DETERMINATION OF CONGENER-SPECIFIC CHLORONAPHTHALENES USING COMPREHENSIVE TWO-DIMENSIONAL GC/QMS

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Introduction

Chloronaphthalenes (CNs) are primarily industrial chemicals[1] and they became popular worldwide in 1910–1970s[2,3]. CNs have been mainly used in electromagnetic equipments including capacitors, transformers, and in cables. Halowax is a trade name for technical CN formulations manufactured in the past by Koppers Co. (USA). Thereafter, other formulations of a similar nature were also manufactured[1–5]. On the other hand, since CNs are persistent and bioaccumulative chemicals, they became widespread globally and have been reported as food and human body contaminants[6–8].

CNs can contain from one to eight chlorine atoms per naphthalene molecule and form a complex mixture of 75 CN congeners. Interestingly, it was well known that characterization and biomagnification of each congener were different. Among the 75 CN congeners, CN congeners such as #1, #2, #5/#7, #20, #36/#45, #52/#60, #66/#67, and #73 are the predominant ones in flue gases[9]. In sea eagles and cormorants, CN congeners such as #42, #52/#60, #54, #58, #61, #64/#68, #66/#67, #69, and #71/#72 are those that are the most enriched ones[8]. Several CN congeners are important when evaluating fingerprint that aimed to understand their sources and persistency and to perform risk assessment. Highly desired are results providing information on the hard to separate pentachloronaphthalenes (nos. #52/#60) and hexachloronaphthalenes (nos. #66/#67).

Our idea was to examine the possibility of congener-specific determinations of some tightly co-eluting CNs by comprehensive two-dimensional GC with the aid of a quadrupole mass spectrometer (GC × GC/QMS). A GC × GC/QMS determination is an analytical tool recently developed and that provides some advantages that help to separate and identify components of very complex matrices when compared to results from a single-dimensional GC/MS[10–12]. Here the focus is on tetrachloronaphthalenes (TeCNs), pentachloronaphthalenes (PeCNs), and hexachloronaphthalenes (HxCNs) of Halowaxes.

Materials and methods

Technical CN formulations (Halowaxes 1000, 1001, 1014, and 1051) were from AccuStndard in the USA. Other Halowaxes (1001, 1014, and 1051) were from Analabs in the USA. Infinity Pure grade methanol used for preparation was from Wako Pure Chemical Industries in Japan.

GC × GC/QMS determinations were performed using a 6890 GC equipped with a 5973 QMS (Agilent Technologies, USA)[11,12]. GC columns used were a combination of Rt-β DEXcst (30 m × 0.25 mm i.d., 0.25 μm film thickness, Restek, USA) and DB-WAX (2 m × 0.1 mm i.d., 0.1 μm film thickness, J&W Scientific, USA). Column oven temperature was programmed from 120 °C (1 min) to 230 °C at a rate of 1 °C/min, with a final hold time of 79 min, and total run time was 190 min (program 1). To separate co-eluting congeners properly, another column oven temperature program was performed [program 2, 160 °C (1 min) to 230 °C at a rate of 0.5 °C/min, with a final hold time of 64 min, and total run time was 205 min]. Injection was performed by cooled injection system, and inlet temperature was programmed from 40 °C (0.20 min) to 230 °C at a rate of 12 °C/min, with a final hold time of 10 min. Pressure was 683 kPa for program 1 and 635 kPa for program 2, respectively. Hot jet gas temperature was programmed from 200 °C to 300 °C at a rate of 1 °C/min. Hot gas duration time was 350 m seconds. Modulation period was 10 seconds for program 1 and 8 seconds for program 2, respectively. Helium was used as the carrier gas. Quadropole MS was operated in scan mode (*m/z*: 150–420) with 21.28 scans/sec using EI ionization. Peak identification was supported by referring to published data[4,6,7,13].

Results and discussion:

-*TeCNs to HxCNs*- Two capillary columns of different polarity that were applied in GC × GC/QMS enabled separation of many co-eluting CNs including 22 of TeCN, 14 of PeCN, and 10 of HxCN.

For TeCNs, 20 CN congeners were detected in Halowaxes, and 10 were identified. Interestingly, separation of TeCN congeners #27/#39, #28/#36, and #33/#34, that are co-eluting when separating by single-dimension GC using DB-5 or DB-17 columns, was achieved completely (Fig. 1). Table 1 shows the numbers of CNs separated, detected, and identified by previous reports[14-17] and this study. Developed method enabled determination of the largest number of congeners among TeCNs. Especially, TeCN congeners #33/#34, which are among the most abundant of TeCNs in Halowaxes, could be separated for the first time. These results suggest that the developed method has a superior capability compared to previous attempts. Unfortunately, numbers of identified TeCN congeners were not enough because of lack of authentic compounds as standards.
For PeCNs, 13 CN congeners were detected and identified. Among them, PeCN congeners #52/#60 were typical ones that require a complete separation. From the results in this study, separation of PeCN congeners #52 and #60 was achieved completely (Fig. 1). However, only PeCN congener #55 remained undetected because of very low concentrations present. This result suggests that the method developed here accomplished the resolution of all the 14 PeCN congeners similar to the method from reports by Helm *et al.*[13,17].
For HxCNs, 10 CN congeners were separated and identified. Similarly to PeCN congeners #52/#60, HxCN congeners #64/#68, #66/#67, and #71/#72 were desired a complete separation. In this study, separation of these CN congeners was also achieved (Fig. 1) but without #64/#68 and #71/#72 using a HPLC connected with a PYE-column[4,6,7].
Other CN compounds such as monochloro- and heptachloronaphthalene congeners, which have 2 CN congeners in each, were separated completely as well as PeCNs and HxCNs. In case of dichloro- and trichloronaphthalenes (DiCNs and TriCNs), 8 and 10 CN compounds were detected, respectively (in principle, there are respectively 10 of DiCN and 14 of TriCN). Eventually, among the 75 CN congeners, 66 compounds have already been determined by GC × GC/QMS. Namely, congener-specific determination of dominant CN congeners among TeCNs to HxCNs was achieved without clean-up using multi-layer column and HPLC. Actually, we are attempting to identify the members of lowest chlorinated compounds among CNs of Halowaxes.

-*Comparison of congener-specific data on Halowax mixtures*- Profiles of CNs in Halowax were often described, while only in a few reports a real congener-specific data are available. Then, by using the developed method, the congener-specific data of TeCNs to HxCNs in several Halowaxes could be examined.
TeCN congener #33 in Halowaxes 1001 and 1014 was at approximately twofold greater concentration than TeCN congener #34 (Fig. 2). Moreover, TeCN congener #46 in Halowaxes 1001 and 1014 provided by AccuStandard was greater than TeCN #VIII (probably TeCN congener #38), while TeCN #VIII in Halowaxes 1001 and 1014 provided by Analabs was at greater concentration than TeCN congener #46. This might be because of batch to batch differences in CN compositions[18–19].
PeCN congener #59 was the predominant one in Halowaxes 1001 and 1014[20] from both companies. Moreover, PeCN congener #60 in all of the measured Halowaxes was more abundant than the PeCN congener #52 as well as the reports by Helm *et al*.[13,17]. In addition, the ratio of PeCN congeners #52 and #60 in Halowax 1001 was larger than that in Halowax 1014. This discussion regarding each of PeCN congeners #52 and #60 will provide new understanding of CNs.
HxCN congener #71 was the predominant one in Halowaxes 1014 and 1051 from both companies.
From the result discussed above, fingerprint of CNs seems to become reliable using congener-specific data such as PeCN congeners #52 and #60. Furthermore, toxic equivalents calculated by 2,3,7,8-tetrachlorodibenzo-*p*-dioxin relative potency factors estimated for specific CN congeners such as the HxCN congeners #66 and #67 may be re-assessed reliably. Indeed, congener-specific data of TeCN congeners is important and good advantages because few reports on these data are available to our knowledge. Therefore, these congener-specific data in this study are obviously useful for reliable fingerprint and risk assessment in not only technical CN formulations but also various environmental matrices.

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References:
1. Falandysz J. (1998); *Environ. Pollut*. 10: 77–90

2. Paasivirta J. ed. (2000); *New Types of Persistent Halogenated Compounds* – Jakobsson E, Asplund L. *Polychlorinated naphthalenes (PCNs)* –: 97–126, Springer-Verlag, Berlin
3. Falandysz J. (2003); *Food Add. Contam*. 21: 995–1014
4. Yamashita N, Taniyasu S, Hanari N, Horii Y, Falandysz J. (2003); *J. Environ. Sci. Health* A38: 1745–59
5. Falandysz J, Kawano M, Ueda M, Matsuda M, Kannan K, Giesy JP, Wakimoto T. (2000); *J. Environ. Sci. Health* A35: 281–98
6. Horii Y, Falandysz J, Hanari N, Rostkowski P, Puzyn T, Okada M, Amano K, Naya T, Taniyasu S, Yamashita N. (2004); *J. Environ. Sci. Health* A39: 583–605
7. Hanari N, Kannan K, Horii Y, Taniyasu S, Yamashita N, Jude DJ, Berg MB. (2004); *Arch. Environ. Contam. Toxicol*. 47: 84–93
8. Falandysz J, Strandberg B, Strandberg L, Bergqvist PA, Rappe C. (1997); *Sci. Total. Environ*. 204: 97–106
9. Takasuga T, Inoue T, Ohi E, Kumar KS. (2004); *Arch. Environ. Contam. Toxicol*. 46: 419–31
10. Marriott PH, Dhellie R. (2002); *TrAC Trends Anal. Chem*. 21: 573–583
11. Ieda T, Horii Y, Petrick G, Yamashita N, Ochiai N, Kannan K. (2005); *Environ. Sci. Technol*. 39: 7202–7
12. Lukaszewicz E, Ieda, T, Horii Y, Yamashita N, Falandysz J. (2007); *J. Environ. Sci. Health* A42: 1607–14
13. Helm PA, Jantunen LMM, Bidleman TF, Dorman FL. (1999); *J. High Resol. Chromatogr*. 22: 639–43
14. Horii Y, Okada M, Amano K, Hanari N, Taniyasu S, Yamashita N. (2002); *Bunseki Kagaku* 51: 1009–18 (in Japanese)
15. Haglund P, Jakobsson E, Asplund L, Athanasiadou M, Bergman A. (1993); *J. Chromatogr*. 634: 79–86.
16. ISO/CD 16780; *Water quality - Determination of polychlorinated naphthalenes (PCN) - Method using gas chromatography (GC) and mass spectrometry (MS)*: ISO publication, Geneva
17. Helm PA, Gewurtz SB, Whittle DM, Marvin CH, Fisk AT, Tomy GT. (2008); *Environ. Sci. Technol*. 42: 1024–31
18. Falandysz J, Nose K, Ishikawa Y, Lukaszewicz E, Yamashita N, Noma Y. (2006); J. Environ. Sci. Health A41: 291–301
19. Falandysz J, Nose K, Ishikawa Y, Lukaszewicz E, Yamashita N, Noma Y. (2006); J. Environ. Sci. Health A41: 2237–55
20. Helm PA, Bidleman TF. (2003); *Environ. Sci. Technol*. 37: 1075–82

Table 1 Comparison to number of detected congeners and identified separated congener on tetrachloro- to hexachloronaphthalenes from previous reports and this study

	Number of detected congeners	Identified separated congener	Reference
Tetrachloronaphthalene	14	#27, #35, #38, #39, #40, #41, #42, #44, #46, #47	Horii 2002
	14	#33, #42, #47	Haglund 1993
	-	#27, #28, #36, #42, #46, #48	ISO/CD 16780
	20	#27, #28, #31, #33, #34, #36, #39, #42, #46, #48	This study
Pentachloronaphthalene	11	#49, #50, #51, #53, #56, #57, #58, #59, #61, #62	Horii 2002
	12	#52	Haglund 1993
	14	all congeners were identified	Helm 1999
	-	#49, #50, #53, #54	ISO/CD 16780
	13	except #55	This study
Hexachloronaphthalene	6	#63, #65, #69	Horii 2002
	6	#63	Haglund 1993

	10	all congeners were identified	Helm 1999
	-	#63, #69, #70	ISO/CD 16780
	10	all congeners were identified	This study

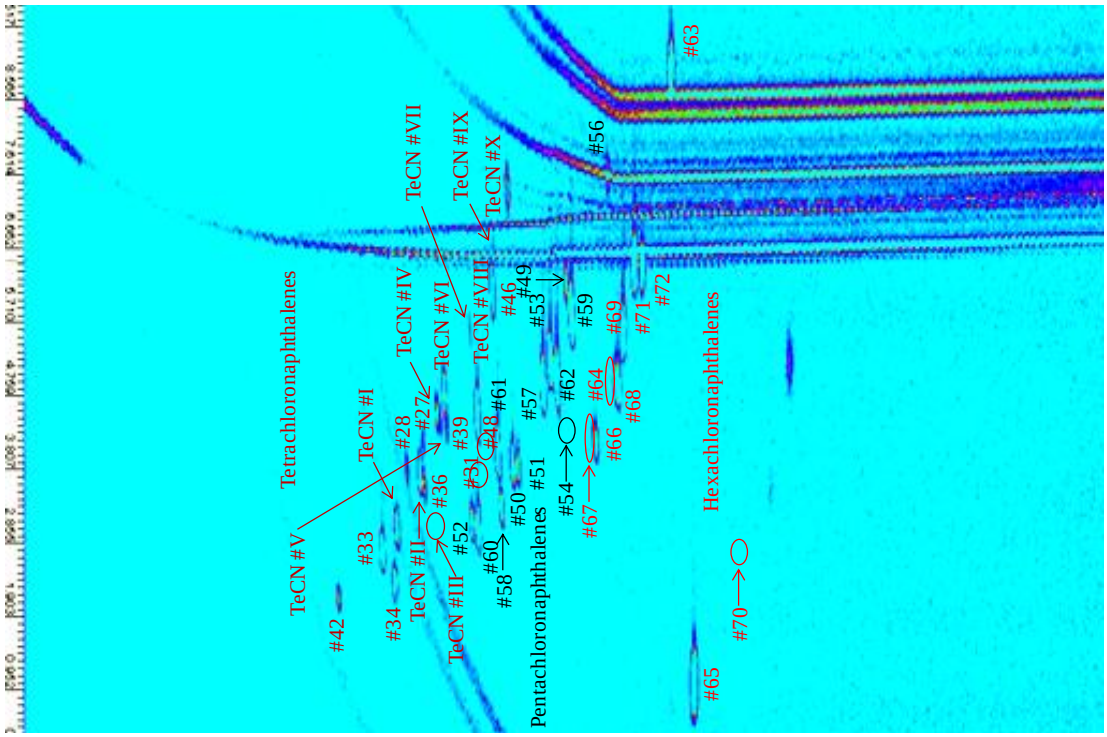

Fig. 1 GC × GC/QMS chromatogram of tetrachloro- to hexachloronaphthalenes of Halowax equivalent mixture separated on Rt-β DEXcst as the 1st and DB-WAX as the 2nd dimension columns

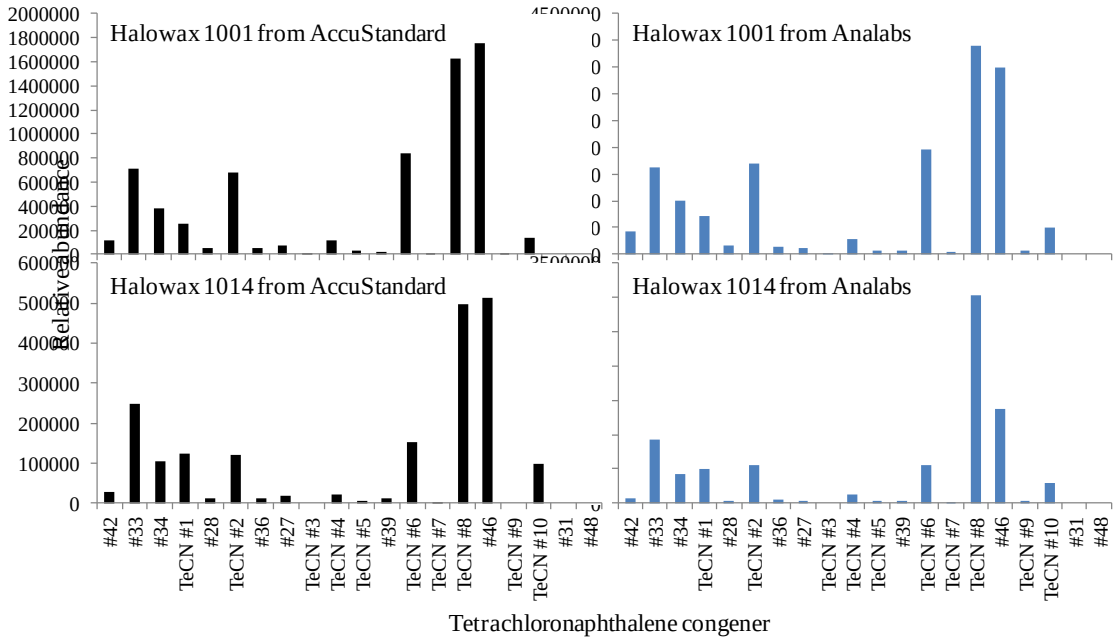

Fig. 2 Tetrachloronaphthalene congener profiles in Halowaxes 1001 and 1014 from AccuStandard and Analabs