes the results of optimization of the extraction of polychlorinated dibenzofurans from municipal incinerator fly ash samples.

The study has shown that quantitative yields of the polychlorinated dibenzofurans can be achieved using supercritical fluid extraction. By shortening the time required for the extraction step, the methodology contributes to reducing the entire analysis time to ca 120 minutes per sample, a significant improvement over the ca. 24 hours/sample required with conventional Soxhlet extraction procedure. The improved protocol also has advantages over organic solvent extraction methodology in terms of occupational health and safety.

## **SOMMAIRE À L'INTENTION DE LA DIRECTION**

Le présent rapport décrit les résultats de l'optimisation de l'extraction des polychlorodibenzofuranes d'échantillons de cendres volantes d'incinérateurs municipaux.

L'étude a montré que les polychlorodibenzofuranes pouvaient être extraits quantitativement par fluide supercritique. En réduisant le temps nécessaire pour l'étape d'extraction, cette méthode permet de réduire la durée totale de l'analyse à env. 120 minutes par échantillon, alors qu'elle était d'env. 24 heures/échantillon avec l'extraction classique au Soxhlet. Un autre avantage de la nouvelle méthode par rapport à l'extraction aux solvants organiques se situe au niveau de la santé et de la sécurité au travail.

## **ABSTRACT**

A multiresidue supercritical fluid extraction procedure for chlorinated dibenzofurans (PCDFs) has been optimized as an efficient method for the determination of these compounds in fly ash samples. The results were compared with those obtained by Soxhlet extraction.

Extracts from the two procedures were analyzed by gas chromatography-mass spectrometry (HRGC-MS) and statistical data confirmed that supercritical fluid extraction provides data with a relative standard deviation of less than 6% while Soxhlet extraction data show a much greater spread.

## **RÉSUMÉ**

On a optimisé une méthode d'extraction par fluide supercritique pour le dosage des polychlorodibenzofuranes (PCDF) dans des échantillons de cendres volantes. Les résultats ont été comparés à ceux obtenus par extraction au soxhlet.

Les extraits obtenus par les deux méthodes ont été analysés par chromatographie en phase gazeuse et par spectrométrie de masse (CPG-SM); l'analyse statistique confirme que l'extraction par fluide supercritique fournit des résultats avec un écart-type inférieur à 6 %, alors que ceux de l'extraction au soxhlet sont beaucoup plus étalés.

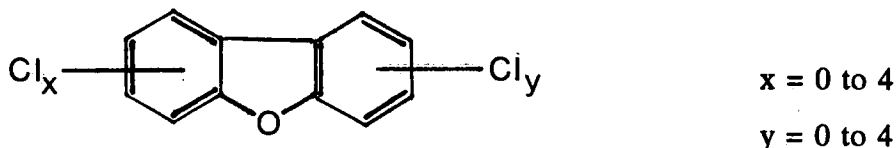
## INTRODUCTION

Owing to their toxicity and widespread distribution in the global environment, chlorinated dibenzofurans have attracted the attention of environmental analytical chemists, toxicologists and regulatory agencies all over the world. Since chlorinated dibenzofurans have been detected in the emissions from municipal incinerators (1), it is important to enhance the capability of analytical methodologies for their fast and more reliable extraction and cleanup from fly ash matrices. Recently, the analytical procedures and instrumentation employed to determine polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) in fly ash have been refined considerably (2,3). Because very low concentrations of PCDFs are being determined, sample extraction and cleanup requires time consuming multistep separation procedures. The PCDFs and PCDDs are normally recovered from fly ash samples by solvent extraction in a Soxhlet apparatus, followed by cleanup and concentrations steps.

In our previous study, we described a supercritical fluid extraction (SFE) technique as a part of the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in sediments (4) and all PCDD-congeners in fly ash (5). Nitrous oxide + methanol (2%) or toluene (5%) were used as the modifiers in the supercritical fluid. It was demonstrated that the SFE of polychlorinated dibenzo-p-dioxins from fly ash matrices is governed by a variety of interrelated parameters, including the affinity of the solutes for the matrix, the solubility and the vapour pressure of the analytes and the diffusivity coefficients of the analytes in the supercritical fluid. Supercritical fluid extraction recoveries are controlled by many variables including SF-density, temperature, extractor geometry, restrictor sizes, modifiers, and sample matrix composition. Although it is well established that the solvation power of the supercritical fluid is related to its supercritical density, little is known about the effects of other controllable parameters for analytical scale supercritical fluid extraction of polychlorinated dibenzofurans. In this paper, experimental

results will be reported for SFE and quantification of PCDFs in municipal incinerator fly ash containing about 9% carbon.

Basic molecular structure and congener structural possibilities for the polychlorinated dibenzofurans are presented in Scheme 1.



## EXPERIMENTAL

To facilitate comparisons between Soxhlet and supercritical fluid extractions the same standards and samples were extracted by each technique.

**Fly Ash Samples:** Two grab samples of fly ash were collected by the Ontario Ministry of the Environment. The fly ash was homogenized by sieving it to 200  $\mu\text{m}$ .

**Soxhlet Extraction and Concentration:** A 10 g sample of fly ash was treated with 3 percent hydrochloric acid (20 mL) for 1 hour. Afterwards, it was filtered under suction using a prewashed fibreglass filter (Whatman GF/A) and washed with 50 mL distilled water. The sample was spiked with chlorinated C-13 labelled PCDFs as internal standards (6). The aliquot (2 g dry weight) was extracted overnight (approx. 20 hours) with 200 mL toluene in a medium porosity Soxhlet thimble. The toluene extract was washed with 100 mL of 0.05 M  $\text{Na}_3\text{PO}_4$ , and further concentrated to 1 mL before cleanup on a Florisil column (7). Polychlorinated benzenes and PCBs were eluted with n-hexane (20 mL) and the PCDFs with n-hexane + diethyl ether (1:1).

**Supercritical Fluid Extraction:** Samples were extracted using a Suprex Model MPS-225 extraction and chromatography system. A schematic diagram of the system was



shown in our previous paper (5). The system uses cryogenic trapping which allows the collection of all extracted compounds in a precise temperature controlled manner. Approximately 25 mg of a homogenized aliquot of fly ash, previously treated with formic or hydrochloric acid (75  $\mu\text{L}$ ), was precisely weighed into a 1 mL volume extractor. The extraction was performed in the static mode as well as in the dynamic mode using nitrous oxide (Linde, Union Carbide, Mississauga, Ont.). The extraction process was pre-programmed using the integrated software to perform the valve switching and to control the temperature via the cryogenic trapping system. A restrictor having an internal diameter of 25  $\mu\text{m}$  and 20 cm in length was used and changed every third extraction. After cold-trapping, the cryogenically collected analytes were retrapped in 5 mL of n-hexane (8). Each sample was reconstituted into 25  $\mu\text{L}$  of toluene. Two microlitres of the extract was injected onto the column.

**Sample Cleanup:** A cleanup procedure must be able to remove most of the interferences and provide acceptable recovery and precision for target PCDFs. Performance with respect to precision, accuracy and recovery must be evaluated and reported. The basic cleanup procedure for sample extracts consisted of the following steps. The extract was first cleaned up on a 20 g Florisil column, with the first fraction of 200 mL of n-hexane containing PCB's and the second fraction of 6% diethyl ether/hexane containing the PCDD/PCDFs. The second cleanup column used 1 g of basic alumina. The column was eluted with 3% methylene chloride in n-hexane and 50% methylene chloride in n-hexane, successively. The first fraction contained the PCDD/PCDFs and the second contained the chlorinated benzenes and PCBs. All sample extracts were concentrated prior to GC-MS analysis by blowing it down to dryness under a gentle stream of prepurified nitrogen. An extract volume of 20  $\mu\text{L}$  of the recovery standard solution of labelled dibenzofurans consisting of one isomer for each congener group was used.

**Instrumentation:** The identification and quantitation of polychlorinated dibenzofurans by means of HRGC/MS was done using a Tribid-VG mass spectrometer in low

resolution mode and a Hewlett-Packard HP5890 GC/MSD system. The data system is operator-programmed for time-sequenced acquisition of selected MS data for each analyte. Data collection is obtained under electron impact mode of positive ions and by using selected ion monitoring (SIM).

Gas Chromatography-Mass Spectrometry Parameters: Optimum operating conditions must be achieved for both the GC-separation and the subsequent MS-analysis of the separated chlorinated dibenzofurans (6). To achieve acceptable GC-separation requires the following set of experimental parameters should be used:

WCOT - column :	30-meter x 0.2 mm SE-52 crosslinked
Carrier gas :	Helium at linear velocity 35 cm/s
Injection :	Cool on-column at 80 °C
Interface :	290 °C

The temperature program of the cool on-column injection consisted of an initial temperature of 80 °C holding for 3 minutes, programmed at 20 °C/min to 180 °C then at 5 °C/min to 270 °C, final holding time 20 minutes. The end of the capillary column was inserted directly into the ion source of the mass spectrometer operated at 70 eV in the electron impact mode. Optimum setting for GC parameters and the appropriate retention time windows for time-sequenced SIM mode of PCDFs on a 30 meter OTC were established from the analysis of window defining mixtures containing the earliest and latest eluting congeners within each homologue group of PCDFs. The electron multiplier voltage was set at 2.2 kV and the dwell time was 200 ms per peak. The order of elution as shown in Table 1 is such that five retention windows can be defined, corresponding to the five levels of chlorine substitution without any overlap. Quantitation of PCDFs was carried out by spiking the fly ash samples with a labelled PCDF mixture as internal standard. Quantitation of the C-13 labelled dibenzofuran mixture was carried out using a reference standard mixture of unlabelled and labelled dibenzofurans consisting of one isomer for each congener group. The ions monitored during the analysis are identified in Table 2.

**Table 1. Elution Order of PCDF Window Defining Mixture on a 30 M SE-52 Open Tubular Column**

Homologue	First Eluting Isomer	Last Eluting Isomer	RT Window (min)
4CDF	1,3,6,8-	1,2,8,9-	14.0 - 18.0
5CDF	1,3,4,6,8-	1,2,3,8,9-	17.5 - 20.0
6CDF	1,2,3,4,6,8-	1,2,3,4,8,9-	20.0 - 24.0
7CDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-	24.0 - 27.0
8CDF	1,2,3,4,6,7,8,9-	1,2,3,4,6,7,8,9-	27.0 - 32.0

Retention time windows are set on the basis of temperature program given above.

The quantitation was performed in triplicate. A selected ion current profile was recorded for each congener at the exact masses specified in Table 2. This was achieved by an authentic standard of the PCDFs as a mixture of known concentration in which there is no interference between closely eluting congeners and by adhering to the analytical protocol described in the text. A 1.0 to 2.0  $\mu\text{L}$  aliquot was injected into the gas chromatograph equipped with a cold on-column injector. A solution containing standards was injected into the HRGC-MS system. The selected ion current profile for each congener was measured and the ion abundance ratios listed in Table 2 were computed and compared to the corresponding theoretical ratio. Each analyte must be within the control limits of the pre-established ion ratios. Should any of these ion ratios not be achieved, then the mass spectrometer must be fine tuned until the results of this test agree with the limits given in the text.

An internal standard method was used to quantify the PCDFs. It relies upon consistent linearity of MS-response over the intervals between a series of calibration

points. It was carried out by spiking the fly ash samples with labelled PCDF mixture as internal standard. The quantitation was performed in triplicate.

**Table 2. Selected Ion Masses for Chlorinated Dibenzofurans**

Window	Compound	Quantitation Ions (m/z)			Ion Ratio
		1st ion	2nd ion	M-COCl	
1	4CDF	303.9	305.9	242.9	M/M+2
	<sup>13</sup> C <sub>12</sub> -TCDF	315.9	317.9	-	M/M+2
2	5CDF	339.9	341.9	278.9	M+2/M+4
	<sup>13</sup> C <sub>12</sub> -PCDF	351.9	353.9	-	M+2/M+4
3	6CDF	373.8	375.8	312.85	M+2/M+4
	<sup>13</sup> C <sub>12</sub> -HxCDF	383.8	385.8	-	M+2/M+4
4	7CDF	407.8	409.8	346.8	M+2/M+4
	<sup>13</sup> C <sub>12</sub> -HpCDF	417.8	419.8	-	M+2/M+4
5	8CDF	441.7	443.7	380.8	M+2/M+4

Internal standard quantitation was based on the use of relative response factors (RRF). A RRF was defined as the ratio of analyte response factor to the response factor of the corresponding labelled surrogate. These RRFs remain unchanged over the range of concentration for which mass spectrometer response is linear. Using these RRFs along with internal standard responses from the sample run, concentrations of PCDFs can be calculated directly, without the necessity of calculating internal standard recoveries. Recoveries were calculated separately. The effect of variables influencing SFE, such as pressure, temperature and time required for extracting PCDFs have been discussed previously and are described elsewhere (5).

## RESULTS AND DISCUSSION

Several sets of experimental conditions were evaluated to optimize the SFE method for PCDFs. These conditions are summarized in Table 3. Experiments 8 and 11 were performed with fly ash having higher PCDF content and remaining the 12 experiments employed fly ash with lower PCDF content.

Upon completion of extractions employing both the Soxhlet and SF-extraction and cleanup steps all samples were analyzed for the PCDFs using the procedures discussed above. Figures 1a to e illustrate HRGC-MS-SIM chromatograms of PCDF. Several peaks corresponding to TCDF congeners fulfill criteria for unambiguous confirmation and quantitation. The isotope ratios for all tetrachlorinated DBFs were in the range of 0.78 to 0.84 considering that required control limits were 0.65 to 0.89. Similarly nine peaks of pentachloro-DBFs fulfilled criteria for their confirmation and were also used for quantitation. Required control limits were between 1.32 to 1.78. The peaks that fell within this range had 1.49 to 1.69 values. Hexachloro-dibenzofuran congeners shown in SIM trace (Figure c) represent 12 peaks with isotope ratios from 1.13 to 1.34 and all of them were used for quantitation. On the other hand, two peaks from heptachloro-DBF SIM trace indicated isotope ratios of 1.02 to 1.12 and the remaining 2 peaks did not fulfil defined criteria (1.26 to 1.30), thus they were rejected. Their retention times (RT 24:36 and 24:45) matched with those of labelled HpCDFs and the M-COCl loss mass was observed.

Our previous studies indicated that PCDDs could be successfully extracted from fly ash and sediment by a mixture of nitrous oxide + 2% methanol. The static mode of extraction was preferred since the required amount of nitrous oxide it consumed per extraction was less than 30% of that utilized for leaching mode extraction and it contributed to background interferences.

With no certified PCDF sample reference material currently available for fly ash samples all extraction data were compared with those obtained by Soxhlet extraction with toluene. The results obtained using the Soxhlet extraction are presented in Table 4. The results from the triplicate analyses are indicative of acceptable standard deviation values for all homologue groups. A summary of the HRGC-MS analyses of PCDFs from fly ash extracts by SF-extraction are given in Tables 5 and 6. The highest overall concentrations of PCDFs were found in two extracts in experiments 13 and 14. Both extracts were obtained with nitrous oxide at 400 atm. Experiment 14, employed static mode of extraction using methanol as a modifier. The extraction provided 122% recovery as compared to Soxhlet extraction. Experiment 13 used the dynamic leaching mode with nitrous oxide at 400 atm. The sample was pretreated with formic acid and toluene was used as a modifier. Recovery of PCDFs shows 110.5% yield. It seems that both techniques are equally efficient for extracting PCDFs under defined conditions. On the other hand, it is worth noting that experiment 3 using SF-CO<sub>2</sub> and toluene as a modifier extracted fly ash pretreated with formic acid with the same efficiency as the Soxhlet extraction in 1/10 of the time.

The homolog composition and extraction yields can be discerned from Figures 2 and 3. Averaged yields of PCDFs from fly ash extraction experiments provide data that were statistically significant.

Results from experiments 2,4,5,6,7 and 12 show that lower pressure (350 atm) and shorter extraction times resulted in incomplete recoveries of PCDFs. Selective removal of aromatic impurities was achieved in experiment 7 by pre-extraction with ethylene at 200 atm, 20 °C for 60 minutes. During this step less than 2% of PCDFs were co-extracted but the extract obtained was much cleaner.

As it was concluded in our previous paper (5), the addition of formic acid to the sample prior its extraction improves extraction yield but this improvement is not so pronounced as for PCDDs. The time for extraction must be regarded as a principal

variable in SFE experiments and it is also dependent on the total amount of sample extracted. In our case, the optimum extraction time for 25 to 30 mg sample should be 120 minutes at 400 atm and 45 °C.

The addition of formic acid pretreatment provides almost 20% increase in yield of PCDFs in comparison to toluene pretreatment. However, even toluene pretreatment provides almost 18% improvement in recovery of PCDFs over Soxhlet extraction.

## CONCLUSION

It may be concluded that under the conditions studied, SFE is a more efficient technique than Soxhlet extraction. Supercritical fluid extraction offers an excellent alternative to Soxhlet extraction of chlorinated dibenzofurans from fly ash matrices. Automated SFE instrumentation, as used in this study, shows great advantage in overcoming the limitations of liquid-solid Soxhlet extraction because extracts can be effectively trapped in a solution or quantitatively transferred onto a capillary column. The working conditions have been optimized for PCDFs in fly ash in the low ppm (mg/kg) range. If lower levels of PCDFs are expected, it would require modification of working conditions as related to the amount of sample, volume of the extraction vessel and time required for a complete extraction. Measures of analytical precision and bias for evaluating and maintaining its performance are necessary requirements needed for the usefulness of results and the cost-effectiveness of analytical tools including the supercritical fluid extraction.

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**CAPTIONS**

**Figure 1. Selected Ion Monitoring Traces for PCDFs Showing Presence of Individual Congeners in Fly Ash. a) tetrachloro DFs; b) pentachloro DFs; c) hexachloro DFs; d) heptachloro DFs; and e) octachloro dibenzofuran.**

**Figure 2. Recovery of Low Levels of PCDFs by SFE : comparison with extraction in a Soxhlet apparatus.**

**Figure 3. Recovery of High Levels of PCDFs : comparison with extraction in a Soxhlet apparatus.**

**Table 1. Elution order of PCDF window defining mixture on a 30 m x 0.25 mm i.d. SE-52 open tubular column.**

**Table 2. Selected ion masses for quantitation of chlorinated dibenzofurans.**

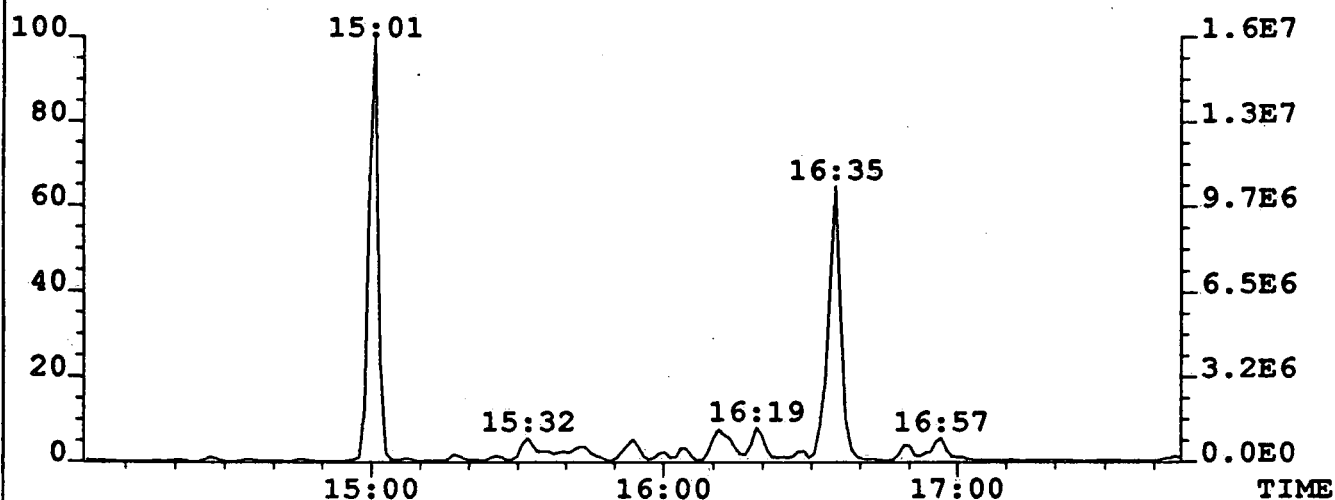
**Table 3. Extraction conditions for PCDFs from Fly Ash.**

**Table 4. Recovery of PCDFs from Fly Ash using Soxhlet Extraction in mg/kg.**

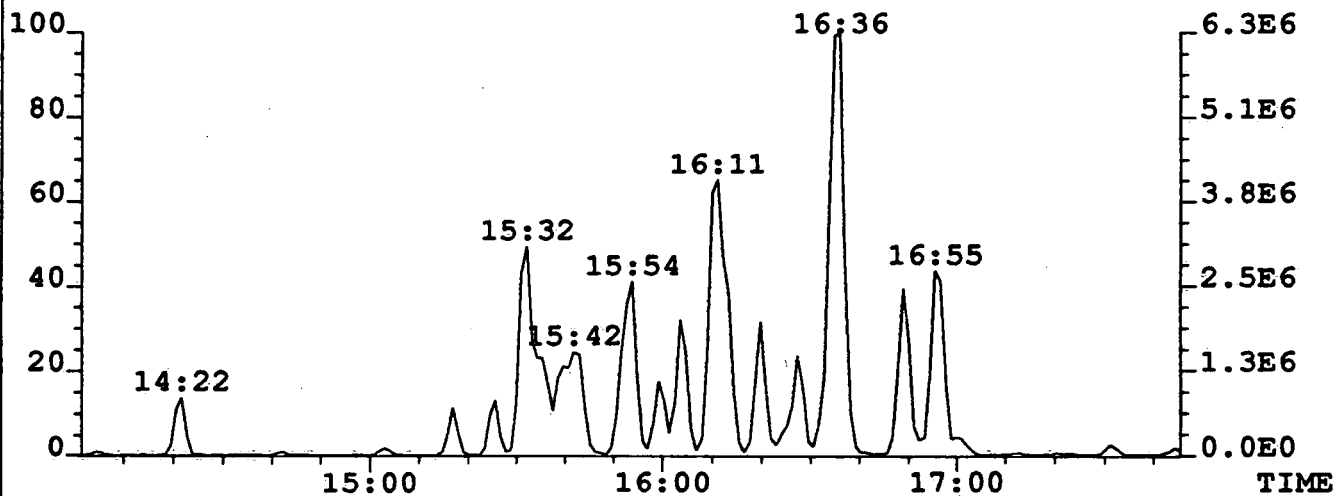
**Table 5. Recovery of PCDFs from Fly Ash using SFE. Low level Samples (mg/kg).**

**Table 6. Recovery of PCDFs from Fly Ash using SFE. High level Samples (mg/kg).**

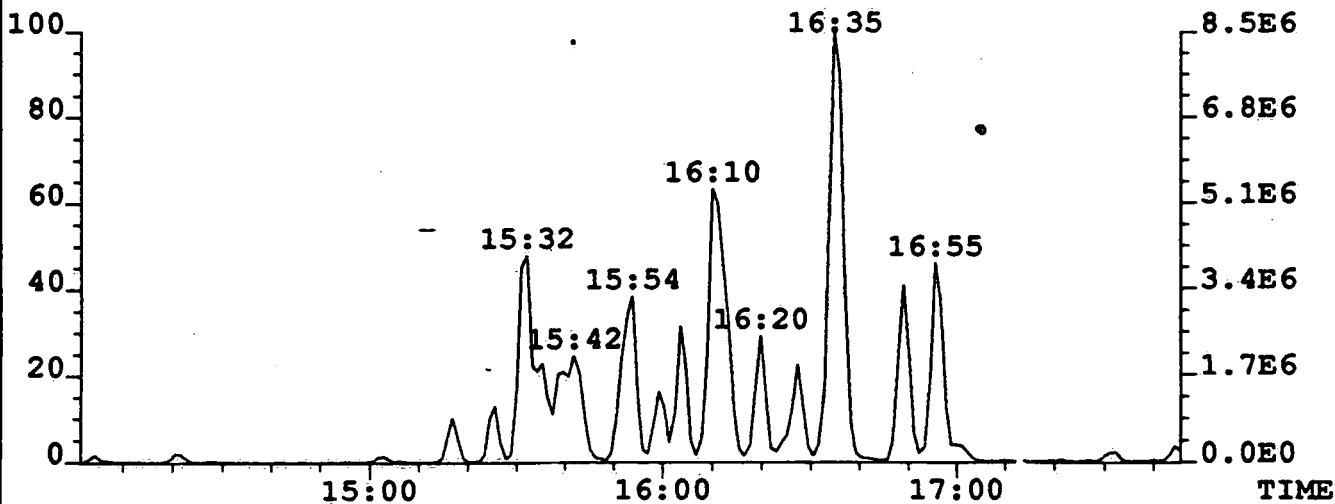
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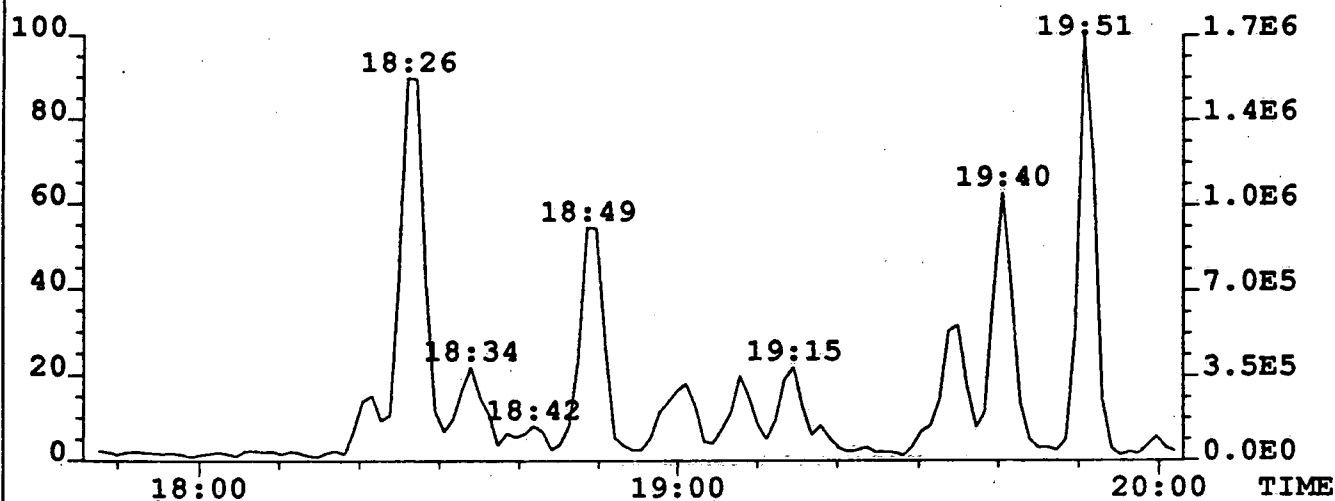
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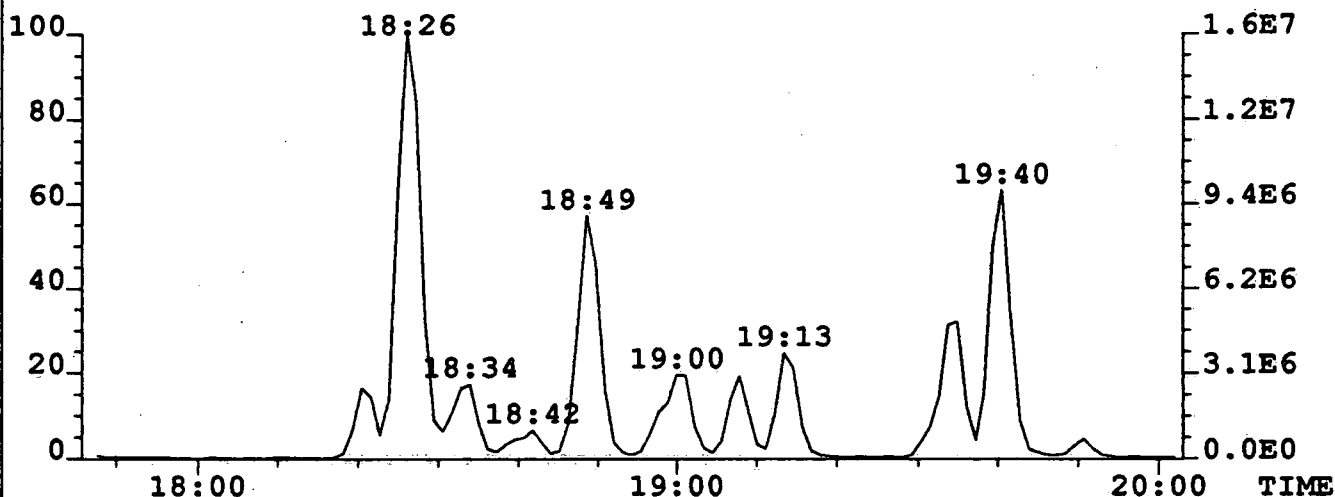
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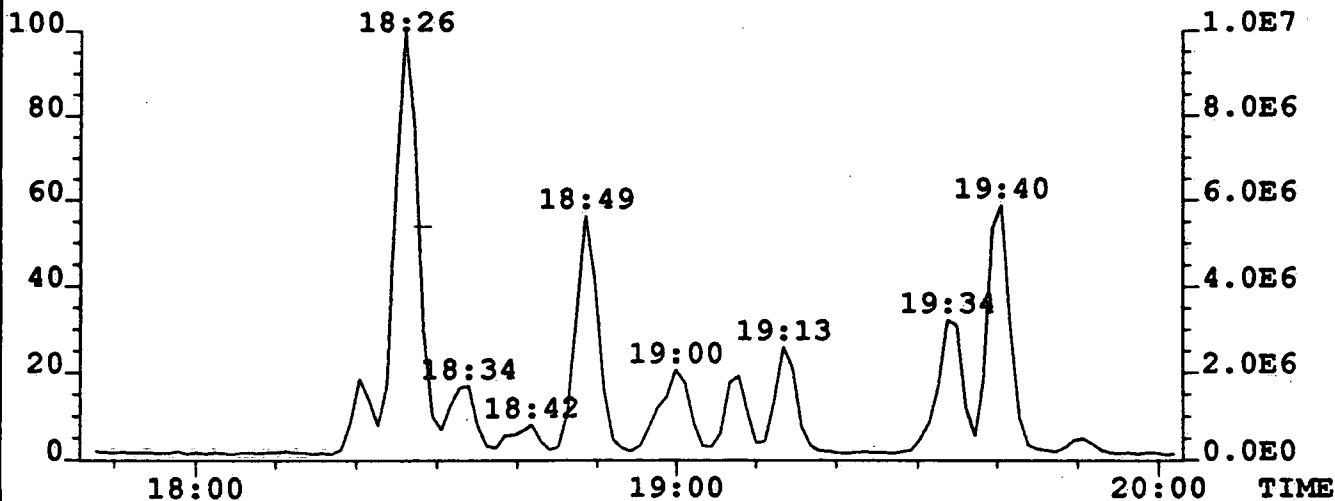
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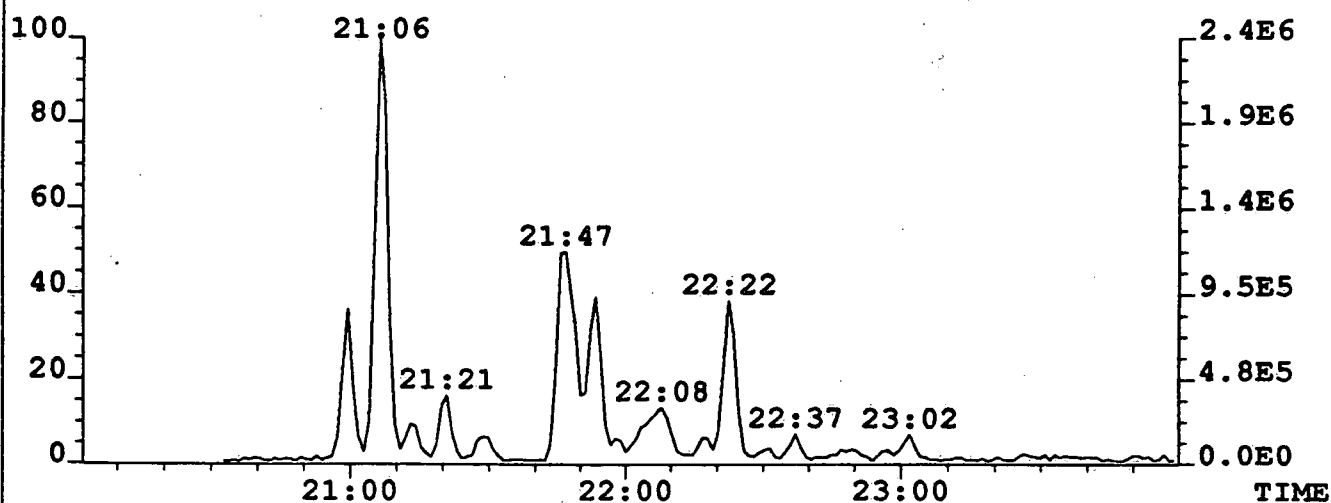
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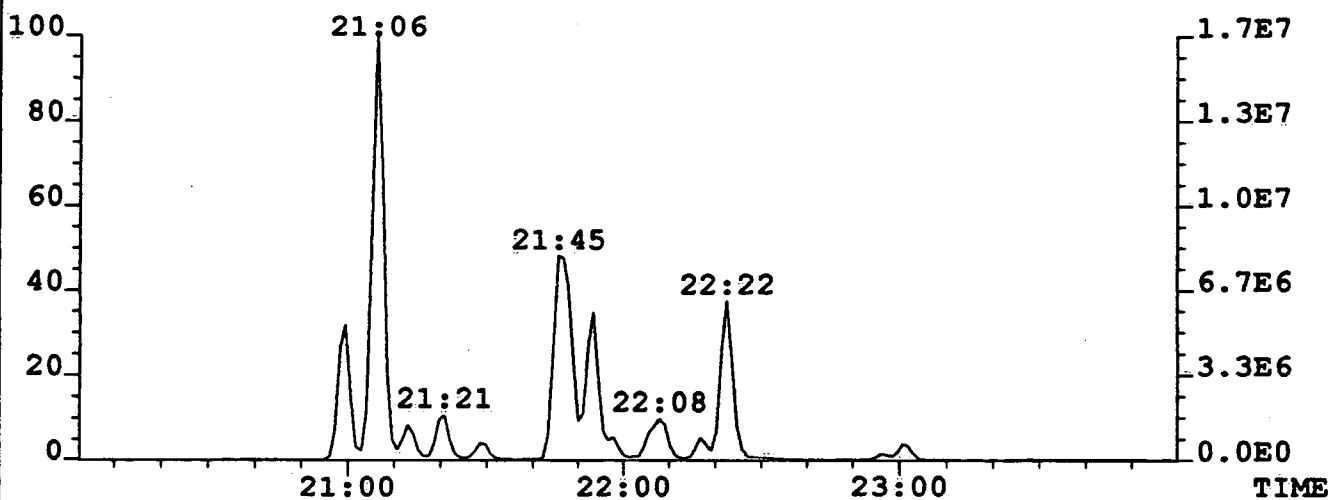
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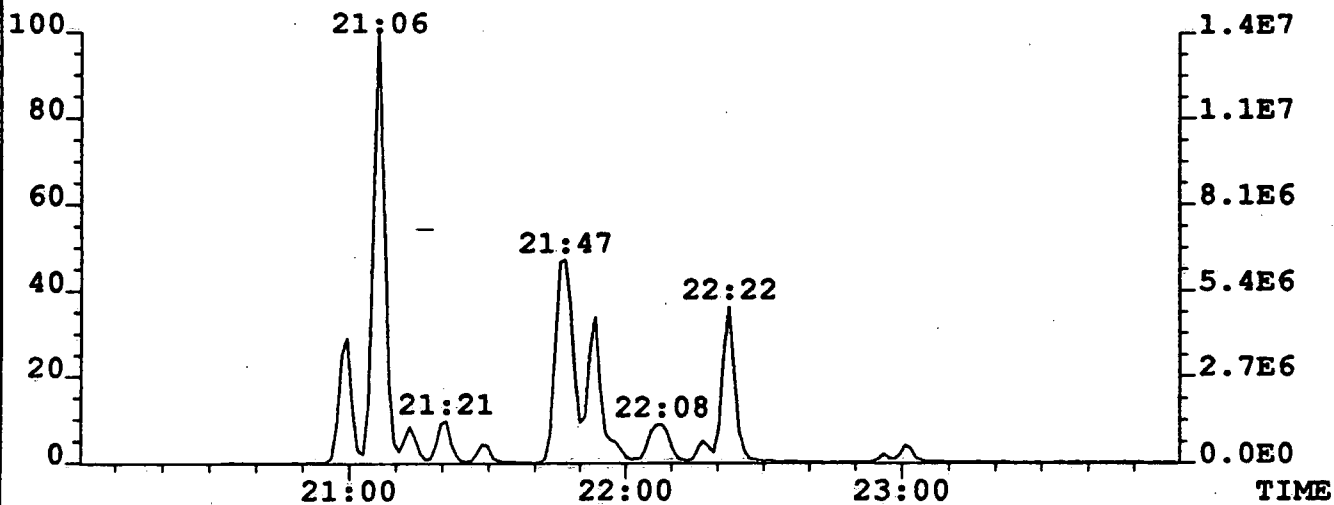
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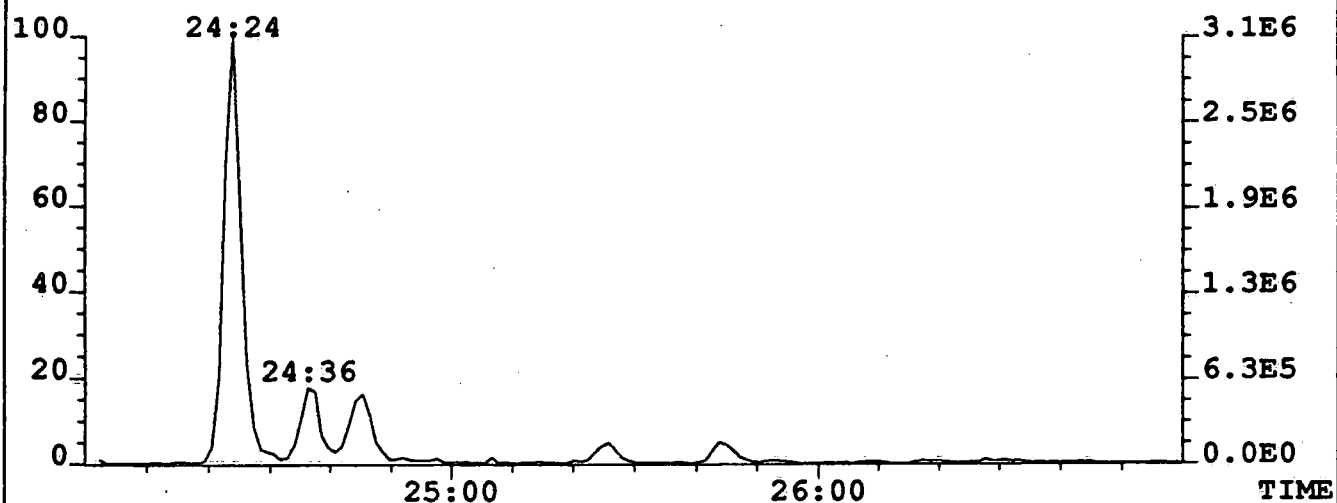
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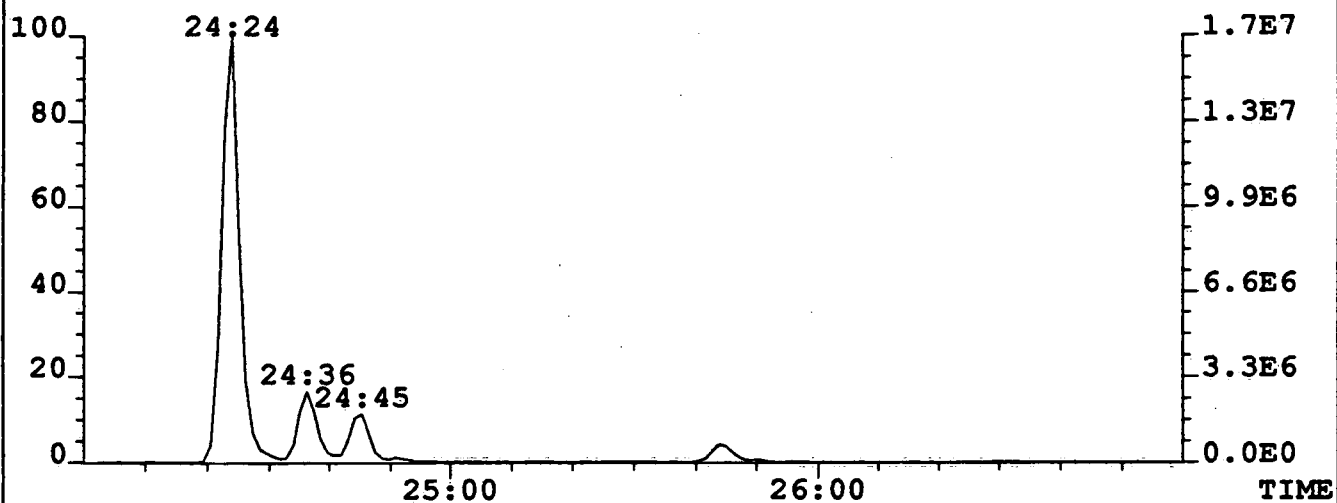
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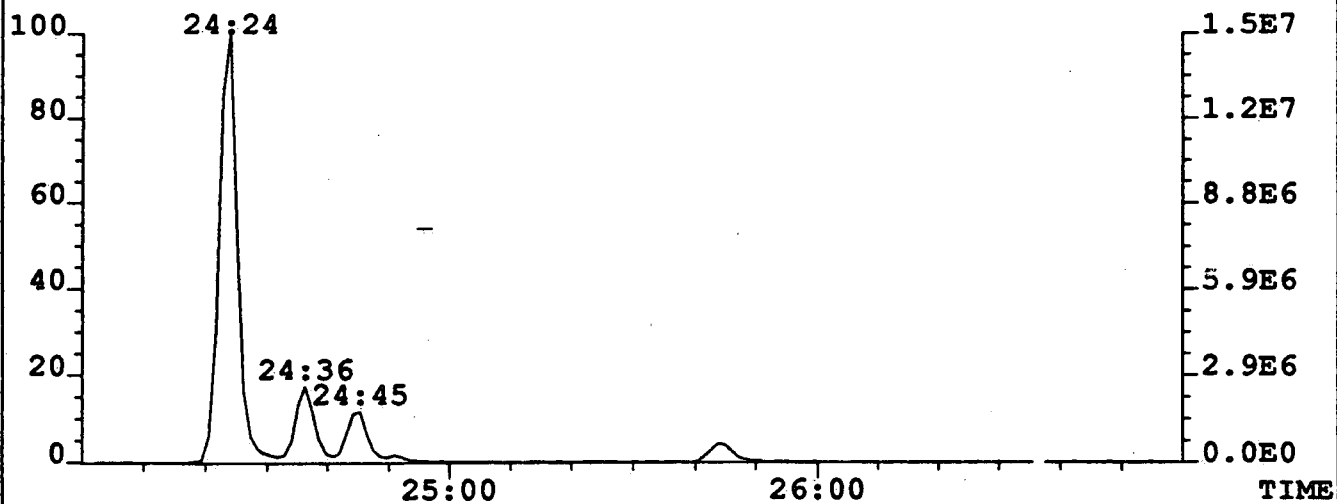
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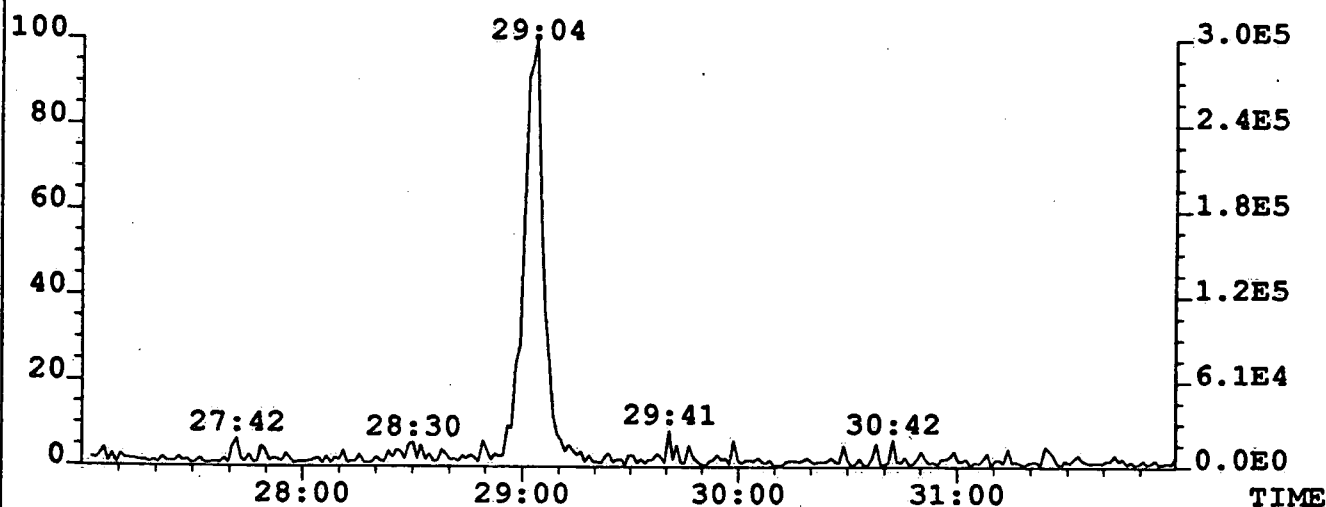
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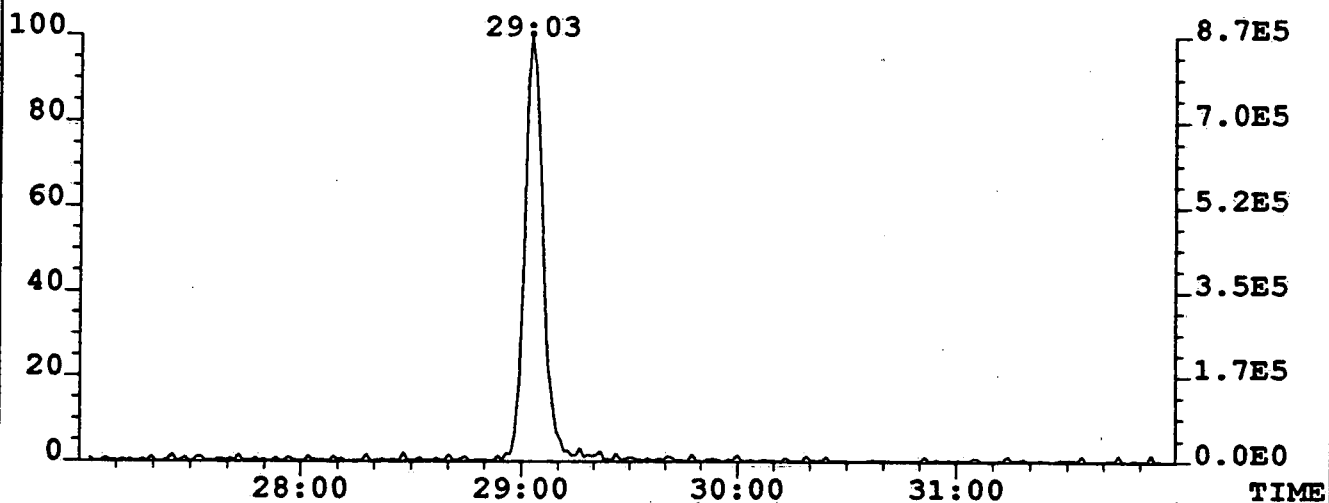
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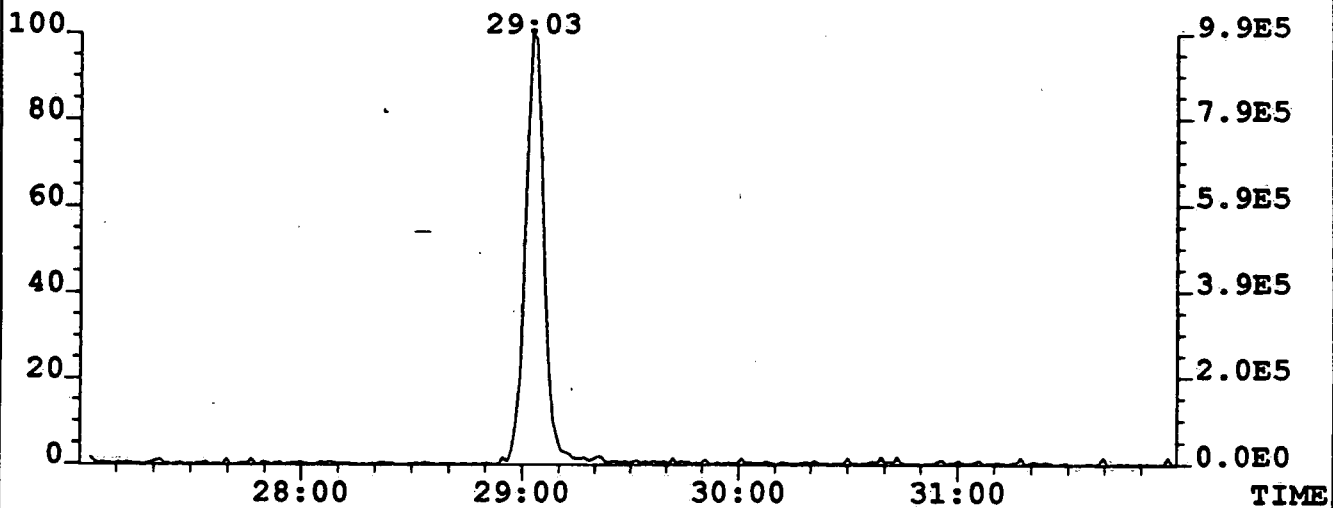
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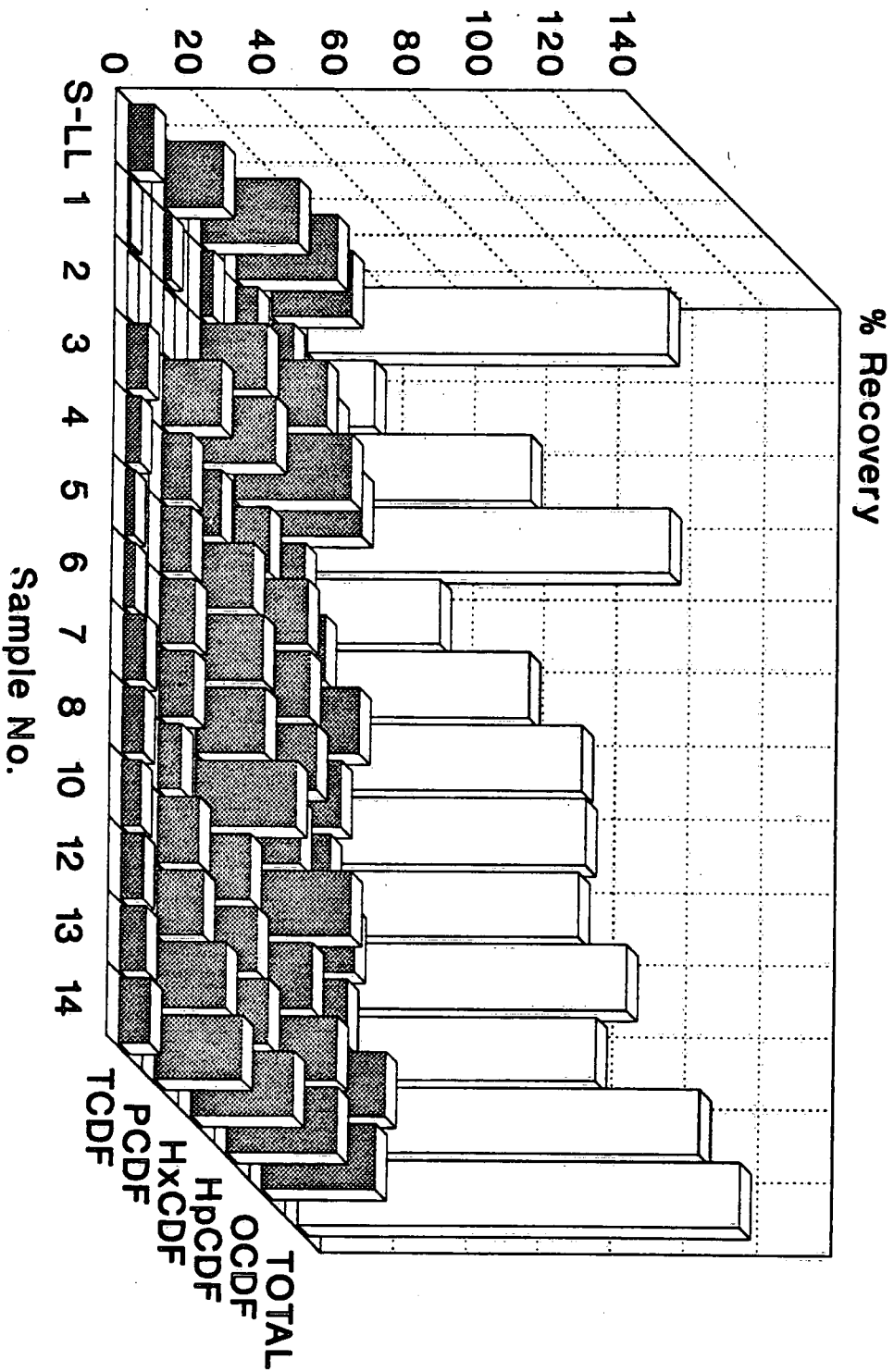


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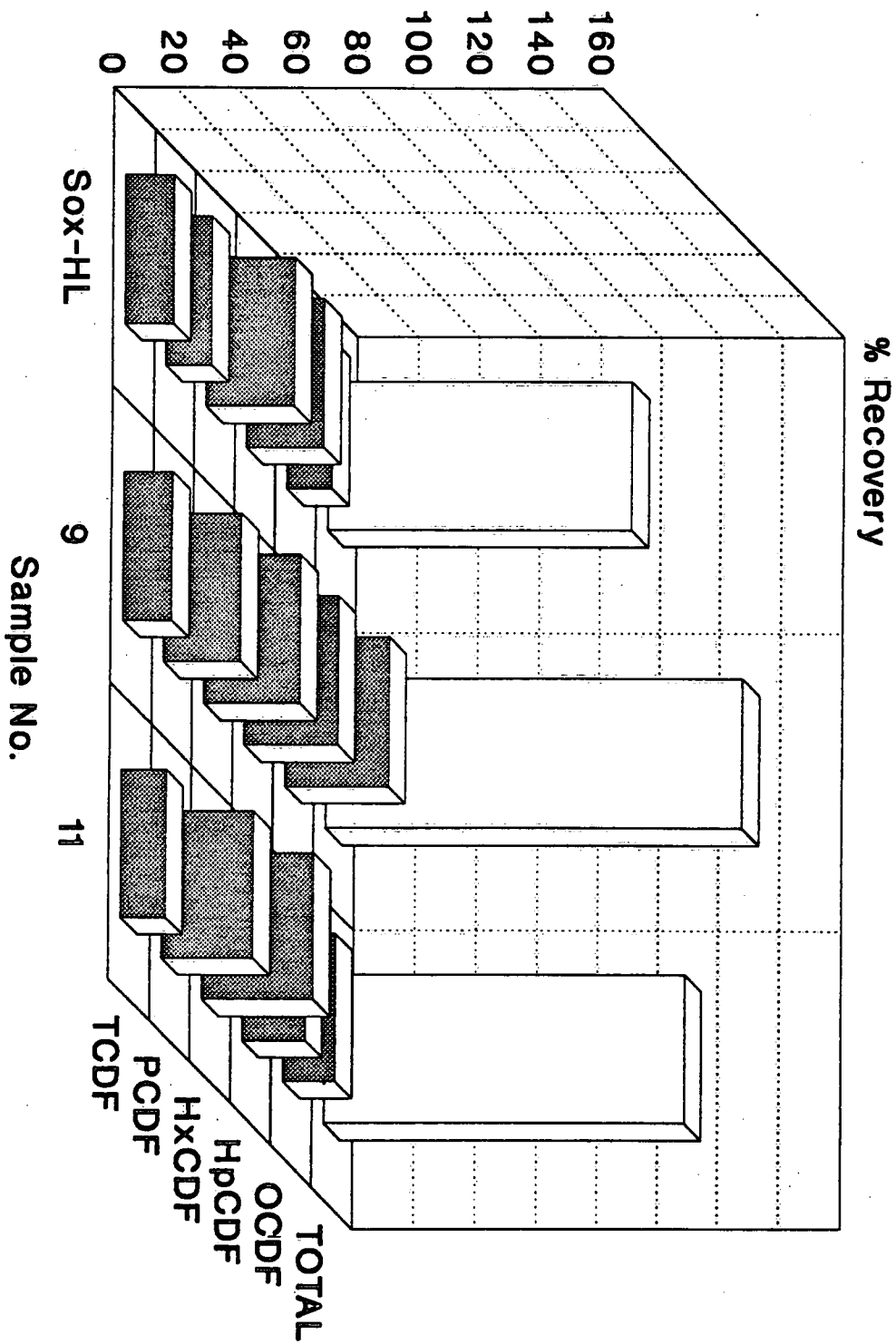


# RECOVERY OF PCDFs

## Low Level



# RECOVERY OF PCDFS High Level





**Table 3. Extraction Conditions for PCDFs from Fly Ash**

Exp. No.	Pressure atm	Replicate #	SF	Modifier	Pretreat	Extraction Time, static leaching minutes		Mode
1	400	2	CO <sub>2</sub>	-	F	64	16	A
2	350	2	CO <sub>2</sub>	M	T	40	10	C
3	400	2	CO <sub>2</sub>	T	F	64	16	A
4	350	3	N <sub>2</sub> O	M	-	-	60	B
5	350	2	N <sub>2</sub> O	M	-	40	10	C
6	350	2	N <sub>2</sub> O	M	T	40	10	C
7	350	2	N <sub>2</sub> O	M	E,F	50	16	D
8	400	3	N <sub>2</sub> O	M	HCl	64	16	A
9	400	2	N <sub>2</sub> O	M	F	64	16	A
10	400	2	N <sub>2</sub> O	T	F	32	8	A
11	400	3	N <sub>2</sub> O	M	T	64	16	A
12	350	2	N <sub>2</sub> O	M	F	120	30	A
13	400	2	N <sub>2</sub> O	T	F	-	60	B
14	400	2	N <sub>2</sub> O	M	-	64	16	A

M - 2% methanol, T - 5% toluene, E - ethylene

F - formic acid, HCl - hydrochloric acid

A - 15 step static extraction (16 min) + 4 min leaching, repeated 2 to 4 times

B - dynamic leaching

C - 20 step static, 20 min equilibration time + 5 min purging, repeated 2 to 6 times

D - 12 step static, 15 min equilibration time + 3 min purging

**Table 4. Recovery of PCDFs using Soxhlet Extraction in mg/kg**

Sample	TCDF	PCDF	HxCDF	HpCDF	OCDF	Total $\pm \sigma$
HL	0.567 $\pm$ 0.038	0.539 $\pm$ 0.027	1.030 $\pm$ 0.056	0.903 $\pm$ 0.009	0.526 $\pm$ 0.003	3.565 $\pm$ 0.462
LL	0.142 $\pm$ 0.008	0.324 $\pm$ 0.015	0.548 $\pm$ 0.029	0.568 $\pm$ 0.003	0.457 $\pm$ 0.001	2.039 $\pm$ 0.268

Samples were run in triplicate

**Table 5. Recovery of PCDFs using SFE in mg/kg  
Low level Samples (LL)**

Exp.No.	TCDF	PCDF	HxCDF	HpCDF	OCDF	Total $\pm \sigma$
1 - LL	0.016	0.044	0.071	0.124	0.128	0.383 $\pm$ 0.031
2 - LL	interfer.	interfer.	0.376	0.516	0.380	1.272 $\pm$ 0.113
3 - LL	0.122	0.324	0.433	0.660	0.521	2.060 $\pm$ 0.163
4 - LL	0.081	0.163	0.128	0.202	0.189	0.763 $\pm$ 0.073
5 - LL	0.053	0.167	0.313	0.421	0.320	1.274 $\pm$ 0.117
6 - LL	0.060	0.191	0.373	0.437	0.517	1.578 $\pm$ 0.074
7 - LL	0.124	0.190	0.390	0.479	0.420	1.603 $\pm$ 0.125
8 - LL	0.119	0.127	0.567	0.391	0.362	1.566 $\pm$ 0.078
10 - LL	0.107	0.225	0.316	0.684	0.506	1.838 $\pm$ 0.127
12 - LL	0.122	0.256	0.359	0.795	0.610	2.142 $\pm$ 0.146
13 - LL	0.144	0.386	0.422	0.614	0.688	2.254 $\pm$ 0.207
14 - LL	0.171	0.481	0.572	0.620	0.636	2.480 $\pm$ 0.176

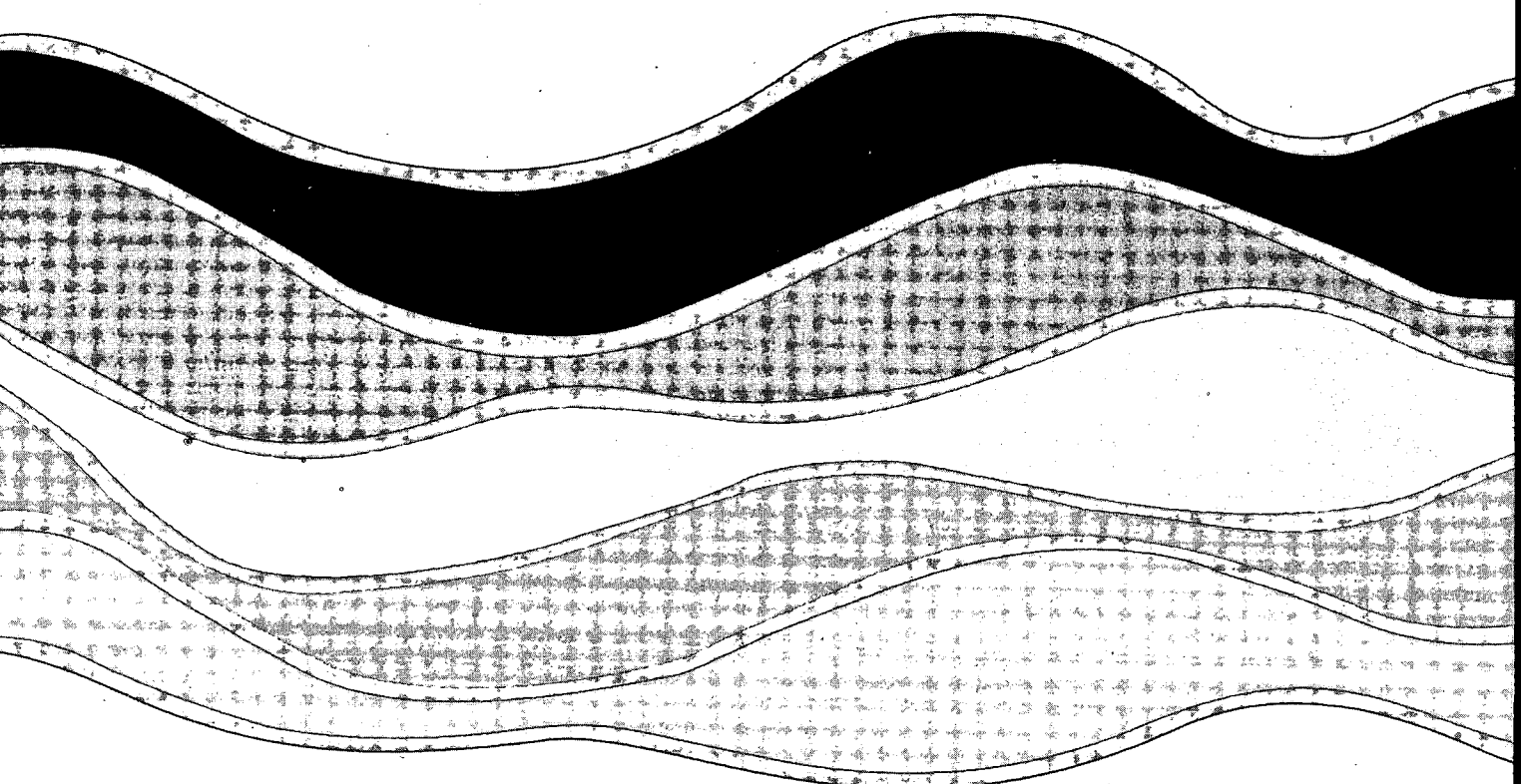
**Table 6. Recovery of PCDFs using SFE in mg/kg  
Higher Level Samples (HL)**

<b>Exp. No.</b>	<b>TCDF</b>	<b>PCDF</b>	<b>HxCDF</b>	<b>HpCDF</b>	<b>OCDF</b>	<b>Total <math>\pm \sigma</math></b>
<b>9 - HL</b>	0.570	0.900	1.120	1.090	1.210	4.89 $\pm$ 0.181
<b>11 - HL</b>	0.520	1.070	1.290	0.730	0.610	4.22 $\pm$ 0.148

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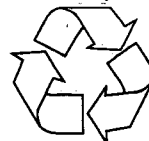
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