ANALYSIS OF ORIGIN OF IMPORTED TECHNICAL PCN FORMULATION

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Introduction

Chloronaphthalenes (CN; polychlorinated naphthalenes, PCNs) are compounds that are environmentally persistent, toxic and can bioaccumulate [1]. CNs form 75 congeners divided into 8 homologue classes. Environmental pollution with CNs is due to vaporization from the materials, products and equipment manufactured using these compounds (i), an unintentional production due to incineration or combustion processes (ii); and manufacture and use of technical PCBs [2-5].

CNs manufactured has been under the trade names such as Halowax, N-Oil, N-wax (USA), Basileum, Nibren wax (Germany), Seekay wax (United Kingdom), Clonacire wax (France), or Cerifal Materials (Italy) in ~1910-~1980. It not known is exactly when production of technical CN formulations started and discontinued could be worldwide, depending on the particular manufacturer and product, and about manufactured volumes. A manufacture of the Halowaxes ceased in 1977 (Koppers Co.), and the last manufacturer in the USA (Chemisphere) ceased their production in 1980 [1,6,7]. Reports did indicate that at least sporadic uses of CNs take place in the 1990s [6]. Recent episodes of unlawful trade and use CN containing product imported from Canada and of technical CN formulation imported from the United Kingdom take place in Japan [8].

Aim of this study was to evaluate and identify origin of technical CN formulation unlawfully imported from the United Kingdom to Japan based on HRGC/HRMS data and multivariate analysis.

Materials and Methods

HRGC/HRMS examination of imported (unidentified) technical CN formulation using Ultra 2 liquid phase for separation performed was under the same procedure and analytical conditions as described recently for the Halowax formulations. [9] Falandysz et al. published details on CN constituents of several batches of seven brands of the Halowaxes obtained by HRGC/HRMS after separation using also Ultra 2 phase. [9,10] Yamashita et al. published absolute concentration data on CNs composition of imported technical CN formulation and Halowax 1001 obtained by HRGC/HRMS after separation using DB 1701 phase[8].

Chloronaphthalenes compositional data of imported technical CN formulation and that of the Halowaxes 1000, 1001 and 1013 examined have been a subject for the graphic presentation of theirs CN congener and homologue group patterns (not shown). These data also served for chemometric analysis and imported mixture identity (name) determination.

Principal Component Analysis (PCA) of data matrix carried out has been with ANCZY 40 software developed by Prof. Jan Mazerski from the Technical University of Gdańsk, Poland. All diagrams with the PCA and Cluster Analysis results drawn were using STATISTICA 6.0, StatSoft Inc.

Results and discussion

A visual resolution of congener-specific (not shown) or homologue class-specific pattern of DiCNs to OctaCN found in Halowax 1031, 1000 and 1001 as well as of imported CN formulation seems inadequate and clearly to complex (Table 1) to recognize (identify) some of these mixtures without chemometric support.

The PCA of CN congener-specific dataset for altogether “six formulations” considered did indicate that compositional variability between them explained could be by four principal components. These four PCs retained accounted for 92 % of the model variance. On the linear map with objects shown in space of Factor 1, Factor 2 and Factor 3 (Fig. 1) no clustering of formulations could be observed. The objects seem dispersed

Table 1: Normalized CN homologue class composition of Halowax 1000, 1001, 1031 and of imported (unidentified; U) technical CN formulation (%), adapted from [8,10]

CN homologue group	*Halowax*				*Imported CN formulation*	
	1031(%) Ultra 2	*1000 (%) Ultra 2*	*1001 (%) Ultra 2*	*1001 (%) DB 1701*	*U (%)* Ultra 2*	*U (%) DB 1701*
DiCNs	85	90	4.3	2.7	1.0	1.2
TriCNs	7.6	6.6	52	36	27	41
TetraCNs	6.4	2.2	40	58	62	52
PentaCNs	1.1	0.50	3.3	3.9	9.8	6.2
HexaCNs	0.15	0.29	0.11	0.058	0.19	0.075
HeptaCNs	0.045	0.071	0.019	0.017	0.021	0.00086
OctaCN	0.085	0.000018	0.000011	0.0083	0.016	0.00086
Cl content (%)	27	35	49	50*	52	50*

Notes: *This study

to be rather in the factors space (Fig. 1). An imported CN formulation characterized was with smaller participation of CNs nos. 20/19, 21/24/14, 64/68, 69, 71/72, 63, 65, 73 and 74 (positive correlation) and greater of CNs nos. 48/35 (negative correlation) related to Factor 1, when compared to Halowaxes 1031 and 1000. Cluster analysis of data considered was as supplementary tool to PCA A structure of dendrogram drawn did indicate that there is no apparent similarity between imported CN formulation and Halowax 1031, 1000 or 1001 (Fig. 2).

The PCA of CN homologue dataset of these formulations did indicate that compositional variability between them explained could be by two PCs. These two PCs retained accounted for 86 % of the model variance. After Varimax rotation two factors obtained could be. Projection of data in space of Factor 1 and Factor 2 given is at Fig. 3.

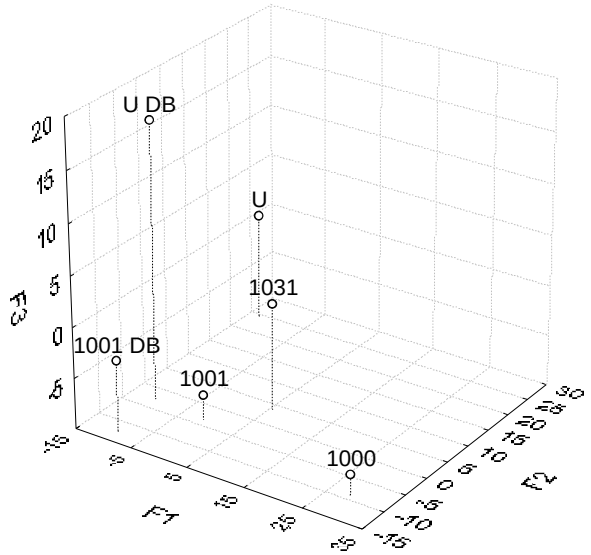

Fig. 1. Linear map of CN congener compositional pattern of technical CN formulations in space of first (F1), second (F2) and third (F3) Factor. Notes: 1000, 1001, 1031 and U refers to Halowax 1000, Halowax 1001, Halowax 1031 and unidentified (imported) CN formulation, respectively, when analyzed using Ultra 2 liquid phase; 1001DB refers to Halowax 1001 and UDB to imported CN formulation when analyzed using DB 1701 phase.

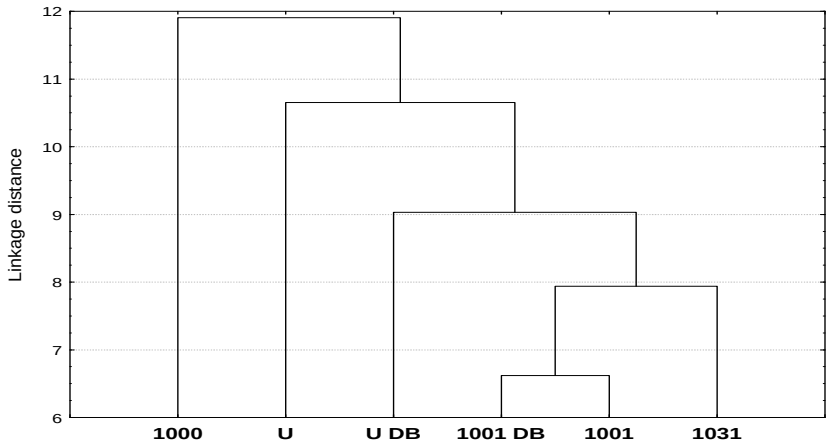

Fig. 2. Cluster diagram of Halowax 1031, 1000 and 1001 and imported CN formulation based on CN congener's composition. The symbols have the same meaning as at Fig. 1.

Dendrogram obtained after Cluster Analysis of CN homologue class data divided formulations examined into two main fractions (as after PCA at Fig. 3) (Fig. 4). First cluster included imported CN formulation and Halowax 1001 due to theirs high similarity of CN homologue classes' content, and second cluster included Halowax 1000 and 1031. Imported (unidentified) CN formulation and Halowax 1001 are less similar after separation with Ultra 2 phase, what results in greater linkage distance.
Multivariate analysis of formulations considered based on CN homologue classes' content shows that imported formulation is similar somehow to that of Halowax 1001, regardless type of liquid phase used for HRGC/HRMS separation.

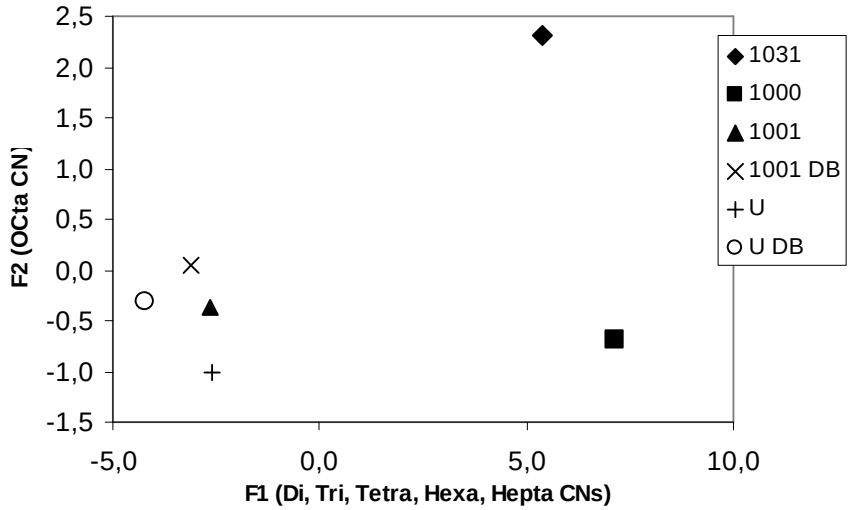

Fig. 3. Projection of Halowax 1031, 1000 and 1001 and imported CN formulation at the Factor 1 (F1) and Factor 2 (F2) planes. The symbols have the same meaning as at Fig. 1.

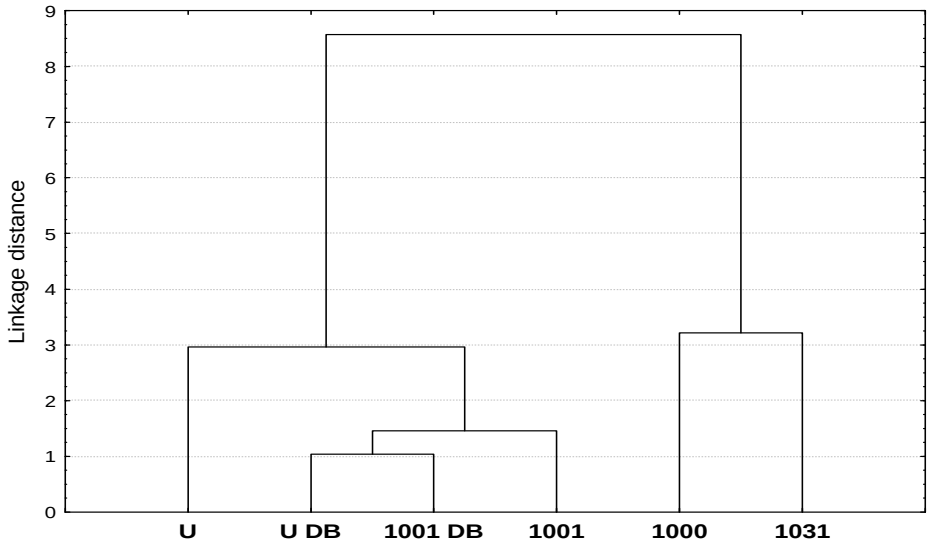

Fig. 4. Cluster diagram of technical CN formulations similarity based on CN homologue classes' composition. Te symbols have the same meaning as at Fig. 1.

Acknowledgments
Acknowledged is support by the Ministry of Higher Education and Science under grant no. 127/02/E-335/2008 [project no. R 169 (T) 5278/2003].

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