

CHLOROBENZENES AND CHLOROPHENOLS IN CHLORONAPHTHALENE HALOWAX FORMULATIONS

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Introduction

Polychlorinated naphthalenes (PCNs; chloronaphthalenes, CNs) are industrial chemicals, that starting from the year 1900 become increasingly popular substances. Initially CNs were used to substitute natural waxes and rubber, next as insulating material in capacitors and for cable manufacture, and further found many other appliances¹⁻⁵. The restrictions on use of CNs, initially largely voluntary but also official in some countries came into force in 1972-1995. CNs were manufactured in Europe (Nibren, Seekay and Clonacire waxes etc.) and USA (Halowax waxes) using gaseous chlorination of molten naphthalene in presence of a catalyst and applying high pressure and temperature³⁻⁶. It can be assumed that technical naphthalene used for manufacture of technical CN mixtures can contain some impurities such as benzene and phenol. These impurities should be chlorinated to form some chlorinated compounds during the production of technical CN preparations⁷. Hence, some toxic outbreaks noted in man and animals after exposure to mixtures of CN can be partly also due to exposure to by-side impurities such as chlorobenzenes (CBzs) and chlorophenols (CPhs).

In this study an attempt has been taken to examine if CBzs and CPhs are formed during synthesis of CNs and contribute as toxic impurities found in a final product, which is represented by seven of various type the technical CN Halowax formulations. There is no earlier report available on contamination by CBzs and CPhs of the Halowaxes.

Materials and methods

Seven technical Halowax formulations studied were Halowax 1000, 1001, 1013, 1014, 1031, 1051 and 1099, which were supplied by the Foxboro C, MA, USA. The native and isotopically labeled $^{13}\text{C}_6$ chlorobenzenes and chlorophenols standard solutions were from the Wellington Laboratories Inc. (Ontario, Canada). All solvents and reagents used were of dioxin analysis grade and purchased by the Kanto Chemicals (Tokyo, Japan). A 10 mg portion of each particular Halowax formulation examined was dissolved with hexane and spiked with clean-up standard solution containing all isotopically labeled chlorobenzene or chlorophenol congeners.

The GC separation of mono- through tetrachlorinated congeners of CBzs and CPhs was achieved using DB-5 coated capillary column (J&W Scientific, Folsom, CA, USA), while for Pe- and HxCBz and PeCPh using Agilent Ultra 2 capillary column. The GC used was the model Hewlett-Packard 6890 GC, which was interfaced with the model JMS-700D (JEOL Co.) MS with resolution $R > 10,000$ MU (10 % valley).

Results and Discussion

Chlorobenzenes: The total amounts of chlorobenzenes in the Halowax formulations varied from 1100 to 9800 ng/g. The lower chlorinated Halowaxes such as Halowax 1031 and 1000 were rather contaminated than the other Halowaxes. The most contributing chlorobenzene homologue group in the technical CN formulations examined were: TeCBzs with 57.1 and 41.8 %, respectively, in a lower chlorinated Halowaxes 1031 (27 % Cl) and 1000 (35 % Cl); HxCBz with 45.8 and 47.7 %, respectively, in Halowax 1099 (51 % Cl) and a highest chlorinated Halowax 1051 (70 % Cl); while DiCBz with 52.5, 67.3 and 45.7 % predominated in the Halowaxes 1001, 1013 and 1014 containing Cl at 49, 54 and 59 %, respectively. As regards to chlorobenzene homologue group profiles found in the Halowax mixtures, there are some unexpected similarities, i.e. between Halowax 1001 and 1013 as well as between Halowax 1099 and 1051 but also a large discrepancies are observed when compared to other Halowax mixtures, and no a clear trend could found.

LEVELS IN INDUSTRIAL AND OTHER MATRICES

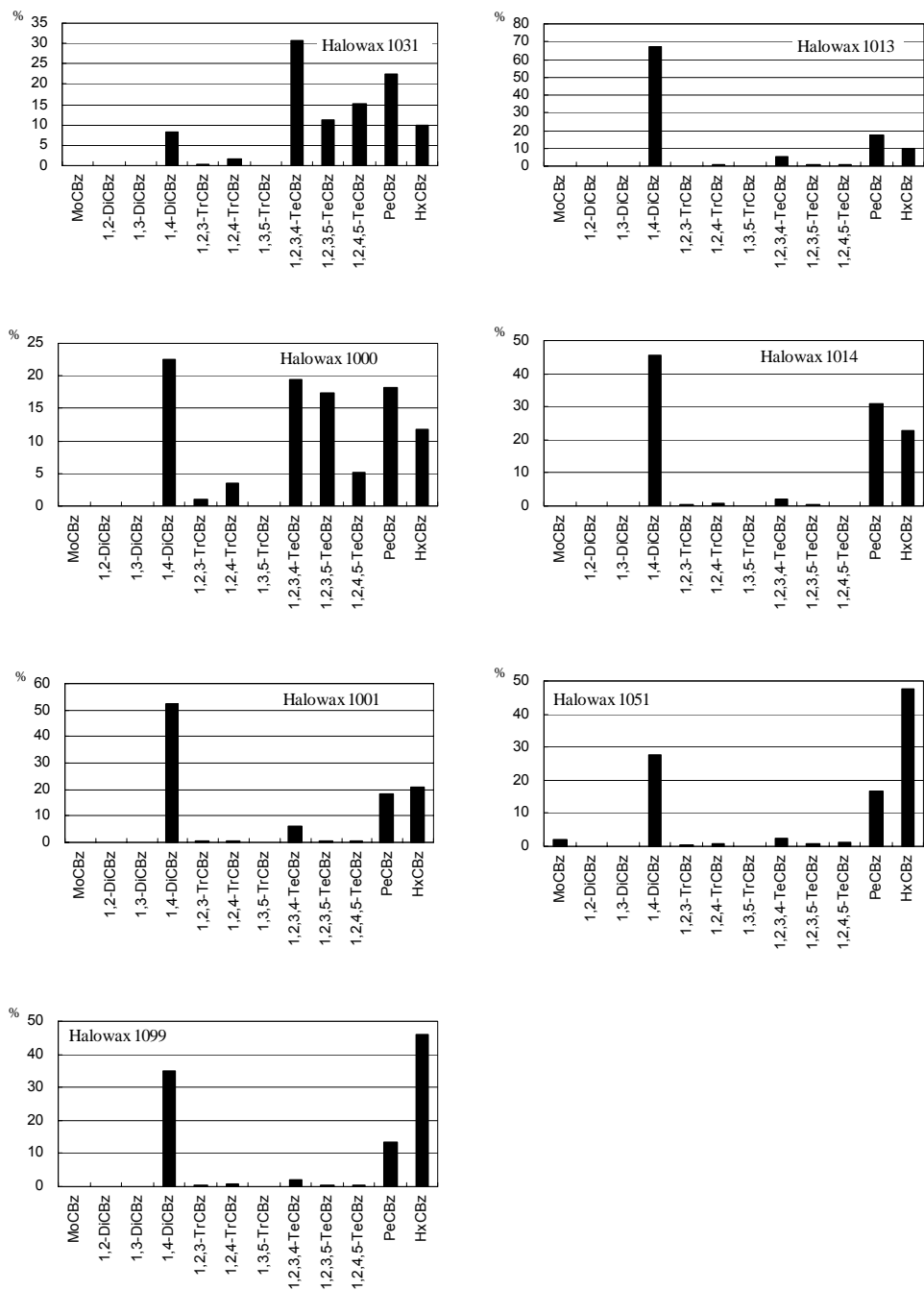


Fig.1. Chlorobenzene congener profiles (%) of the Halowax formulations.

Trichlorobenzenes alone or MoCBz plus TrCBzs but sometimes also including TeCBzs were minor compounds.

The process of chloronaphthalenes manufacture is largely similar to that of chlorobenzenes when using gaseous chlorine but difference is in the range of the temperature regime applied. Chlorobenzenes can be obtained in technical scale by gaseous chlorination of benzene in presence of the catalyst (ferric chloride, antimony chlorides). Firstly is produced mainly MoCBz, while 1,2-Di- and 1,4-DiCBz are minor constituents. When chlorination process is continued with higher yield tri-, tetra-, penta- and finally mainly HxCBz are obtained. After one substitution take place, the established chlorine substituents exert an orientating effect, so, certain congeners are preferentially formed ⁶.

On the other hand technical mixtures of CNs are adequately manufactured by gaseous chlorination of molten naphthalene at temperature range increasing from 80 to close to 180 °C and in a catalytic presence of ferric chloride or antimony pentachloride ⁶. A prolonged time and an elevated temperature close to 180 °C led to formation of perchlorinated naphthalene i.e., OcCN (81 %) and less of HpCNs (17 %), which both are found in highly chlorinated mixture of Halowax 1051 (70 % Cl) ⁷. It can be supposed that a course of the synthesis of Halowax 1051 in presence of trace amount of benzene as impurity theoretically should lead to high yield both of OcCN and HpCNs, and it parallel, also to co-synthesis and predominance of highest molecular weight congeners of chlorobenzene such as HxCBz and PeCBz.

A stepwise increase of temperature and pressure but also prolonged time of chlorination lead to a somehow similar profile of congeners of CBzs formed and a particular predominance of 1,4-DiCBz, PeCBz and HxCBz in Halowax 1001, 1099, 1013, 1014 and 1051, while for Halowax 1031 the profile of CBz congeners was different and 1,2,3,4-TeCBz predominated (Fig. 1). Apparently, during manufacture of the Halowax mixtures and after an initial by-side formation of monochlorobenzene and due to a steric hindrance effect further chlorine atom entering the ring is substituted in para position, i.e., 1,4-DiCBz is preferentially formed. In a next step and because of the effect mentioned a continuing chlorination and a rise in temperature and pressure which led to preferential formation also of PeCBz and HxCBz.

Chlorobenzenes are common by-side impurities in technical CN mixtures as indicated for the Halowax formulations in this study. So, manufacture and use of the Halowax formulations become at least a source of environmental pollution both with CNs and CBzs. HxCBz is very persistent and toxic compound ⁸. Nevertheless, contribution of HxCBz altogether with other co-occurring

chlorobenzenes found in the Halowaxes to toxic effects exerted by those formulations during occupational exposure seems to be low. This is because of relatively small CBzs content of the Halowaxes and in parallel also to a much higher potency of some CN congeners as dioxin-like compounds itself when compared to CBzs^{5, 9}. In earlier published papers CBzs were not claimed to be involved in outbreaks of chloracne among occupationally exposed man but are claimed in a recent report by Vazquez et al.¹⁰.

Chlorophenols: Chlorine content of the technical Halowax mixtures in this study followed gradually increasing trend, i.e. 27, 35, 49, 51, 54, 59 and 70 % in Halowax 1031, 1000, 1001, 1099, 1013, 1014 and 1051, respectively. The absolute concentration of chlorophenols in the Halowaxes varied between 1050 and 32400 ng/g and decreased with increasing from 27 to 51 % chlorine content of the particular formulation, while for higher chlorinated Halowaxes with 51 to 70 % Cl content remained relatively constant. Nevertheless, the most chlorinated Halowax formulations varied in composition of chlorophenol congeners (Fig. 2).

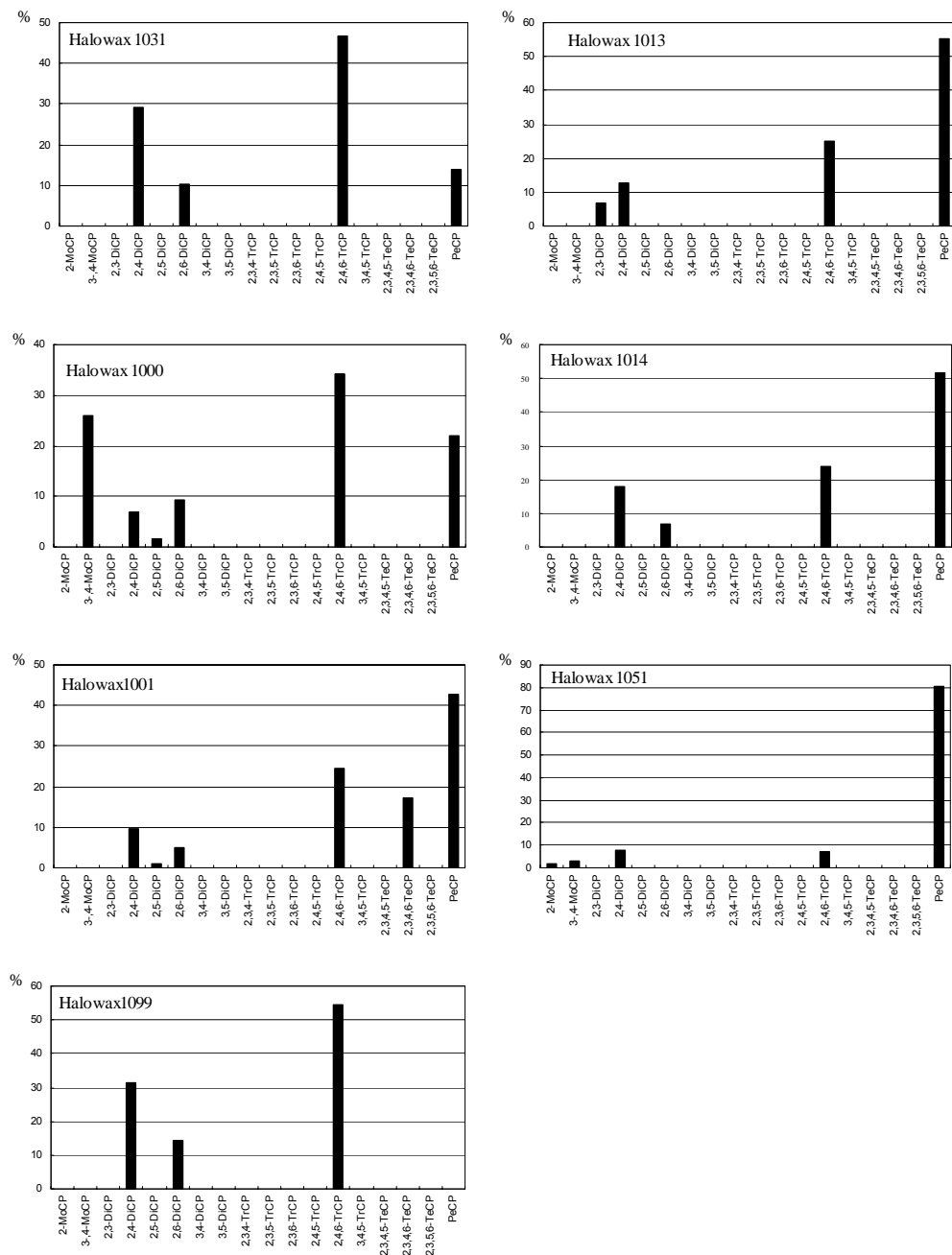


Fig. 2. Fingerprint (%) of chlorophenols in the Halowax formulations.

The profile (%) of higher chlorinated CPh homologues like PeCPh in the Halowaxes followed somehow a degree of chlorination (Cl %) of the parent mixture, i.e. increased from 14, 22, 43, 55, 52 to 80 %, respectively, but exception was free of PeCPh the Halowax 1099. And contrary, for a lower chlorinated DiCPhs and TrCPhs their relative proportions decreased but again an exception was Halowax 1099.

2,4-DiCPh, 2,6-DiCPh, 2,4,6-TrCPh and PeCPh were noticed as relatively abundant by-side chlorophenols found in the Halowaxes. These particular chlorophenol congeners are also amongst of main CPhs formed during industrial technical chlorophenol synthesis process when phenol and chlorine are used as substrate. 2,4,5-TrCPh, which is an indicative congener to CPhs obtained by alkaline hydrolysis of chlorobenzenes, was absent in the Halowax formulations examined. That observation implies that aqueous alkaline washing of crude Halowax mixtures before their vacuum distillation step did not produced any additional chlorophenol congeners even if chlorobenzenes were present. Hence, phenol, which co-occurred as impurity to technical naphthalene, is suggested as by-side agent responsible for occurrence of chlorophenols in the CN formulations of the Halowax series.

Since chlorophenols for the first time were identified as technical impurity in the Halowax formulations the contribution of those by-side products to toxic effects exerted by technical chloronaphthalenes noticed earlier can't be neglected. Chloronaphthalenes from early decades of the 20th century are environmental contaminants on a global scale due to widespread use in the past of technical CN mixtures, and as indicated in this study that mixtures also contributed in part to environmental release of CPhs. Additionally, finding of CPhs in the Halowaxes implies on co-occurrence in these formulations also of highly toxic PCDDs and PCDFs.

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