

Isomerspecific separation and determination of chlorinated compounds by High Resolution Gas Chromatography (HRGC) and Low Resolution Negative Chemical Ionisation Mass Spectrometry (LRNCIMS).

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1. INTRODUCTION

It is possible and acceptable from the toxicologic point of view to evaluate equivalents constants (TEFs) for co-planar PCBs related to 2,3,7,8-TCDD<sup>1</sup>. TEFs values for three co-planar PCB are presented in Table 1.

Table 1.

TEFs values for three co-planar PCB according to Safe (1990).

PCB compound	TEF value
<sup>13</sup> C #77 3,3',4,4' - Tetra CB	0,01
<sup>13</sup> C #126 3,3',4,4',5 - Penta CB	0,1
<sup>13</sup> C #169 3,3',4,4',5,5' - Hexa CB	0,05

PCB are included in the swedish protocol for the analysis of the sewage sludge<sup>2</sup>. We have developed a clean-up and a mass spectrometric procedure for determination of the co-planar PCB together with PCDD/PCDF and we have completed the swedish protocol with analysis of the PCDD/PCDF.

No single column GC/ECD system is able to resolve non-ortho PCB from PCBs with one chlorine atom in an ortho-position. A multidimensional GC system can solve the problem of the separation successfully, but such a system is less suitable for the routine work. Gas chromatographic resolution of the co-planar isomers can be achieved on the SB-Smectic column. SB-Smectic is a liquid polysiloxane phase and its selectivity is based on molecular geometry, related to size and shape of the solute rather than partial pressure and adsorptive characteristics. A simple solution to the separation problems is to use a good general purpose GC column and a mass spectrometer as detector.

2. EXPERIMENTAL

Sample preparation procedure is based on classical destructive clean-up with fuming Sulphuric acid, followed by column chromatography on Silica gel.

An extract dissolved in 2 ml of 5% Chlorobutane in *n*-Hexane in a test tube is treated with a solution of 10% fuming Sulphuric Acid in concentrated Sulphuric Acid. The phases are thoroughly mixed by vortexing and sonication. Following centrifugation, the acid is solidified by immersion in liquid nitrogen. The organic layer is collected using a pasteur pipett. The acid layer is subsequently thawed and reextracted with 2 ml of 5% Chlorobutane in *n*-Hexane to ensure good recoveries. For highly impure extracts originating from sludge or soil, the whole procedure is repeated to remove remaining interfering aromatic matrix components.

The combined extracts are subsequently passed through a silica gel column using *n*-Hexane as a mobile phase to remove traces of sulfonating acid and remaining polar components from the matrix.

For sludge extracts, which usually contain large quantities of long chain hydrocarbons, the solvent of the extract is exchanged to Acetonitrile. The Acetonitrile solution is passed through a column filled with octadecylsilane silica, that retains hydrophobic hydrocarbons.

Low Resolution Negative Chemical Ionisation Mass Spectrometry is used for detection and quantification of the PCBs because of its higher sensitivity and good selectivity.

Two different chromatographic systems are operated:

**Column 1:**  
 25mx0.20mmx0.15 $\mu$ m SB-SMECTIC,  
 Lee Sci., USA  
 Carrier: 50 kPa Helium  
 Inj.vol: 2 $\mu$ l Splitless  
 Inj.temp: 280 $^{\circ}$ C  
 Init.temp: 155 $^{\circ}$ C  
 Init.time: 3.0 min  
 Prog: 4 $^{\circ}$ C/min  
 Final temp: 250 $^{\circ}$ C  
 Final time: 45 min

**Column 2:**  
 60mx0.32mmx0.25 $\mu$ m, DB-5 J&W, USA  
 Carrier: 100 kPa Helium  
 Inj.vol: 2 $\mu$ l Splitless  
 Inj.temp: 290 $^{\circ}$ C  
 Init.temp: 125 $^{\circ}$ C  
 Init.time: 2.0 min  
 Prog: 4 $^{\circ}$ C/min  
 Final temp: 300 $^{\circ}$ C  
 Final time: 45 min

The following mass spectrometric conditions are used during analysis:

Ionisation method:	Negative Chemical Ionisation (NCI)
Reaction gas:	Methane
Ion source temp:	130 $^{\circ}$ C
Ion source press:	0.95 torr
Electron energy:	100 eV
Multiplier voltage:	2500 V
Ions used during scanning in [amu]:	255.9, 257.9, 289.9, 291.9, 301.9, 303.9, 325.9, 327.9, 333.9, 335.9, 337.9 339.9, 359.9 361.9, 371.9, 373.9, 393.9 and 395.9

### 3. RESULTS

The efficiency of the described method have been proved in the large international intercomparison test<sup>3</sup> with good results. The subject of analysis were samples of fish oil. Recovery of Internal Standards after the clean-up procedure, received in the intercomparison study are presented in Table 2.

Table 2.

Recovery of Internal Standards after the clean-up procedure, received in the intercomparison test (in percent). Each value is a mean value for five different determinations.

PCB compound	Sample #1	Sample #2	Sample #3
<sup>13</sup> C #77	86	73	81
<sup>13</sup> C #126	81	73	77
<sup>13</sup> C #169	81	69	78

Relative Standard Deviation for determination of three PCB compounds have been investigated and is presented in Table 3. Each value represents five different determinations.

Table 3.

Relative Standard Deviation for determination of three PCB compounds.

PCB compound	Sample #1	Sample #2	Sample #3
<sup>12</sup> C #77	RSD=2,4%	RSD=3,9%	RSD=1,4%
<sup>12</sup> C #126	RSD=4,6%	RSD=6,6%	RSD=3,6%
<sup>12</sup> C #169	RSD=3,1%	RSD=4,7%	RSD=3,1%

About hundred samples of sewage sludge have been investigated by the method. Levels of the PCB #28, #52, #101, #118, #138, #153 and #180, have been determined according to Method DIN 51527<sup>4</sup>. PCB determinations in sewage sludge for several samples have been completed with analysis of PCDDs and PCDFs. After the determinations of both PCBs and PCDDs/PCDFs the toxic equivalent values have been calculated. The contribution of PCB to the total TEF values is shown in Table 4.

Table 4.

Total TEFs values (PCDD/PCDF + PCB) determined in the sewage sludge [pg/g].

Equivalent	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5
Eadon Equiv	16	0,99	1,8	4,4	1,3
PCB acc. to Safe	22	16	5,4	3,1	18
TEF <sup>Eadon+Safe</sup>	38	17	7,2	7,5	19

#### 4. CONCLUSIONS

I. Concentrations of co-planar PCB, ie.: #77, #126 and #169 are considerable enhanced in the sewage sludge compared with normal PCB profiles<sup>5</sup>.

II. Levels of tetra-, penta-, and hexa chlorinated PCDD/PCDFs do not make a significant contribution to the total TEF value in the sewage sludge samples.

III. Co-planar PCBs are the most significant contributors to the TEF value in the sewage sludge samples investigated in this series<sup>6</sup>.

#### REFERENCES:

1. Safe S. Polychlorinated Biphenyls (PCBs), Dibenso-p-Dioxins (PCDDs), Dibensofurans (PCDFs) and related compounds: Environmental and mechanistic considerations which

- support the development of toxic equivalency factors (TEFs). *Crit. Rev Toxicol*, 21, pp 51-88, (1990).
2. Swedish Environmental Protection Agency. Rapport 3829. *Sampling and analytical methodology for sewage sludge*. (in Swedish). ISBN 91-620-3829-X, ISSN 0282-7298.
  3. Swedish Environmental Protection Agency, Special Analytical Laboratory: *Intercomparison of non-ortho and 1-ortho chlorine substituted chlorobiphenyls*. S-171 85 Solna, Sweden, March 1991.
  4. Deutsche Norm. DIN 51527: *Bestimmung polychlorierter Biphenyle (PCB)* (in German), May 1987.
  5. Kannan N, Tanabe S, Wakimoto T, Tatsukawa R, Coplanar polychlorinated biphenyls in Aroclor and Kanaclor mixtures. *J. Assoc. Off. Anal. Chem*, 70, pp 451-454, (1987).
  6. Warman K, Report on distribution of chlorinated aromatics around a remote-located industrial site. *Chemosphere*, 20, Nos 10-12, pp 1511-1516, (1990).