

THE ANALYSIS OF ORGANOHALOGEN COMPOUNDS (PCDDs, PCDFs and PCBs) IN COMPLEX MATRICES

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ABSTRACT

Methods for the isomer-specific analysis of PCDDs, PCDFs and PCBs in a variety of sample matrices including deduster sludge, soils, fragmentiser residues, slaked lime scavengers and incinerator stack effluents derived from clinical waste, dried sewage sludge, bituminous coal etc. are described. Results indicate that the levels of higher chlorinated dioxins contribute significantly to TEQ values for some of the sample analysed.

Introduction

The methods of determination for PCDDs, PCDFs and PCBs are largely dependent on the sample matrix and the levels of analyte present.

The matrices encountered are varied and include incinerator stack effluents derived from clinical wastes, dried sewage sludge, domestic refuse, bituminous coal etc., soils, slaked lime scavengers and ambient air, for dioxins; and, fragmentiser residues, recyclable metals from domestic appliances, and deduster sludge for PCBs.

The complexity of the analyses arises from the combination of matrices with high levels of potential organic co-extractives, and relatively low levels of the target analytes.

The 2,3,7,8-chloro substituted PCDDs and PCDFs are individually determined as are nine PCB isomers including the 6 draft legislation isomers (1) and three of the most toxic (2) non-ortho substituted isomers (Table 1).

In view of the high levels of co-extractives the analytical methodology is based on thorough sample preparation with the use of both, high and low resolution mass spectrometry.

Experimental

The internal standards used in the analyses are indicated in Table 1. All of these were Carbon-13 labelled.

Additionally, 2,3,7,8-TCDD ($^{37}\text{Cl}_4$ labelled) was used as a syringe standard and, 1,2,3,4-T₄CDD ($^{13}\text{C}_{12}$ labelled) was used as the internal sampling standard (pre-sampling, filter spike).

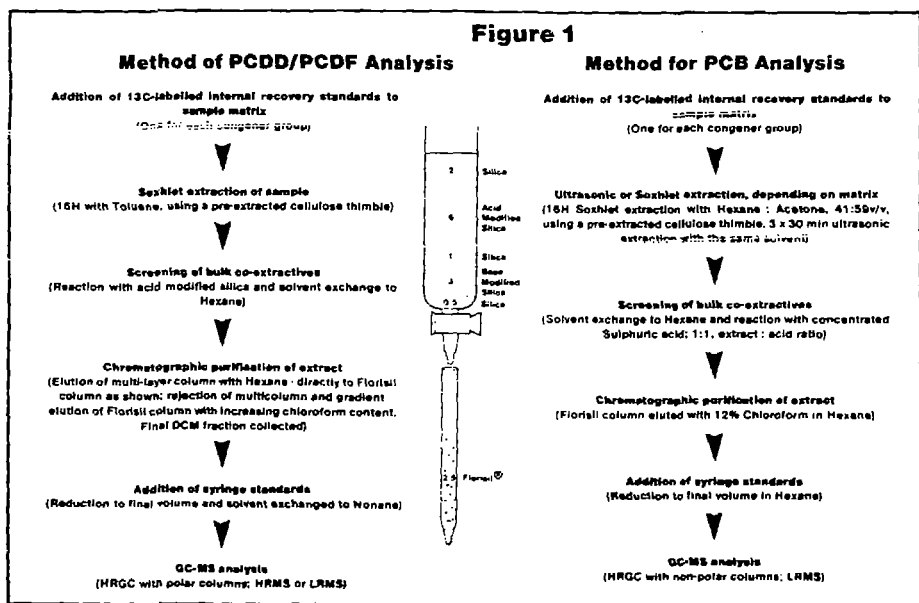
General procedures for dioxin and PCB analyses are summarised in Fig. 1. GC-MS(SIM) analyses were carried out on a Hewlett-Packard 5890A/MSD system or a VG 70/11-250J mass

Table 1
List of Specific Analytes

PCDDs and PCDFs	PCBs
2,3,7,8- T_4 CDD *	2,4,4'- T_2 CB (28) *
1,2,3,7,8- P_5 CDD *	2,5,2',5'- T_4 CB (52) ○
1,2,3,4,7,8- H_6 CDD	3,4,3',4'- T_4 CB (77) *
1,2,3,6,7,8- H_6 CDD	2,4,5,2',5'- P_5 CB (101) ○
1,2,3,7,8,9- H_6 CDD *	(2,4,5,3',4'- P_5 CB) (118)
1,2,3,4,6,7,8- H_7 CDD *	3,4,5,3',4'- P_5 CB (126) *
OCDD *	2,3,4,2',4',5'- H_6 CB (138) *
2,3,7,8- T_4 CDF	2,4,5,2',4',5'- H_6 CB (153) ○
1,2,3,7,8- P_5 CDF	3,4,5,3',4',5'- H_6 CB (169) ○
2,3,4,7,8- P_5 CDF *	2,3,4,5,2',4',5'- H_7 CB (180) *
1,2,3,4,7,8- H_6 CDF	
1,2,3,6,7,8- H_6 CDF	
1,2,3,7,8,9- H_6 CDF ○	
2,3,4,6,7,8- H_6 CDF	
1,2,3,4,6,7,8- H_7 CDF ○	
1,2,3,4,7,8,9- H_7 CDF	
OCDF ○	

* - recovery/quantitation standards
○ - syringe standards

Figure 1



spectrometer coupled to an HP 5890 Series II gas chromatograph. A 0.22 x 60m SP2331 column was used for the PCDD/PCDF analyses, while that for the PCB separations was a 0.22 x 60m DB-5. The following GC oven temperature programmes were used:

PCDDs/PCDFs - 140°C for 1 min to 228°C at 17°C/min for 4 min, then 0.8°C/min to 245°C, then 1°C/min to 260°C, then 3°C/min to 275°C for 19 min.

PCBs - 60°C for 1 min to 190°C at 20°C/min for 4 min, then 1.4°C/min to 270°C, then 10°C/min to 285°C.

The m/z values of the ions monitored during the GC-MS(SIM) runs are well documented (5,6). Additionally, the following ions corresponding to the ¹³C₁₂ labelled PCB isomers were monitored: m/z 268,270,302,304,338,340,372,374,406 and 408.

Similar positive identification criteria (3,4) were applied to all classes of analytes. Quality control measures included random use of glassware for blanks, daily pre-analysis monitoring of GC-MS performance evaluation standards, checks on recoveries of sampling and quantitation standards and monitoring of lock mass and lock mass checks (for HRGC-HRMS). Additionally, duplicate samples and an internal quality assurance sample were run as a test of reproducibility and overall method performance.

Results and Discussion

The analytical methods described in this report are applicable to a wide variety of sample types. Critical to the sample preparation stage is the screening of co-extractives, the successful removal of which, greatly facilitates the chromatographic purification of the extract.

Direct elution of the multicolumn to the Florisil[®] column results in a shorter analysis time as well as smaller analyte losses.

Prior to routine analysis the methods were extensively validated. Relevant data is summarised in Table 2.

The results of dioxin and PCB determinations for a range of sample types is presented in Table 3. Results of dioxin determination for a number of different matrices show - a. the presence of the whole range of 2,3,7,8- substituted isomers and b. on a TEQ basis, significant levels of the higher chlorinated PCDDs and PCDFs for some samples.

PCB results indicate that relatively higher level of moderately chlorinated isomers (3,4 and 5-Cl) are present in the samples analysed and that the levels of the co-planer PCBs are generally lower with undetected levels of isomer 169.

The analytical methods described are well-validated and are generally applicable to the PCDD, PCDF and PCB analysis of a range of non-biological sample matrices with the results of routine analyses being confirmable by HRGC-HRMS.

References

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2. N. Kannan et al, JAOAC, 70, 45, (1987).
3. C.S. Creaser, A.R. Fernandes, S.J. Harrad and E.A. Cox, Chemosphere (1990) (in press).
4. C. Rappe, Chemosphere 18, 17, (1989).
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6. A.R. Fernandes, PhD Thesis, University of East Anglia (1988).

Table 2
Summary of Validation Data

1. PCDDs and PCDFs

Recovery		Precision (Cov)		Limit of Detection
Range	Mean	Range	Mean	
67-110%	83%	4-13.7%	8.6%	5pG-20pG (LRMS)

2. PCBs

88-96%	93%	4.8-12.6%	8.05%	1pG
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Table 3
Levels of Analytes Determined

1. PCDDs and PCDFs [⊙]

Analyte	Sample Matrix		
	Incinerator stack effluent sewage sludge	Incinerator stack effluent domestic refuse	Incinerator stack effluent bituminous coal
2,3,7,8-T ₄ CDD	0.08 (0.08)	0.64 (0.64)	n.d. (0)
1,2,3,7,8-P ₅ CDD	0.51 (0.26)	5.64 (2.82)	0.003 (0.0015)
1,2,3,4,7,8-H ₆ CDD	0.67 (0.07)	7.09 (0.71)	0.003 (0.0003)
1,2,3,6,7,8-H ₆ CDD	1.21 (0.12)	15.61 (1.56)	0.003 (0.0003)
1,2,3,7,8,9-H ₆ CDD	0.91 (0.09)	10.77 (1.06)	n.d. (0)
1,2,3,4,6,7,8-H ₇ CDD	18.63 (0.20)	167 (1.67)	0.030 (0.0003)
OCDD	80.54 (0.08)	410 (0.41)	0.025 (0)
2,3,7,8-T ₂ CF	0.62 (0.06)	5.73 (0.57)	0.012 (0.0012)
1,2,3,7,8-P ₂ CF	0.69 (0.04)	9.33 (0.47)	0.020 (0.001)
2,3,4,7,8-P ₂ CF	1.32 (0.66)	13.9 (6.95)	0.021 (0.011)
1,2,3,4,7,8-H ₂ CF	2.02 (0.20)	20 (2.0)	0.022 (0.0022)
1,2,3,6,7,8-H ₂ CF	1.84 (0.18)	18.4 (1.84)	0.018 (0.0018)
1,2,3,7,8,9-H ₂ CF	6.94 (0.58)	4.36 (0.44)	n.d. (0)
2,3,4,6,7,8-H ₂ CF	15.5 (1.55)	48 (4.8)	0.020 (0.0020)
1,2,3,4,6,7,8-H ₂ CF	3.4 (0.03)	106 (1.06)	0.053 (0.0006)
1,2,3,4,7,8,9-H ₂ CF	n.d. -	12.6 (0.13)	0.024 (0.0002)
OCDF	n.m. -	-	n.d. (0)

2. PCBs [⊙]

Analyte	Fragmentiser residue	Sample Matrix		
		Sewage sludge	Recyclable metals	Domestic refuse
2,4,4'-T ₂ CB	880	11200	25	35
2,5,2',5'-T ₂ CB	340	6000	16	104
3,4,3',4'-T ₂ CB	33	580	2.7	8
2,4,5,2',5'-P ₂ CB	230	6160	8.3	180
3,4,8,3',4'-P ₂ CB	n.d.	27	n.d.	n.d.
2,3,4,2',4',5'-H ₂ CB	68	2380	5.2	123
2,4,6,2',4',5'-H ₂ CB	59	1690	3.4	79
3,4,6,3',4',5'-H ₂ CB	n.d.	n.d.	n.d.	n.d.
2,3,4,5,2',4',5'-H ₂ CB	17	400	1.2	15

⊙ Levels in ng m⁻³ (2,3,7,8-T₄CDD equivalents)

n.d. - not detected

⊙ Levels in µg kg⁻¹

n.m. - not measured