

Use of Chlorobornanes as Analytical Standards for Toxaphene Analysis

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1. Introduction

Some recently isolated Chlorobornanes have been used in analysis of Toxaphene residues¹⁾. Only 4 have been found in significant amounts, while the remaining Nona- and Decachlorobornanes have not been found in environmental samples, despite their presence in technical Toxaphene. Therefore we have undertaken an investigation into isolation of Heptachlorobornanes and then used isolated compounds as analytical standards for fish oil specimen analysis.

2. Isolation of Chlorobornanes

The process was described by us previously²⁾. 2-exo,10,10-Trichlorobornane (TrCB-2049) was chlorinated to the desired extent, and the resulting mixtures were separated on 2m column of specially prepared silica gel. Some fractions deposited crystals on standing, which were further purified. The diagram (Fig 1) demonstrates the separation process, in comparison to similar separation, described by Parlar et. al.³⁾. It is clear, that we have isolated a set of compounds with broader range of retention volumes, and, therefore, HpCB-4661 and NCB-7047 are "the most polar" and "the least polar" chlorobornanes.

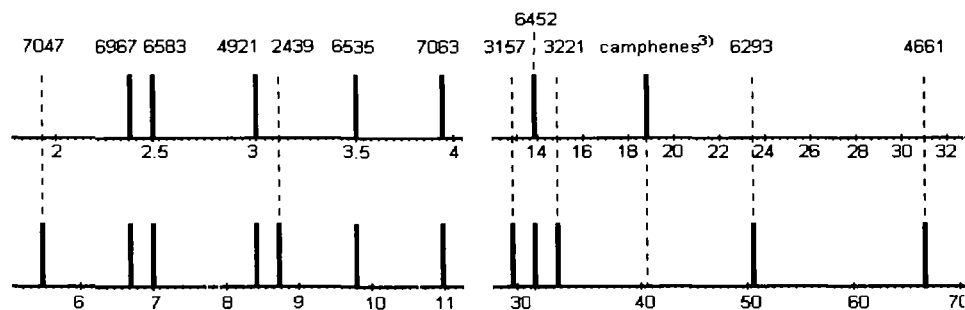


Fig.1. Retention volumes (L) of Chlorobornanes. Top - Parlar et. al.³⁾, bottom - this work.

TOXA

3. Analytical Standards

11 compounds have been chosen.

The compounds are numbered according to binary-decimal nomenclature⁴⁾.

NCB-4925: 2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-NonaChloroBornane(Toxicant A_C)

OCB-4921: 2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-OctaChloroBornane

NCB-6551: 2,2,5,5,8,9,9,10,10-NonaChloroBornane

OCB-6535: 2,2,5,5,9,9,10,10-OctaChloroBornane

HpCB-6452: 2,2,5-*endo*,6-*exo*,8,9,10-HeptaChloroBornane(Toxicant B)

HpCB-2439: 2-*exo*,5,5,9,9,10,10-HeptaChloroBornane

HpCB-2837: 2-*exo*,3-*exo*,5-*endo*,8,9,10,10-HeptaChloroBornane

HpCB-3157: 2-*exo*,3-*endo*,6-*endo*,8,9,10,10-HeptaChloroBornane

HpCB-3221: 2-*exo*,3-*endo*,5-*exo*,8,9,10,10-HeptaChloroBornane

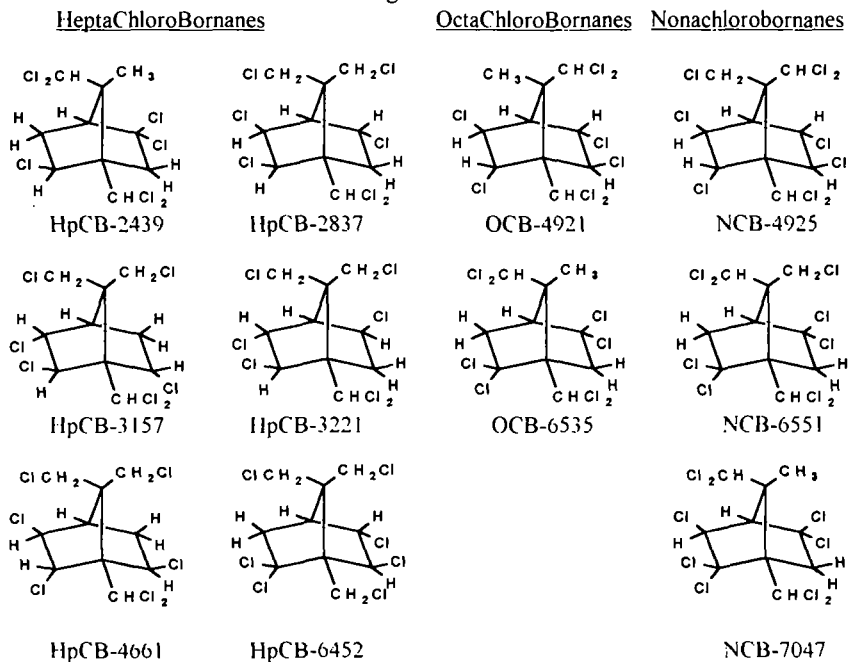
HpCB-4661: 2-*endo*,3-*exo*,6-*exo*,8,9,10,10-HeptaChloroBornane

NCB-7047: 2,2,3-*exo*,5,5,9,9,10,10-NonaChloroBornane

OCB-4921 and NCB-4925 are the major Toxaphene components in environmental samples, especially in marine mammals⁵⁾, along with NCB-6551 and HpCB-6452 they are subject for certification in NIST CRM-1588 (Cod liver oil). The first three congeners form a group of four structurally related compounds with OCB-6535.

NCB-7047 and HpCB-4661 are the very first and the very last eluting congeners on SiO₂/Hexane column, therefore, they are important for recovery control.

The structures of 11 chlorobornanes are given below :



4. Analysis of fish oil sample

We used fish oil for dogs from a supermarket. It was labelled as :
 {Bogena B.V. Waailwijk Holland Levertraan "Huile de foie de morue"}
 20 ml of oil have been put on top of a SiO₂-column (200g of silica gel, prepared in the same way, as for isolation of chlorinated bornanes) and eluted with 4 liters of hexane (volume, estimated to be sufficient for elution of all congeners from NCB-7047 to HpCB-4661). Hexane solution was evaporated to 50 ml and the remaining fat was removed by shaking with sulfuric acid 5x5ml, until acid layer remained colourless. Solution was washed from acid, passed through a small silica gel column, hexane was evaporated to dryness, and a sample was redissolved in 10ml of iso-octane.
 GC/ECD analysis was carried out on "Model-3700" Gas-chromathograph with ECD ⁶³Ni at 290°C. Column: 25m, 0.2mm i.d. SE-54, 0.25µm "KKK". Carrier gas - nitrogen at 1 ml/min. Split/splitless injection, 2µl. Injection port at 280°C. Temperature programm : 90°C(1min),10°C/min to 280°C, 280°C(12min).

Concentrations of Chlorobornanes in fish oil in ng/g are given in **Table 1**.

HpCB-2429	HpCB-2837	HpCB-4661	OCB-4921	OCB-6535	NCB-4925	NCB-6551	NCB-7047
3.6	3.9	18.5	11.1	2.8	22.5	15.9	1.7

Chromatograms of standard mix(250ng/ml each) and of an oil sample are shown on **Fig.2**

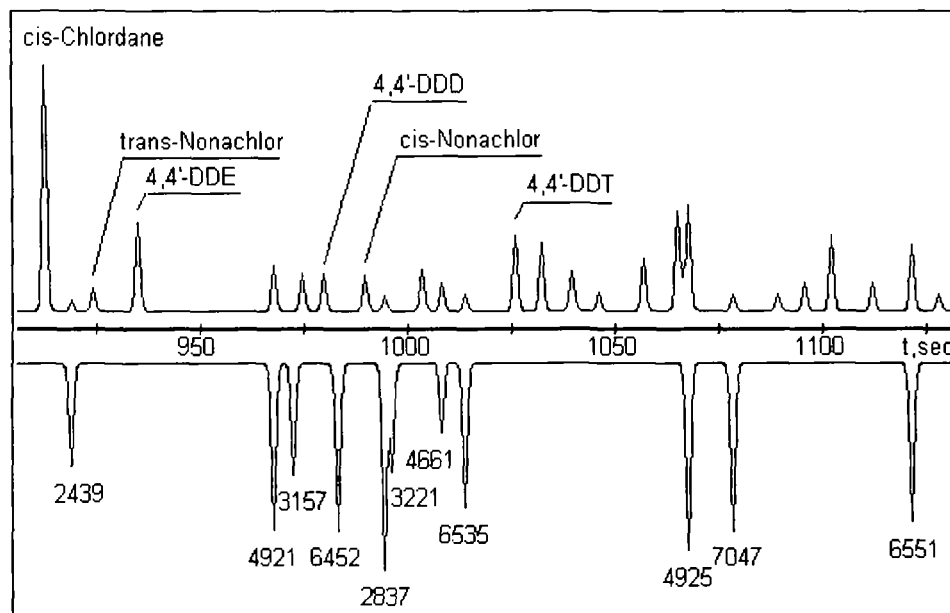


Fig.2. Top - fish oil, bottom - standard mixture. Conditions - see text.

5. Acknowledgements

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6. References

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