

CONGENER-SPECIFIC DATA OF CHLORONAPHTHALENES IN VARIOUS LOTS OF SEVERAL HALOWAX FORMULATIONS

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Introduction

Chloronaphthalenes (CNs) can compose a mixture of up to 75 congeners and eight CN homologue groups, *i.e.* from mono- to octa-CN. A large scale manufacture of CNs and their main use from 1910 till 1970s as popular industrial compounds become a main source of environmental pollution with those substances¹⁻². Nevertheless, even very recently but unlawfully trade and use of CNs attracted chemical industry³. CNs are environmentally persistent chemicals, and accumulates and biomagnify in food-chains, while many of the CN congeners shows relatively high dioxin-like activity⁴⁻⁸. Chloronaphthalenes were recently identified as common contaminants of food and feed in Europe and Japan^{9,10}. Seafood from various regions of the world usually also contains residues of CNs¹¹.

Perfect quantification of all CN congeners found in environmental or technical matrices is still difficult due to congener separation problems. Large improvements have been made recently in CNs analysis using graphitized porous carbon and pyrenyl silica for their HPLC fractionation and further using DB-17 liquid phase and HRGC-HRMS for final separation, detection, identification and quantification¹². Also a cyclodextrin liquid phase of Rt- β DEXcst used in HRGC-HRMS permitted full separation of all penta- and hexa-CN¹³.

Halowax 1014 is considered as highly chlorinated (59 % Cl) and relatively popular CNs mixture, which was often used also as analytical standard for CNs determination in environmental samples^{14,15}. Due to a relative popularity of the Halowax 1014 elucidation of its CNs composition becomes a subject for several earlier studies. Also relative composition of Equi-Halowax which is an equivalent mixture of all seven Halowax formulations becomes known and very recently also on CNs composition of all seven types of the Halowax formulations alone^{16,17}. When analyzing two lots of Halowax 1014 some discrepancies have been found in its CNs composition¹³. In this communication are presented a preliminary data on CNs composition of various lots of several Halowax formulations after HRGC-HRMS analysis. A new analytical and toxicological data on CNs and including their technical formulations are increasingly important since those mixtures are considered as equipotent to

planar chlorobiphenyls (CBs) or even a main source of environmental load of dioxin-like activity released in recent decades of years ¹⁷.

Materials and methods

A several lots of Halowax 1001, 1000, 1099, 1013, 1014 and 1051 of the Koppers C. Inc., Pittsburg, USA were obtained from the Accu Standard, Analabs and Foxboro (USA) analytical standards trade companies. The analytical method used was described in detail elsewhere, while for final HRGC-HRMS quantification of CN congeners an Agilent Ultra 2 capillary column (25 m x 0.2 mm i.d., d.f. = 0.33 μ m) and an Agilent Model 6890 gas chromatograph coupled with a JEOL JMS-700 mass spectrometer were used ¹⁷. The standard solution of native CNs (PCN-MXB) was from the Wellington Laboratories Inc. (Canada), while isotopically labeled ¹³C₁₀ CN standards were purchased by the Cambridge Isotope Laboratories Inc. (USA). All solvents and reagents used were of dioxin analysis grade and purchased by the Kanto Chemicals (Tokyo, Japan).

Results and Discussion

The data obtained on CN composition of the several lots of the particular types of the Halowax formulations examined revealed a distinct variation in abundance of the particular homologue groups and congeners. At the figures from 1 to 4 are presented, respectively, CN homologue group and congener profiles for Halowax 1099 and 1013, which are formulations chlorinated at 49-51 % and 54-55 %, by weight. Generally, as found in Equi-Halowax study, when analyzing individual Halowax formulations a similar pattern of CN congeners within each CN homologue group is noted but their abundance vary depending on the formulation lot (Figs. 3 and 4) ¹⁶.

The technical formulations of the Halowax series form a complex mixture of CNs as primary compounds but also of many by-side and highly toxic impurities and at least of chlorinated dibenzo-*p*-dioxins (CDDs), chlorinated dibenzofurans (CDFs), chlorinated biphenyls (CBs), chlorophenols (CPhs) and chlorobenzenes (CBzs) ¹⁷⁻¹⁹. In an earlier study of on the composition of CNs of the Equi-Halowax mixture (an equivalent by weight mixture of the Halowax 1000, 1001, 1031, 1013, 1014, 1099 and 1051; 1:1:1:1:1:1), a few congeners, *i.e.* 2,3-DiCN (No. 10), 1,6,7-TriCN (No. 25), 2,3,6-TrCN (No. 26), 1,3,6,7-TeCN (No. 44), 1,2,3,6-TeCN (No. 29), 1,2,3,8-TeCN (No. 31), and 1,2,3,6,7,8-HxCN (No. 70) were and not detected above the method limit of quantification and suggestion was made on their absence or possible absence, respectively ¹⁶. Chloronaphthalene congener's No. 29, 31, 44 and 70 were not found also in present study when examining all seven Halowax formulations separately. On the other side in a particular Halowax formulations examined were found CN congener such as: No. 10 and 25/26, which co-eluted (Figs. 3 and 4). In another study CN congener No. 29 was found in Halowax 1001, while No. 44 and 70 were found as by-side impurity in a several technical chlorobiphenyl formulations ^{3,20}.

Some of the Di- and Tr-CNs detected co-eluted at the HRGC-HRMS used, *i.e.* 1,4-/1,6- (No. 5/7), 1,5-/2,7- (No. 6/12), 2,6-/1,7- (No. 11/8), 1,3,6-/1,3,9- (No. 20/19), 1,3,7-/1,4,6- (No. 21/24) and 1,6,7-/2,3,6- (No. 25/26) (Figs. 3 and 4), and some of them (No. 20 and 24) can be also absent in the Halowaxes. A further improvement in Di- and Tri-CNs separation should be helpful to understand their environmental sources and fate.

LEVELS IN INDUSTRIAL AND OTHER MATRICES

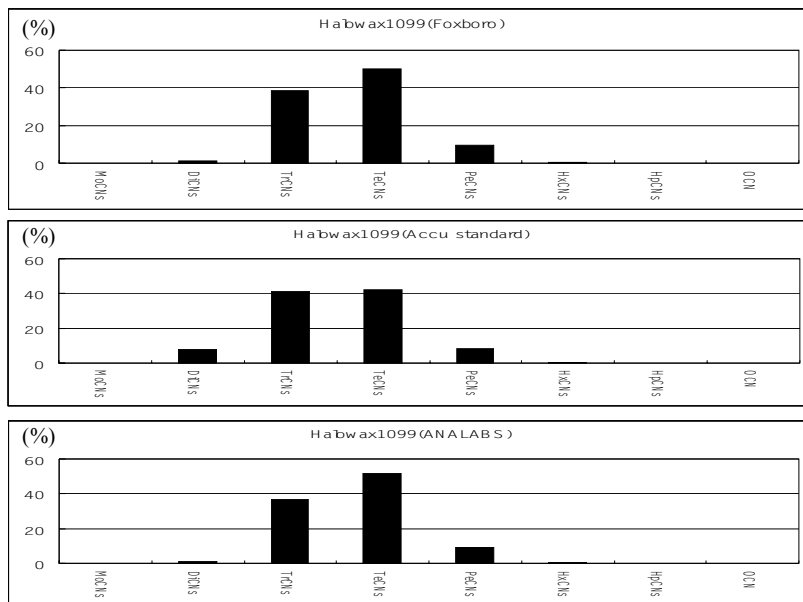


Fig. 1. Fingerprint of CN homologue groups in various lots of Halowax 1099.

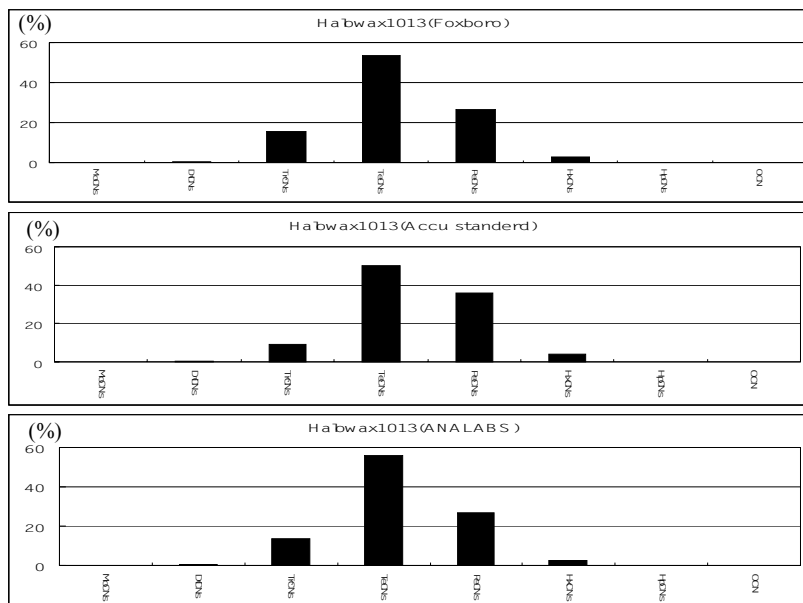


Fig. 2. Fingerprint of CN homologue groups in various lots of Halowax 1013.

LEVELS IN INDUSTRIAL AND OTHER MATRICES

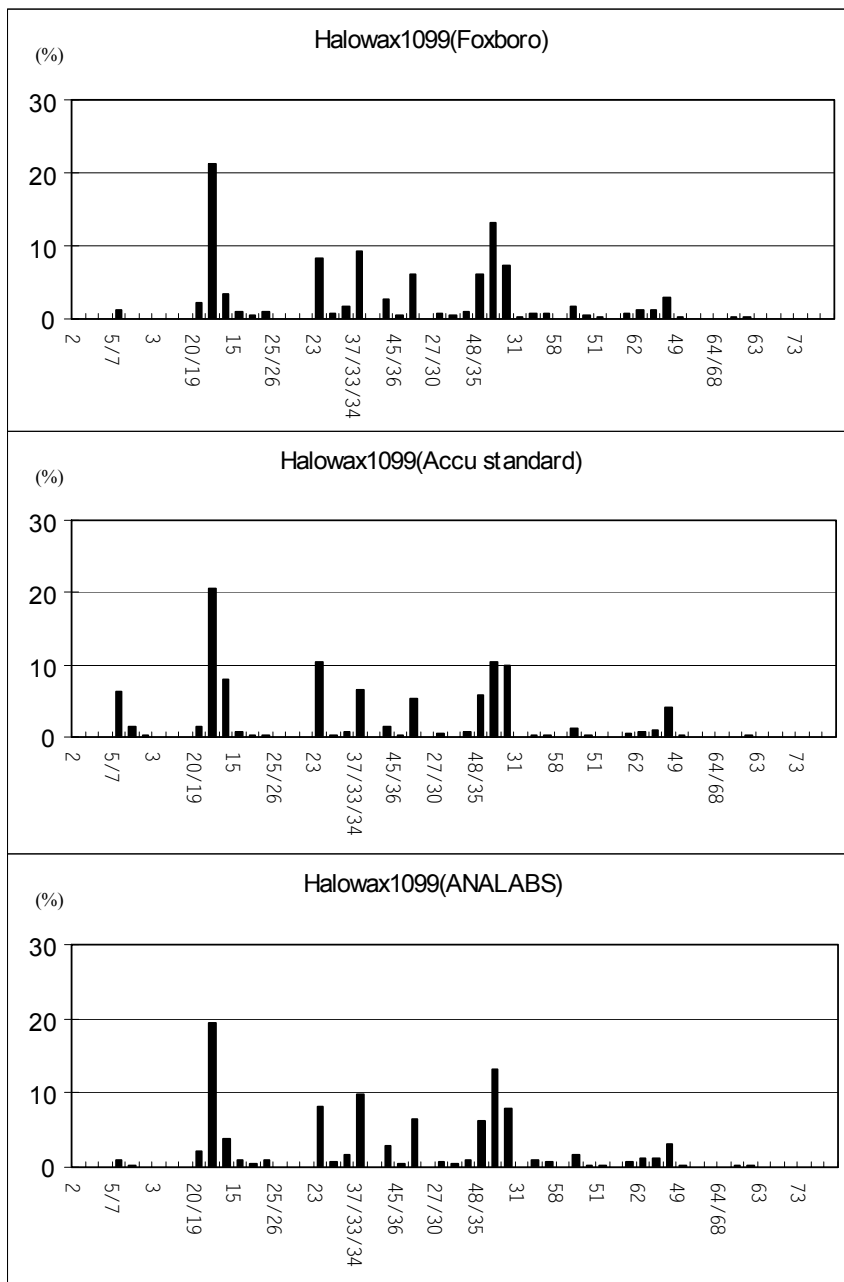


Fig.3. Fingerprint of CN congeners in various lots of Halowax 1099.

LEVELS IN INDUSTRIAL AND OTHER MATRICES

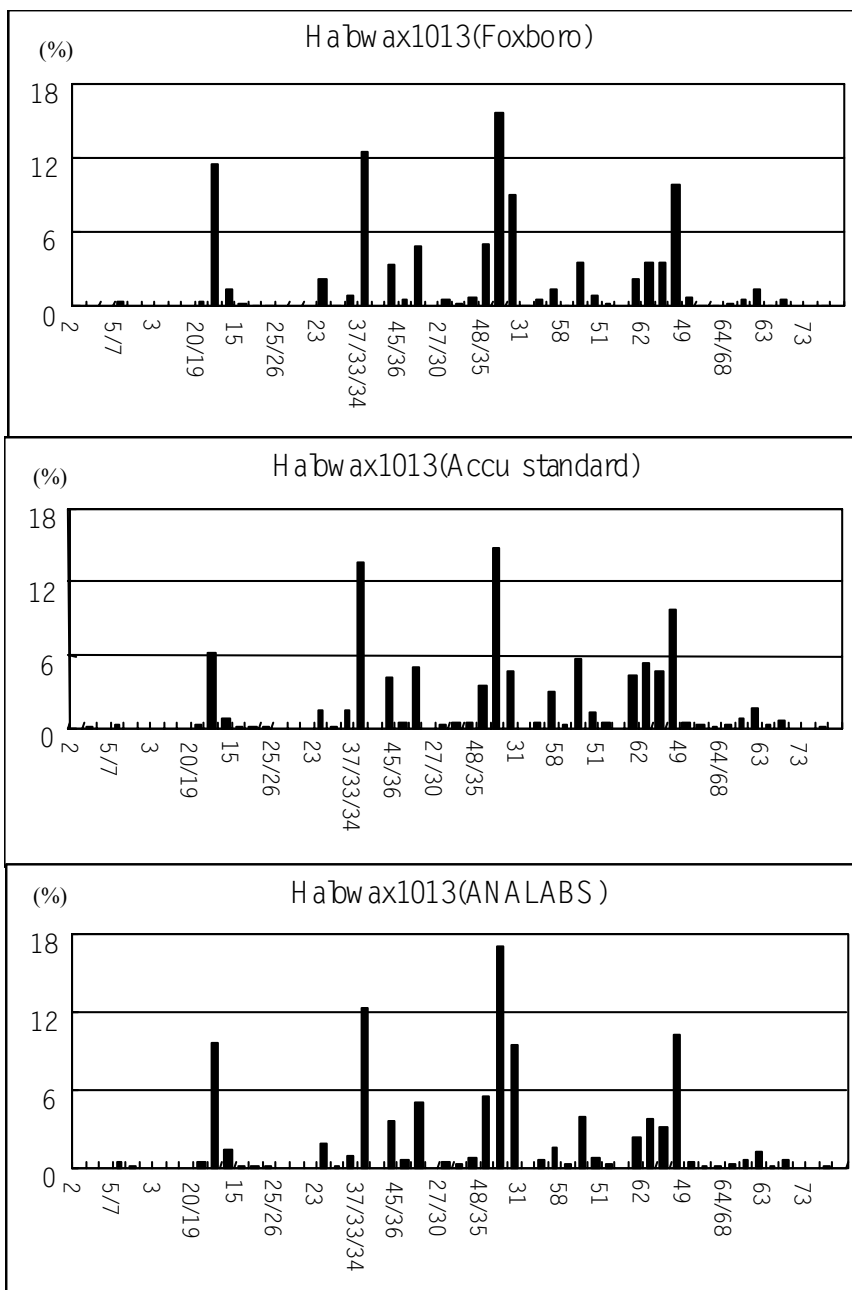


Fig. 4. Fingerprint of CN congeners in various lots of Halowax 1013.

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