clear that with MIBK, acetone, and methanol carriers, the length of the coil has relatively little effect on the signal. With water and ethanol the effect is more significant, although the signal with ethanol levels off after 55 cm. In the case of MIBK, the dispersion would be limited by limited water solubility. In the case of totally water-miscible solvents, the organic solvent effect probably counters the increased spreading of the sample plug.

Time of Analysis. The FIA/AA peak emerges 4 s after injection. The peak width of the base line was 12 s for water, methanol, ethanol, and acetone carriers. It was only 6 s when MIBK carrier was used. Hence, it is possible to achieve as high as 200 measurements/h when water, methanol, ethanol, or acetone is used as carrier and in excess of 300 measurements/h when MIBK is used as carrier.

It is demonstrated in this study that it is possible to increase the FIA/AA sensitivity by 8-fold if the optimum carrier–sample solvent combination is used, allowing the analyst to determine trace metals at lower concentration levels, and should be particularly useful when dealing with biological samples. More dilution of the sample with the appropriate solvent is possible. This method is reproducible and does not require extra addition to the equipment or chemicals usually available to the analyst.

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; acetone, 67-64-1; methyl isobutyl ketone, 108-10-1; copper, 7440-50-8.

LITERATURE CITED

(1) Henry, R. J.; Cannon, D. C.; Winkelman, J. W. "Clinical Chemistry, Principles and Technics"; Harper and Row: Hagerstown, MD, 1974.
(2) Tietz, N.; "Fundamentals of Clinical Chemistry"; W. B. Saunders Co.: Philadelphia, PA, 1970.
(3) Marshall, J.; Ottaway, M. *Talanta* **1983**, *30*, 571.
(4) Christian, G. D.; Feldman, F. J. "Atomic Absorption Spectroscopy. Applications in Agriculture, Biology and Medicine"; R. E. Krieger Publishing Co.: New York, 1979.
(5) Kniseley, R. N.; Fassel, V. A.; Butler, C. C. *Clin. Chem. (Winston-Salem, N.C.)* **1973**, *19*, 807.
(6) Aziz, A.; Broekaert, J. A. C.; Leis, F. *Spectrochim. Acta, Part B* **1981**, *36B*, 251.
(7) Bauer, H. H.; Christian, G. D.; O'Reilly, J. E. "Instrumental Analysis"; Allyn and Bacon: Boston, MA, 1978.
(8) Christian, G. D.; Feldman, F. J. *Can. Spectrosc.* **1969**, *14*, 1.
(9) Ruzicka, J.; Hansen, E. H. "Flow Injection Analysis"; Wiley: New York, 1981.
(10) Ruzicka, J. *Philos. Trans. R. Soc. London, Ser. A* **1982**, *A305*, 645.
(11) Stewart, K. K. *Anal. Chem.* **1983**, *55*, 931A.
(12) Rocks, B. F.; Riley, C. *Clin. Chem. (Winston-Salem, N.C.)* **1982**, *28*, 409.
(13) Rocks, B. F.; Sherwood, R. A.; Riley, C. *Clin. Chem. (Winston-Salem, N.C.)* **1982**, *28*, 440.
(14) Jacintho, A. O.; Zaggatto, E. A. G.; Bergamin, H.; Krug, F. J.; Reis, B. F.; Bruns, R. E.; Kowalski, B. R. *Anal. Chim. Acta* **1981**, *130*, 243.
(15) Rocks, B. F.; Sherwood, R. A.; Bayford, L. M.; Riley, C. *Ann. Clin. Biochem.* **1982**, *19*, 338.
(16) Attiyat, A. S.; Christian, G.D. *Clin. Chim. Acta*, in press.

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Isomer-Specific Separation of 2378-Substituted Polychlorinated Dibenzo-*p*-dioxins by High-Resolution Gas Chromatography/Mass Spectrometry

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All polychlorinated dibenzo-*p*-dioxin (PCDD) isomers containing four and more chlorine substituents were prepared by micropyrolysis of chlorophenates. The syntheses included the preparation of all 22 tetra-, 14 penta-, 10 hexa-, 2 hepta-, and octachlorinated species (tetra- to octa-CDD). The gas chromatographic and mass spectrometric properties of these isomers were studied. High-resolution gas chromatography (HRGC) on a 55-m Silar 10c glass capillary column allowed the separation of many of these isomers and allowed the unambiguous assignment of the toxic and environmentally hazardous 2378-substituted isomers (2378-tetra-, 12378-penta-, 123478-, 123678-, and 123789-hexa-CDD). Analyses were carried out to determine the occurrence of these isomers in environmental samples and in fly ash from municipal incinerators.

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are a group of toxic and environmentally hazardous compounds. The tricyclic aromatic compounds are substituted with up to eight chlorine atoms. There is a total of 75 PCDD isomers ranging from the mono- to the octachloro compounds (mono- to octa-CDD) (see Table I).

Table I. Number of Isomers and Substitution Pattern of PCDDs

compounds	substitution type (x:y)[a]	no. of isomers	total no. of isomers
mono-CDDs	1:0	2	2
di-CDDs	1:1	6	
	2:0	4	10
tri-CDDs	2:1	12	
	3:0	2	14
tetra-CDDs	2:2	13	
	3:1	8	
	4:0	1	22
penta-CDDs	3:2	12	
	4:1	2	14
hexa-CDDs	3:3	6	
	4:2	4	10
hepta-CDDs	4:3	2	2
octa-CDD	4:4	1	1
			75

[a] x and y are the number of chlorine substitutents in each carbon ring of the dioxin molecule.

Some PCDDs have extraordinary toxic properties (*1–4*). Toxicity depends on the number and position of the chlorine substituents and is highest for the tetra-, penta-, and hexa-

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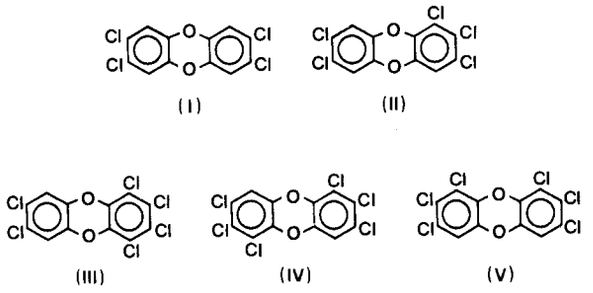

Figure 1. Structure of 2378-substituted PCDDs: (I) 2378-tetra-, (II) 12378-penta-, (III) 123478-, (IV) 123678-, and (V) 123789-hexa-CDDs.

chloro compounds. The most toxic isomers apparently belong to the 2378-group (chlorine substituted at carbons in lateral 2-, 3-, 7-, and 8-positions). This group includes the 2378-tetra-, 12378-penta-, and 123478-, 123678-, and 123789-hexa-CDD (notation excludes the commas necessary in full names; structures are given in Figure 1). 2378-Tetra-CDD is a strong cocarcinogen (*5*) and appears to be the most toxic isomer. It is chemically and biologically stable, and only recently have mammalian metabolites been found and identified (*6*). The 12378-penta-CDD is reported to be very close to the 2378-tetra-CDD in toxicity and biological activity (*7*).

The PCDDs are known as highly stable contaminants of some industrial chemicals such as chlorinated phenols and their derivatives (phenoxy acid herbicides). More recently PCDDs have been detected in emissions of some combustion sources (*8–10*). The origin of the PCDDs in these emissions is not completely clear; PCDDs could not only originate from combustion of specific organochlorine compounds but possibly also from de nuovo syntheses via nonspecific chlorination reactions. PCDDs, including 2378-tetra-CDD, have been implicated in several industrial accidents and they caused severe environmental contaminations, most recently at Times Beach, MO (*11*). There is a growing concern on the more recently detected wide-spread occurrence of these compounds in the environment (*12*).

Because of the extreme toxicity of some PCDDs there is a special need for unusually sensitive and specific analytical methods to monitor levels of these compounds in the environment. Pronounced differences in biological and toxicological effects between different isomers require especially selective, isomer-specific analyses. Desirable detection limits for the toxic 2378-substituted isomers are in the part-per-trillion (pptr) range. Essential requirements for such analytical procedures are efficient extraction and purification of the extract, followed by highly specific and selective separation and detection means. The most sensitive methods make use of mass spectrometry (MS).

Various analytical methods for PCDDs have been described in the literature (*13*). These methods include elaborate cleanup schemes sometimes involving high-performance liquid chromatography (HPLC) and attempting the isolation of selected isomers. More desirable however are procedures designed to collect all PCDDs as a group with later analysis for all or selected isomers.

In previous reports we described the use of high-resolution gas chromatography (HRGC) and MS for the analysis of PCDDs (*14–16*). By use of a Silar 10c (cyanosiloxane) HRGC column it was possible to distinguish 2378- from all the other 21 tetra-CDD isomers (*16*). In the present paper we describe the preparation, analysis, and identification of all PCDD isomers containing four and more chlorine substituents. This includes 22 tetra-, 14 penta-, 10 hexa-, 2 hepta-, and 1 octa-CDD which were prepared via microsyntheses. Analytical conditions were found that allow an isomer-specific separation and detection of all the 2378-substituted isomers using HRGC and MS. Application of the procedure is demonstrated in the analysis of environmental samples.

EXPERIMENTAL SECTION

Synthesis of PCDDs. Tetra-, hexa-, hepta-, and octa-CDD were prepared as previously described (*16, 17*). Penta-CDDs were synthesized by micropyrolysis of various potassium chlorophenate combinations: 3:2 type isomers (total of 12) from mixtures of tri- and tetrachlorophenates (tri- and tetra-CPs), 4:1 type isomers (total of 2) from mixtures of di- and pentachlorophenates (di- and penta-CPs). The chlorophenols used were 23- and 24-di-, 234-, 236-, 245-, and 246-tri-, 2345- and 2356-tetra-, and pentachlorophenol, all of analytical quality from Fluka (Buchs, Switzerland). The experimental conditions were as previously described and the PCDDs were characterized by HRGC and MS without further purification of the samples (*16, 17*).

Additional Reference Samples. Additional reference samples were 2378-tetra-CDD (Stickstoffwerke Linz, Austria); 1234-tetra-CDD (K. Andersson, University of Umeå, Sweden), and 12378- and 12478-penta-, 123678- and 123789-hexa-, 1234678- and 1234679-hepta-CDD (D. Firestone, Food and Drug Administration, Washington, DC).

Preparation and Purification of Environmental Samples. Purified extracts of fish and herring gull from various water sheds were obtained from D. Stalling, Columbia National Fisheries Research Laboratory (CNFRL), Columbia, MO. The extracts were purified at CNFRL by gel permeation, cesium silicate and carbon chromatography resulting in an improved enrichment of planar aromatic contaminants. Some of the samples were analyzed and results reported previously (*12*). An extract of a soot sample from the transformer fire in the state office building in Binghampton, NY, was obtained (courtesy D. Stalling, CNFRL, Columbia, MO). It was cleaned up by CNFRL using the above procedure. Fly ash from municipal incinerators of Switzerland and Canada (courtesy R. C. Lao, Air Pollution Technology Center, Ottawa) was treated with HCl and extracted with toluene (*18*) and the extracts were purified by chromatography on silica and alumina as previously described (*17*).

GC/MS Analyses. A 55-m Silar 10 c HRGC glass capillary column (0.26 mm i.d.) was coupled via a fused silica interface to a Finnigan 4000 quadrupole MS operated in the electron-impact (EI) mode (70 eV, 250 °C). The column was prepared in this laboratory (soft glass, HCl etched, Carbowax 20M deactivated) but may be replaced by columns from commercial sources. Sample aliquots of 1–2 μL containing 100–1000 picograms (pg) of a PCDD in hexane or toluene were injected splitlessly (60 s) and the column temperature was programmed as follows: 60 °C (samples in hexane) or 100 °C (samples in toluene), 2 min isothermal, 20 °C/min to 180 °C, 2 °C/min to 250 °C. Single or multiple ion monitoring at m/z 320, 354, 388, 424, and 458 was used for the detection of tetra- to octa-CDD. Complete mass spectra were recorded as previously described (*16*). Isomer identifications were based on coinjection with reference samples using single ion detection; absolute retention times were used for guidance only. Analysis time was 53 to 55 min.

RESULTS AND DISCUSSION

All PCDDs containing four to eight chlorine substituents (49 isomers) were synthesized by micropyrolysis of various chlorophenates and their combinations as summarized in Table II. Micropyrolysis was found to be a simple and safe route for the preparation of microgram amounts of PCDDs from readily available starting materials. No elaborate isolation was required and the synthesis involved minimal sample handling.

PCDDs form through condensation of chlorophenates and various isomers may form through involvement of a Smiles rearrangement as outlined in Figure 2. The number of isomers expected from these reactions and those actually observed are usually in agreement. However, assignment of the correct structure to each of the isomers may not always be possible. In some cases, assignment of Smiles related tetra- and penta-CDDs was possible from results of a photolysis experiment with two isomeric hexa-CDDs (*19*).

Table II. Properties and Route of Preparation of PCDDs Investigated

sample no.	PCDD isomer	substitution pattern	Smiles relationship	elution temp,[a] °C	chlorophenates reacted	remarks
1	1267-tetra-	2:2	Sm	223.4	234-tri-CP	*b*
	1289-	2:2		227.4		
2	1368-tetra-	2:2	Sm	205.6	246-tri-CP	*b*
	1379-	2:2		208.2		
3	2378-tetra-	2:2		215.8	245-tri-CP	*c*
4	1269-tetra-	2:2		222.1	236-tri-CP	*d*
	1469-	2:2		220.3		
5	1278-tetra-	2:2		220.0	245- + 234-tri-CP	*e*
6	1378-tetra-	2:2		210.9	245- + 235-tri-CP	*e*
7	1478-tetra-	2:2		215.5	245- + 236-tri-CP	*e*
8	1268-tetra-	2:2	Sm	214.2	246- + 234-tri-CP	*b, e*
	1279-	2:2		217.5		
9	1369-tetra-	2:2		212.6	235- + 236-tri-CP	*e*
10	1236-tetra-	3:1	Sm	217.5	23-di- + 2345-tetra-CP	*b, e*
	1239-	3:1		220.8		
11	1237/1238-tetra-	3:1	Sm	216.5, 216.7	25-di- + 2345-tetra-CP	*e*
12	1246/1249-tetra-	3:1	Sm	216.4, 216.4	26-di- + 2356-tetra-CP	*e*
13	1247/1248-tetra-	3:1	Sm	212.8, 212.8	24-di- + 2356-tetra-CP	*e*
14	1234-tetra-	4:0		216.3	23-di- + penta-CP	*c, e*
15	12368-penta-	3:2	Sm	223.6	246-tri- + 2345-tetra-CP	*b*
	12379-	3:2		226.4		
16	12367-penta-	3:2	Sm	232.5	234-tri- + 2345-tetra-CP	*b, f*
	12389-	3:2		236.2		
17	12378-penta-	3:2		229.6	245-tri- + 2345-tetra-CP	*c*
18	12369-penta-	3:2		230.5	236-tri- + 2345-tetra-CP	*g*
19	12468/12479-penta-	3:2	Sm	222.2, 222.2	246-tri- + 2356-tetra-CP	*h*
20	12467/12489-penta-	3:2	Sm	230.9, 231.2	234-tri- + 2356-tetra-CP	*i*
21	12478-penta-	3:2		225.4	245-tri- + 2356-tetra-CP	*c, f*
22	12469-penta-	3:2		228.8	236-tri- + 2356-tetra-CP	*k*
23	12346-penta-	4:1		232.1	23-di- + penta-CP	*e*
24	12347-penta-	4:1		228.8	24-di- + penta-CP	*e*
25	123678-hexa-	3:3	Sm	242.2	2345-tetra-CP	*c*
	123789-	3:3		245.3		
26	123679/123689-hexa-	3:3	Sm	240.0, 240.2	2346-tetra-CP	*i, l*
27	124679/124689-hexa-	3:3	Sm	237.6, 237.6	2356-tetra-CP	*h*
28	123467-hexa-	4:2		247.1	234-tri- + penta-CP	*e*
29	123468-hexa-	4:2		237.8	246-tri- + penta-CP	*e*
30	123478-hexa-	4:2		241.8	245-tri- + penta-CP	*e*
31	123469-hexa-	4:2		244.2	236-tri- + penta-CP	*e, m*
32	1234678-hepta-	4:3		250	2345-tetra- + penta-CP	*c, e*
33	1234679-hepta-	4:3		250	2356-tetra- + penta-CP	*c, e*
34	12346789-octa-	4:4		250	penta-CP	*c*

[a] 55-m Silar 10c HRGC column, see Figure 3 and Experimental Section. [b] Assignment via photolysis of hexa-CDDs, ref 19. [c] Additional reference sample, see Experimental Section. [d] 1267- and 1289-tetra-CDD additionally formed, see sample 1; 1469-tetra-CDD assigned via photolysis of octa-CDD, ref 16. [e] Additional PCDDs from individual chlorophenates. [f] Some dechlorination observed. [g] 12367- and 12389-penta-CDD additionally formed, see sample 16. [h] Smiles related isomers not separated, full assignment not possible. [i] Smiles related isomers separated but full assignment not possible. [k] 12467- and 12489-penta-CDD additionally formed, see sample 20. [l] Also minor amounts of 124679-/124689-, 123678-, and 123789-hexa-CDD. [m] 123467-hexa-CDD additionally formed, see sample 28.

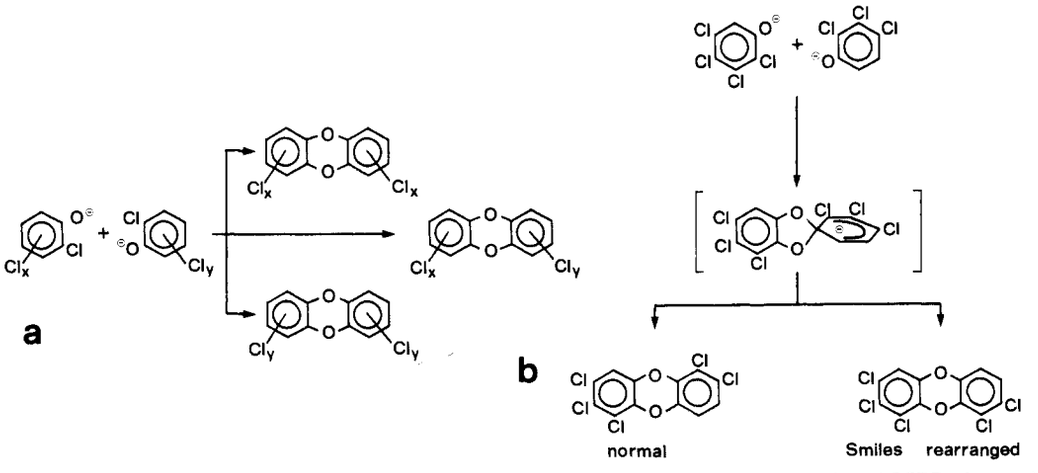

Figure 2. (a) Simplified reaction scheme showing synthesis of symmetrically and unsymmetrically substituted PCDDs from mixed pyrolysis of chlorophenates. (b) Condensation scheme involving Smiles rearrangement leading to 12367- and 12389-penta-CDD as the normal and the Smiles rearranged products from the condensation of 234-tri- and 2345-tetra-CP.

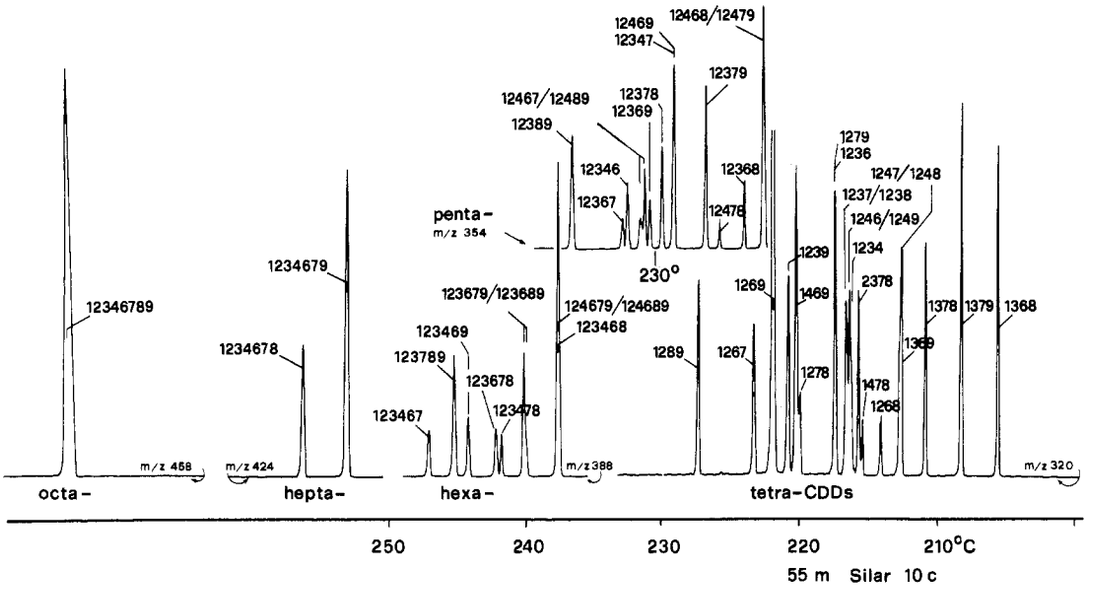

Figure 3. Chromatogram of a composite sample showing elution of all 22 tetra-, 14 penta-, 10 hexa-, 2 hepta- and 1 octa-CDDs on 55-m Silar 10c HRGC column.

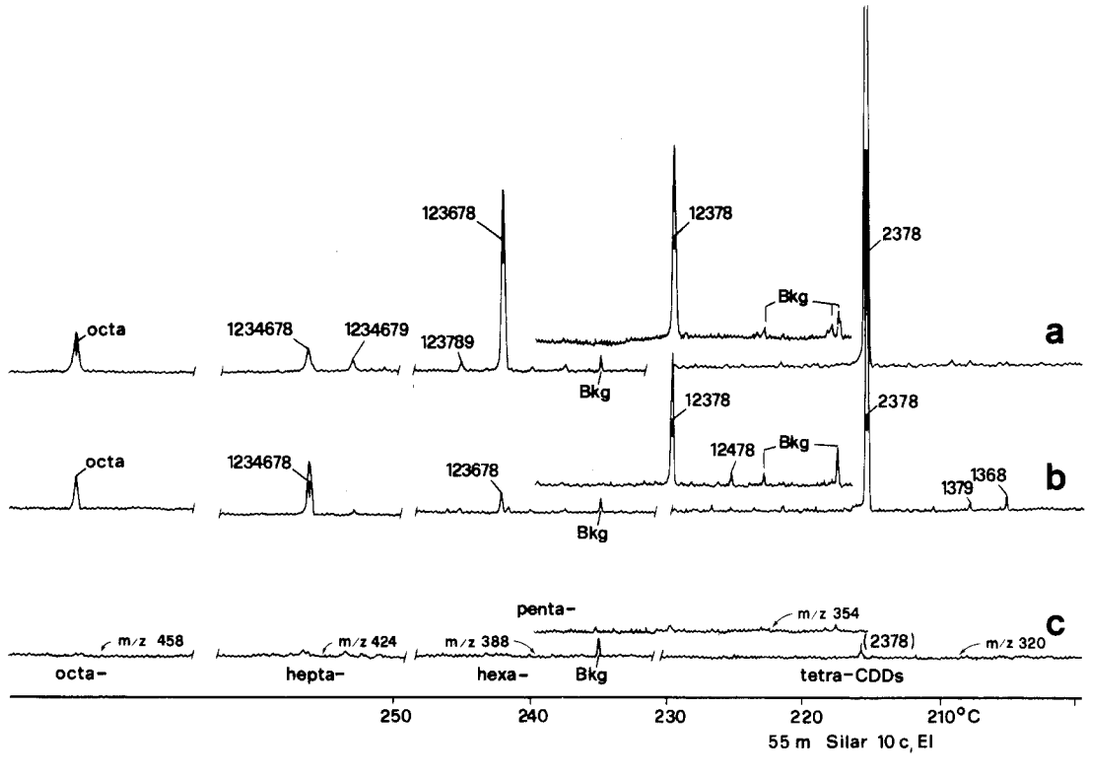

Figure 4. Chromatograms showing elution of some 2378-substituted PCDDs in extracts of (a) herring gull, Lake Huron, and (b) yellow perch, Woods Pond, MA, and (c) no detectable PCDDs in extract of perch, Lake Zurich, Switzerland, except 1 pptr 2378-TCDD due to internal standard addition.

All the tetra-, hexa-, hepta-, and octa-CDDs were prepared as previously described (*16*, *17*). Tetra- and hexa-CDDs were also synthesized by an independent group using a similar procedure (*20*, *21*). The 14 penta-CDDs were prepared from combinations of various tri- and tetra-CPs (formation of 3:2 type penta-CDDs) and from di- and penta-CPs (formation of 4:1 type penta-CDDs). The use of 2345-tetra-CP leads to 3:2 type penta-CDDs with 123-chlorine substitution and the use of 2356-tetra-CP to 3:2 type penta-CDDs with 124-chlorine substitution (see Table II). In some pyrolysis experiments, dechlorination of higher PCDDs was observed as indicated in Table II. Repeating pyrolysis at lower temperatures (260 °C), however, produced proportionally less dechlorinated products and thus aided in their identification.

EI mass spectra of PCDDs show intense (usually base peak) molecular ions (M^+). Fragmentation leads to $M^+ - COCl$ and $M^+ - 2COCl$; minor ions are observed at $M^+ - Cl$ and $M^+ - Cl_2$. Fission of the C–O bonds followed by loss of Cl, HCl, or Cl_2 leads to ions in the lower mass range that contain information on the substitution type of an isomer and allow a determination of the number of chlorine substituents attached to the two carbon rings of a PCDD. Further distinction among isomers of the same substitution type is not possible from EI data. The m/z values used for monitoring PCDDs (single ion detection) were 320 (M^+), 354 (M^+), 388 (M^+), 424 ($M^+ + 2$) and 458 ($M^+ + 2$) for tetra- to octa-CDD ($M^+ + 2$ ions of hepta- and octa-CDD were used for compensating lower MS sensitivity to these compounds).

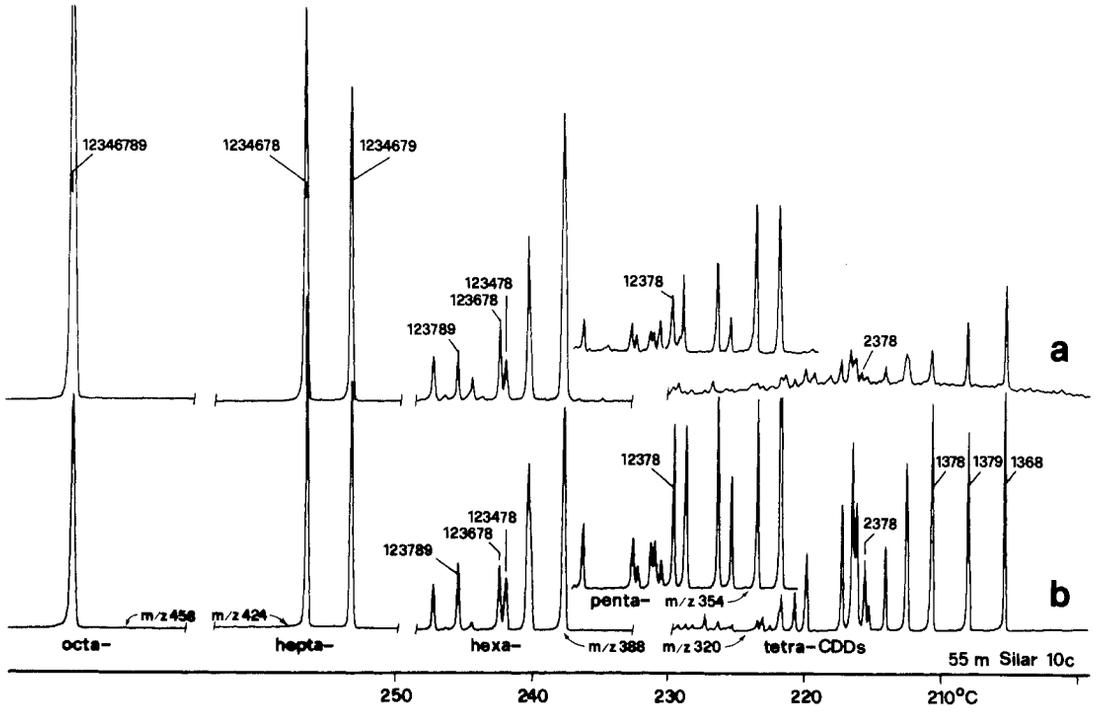

Figure 5. Chromatograms showing elution of PCDDs in extracts of fly ash from municipal incinerators of (a) Zurich, Switzerland, and (b) Ontario, Canada; 2378-substituted isomers are present, but not as the main PCDD components.

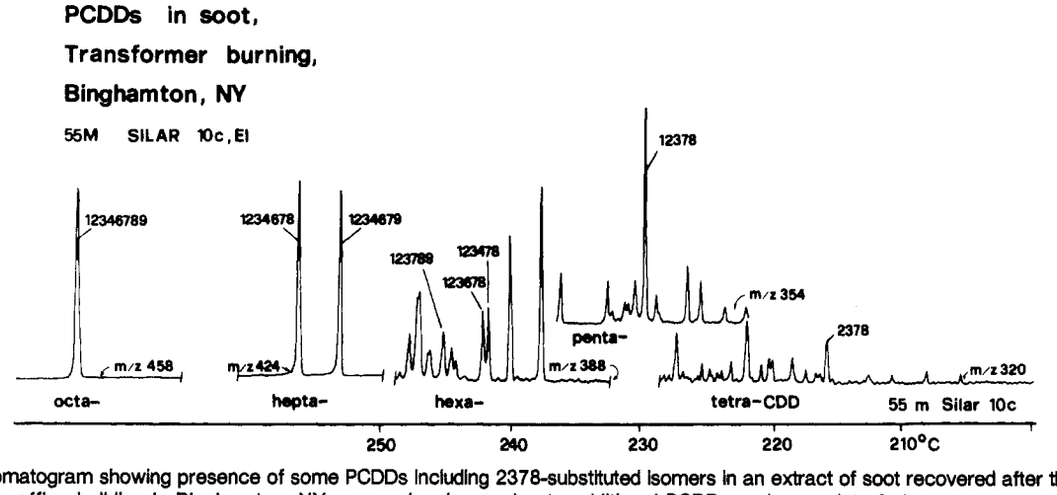

Figure 6. Chromatogram showing presence of some PCDDs including 2378-substituted isomers in an extract of soot recovered after the transformer fire in the state office building in Binghamton, NY; some signals are due to additional PCDDs and some interfering components.

HRGC of PCDDs using glass capillary columns of different polarity showed highest selectivity toward isomer separation for Silar 10c (*14*, *16*). A special, narrow-bore (0.25 mm i.d.), 55-m Silar 10c HRGC column allowed the separation of 2378-tetra-CDD from all other tetra-CDD isomers (*16*). In the present study a similar Silar 10c column was used (55 m, 0.26 mm i.d.). Retention data (elution temperatures) of all the PCDDs studied are included in Table II. The values for other Silar 10c columns may vary, but the same order of elution is expected.

A chromatogram of a composite sample containing all 49 PCDDs with four to eight chlorine substituents is shown in Figure 3. The elution temperatures of the various PCDDs were 205–228 °C for tetra-CDDs, 222–236 °C for penta-CDDs, 238–248 °C for hexa-CDDs, and hepta- and octa-CDD at 250 °C. Retention times increased with increasing number of chlorine substituents except for some overlapping of tetra- and penta-CDDs.

Not all the isomers are fully separated, as indicated in Figure 3. Some of these coeluting PCDDs however may be separated on OV-17 or OV-101 HRGC columns (1469- from 1278-; 1236- from 1279-; 1369- from 1247/1248-tetra-CDD; 12347- from 12469-penta-CDD; 123468- from 124679/124689-hexa-CDD) but several isomers, especially Smiles related isomers with 124-substitution, proved difficult to separate (see Table II). These are (1) 1246- and 1249-, (2) 1247- and 1248-tetra-CDD, (3) 12468- and 12479-, (4) 12467- and 12489-penta-CDD, (5) 123679- and 123689-, and (6) 124679- and 124689-hexa-CDD. The HRGC column used in the present investigation allowed full separation of isomer pair (4) and partial separation of isomer pairs (1), (2), and (5) under slow (0.5 °C/min) temperature programming conditions. In case of isomer pairs (3) and (6), the presence of two isomers was only deducible from peak width considerations. The presence of two hexa-CDDs in isomer pairs (5) and (6) was not recognized previously when shorter columns were used (*14*, *17*).

The elution order of PCDDs on Silar 10c shows the following general dependence on chlorine substitution (increasing retention from left to right): 13- < 14- < 12- < 124- < 123- < 1234- and $-68 \leq -79 < -78 < -69 < -67 \leq -89$.

The chromatogram in Figure 3 also shows the elution of

the 2378-type isomers. 2378-Tetra-, 12378-penta-, 123478-, 123678-, and 123789-hexa-CDD are separated from other isomers. Shorter HRGC columns (25 m Silar 10c) failed to separate the 2378-tetra-CDD from the other isomers; however, the 2378-type penta- and hexa-CDDs were still separated. The 55-m Silar 10c column thus allowed the separation of all the 2378-type isomers and therefore allows an unambiguous assignment of these important isomers.

In the following examples we illustrate the application of HRGC and MS for the isomer-specific separation of 2378-substituted PCDDs in environmental samples. The procedure was applied to extracts of fish and herring gull from different water sheds. The extracts were cleaned up by CNFRL using gel permeation, adsorption, and carbon chromatography. This cleanup results in exceptionally clean extracts containing all the PCDDs and the related polychlorinated dibenzofurans (PCDFs) but only very minor amounts of other chlorinated pollutants and coextracted materials. Recovery rates were determined with a series of PCDDs and PCDFs and ranged from 60 to 100%, ^{13}C-2378-tetra-CDD added at a level of 100 pptr is used as an internal standard. Results of a series of fish and herring gull samples analyzed for PCDDs and PCDFs were reported previously (*13*). A selected number of these were reanalyzed in the present investigation for the occurrence of specific PCDD isomers. In Figure 4a the chromatogram of a herring gull (Lake Huron) reveals the presence of significant amounts of 2378-tetra-CDD (75 pptr), 12378-penta-CDD (18 pptr), and 123678-hexa-CDD (17 ppm) in addition to some 123789-hexa-, hepta-, and octa-CDD. As the chromatogram shows, practically no other PCDDs are detectable. The chromatogram of the extract of yellow perch (Woods Pond, MA, Figure 4b) reveals again the almost exclusive presence of 2378-substituted PCDDs (2378-tetra-CDD, 26 pptr; 12378-penta-CDD, 10 pptr; 123678-hexa-CDD, 2 pptr). The results indicate some contamination of these two watersheds with these specific PCDDs. For comparison, Figure 4c shows the chromatogram of an extract of fish (perch) from Lake Zurich (Switzerland) revealing an almost complete absence of PCDDs and indicating a so far uncontaminated watershed (presence of ~1 pptr 2378-tetra-CDD due to internal standard addition).

In a further application we studied the presence of 2378-substituted PCDDs in fly ash from municipal incinerators. In Figure 5a is the chromatogram of an extract of fly ash from a municipal incinerator at Zurich. The presence of tetra- (3 ppb), penta- (20 ppb), hexa- (50 ppb), hepta- (180 ppb), and octa-CDD (210 ppb) is indicated, revealing increased amounts of the higher chlorinated species. As indicated 2378-substituted isomers may be present to some extent but not as the main PCDD components (maximal 2, 14, and 24% of total tetra-, penta-, and hexa-CDD, respectively). The chromatogram of a Canadian fly ash sample in Figure 5b shows a more uniform distribution of PCDDs; the sample contained tetra- (150 ppb), penta- (550 ppb), hexa- (900 ppb), hepta- (850 ppb), and octa-CDD (400 ppb). Although this sample in comparison to the Swiss fly ash shows significantly higher levels of PCDDs and a changed distribution maximizing for hexa-CDD, it has surprisingly similar proportions of 2378-substituted PCDDs (4, 12, and 27% of total tetra-, penta- and hexa-CDDs, respectively). So far it is not known whether the higher levels of PCDDs result from different operating conditions of the incinerators, different feed stock, or different collection conditions (temperature) of the fly ash. However, the similar isomer distribution pattern of these fly ashes may point to common processes of formation of these PCDDs.

Finally, in Figure 6 is a chromatogram of an extract of soot recovered after the transformer fire in the state office building in Binghampton, NY (*22*). Soot from this accident not only contained the expected polychlorinated biphenyls (PCBs), but also PCDFs, PCDDs, and polychlorinated biphenylenes. The PCDDs were formed in high-temperature reactions from chlorobenzenes (*23*) present in the PCB transformer fluid. The chromatogram shows the presence of 2378-tetra-CDD (0.6 ppm), 12378-penta-CDD (2.5 ppm), and some hexa-CDDs. Complete mass spectra recorded revealed the presence of interfering components in addition to PCDDs. These interfering components were present in this extract despite the efficient cleanup procedure used.

These applications demonstrate the use of HRGC and MS for the isomer-specific separation of 2378-substituted PCDDs allowing an unambiguous assignment of these toxic isomers. Furthermore, isomer distribution pattern from such analyses may aid in identifying origin and sources of PCDDs and may help in determining routes of formation of these hazardous compounds.

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Registry No. 1267-tetra-CDD, 40581-90-6; 1368-tetra-CDD, 33423-92-6; 2378-tetra-CDD, 1746-01-6; 1269-tetra-CDD, 40581-91-7; 1278-tetra-CDD, 34816-53-0; 1378-tetra-CDD, 50585-46-1; 1478-tetra-CDD, 40581-94-0; 1268-tetra-CDD, 67323-56-2; 1369-tetra-CDD, 71669-24-4; 1236-tetra-CDD, 71669-25-5; 1237-tetra-CDD, 67028-18-6; 1246-tetra-CDD, 71669-27-7; 1247-tetra-CDD, 71669-28-8; 1234-tetra-CDD, 30746-58-8; 12368-penta-CDD, 71925-16-1; 12367-penta-CDD, 71925-15-0; 12378-penta-CDD, 40321-76-4; 12369-penta-CDD, 82291-34-7; 12468-penta-CDD, 71998-76-0; 12467-penta-CDD, 82291-35-8; 12478-penta-CDD, 58802-08-7; 12469-penta-CDD, 82291-36-9; 12346-penta-CDD, 67028-19-7; 12347-penta-CDD, 39227-61-7; 123678-hexa-CDD, 57653-85-7; 123679-hexa-CDD, 64461-98-9; 124679-hexa-CDD, 39227-62-8; 123467-hexa-CDD, 58200-66-1; 123468-hexa-CDD, 58200-67-2; 123478-hexa-CDD, 39227-28 6; 123469-hexa-CDD, 58200-68-3; 1234678-hepta-CDD, 35822-46-9; 1234679-hepta-CDD, 58200-70-7; 12346789-octa-CDD, 3268-87-9; 123789-hexa-CDD, 19408-74-3; 123689-hexa-CDD, 58200-69-4; 124689-hexa-CDD, 58802-09-8; 1289-tetra-CDD, 62470-54-6; 1379-tetra-CDD, 62470-53-5; 1469-tetra-CDD, 40581-93-9; 1279-tetra-CDD, 71669-23-3; 1239-tetra-CDD, 71669-26-6; 1238-tetra-CDD, 53555-02-5; 1249-tetra-CDD, 71665-99-1; 1248-tetra-CDD, 71669-29-9; 12379-penta-CDD, 71925-17-2; 12389-penta-CDD, 71925-18-3; 12479-penta-CDD, 82291-37-0; 12489-penta-CDD, 82291-38-1; 234-tri-CP, 58200-71-8; 246-tri-CP, 2591-21-1; 245-tri-CP, 35471-43-3; 236-tri-CP, 58200-73-0; 235-tri-CP, 58200-72-9; 23-di-CP, 88211-72-7; 25-di-CP, 68938-81-8; 26-di-CP, 18396-74-2; 24-di-CP, 50884-30-5; 2345-tetra-CP, 58200-74-1; 2356-tetra-CP, 58200-75-2; penta-CP, 7778-73-6; 2346-tetra-CP, 88211-73-8.

LITERATURE CITED

(1) Nicholson, W. J., Moore, J. A., Eds *Ann. N.Y. Acad. Sci.* **1979**, *320*.
(2) Poland, A.; Glover, E.; Kende, A. S. *J. Biol. Chem.* **1976**, *251*, 4936–4946.
(3) McConnell, E. E.; Moore, J. A.; Haseman, J. K.; Harris, M. W. *Toxicol. Appl. Pharmacol.* **1978**, *44*, 335–356.
(4) Leng, M. L. In "CIPAC Proceedings Symposium Papers;" Bontoyan, W. R., Ed.; Collaborative International Pesticides Analytical Council Publications: Harpenden, U.K., 1979.
(5) Poland, A.; Palen, D.; Glover, E. *Nature (London)* **1982**, *300*, 271–273.
(6) Poiger, H.; Buser, H. R.; Weber, H.; Zweifel, U.; Schlatter, C. *Experientia* **1982**, *38*, 484–486.
(7) Goldstein, J. A. In "Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzo-dioxins and Related Products;" Kimbrough, R. D., Ed.; Elsevier/North Holland Biomedical Press: Amsterdam, 1980; Chapter 6.
(8) Olie, K.; Vermeulen, P. L.; Hutzinger, O. *Chemosphere* **1977**, *6*, 455–459
(9) Buser, H. R.; Bosshardt, H. P.; Rappe, C. *Chemosphere* **1978**, *7*, 165–172.
(10) The Chlorinated Dioxin Task Force, "Trace Chemistries of Fire—A Source of and Routes for the Entry of Chlorinated Dioxins into the Environment"; Dow Chemical: Midland, MI, 1978.
(11) Sun, M. *Science* **1983**, *219*, 367–369.
(12) Stalling, D. L, Smith, L. M.; Petty, J. D.; Hogan, J. W.; Johnson, J. L.; Rappe, C.; Buser, H. R. In "Human and Environmental Risks of Chlo-

rinated Dioxins and Related Compounds"; Tucker, E. J., Young, A. L., Grey, A. P. Eds.; Plenum: New York, 1983.
(13) Crummet, W. B. *Chemosphere* **1983**, *12*, 429-446.
(14) Buser, H. R. *Anal. Chem.* **1979**, *48*, 1553-1557.
(15) Buser, H. R. *Anal. Chem.* **1977**, *49*, 918-922.
(16) Buser, H. R.; Rappe, C. *Anal. Chem.* **1980**, *52*, 2257-2262.
(17) Buser, H. R. *J. Chromatogr.* **1975**, *114*, 95-108.
(18) Kooke, R. M. M.; Lustenhouwer, J. W. A.; Olie, K.; Hutzinger, O. *Anal. Chem.* **1981**, *53*, 461-463.
(19) Buser, H. R. *Chemosphere* **1979**, *8*, 251-257.
(20) Nestrick, T. J.; Lamparski, L. L.; Stehl, R. H. *Anal. Chem.* **1979**, *51*, 2273-2281.
(21) Lamparski, L. L.; Nestrick, T. J. *Chemosphere* **1981**, *10*, 3-18.
(22) Schecter, A. *Chemosphere* **1983**, *12*, 669-680.
(23) Buser, H. R. *Chemosphere* **1979**, *8*, 415-424.

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Formaldehyde Surface Emission Monitor

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A passive surface emission monitor has been developed for nondestructive measurement of formaldehyde (CH_2O) emission rates from CH_2O resin-containing materials such as urea–formaldehyde foam insulation (UFFI) and pressed-wood products. Emitted CH_2O is sorbed by a planar distribution of 13X molecular sieve supported inside the monitor and analyzed by using a water-rinse desorption, colorimetric analysis procedure. A detection limit of $\simeq$0.025 mg of CH_2O/(m^2 h) is achieved with a 20.3 cm diameter monitor and a 2-h collection period. Measurements of CH_2O emission rates from pressed-wood products and UFFI encased in simulated wall panels show a strong correlation with reference chamber techniques. The surface monitor has been used to measure the CH_2O emission rate from interior walls and floors in one UFFI and two non-UFFI homes. By application of a simple single compartment model to predict indoor CH_2O concentrations from in situ CH_2O emission rate and tracer gas infiltration rate measurements, a good correlation between the predicted and measured CH_2O concentrations was achieved.

Formaldehyde-based resins are incorporated in a wide variety of construction and consumer products (*1*). Generic product lines include pressed-wood products, urea–formaldehyde foam insulation (UFFI), fiberglass products, and textiles. Exposures to temperature and water vapor concentration levels typical in indoor environments cause degradation of the CH_2O resins and release of formaldehyde (CH_2O) gas. The potential impact of these emissions on indoor air quality is a subject of increased concern, especially with the current emphasis on energy-efficient homes with reduced air-exchange rates (*2*).

Current field monitoring techniques for CH_2O focus on the measurement of airborne CH_2O concentrations and are generally inappropriate for in situ characterization of individual source emission rates (*3–5*). Available methods for source identification and measurement are also undesirable because they require the removal of samples for subsequent laboratory analysis (*6*). The cosmetic problems associated with a destructive sampling procedure can result in inadequate sampling to properly characterize the location and emission rates (ERs) of important CH_2O emitters. In addition, unknown changes can occur in the CH_2O ERs of specimens upon removal from their original environment.

Sample destructive techniques are also currently used for quality control measurements of CH_2O emissions from CH_2O resin-containing products (*7*, *8*). For example, the 2-h desiccator test of the Hardwood Plywood Manufacturers Association, National Particleboard Association is commonly applied in the U.S. to particleboard and decorative paneling products used in mobile homes (*7*). Small cut specimens are placed inside a sealed desiccator for 2 h with an open dish of water to collect emitted CH_2O. Although the procedure is attractively simple to perform, there are several potential disadvantages. First, the destructive sampling protocol discourages the testing of adequate numbers of boards to properly characterize the distribution of CH_2O ERs from each lot of product (*9*). Second, the small specimens expose an atypically large amount of edge surface area that must often be corrected by sealing the edges with paraffin (*9*). Third, the low CH_2O collection rate of the water sorbent (due to limited exposure in a small dish) and large pressed-wood surface area (i.e., $\simeq$0.18 m^2) allows the buildup of CH_2O in the atmosphere inside the desiccator. The elevated CH_2O concentrations suppress the CH_2O ER of the product in comparison to the CH_2O ER that would be observed in typical domestic environments where CH_2O concentrations are generally low (e.g., 0.01–0.25 ppm) (*10*).

A passive formaldehyde surface emission monitor (FSEM) has been developed to address a broad need for semiquantitative, nondestructive measurement of CH_2O ERs from CH_2O resin-containing products. Potential applications include (1) in situ measurements of products incorporated in domestic environments, such as decorative paneling or UFFI that are openly accessible or covered by diffusion barriers and (2) a convenient quality control method for pressed-wood products that is selective to CH_2O emission from the face of the product. The FSEM has been designed to closely simulate environmental chamber tests where the CH_2O concentration is maintained at levels consistent with those in residential housing.

EXPERIMENTAL SECTION

Monitor Construction and Use. The FSEM is constructed from a 20 cm brass mechanical sieve (No. 20 mesh) and cover (Figure 1). A circular flange, 3.0 cm wide and 1.9 cm thick, is attached in a concentric manner to the bottom of the mesh container. The flange is fabricated from Plexiglas and 0.3 cm thick neoprene sponge gasket (ASTM D1056). The sorbent-test media

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