Quantitative Analysis of Organic Trace Compounds by Isotope Dilution: Formation of the Non-*ortho* PCBs 77, 126, 169 during Incineration.

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Abstract

An analytical method establishing the concentration of PCDDs, PCDFs, non-*ortho* PCBs, total PCBs, PAHs, chlorobenzenes and chlorophenols of incineration samples is presented. As an example the levels of the non-*ortho* PCBs 77, 126, 169 on fly ash and the formation parameters of these compounds in a pilot incinerator are reported.

Introduction

Incineration of municipal waste, industrial waste and industrial processes involving chlorine and elevated temperatures are known sources for the emission of organic trace compounds. Monitoring the emission of chlorinated compounds in general only PCDDs and PCDFs are taken in consideration. Quantitatively information about suspected precursors (PAHs, chlorophenols, chlorobenzenes) and about other toxic compounds (non-*ortho* PCBs) is often not reported. In order to gain more information an analytical method quantitatively establishing the concentrations of a large number of organic trace compounds is a necessity. In this paper such a method, which simultaneously quantitatively establishes the amounts of PCDDs, PCDFs, non-*ortho* PCBs, total PCBs, PAHs, chlorobenzenes and chlorophenols, is presented. This method was applied in a study on the formation of PCDDs/PCDFs using a pilot incinerator. This pilot incinerator, the experimental design as well as the results for PCDDs and PCDFs where described elsewhere[1], results concerning chlorobenzenes and PAHs and new experiments with the pilot incinerator are presented in this issue[2,3].

As an example, results concerning the formation and occurrence of the non-ortho PCBs 77, 126 and 169 are discussed. Non-*ortho* PCBs are known to be formed during the incineration of municipal waste[4,5] but quantitative results have not yet been reported. This thermal formation as well as metabolism could be one of the reasons why PCB level in humans[6] and fish[7] have unsuccessfully been related to commercial PCB mixtures like Arochlor or Clophen by multivariate statistical methods (PLS, PCA).

Material and methods

The clean up and sample preparation is an extension of earlier presented methods[8] and a scheme of this clean up is given in figure 1. The following labelled ^{13}C spikes were used in the PCB analysis: ^{13}C PCB 77, ^{13}C PCB 126, ^{13}C PCB 169, ^{13}C 1,2,3,7,8-PeCDF.

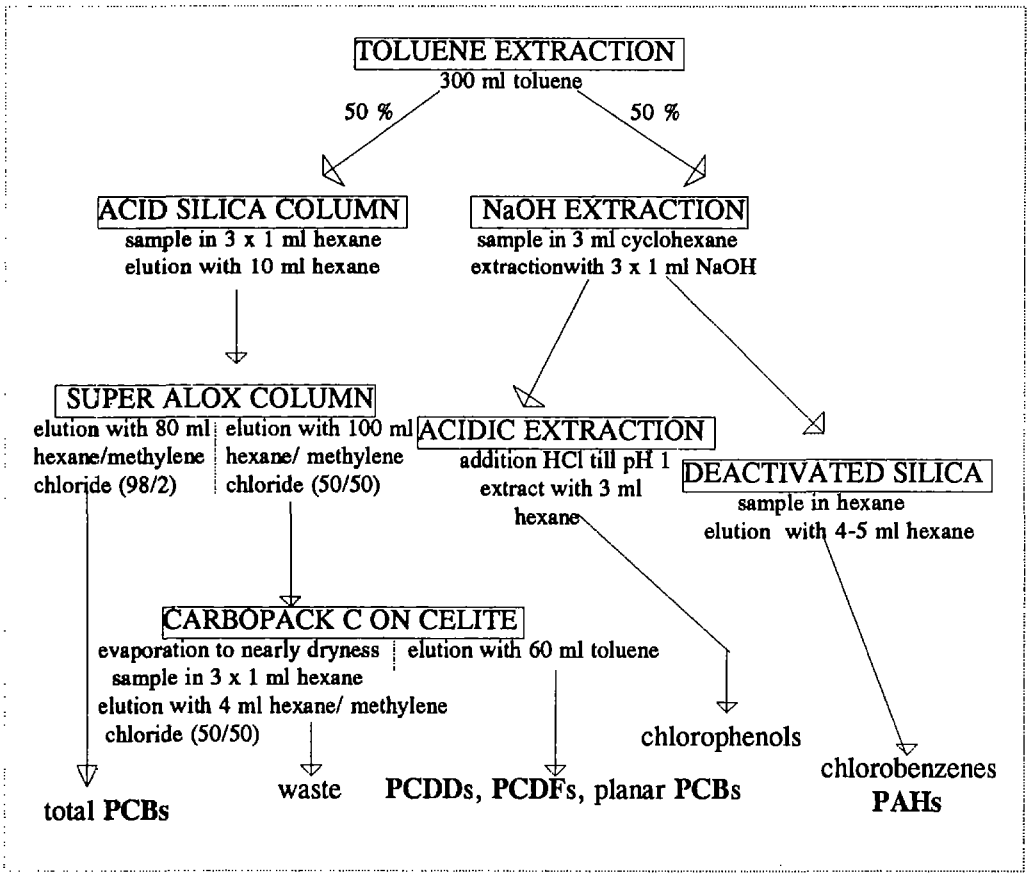

Figure 1. Scheme of the sample pre treatment and clean up.

With regard to the analysis of the non-*ortho* PCBs, after the sample preparation and clean up the samples were analysed on a HRGC/HRMS (VG 70 250) using non polar Rtx-5 GC-column, operating the MS at a resolution of 5000. The following masses were monitored using the selective ion mode to acquire data: 291.92, 293.92, 303.96, 325.88, 327.88, 337.92, 351.90, 359.84, 361.84, 371.88, 393.80, 395.80. These masses represent the native ^{12}C (M^+, M^++2), the ^{13}C spike (M^+) and the recovery spike 1,2,3,7,8-PeCDF ^{13}C (M^+) molecular ions. The analyses of PCDds and PCDFs were preformed using a polar Rt 2330 GC-column.

Results and discussion

Planar PCBs on fly ash

The results for the analysis of two fly ash for the non-*ortho* PCBs IUPAC no. 77, 126 and 169 are shown in table 1. Recoveries of the ^{13}C spikes over 50% were achieved using the sample pre treatment and clean up as described in figure 1.
Further more the results show that the three non-*ortho* PCBs account for a considerable percentage of the TEQ value as the TEF factors as proposed by Safe[9] are used in the calculation.

Table 1 Levels of the non-ortho PCBs 77,126,169 and PCDD/PCDFs on fly ash.

	sample 1		sample 2			
	concentration*	recovery	concentration*	recovery	N-TEF**	I-TEF***
PCB congener						
77	788	68 %	479	52 %	0.0005	0.01
126	982	68 %	625	52 %	0.1	0.1
169	289	60 %	205	62 %	0.01	0.05
PCDD/PCDF congeners						
2,3,7,8-TCDF	250	60 %	230	68 %	0.1	0.1
2,3,7,8-TCDD	80	65 %	70	65 %	1	1
1,2,3,7,8-PeCDF	770		750		0.01	0.05
2,3,4,7,8-PeCDF	500	60 %	500	71 %	0.5	0.5
1,2,3,7,8-PeCDD	310	70 %	300	80 %	0.5	0.5
1,2,3,4,7,8-HxCDF	520		790		0.1	0.1
1,2,3,6,7,8-HxCDF	670	35 %	710	65 %	0.1	0.1
1,2,3,7,8,9-HxCDF	20		70		0.1	0.1
2,3,4,6,7,8-HxCDF	1030		710		0.1	0.1
1,2,3,4,7,8-HxCDD	300		330		0.1	0.1
1,2,3,6,7,8-HxCDD	460	55 %	450	62 %	0.1	0.1
1,2,3,7,8,9-HxCDD	420		450		0.1	0.1
1,2,3,4,6,7,8-HpCDF	2300		2630		0.01	0.01
1,2,3,4,7,8,9-HpCDF	[1]	[1]	250	115 %	0.01	0.01
1,2,3,4,6,7,8-HpCDD	3410	80 %	3250	123 %	0.01	0.01
OCDF	<25		40		0.001	0.001
OCDD	5370	87 %	5280	112 %	0.001	0.001
I-TEQ (only p-PCB)*	121		78			
I-TEQ (total)*	1071		1028			
percentage	11 %		8 %			
N-TEQ (only p-PCB)	102		66			
N-TEQ (total)*	1022		986			
percentage	10 %		10 %			

* pg/g
[1] not analysed
** proposed Nordic TEF values
*** proposed ref. 9

Formation planar PCBs

In the study on the formation of planar PCBs with the pilot incinerator, a reduced factorial design was used to screen the influence of the following 6 parameters: bed temperature, oxygen concentration, concentration of HCl in the flue gas, concentration of H_2O, residence time in the cooling section and flue gas temperature at the sampling point. The residence time and the temperature in the cooling zone were found to have the most influence on formation the non-*ortho* PCBs 77, 126, 169. These are the same parameters that were found to be most important in the formation PCDD/PCDFs and chlorobenzenes[2].

Conclusions

Quantification by isotope dilution after a balanced sample pre treatment and clean up offers the possibility of simultaneously establishing the concentration of PCDDs, PCDFs, total PCBs, non-*ortho* PCBs, PAHs, chlorophenols and chlorobenzenes in incineration samples

The non-*ortho* PCBs 77, 126, 169 are formed during incineration of municipal waste and account for up to 11 % of the total toxic equivalents calculated for fly ash samples.

The same parameters as involved in the formation of PCDD/PCDFs with the pilot reactor are of importance in the formation of the non-*ortho* PCBs 77, 126, 169. These parameters are the residence time and the temperature in the cooling zone.

References

1. Fängmark I., Marklund S., Rappe C., Strömberg B., Berge N. Use of a synthetic refuse in a pilot combustion system for optimizing dioxin emission, part II. *Chemosphere 1992, 23, 1233-1243.*
2. Fängmark I., van Bavel B., Marklund S., Rappe C., Strömberg B., Berge N. Formation of PCDD, PCDF, PCBz, PAH and PCB in a pilot incinerator. *Short Papers, Dioxin '92, this issue.*
3. Fängmark I., Marklund S., Rappe C., Strömberg B., Berge N. The influence of post combustion temperature profile on the formation of PCDDs and PCDFs in a pilot incinerator. *Short papers Dioxin '92, this issue.*
4. Ballschmiter K., Schäfer W., Buchert H. Isomer-specific identification of PCB congeners in technical mixtures and environmental samples by HRGC-ECD and HRGC-MSD. *Fresenius Z. Anal. Chem. 1987, 326, 253-257.*
5. Ballschmiter K., Niemczyk R., Schäfer W., Zoller W. Isomer-specific identification of poychlorinated benzenes (PCBz) and -biphenyls (PCB) in effluents of municipal waste incineration. *Fresenius Z. Anal. Chem. 1987. 328, 583-587.*
6. Luotamo M., Aitio A., Wold S. Serum Polychlorinated Biphenyls: Quantification and Identification of Source of Exposure by the SIMCA Pattern Recognition Method. *Chemometrics and Intelligent Laboratory Systems 1988, 4, 171-181.*
7. Schwartz T.R., Stalling D.L. Chemometric Comparison of Polychlorobiphenyls Residues and Toxicologially Active Polychlorobiphenyl Congeners in the Eggs of Forster's Terns (*Sterna fosteri*). *Arch. Environ. Contam. Toxicol. 1991, 20 183-199.*
8. Marklund S. Dioxin emision and environmental imission. *Thesis University of Umeå 1990.*
9. Safe S. Polychlorinated Biphenyls (PCBs), Dibenzo-p-Dioxins (PCDDs), Dibenzofurans (PCDFs), and Related Compounds: Environmental and Mechanistic Considerations Which Support the Development of Toxic Equivalency Faktors (TEFs). *CRC Crit. Rev. Toxicol. 1990, 21, 51-88.*