

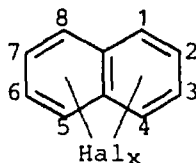
HALOGENATED NAPHTHALENES AS PRECURSORS AND PRODUCTS IN FLAME
CHEMISTRY

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Halogenated naphthalenes in flame chemistry

The reaction pathways in flame chemistry are governed by the formation of stable radicals and of olefinic and acetylenic compounds which in part lead to a complex but defined spectrum of thermodynamic stable aromatic compounds¹. In case that chlorinated precursors are present or the HBr-HCl/O₂/Br₂-Cl₂ equilibrium delivering halogene radicals has to be considered the corresponding halogenated compounds can be expected.



The naphthalene moiety is next to the benzene and styrene moiety a central unit in organic flame chemistry². Halogenated naphthalenes (PCN, Cl_x/Br_xN, C₁₀H_{8-x}Cl_x/Br_x) will be formed as one major and relevant group of aromatic compounds among others, e.g. such as polychlorobenzenes or polychlorobiphenyls. Like for the polychlorinated dibenzodioxins (PCDD) 75 congeners are possible. They can be systematically numbered in the same way as the dioxins. The build-up of Hal_xN can either occur by the reaction of 1.) benzene with butadiene (C₄) or of 2.) styrene with ethene/ethine (C₂) or by 3.) the direct halogenation of the naphthalene molecule by chlorine or bromine radicals. In the first two cases halogenated benzenes (Hal_xBz) and styrenes (Hal_xSt) have to be considered as precursor molecules. They can be formed themselves out of haloethene and haloethine units.

Halogenated naphthalenes as technical products

Polychlorinated naphthalenes are technically synthesized by chlorination of melted naphthalene resulting in mixtures containing the desired amount of chlorine (e.g. Halowax)³. Because of their physical and chemical properties that are similar to those of the polychlorinated biphenyls (PCB) the Halowax mixtures have been used in many corresponding applications. It cannot be excluded that there could be a direct input in municipal waste for the Cl_xN.

The higher chlorinated naphthalenes are inductors of several hepatic microsomal enzymes in rats, the congeners with substitution in the lateral 2,3,6,7-position probably being more potent than the others⁴.

Trace analysis of halogenated naphthalenes

In our study we analysed Cl_xN in a fly ash sample from a waste incineration plant. 5 gr fly ash were digested with 5 ml hydrochloric acid and refluxed under stirring for 30 hours with a mixture of ethylene glycol methyl ether and toluene. The following clean up procedure uses silica gel covered with sulfuric acid as oxidative medium placed in a column and hexane as eluent. Finally liquid chromatography on superactive basic aluminium oxide was performed with benzene as fraction 1, hexane/dichloromethane (98:2) as fraction 2 and hexane/dichloromethane (50:50) as third fraction to remove the sulphur and to separate preliminary. HRGC was done on DB Dioxin (44% methyl-, 28% phenyl-, 20% cyanopropylpolysiloxane, 8% polyethyleneglycole; J&W), SP 2331 (90% biscyanopropyl-, 10% phenylcyanopropyl(1:1)-polysiloxane; Supelco) and on the liquid crystalline phase SB Smectic (Supelco) with mass selective detection in EI mode (monitored masses are given in table 1).

Table 1: Most intense molecular ion masses of Cl_xN used for detection in GC-MS

group of homologues	ion masses	relative intensity
Cl_1N	162.024	100%
	164.021	33%
Cl_2N	195.985	100%
	197.982	65%
Cl_3N	229.946	100%
	231.943	97%
Cl_4N	263.907	88%
	265.904	100%
Cl_5N	299.865	100%
	301.859	64%
Cl_6N	333.826	100%
	335.823	80%
Cl_7N	367.787	100%
	369.784	96%
Cl_8N	401.748	87%
	403.745	100%

While hexane/dichloromethane (98:2) eluate the mono- and dichloronaphthalenes and some of the three- to pentachloronaphthalenes in the Al_2O_3 -LC separation (s. figure 1), most of the Cl_3 -, Cl_4 - and Cl_5 -isomeres and the higher chlorinated congeners can be found in the fraction with hexane/dichloromethane (50:50) as eluent (figure 2). Only minute amounts of the dichloro- and the heptachloronaphthalenes could be detected. One isomer of the Cl_1N , twelve of the Cl_3N , seventeen of the Cl_4N , twelve of the Cl_5N and four of the Cl_6N isomeres could be separated and identified. The thermal pattern of congeners is totally different to that of the technical mixtures. Thus we assume that all Cl_xN identified were de novo formed in the combustion process as observed for the chlorobiphenyls⁵.

- 1 Hucknall DJ. Chemistry of Hydrocarbon Combustion. Chapman and Hall. London 1985
- 2 Ballschmiter K, Zoller W, Scholz Ch, Nottrodt A. *Chemosphere* 1983; 12: 585-594;
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Ballschmiter K, Braunmiller I, Niemczyk R, Swerev M. *Chemosphere* 1988; 17: 995-1005
- 3 Brinkman U.A.Th, Reymer H.G.M.; *J. Chromatogr.* 1976; 127, 203-243
- 4 Campbell MA, Bandiera S, Robertson L, Parkinson A, Safe S. *Toxicology* 1983; 26: 193-205
- 5 Ballschmiter K, Niemczyk R, Schäfer W, Zoller W. *Fresenius Z. Anal. Chem.* 1987; 328: 583-587

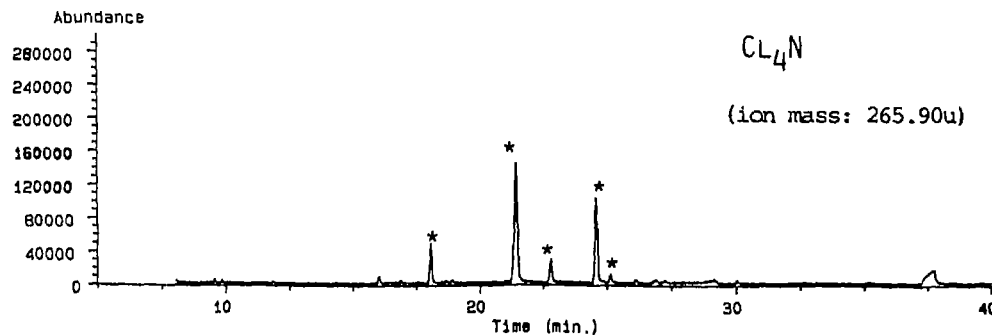
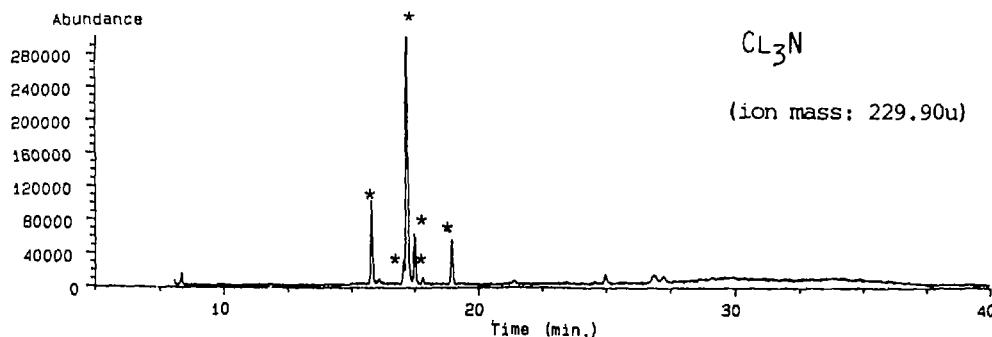
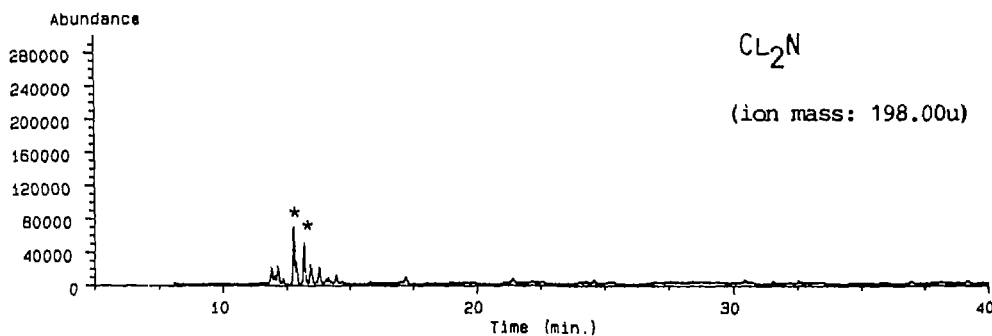
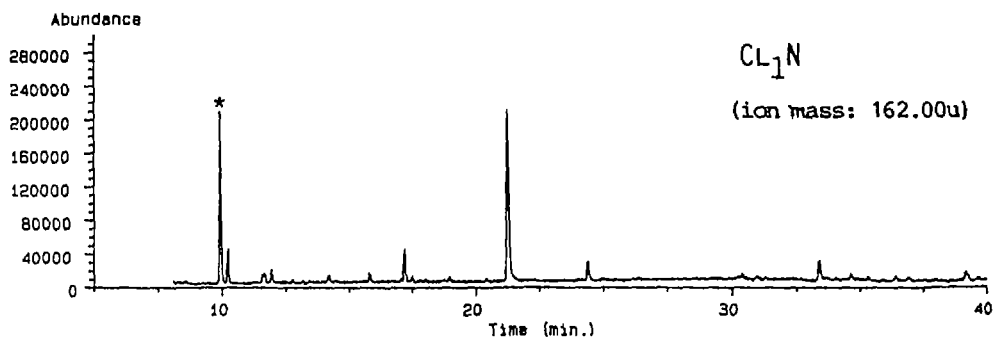


Figure 1: HRGC-MS (SIM) of polychlorinated naphthalenes in a MWI fly ash sample; second LC-fraction (hexane/dichloromethane=98:2). Stationary phase: SP2331. Identified Cl_xN are marked with *; unmarked peaks are not identified.

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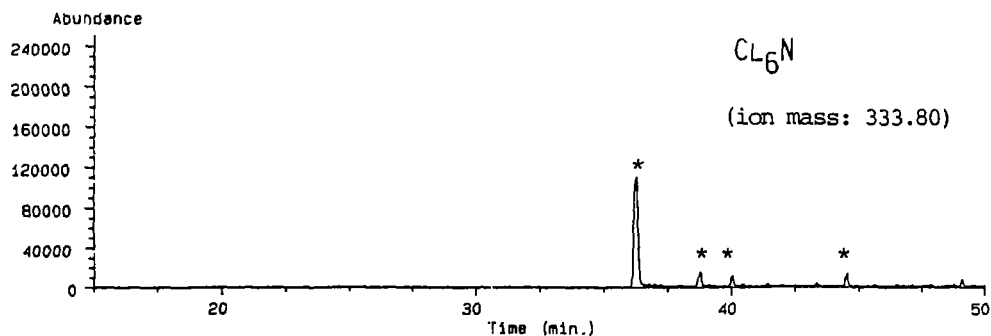
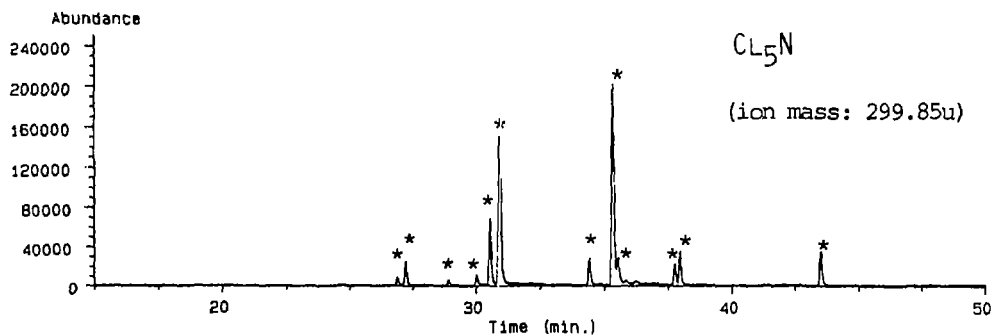
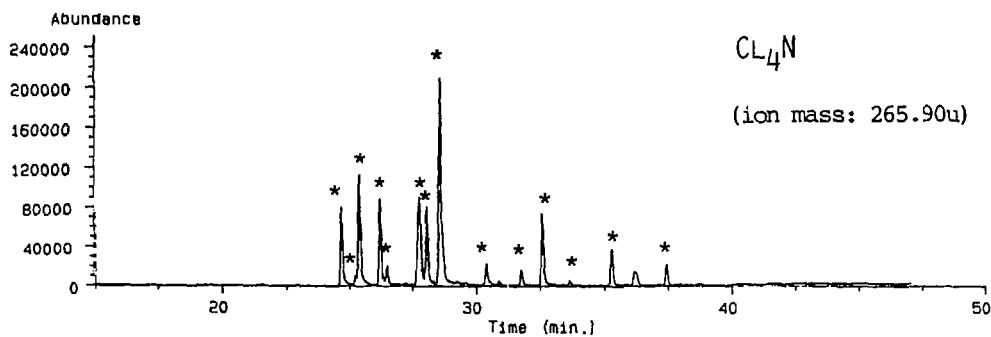
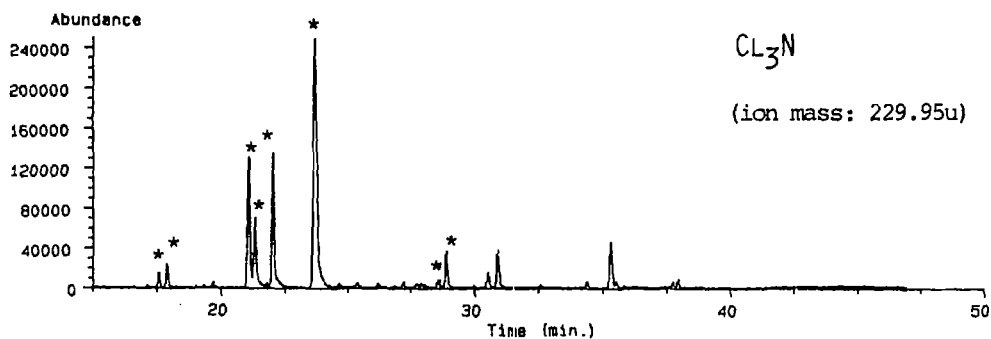


Figure 2: HRGC-MS (SIM) of polychlorinated naphthalenes in a MWI fly ash sample; third LC fraction (hexane/dichloromethane=50:50). Stationary phase: SP2331. Identified Cl_xN are marked with *; unmarked peaks are not identified.