

## GC x GC ANALYSIS OF TETRACHLORONAPHTHALENES

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The GC x GC as one of an alternative and relatively novel techniques of so called "multidimensional gas chromatography" has been developed to improve separation of very complex mixtures. In GC x GC the compounds are being separated into two dimensions. The best resolution of constituents of very similar physical and chemical nature is achieved when separation mechanisms in those two dimensions are fundamentally different and independent, that is they must be orthogonal<sup>1,2</sup>. In the consequence, substances belonging to the same chemical group as the congeners and isomers of chloronaphthalene (CN) could be arranged in strands along oblique lines on two-dimensional chromatogram<sup>3</sup>. A use of two columns of different properties, e.g. containing a non-polar phase as the 1<sup>st</sup> one and a polar- or shape selective phase as the 2<sup>nd</sup> one, allows getting two retention time's for the same searched compound of examined mixture<sup>2</sup>. A mentioned nature of two-dimensional chromatogram could aid considerably in identification and quantification of compounds, and what is especially useful for the constituents which co-elute during single capillary column GC separation<sup>3</sup>.

Chloronaphthalenes (CNs) form a complex mixture of up to 75 congeners and become ubiquitous environmental contaminants<sup>4</sup>. A several CN congeners, e.g. 1,4-/1,6- (# 5/7) 1,5-/2,7- (# 6/12) and 2,5-/1,7- (# 11/8) of di-CN's; 1,3,6-/1,3,5- (# 20/19), 1,2,7-/1,4,6- (# 21/24) and 1,6,7-/2,3,6- (#25/26) of tri-CN's; 1,2,5,7-/1,2,4,8-/1,2,4,7- (# 37/33/34), 1,3,6,8-/1,2,5,6- (# 45/36), 1,2,3,5-/1,3,5,8- (# 28/43), 1,2,3,4-/1,2,3,7- (# 27/30), 2,3,6,7-/1,2,4,8- (# 48/35) and 1,2,5,8-/1,2,6,8- (# 38/40) of tetra-CN's; 1,2,3,5,7-/1,2,4,6,7- (# 52/60) and 1,2,3,5,8-/1,2,3,6,8- (# 53/55) of penta-CN's; and 1,2,3,4,6,7-/1,2,3,5,6,7- (# 66/67), 1,2,3,4,5,7-/1,2,3,5,6,8- (# 64/68) and 1,2,4,5,6,8-/1,2,4,5,7,8- hexa-CN's (# 71/72) usually co-elute during monochromatic GC separation<sup>5-10</sup>. The aim of this work is to develop the GC x GC system to quantify all CNs as single compounds in various technical and environmental matrices. Within an attempt undertaken in this report data are presented on separation of some of tetra-CN's, which are relatively less studied<sup>8</sup>, and their existence or not in technical CN Halowax formulations, pine needles and soil.

**Materials and Methods**

**Matrices.** Seven types of Halowax formulations examined were of various batches and manufactured by the Koppers C. Inc., Pittsburg, USA, and Equi-Halowax mixture was made ourselves. Pine needles and soil samples originated from Poland, and details of their preparation including extract clean-up using Hypercarb-HPLC and PYE-HPLC are as reported previously<sup>9</sup>.

**Instruments.** All experiments were performed using the Agilent 6890A GC equipped with a 5973A mass-selective detector (Agilent Technologies, Palo Alto, CA, USA) and Zoex KT2003 system (Zoex Inc., Lincon, NE, USA). DB-5MS (30 m x 0.25 mm i.d. x 0.25  $\mu$ m film thickness, J&W Agilent) and LC-50 (1 m x 0.1 mm i.d. x 0.1  $\mu$ m film thickness, J&K Scientific) were used as the 1<sup>st</sup> and 2<sup>nd</sup> dimension columns, respectively. The initial oven temperature was 90 °C (2 min), followed by a temperature ramp of 30 °C/min to 165 °C (0 min), then at 1.5 °C to 270 °C (20.50 min). Total run time was 85 min. Helium was used as carrier gas at a constant flow mode of 1.44 ml/min. Inlet temperature was maintained at 280 °C and the splitless injection mode (2 min) was used. The pressure during the analysis was 263 kPa. The hot jet gas temperature was 200 °C, followed by a temperature ramp of 10 °C/min to 300 °C, and modulation period was 4 seconds and hot gas duration time 250 ms. The MS was operated in the scan mode (Halowax), and SIM mode (pine needle and soil) using EI ionization. The scan ranges were: m/z from 161 to 270 (for mono- to tetra-CN's) with 26.60 scans/sec, and from 296 to 408 (for penta- to octa-CN) with 26.37 scans/sec. All samples were injected manually. The peaks identification, besides literature data, was supported by the use of a linear retention data and an individual congener's standards solution.

**Results and Discussion**

**GC x GC Separation.** A combination of non-polar and shape selective columns in GC x GC system used allows to get better separation of some tetra-CN's (Figs. 1 and 2) which co-eluted at the HRGC-HRMS systems used previously<sup>5-11</sup>.

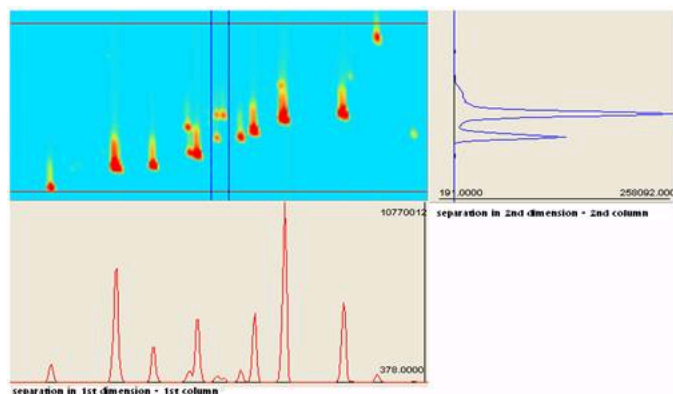


Fig. 1. Chromatograms of tetra-CN of Equi-Halowax obtained in two dimensions (1<sup>st</sup> dimension-red one; 2<sup>nd</sup> dimension- blue one).

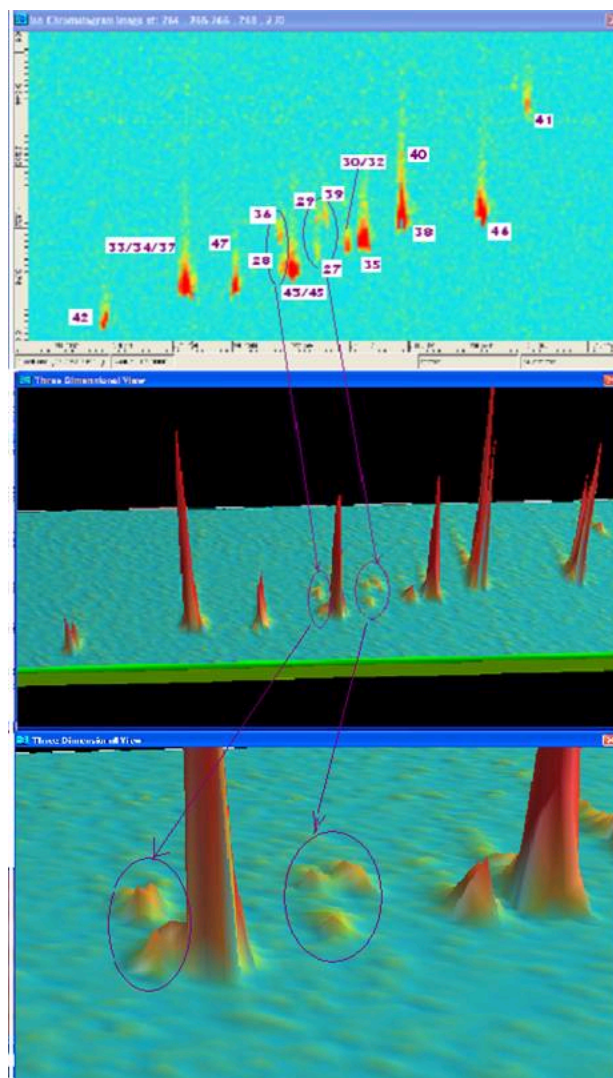


Fig. 2. GC x GC chromatograms of tetra-CN of Halowax 1099 based on DB-5MS as 1<sup>st</sup> and LC-50 as 2<sup>nd</sup> column.

An elution order of isomers of tetra-CN after first column (DB-5MS, which is analogous to DB-17) is as follow (Fig. 2): nos. 42, 33/34/37, 44, 47, 28/36, 43/45, 27/29/39, 48, 30/32, 35, 38/40, 31, 46 and 41, while a somewhat different is on DB-5<sup>7,9</sup>. Because of the co-elution problem existence of some isomers of tetra-CN in Halowax formulations and environmental samples couldn't be undoubtedly indicated<sup>7,10,11</sup>. Amongst of tetra-CN the isomers nos. 27, 29 and 39 but also nos. 28 and 36, and 38 and 40 could be well separated, and by the GC x GC system used, but 33/34/37, 43/45 and 30/32 still co-eluted (Fig. 2). Six of these seven well separated isomers have been found in trace amount and only 1,2,5,8-tetraCN (no. 38) was somewhat more abundant in Halowax mixtures examined but also in soil and pine needles. In an earlier efforts when various liquid phases packed into a single capillary column and GC were used to elucidate composition of Halowax formulations 1,2,3,6-tetraCN (# 29) was absent or not found at concentration above the method limit of quantification (< 0.0005 mg/g) for all types and different batches of Halowaxes<sup>7,10,11</sup>. Also 1,3,6,7-tetraCN (no. 44) and 1,2,3,8-tetraCN (no. 31) were absent or undetected (<0.0005 mg/g) in Halowax formulations during previous trials and were not found after GC x GC in this study (Fig. 2)<sup>7,10,11</sup>.

The CNs nos. 27/30 co-elute on Agilent Ultra 2 column, while nos. 30/32 co-elute on DB-17 column<sup>9-11</sup>. An existence or not of CN no. 30 in Halowax formulations couldn't be confirmed also after GC x GC in this study (Fig. 2). 2,3,6,7-tetraCN (no. 48) and 1,2,4,6-tetraCN (no. 35) (pair 48/35 co-elute on Agilent Ultra 2 and DB-5)<sup>7,10,11</sup> are well separated by DB-17 and GC x GC system employed, and no. 48 was absent, while no.35 was relatively abundant in the Halowax formulations examined (Fig. 2)<sup>9</sup>.

Further CNs nos. 45/36 but also 28/43 co-elute on Agilent Ultra 2 and as such were found in the Halowax formulations<sup>7,10,11</sup>. Since both CNs nos. 36 and 28 were separated by GC x GC and confirmed in the Halowax formulations, while nos. 43/45 couldn't be separated by DB-17 and GC x GC used, their existence or absence, alone or both, in those formulations couldn't be excluded or confirmed in this study.

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