

Composition of Chloronaphthalene Isomers and Congeners in Technical PCN Formulations of the Halowax Series

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Abstract

The composition of chloronaphthalene isomers and congeners was determined in Halowax 1000, 1001, 1099, 1013, 1014 and 1051 technical formulations and in Equi-Halowax mixture. The congeners of chloronaphthalene in the Halowax formulations were separated, identified and quantified using DB-5 capillary column gas chromatography and low resolution (1000 amu) mass spectrometry (HRGC/LRMS). Chloronaphthalenes such as 2,3-DiCN (no. 10), 1,3,6-TrCN (no. 20), 1,2,3,6-TeCN (no. 29), 1,2,3,8-TeCN (no. 31), 1,3,6,7-TeCN (no. 44) and 1,2,3,6,7,8-HxCN (no. 70) were absent in the Halowax formulations. 1,2,4,5,7-PeCN (no. 58) is only a minor constituent. Two trichloronaphthalenes, *i.e.* 1,2,3-TrCN (no. 13) and 1,3,8-TrCN (no. 22) were present in very small amount while two others, *i.e.* 1,6,7-TrCN (no. 25) and 2,3,6-TrCN (no. 26) are absent or coelute with 1,2,7-TrCN (no. 17). Many other congeners dominated in one or more of the particular Halowax formulations. Normalized pattern (DB-5) of PCNs is presented for all technical Halowax formulations and for Equi-Halowax mixture.

Keywords: Polychlorinated naphthalenes, chloronaphthalenes, PCNs, CNs, Halowax.

Introduction

Polychlorinated naphthalenes (PCNs) are chemically inert and lipophilic substances, which were introduced to market as industrial chemicals shortly before the production of polychlorinated biphenyls (PCBs) in 1929. Koppers Company, Inc. was a greatest producer of technical chloronaphthalenes in the USA until 1977. The Chemisphere company manufactured PCNs in the USA until 1980 (1, 2). Polychlorinated naphthalenes were produced in the United States under the trade names such as Halowax (Koppers Co.), N-Oil and N-Wax (Halochem; former Farbenindustrie), while in Europe as Nibren Wax (Bayer AG, former Farbenindustrie,

former Farbenindustrie), while in Europe as Nibren Wax (Bayer AG, former Farbenindustrie, Germany), Seekay Wax (ICI, Great Britain), Clonacire Wax (Prodelec, France) and Cerifal Materials (Caffaro, Italy) (3). The exact quantity of the technical PCN formulations produced worldwide is unknown. The world cumulative output of technical PCNs is roughly assessed to be 150 000 tonnes, *i.e.* an equivalent of 10% of PCBs produced (4, 5). The worldwide production of technical PCNs ceased during 1960s ~ 1980s, and products and materials containing these substances were sold or used even after 1980s. For example, technical PCNs were as casting materials in Germany until 1989 (6), in a factory in former Yugoslavia (7), and also recently were found in an old type and still in service electric equipment (cables) (8).

Seventy five congeners of chloronaphthalene containing one to eight chlorine atoms per molecule are theoretically possible. Due to the different congener composition, physical properties of technical PCN mixtures range from mobile liquids to waxes with melting point at 185°C (3). PCNs have physical and chemical properties largely similar to that of PCBs. Those compounds are hydrophobic, have high chemical and thermal stability, good weather resistance, good electrical insulating properties, low flammability and are compatible with other materials. Technical PCN formulations have found numerous industrial applications (1, 9) such as: dielectrics for flame-proofing and insulating, electric and automobile industry as impregnants in capacitors, transformers, cables, wires and conductors, as preservatives in wood, paper and textile industry (for timber preservation, in plywood, impregnation and as coatings); impregnate in paper inlays in gasmasks; additives in engines (gear oil additives and cutting compounds, crank case additives and ingredients in motor tune-up compounds); lubricants for graphite electrodes, separators in batteries; in grinding wheel lubricants; high boiling capacity solvents; heat exchange fluids; dye carriers (dye dispersion) and in dye production; moisture proof sealant for chemically resistant gauge fluids and instrumental seals; temporary binders in the manufacture of ceramic components; casting materials for alloys; refractive index testing materials; additives in rubber products; flame retardant and masking (stop-off) compounds in electroplating.

Since a detailed qualitative and quantitative composition of chlorinated naphthalenes of a particular technical PCN mixture till now remains largely unknown, this study was conducted to provide some basic data of the patterns of PCN congener in Halowax series.

Materials and Methods

Halowax 1000, 1001, 1099, 1013, 1014 and 1051 were from the depository of Environment Protection Agency, Research Triangle Park, USA. A gas-chromatograph (HP 5890 Series II GC) coupled to JEOL JMS-GC MATE (resolution 1,000 amu) were used for the quantification of PCN congeners. A DB-5 fused silica capillary column (60 m x 0.25 mm i.d.) coated with cross-linked 5% diphenyl-95% dimethyl polysiloxane with a film thickness of 0.25 μm was employed for the separation of PCNs. The oven of GC was temperature programmed: 70°C (1 min) \rightarrow rate 5°C/min, 180°C (1 min) \rightarrow rate 4°C/min \rightarrow 280°C (21 min); total run was 70 min. The ion source was operated under electron ionization (EI) conditions at 70 eV, and the MS was tuned in the selected ion monitoring (SIM) mode.

The congeners of chloronaphthalene were identified on the basis of retention times and mass spectrum, and quantified on the basis of molar responses of authentic mono- through octa-CN congeners. Chromatographic data published for Equi-Halowax and the sets of individually synthesized congeners of chloronaphthalene (9, 11, 12, 13) were used to identify elution pattern of mono- through tri-CN's on the DB-5 capillary column, and for tetra- through hepta-CN's the elution pattern was as established in an earlier work (2). The normalized pattern of chloronaphthalenes in Halowax formulations and in an equivalent mixture of Halowax 1031, 1000, 1001, 1099, 1013, 1014 and 1051 (1:1:1:1:1:1:1) (Equi-Halowax) have been made by the manner, that the highest peak of isomer from the particular homologue group is calculated as 1 and the other isomers were normalised as their peak heights comparing with the highest peak of the same homologue group.

Results and discussion

The normalised pattern of PCNs in Halowax formulations and Equi-Halowax is presented in Table 1. There are 67 congeners of chloronaphthalene that can be identified in the technical PCN formulations of the Halowax series. Congeners such as 2,3-DiCN (no. 10), 1,3,6-TrCN (no. 20), 1,2,3,6-TeCN (no. 29), 1,2,3,8-TeCN (no. 31), 1,3,6,7-TeCN (no. 44) and 1,2,3,6,7,8-HxCN (no. 70) were absent in Halowax formulations examined.

Till now all congeners of chloronaphthalene present in technical Halowax formulations have not been separated completely. Some of di-, tri-, tetra-, penta- and hexa-CN's, and depending on the liquid phase used, coelute in pairs or triplicate when analyzed using liquid capillary gas chromatography (2, 3, 9, 11, 12, 14, 15). Because of inadequate resolution, a few di- to hexa-CN congeners were not identified as a separated compounds even during capillary gas chromatography/mass spectrometric separation (Table 1).

Among trichloronaphthalenes, two peaks (Peak nos. 13 and 22; Figure 1) recorded for Halowax 1001 and 1014 are very low and indicate extremely low concentration of these isomers. Based on the available chromatographic characteristics of PCNs (9, 11-13) these two peaks were tentatively identified as 1,2,3-TrCN (no. 13) and 1,3,8-TrCN (no. 22). There are no standards available to confirm or exclude the presence of 1,6,7-TrCN (no. 25) and 2,3,6-TrCN (no. 26) in Halowax mixtures.

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Table 1. Normalised pattern (DB-5) of PCNs in technical Halowax formulation

PCN No.	Structure	Halowax							Mixture
		1031	1000	1001	1099	1013	1014	1051	
Monochloronaphthalenes									
2	2-MoCN	0.0646	0.0735	0*	0	0	0	0	0.105
1	1-MoCN	1	1	1	0*	1	1	0	1
Dichloronaphthalenes									
4	1,3-DiCN	0.0205	0.0154	0.00218	0*	0.00738	0.00849	0	0.0498
5/7	1,4-/1,6-DiCN	1	0.686	1	1	1	1	0	1
6/12	1,5-/2,7-DiCN	0.288	0.193	0.0948	0.0704	0.135	0.139	0	0.229
11/8	2,6-/1,7-DiCN	0.212	0.140	0.104	0.0867	0.110	0.126	0	0.192
3	1,2-DiCN	0.121	0.102	0.0347	0.0268	0.0767	0.0812	0	0.0776
10	2,3-DiCN	0	0	0	0	0	0	0	0
9	1,8-DiCN	0.807	1	0.148	0.149	0.471	0.914	0	0.00912
Trichloronaphthalenes									
20	1,3,6-TrCN	0	0	0	0	0	0	0	0
19/21	1,3,5/1,3,7-TrCN	0.122	0.167	0.131	0.0940	0.0312	0.118	0	0.0948
24	1,4,6-TRCN	1	1	1	1	1	1	0	1
14	1,2,4-TrCN	0.159	0.201	0.176	0.147	0.0919	0.185	0	0.140
15	1,2,5-TrCN	0.0377	0.0559	0.0481	0.0365	0.0148	0.0563	0	0.0384
16	1,2,6-TrCN	0.0194	0.0127	0.0140	0.0137	0.00542	0.0138	0	0.0212
17	1,2,7-TrCN	0.0444	0.0365	0.0408	0.0354	0.0117	0.0431	0	0.0462
25	1,6,7-TrCN**	0	0	0	0	0	0	0	0
26	2,3,6-TrCN**	0	0	0	0	0	0	0	0
13	1,2,3-TrCN	0	0	0*	0	0	0*	0	0
22	1,3,8-TrCN	0	0	0*	0	0	0*	0	0
23	1,4,5-TrCN	0.257	0.275	0.436	0.377	0.180	0.592	0	0.367
18	1,2,8-TrCN	0.0195	0.0147	0.0258	0.0205	0.00799	0.0432	0	0.00396
Tetrachloronaphthalenes									
42	1,3,5,7-TeCN	0.136	0.176	0.119	0.100	0.0379	0.0277	0	0.106
33/34	1,2,4,6-/1,2,4,7- /37	1	1	0.892	0.782	0.696	0.634	0	0.714
44	1,3,6,7-TeCN	0	0	0	0	0	0	0	0
47	1,4,6,7-TeCN	0.175	0.197	0.191	0.176	0.158	0.182	0	0.220
45/36	1,3,6,8-/1,2,5,6-TeCN	0.0445	0.0242	0.0442	0.0453	0.0269	0.0243	0	0.0370
28/43	1,2,3,5-/1,3,5,8-TeCN	0.524	0.417	0.701	0.606	0.351	0.317	0	0.399
29	1,2,3,6-TeCN	0	0	0	0	0	0	0	0
30/27	1,2,3,7-/1,2,3,4- /39	0.0596	0.0265	0.0421	0.0382	0.0168	0.0137	0	0.0665
32/48	1,2,4,5-/2,3,6,7-TeCN	0.0624	0.0465	0.0743	0.648	0.0362	0.0469	0	0.0696
35	1,2,4,8-TeCN	0.521	0.281	0.564	0.529	0.338	0.240	0	0.370
38/40	1,2,5,8-/1,2,6,8-TeCN	0.843	0.611	1	1	1	1	0	1
46	1,4,5,8-TeCN	0.562	0.311	0.685	0.686	0.659	0.360	0	0.504
31	1,2,3,8-TeCN	0	0	0	0	0	0	0	0
41	1,2,7,8-TeCN	0.0527	0.0113	0.0367	0.0415	0.0201	0.0227	0	0.0528
Pentachloronaphthalenes									
52/60	1,2,3,5,7-/1,2,4,6,7-PeCN	0.243	0.250	0.142	0.141	0.0857	0.259	0*	0.249
58	1,2,4,5,7-PeCN	0	0.0463	0.0283	0.0250	0.0153	0.0399	0	0.0325
61	1,2,4,6,8-PeCN	0.502	0.494	0.520	0.474	0.320	0.486	0	0.385
50	1,2,3,4,6-PeCN	0.151	0.147	0.119	0.112	0.0741	0.149	0	0.0923
51	1,2,3,5,6-PeCN	0.0402	0.0353	0.0328	0.0326	0.0225	0.0390	0	0.0315
54	1,2,3,6,7-PeCN	0	0	0*	0*	0*	0*	0	0*

Table 1, continued

Table 1, continued

PCN No.	Structure	Halowax							Mixture
		1031	1000	1001	1099	1013	1014	1051	
Pentachloronaphthalenes									
57	1,2,4,5,6-PeCN	0.248	0.337	0.133	0.144	0.122	0.366	0	0.380
62	1,2,4,7,8-PeCN	0.342	0.571	0.240	0.268	0.221	0.515	0	0.556
53/55	1,2,3,5,8-/1,2,3,6,8-PeCN	0.330	0.540	0.325	0.321	0.256	0.604	0	0.442
59	1,2,4,5,8-PeCN	1	1	1	1	1	1	0*	1
49	1,2,3,4,5-PeCN	0.0575	0.0255	0.0347	0.0386	0.0218	0.0194	0	0.0415
56	1,2,3,7,8-PeCN	0*	0*	0.0490	0.0820	0.0293	0.0316	0	0.0135
Hexachloronaphthalenes									
66/67	1,2,3,4,6,7- /1,2,3,5,6,7-HxCN	0	0.0232	0.0354	0.0371	0.0135	0.0162	0.117	0.0894
64/68	1,2,3,4,5,7- /1,2,3,5,6,8-HxCN/	0*	0.113	0.0911	0.133	0.0672	0.0886	0.0924	0.258
69	1,2,3,5,7,8-HxCN	0*	0.278	0.239	0.349	0.196	0.244	0.257	0.548
71/72	1,2,4,5,6,8- /1,2,4,5,7,8-HxCN	0*	1	1	1	1	1	1	1
63	1,2,3,4,5,6-HxCN	0*	0.0620	0.0612	0.0552	0.0366	0.0422	0.0152	0.179
65	1,2,3,4,5,8-HxCN	0*	0.365	0.287	0.249	0.290	0.261	0*	0.349
70	1,2,3,6,7,8-HxCN	0	0	0	0	0	0	0	0
Heptachloronaphthalenes									
73	1,2,3,4,5,6,7-HpCN	0	0	0*	0.362	0.121	0.138	0.183	0.259
74	1,2,3,4,5,6,8-HpCN	0	0	0*	1	1	1	1	1
Octachloronaphthalenes									
75	1,2,3,4,5,6,7,8-OCN	0	0	0	0	0	1	1	1

0 (absent) in Halowax; *a congener present in extremely low concentration; **a congener, that can be absent in Halowax

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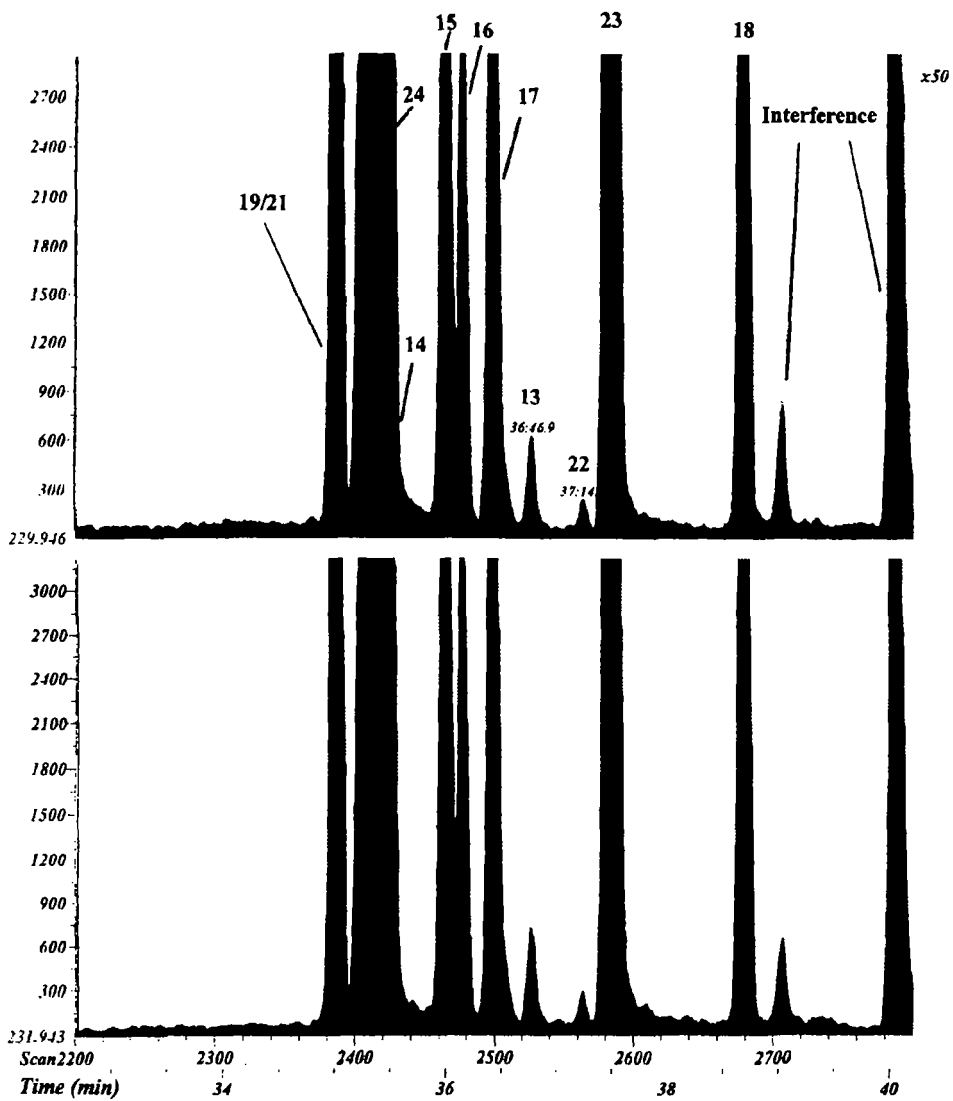


Figure 1. Normalized HRGC/LRMS chromatogram of Tr-CNs in Halowax 1014.