

Potential of Comprehensive Two-dimensional Gas Chromatography (GC x GC) in Analyzing Samples Exposed to Organochlorine Pesticides for Presence of Trace Level PCBs

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Introduction

The regulations for persistent organochlorine pesticides (OCPs) and polychlorinated biphenyls in food products are becoming far more stringent due to the extensive research and the toxic hazards they pose to humans and animals. The need for a method which can chromatographically resolve several trace level PCBs congeners from complex sample matrices and even other organochlorinated compounds lends itself nicely to comprehensive two-dimensional Gas Chromatography (GC x GC), also coupled to a time-of-flight mass spectrometer (TOF-MS). GC x GC dramatically increases the separation power of the chromatographic system while increasing the detectability of analytes through the "cryo-focussing" effects of thermal modulation. The TOF-MS detector offers the required acquisition speed (even at full mass range) necessary to define ultra-narrow two-dimensional chromatographic peaks. The sensitivity of the TOF-MS at full-mass range also gives it a valuable advantage for characterization of non-target PCBs and/or other contaminants/residues. The ChromaTOF software allows the ability to generate highly structured two-dimensional chromatograms with classification regions defining the specific congener types. To demonstrate the applicability of Pegasus 4D i.e. GC x GC technique and software ChromaTOF for detection and identification of PCBs apart from OCPs and other contaminants.

Samples

Std stock solution of OCPs pesticides (1 ug/mL)
Std stock solution of PCBs (10-20 ug/mL)
Pork meat extracts spiked at 1-200 ng/mL

Sample preparation

The mixed working standard solution was prepared (concentration 0.9 ug/mL PCBs, 2 ug/mL OCPs) and analyzed by GC x GC-TOF MS. This mixture has been used for Gas Chromatography method optimization.

The pork extracts spiked with OCPs and PCBs to the final concentration 1-200 ng/mL has been used for preparation of matrix standards and analyzed by GC x GC-TOF MS. These standards have been used for estimating working characteristics of the analytical method.

The extract was prepared as follows: 55 g of pork meat was homogenized with 150 g of anhydrous Na₂SO₄. Afterwards the powder was placed into paper extraction cell and stored in exsicator for 2 hours. The extraction took place in Soxhlet extractor using 400 mL hexane-dichloromethan (1:1). The clean-up was performed using HPGPC (PL-gel).

GC x GC-TOF MS analysis using LECO Pegasus 4D

Gas Chromatography: 1st dimension column BPX-5 (20 m x 0.18 mm x 0.18 μm, SGE Analytical Science), 2nd dimension column BPX-50 (2 m x 0.1 mm x 0.1 μm); injection conditions: splitless, 1 min, 260 °C; oven program: 50 °C, 2 min, 20 °C/min to 180 °C, 4 °C/min to 300 °C; oven program of the secondary oven: 50 °C, 2 min, 20 °C/min to 190 °C, 4 °C/min to 310 °C; modulator temperature offset: 50 °C; modulation time: 3 s; hot pulse time: 0.6 s; carrier gas: He; column flow: 1 ml/min; transfer line temperature: 250 °C.

Mass Spectrometry: ionisation: EI; ion source temperature: 250 °C; acquisition rate: 200 Hz; mass range: 45-500; detector voltage: -1750 V; solvent delay: 210 s; analysis time: 37.5 min.

Results

As long as, all the analyzed sample has been processed by automated peak finding and deconvolution function the potential coelutions could have been traced. Within peak finding, the ChromaTOF software automatically detects peaks at all acquired single masses above certain signal-to-noise level (S/N=50 was used in the given case). After that, deconvolution algorithm mathematically separates mass spectra of chromatographically coeluted compounds. Deconvoluted spectra are then compared to NIST library and the identification is performed automatically. The TOF-MS in this work have been used in order to evaluate the separation potential of orthogonal two-dimensional GC system. In Figure 1 contour plot from GC x GC-TOF MS analysis of mixed standard solution is shown. In GC x GC two columns of different selectivity are applied for the separation of each mixture component and therefore higher separation capacity is achieved. In the particular application, BPX-5 column was used for the first dimension and BPX-50 for the second dimension. Therefore, compounds differing by either volatility or polarity have been effectively resolved. In particular, peaks of columns bleed are positioned higher in the contour plot, followed by more polar oxy-compounds, chlorinated aromatic compounds, less polar OCPs and hydrocarbons at the bottom. The more polar functional groups are contained in structure, the higher in contour plot a compound is found. A good example is shown in Figure 2B, where GC x GC separation of compounds unresolved, if only 1D GC had been used (PCB 28, HCH in given case), are shown. In Figure 2A a part of contour plot where target analytes is zoomed. The method gave excellent linearity and limits of detection when applied to spiked pork meat (Table 1).

Conclusions

In this application GC x GC-TOF MS was used in analysis of PCBs and OCPs in solvent standards and real sample. The aim was to show the compatibility and separation potential of GC x GC within this particular task. The TOF MS system was used to trace down potential coelution and confirm the presence of analytes. The GC x GC, applying right column set-up (BPX-5, BPX-50 in our study) caused the enhancement of separation of target analytes. So the identification of target analytes, thanks to sufficient separation, may be also done only based on retention times in first and second dimension of GC x GC i.e. without mass spectral information. The connection of GC x GC to other more specific detector such as electron capture detector (ECD) would provide additional sensitivity.

Compound	Repeatability (RSD, %, n=5)	Linearity (R ² , 5-200 ng/g)	LOD (ng/g)
Pesticides			
HCB	2	0,9980	0,5
DDT	5	0,9891	0,5
DDE	7	0,9967	0,5
DDD	9	0,9984	1,5
lindan	4	0,9990	2
endrin	11	0,9956	2,5
dieldrin	12	0,9968	2,5
chlorpiryfos	9	0,9979	4
heptachlor	8	0,9989	3
PCBs			
PCB 28	5	0,9982	2,5
PCB 52	9	0,9965	3
PCB 101	6	0,9945	5
PCB 118	11	0,9967	3
PCB 138	17	0,9941	2
PCB 153	13	0,9970	4,5

Table 1. Selected compounds limits of detections (LODs) and repeatability of measurement from spiked pork meat samples by GC x GC-TOF MS.

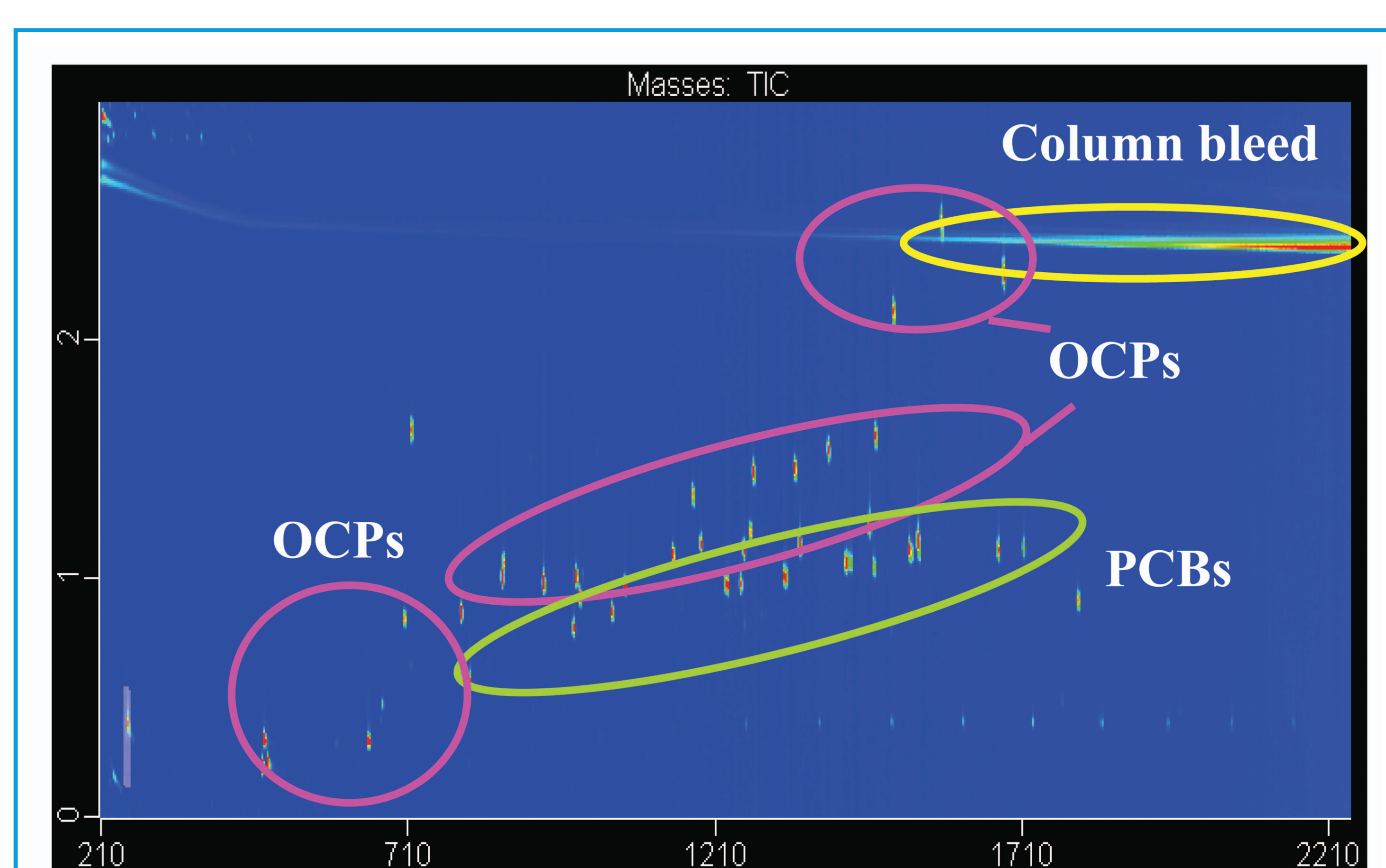


Figure 1: Contour plot obtained by GC x GC-TOF MS analysis of mixed solvent standard at concentration 100 ng/mL of OCP and PCB mixture.

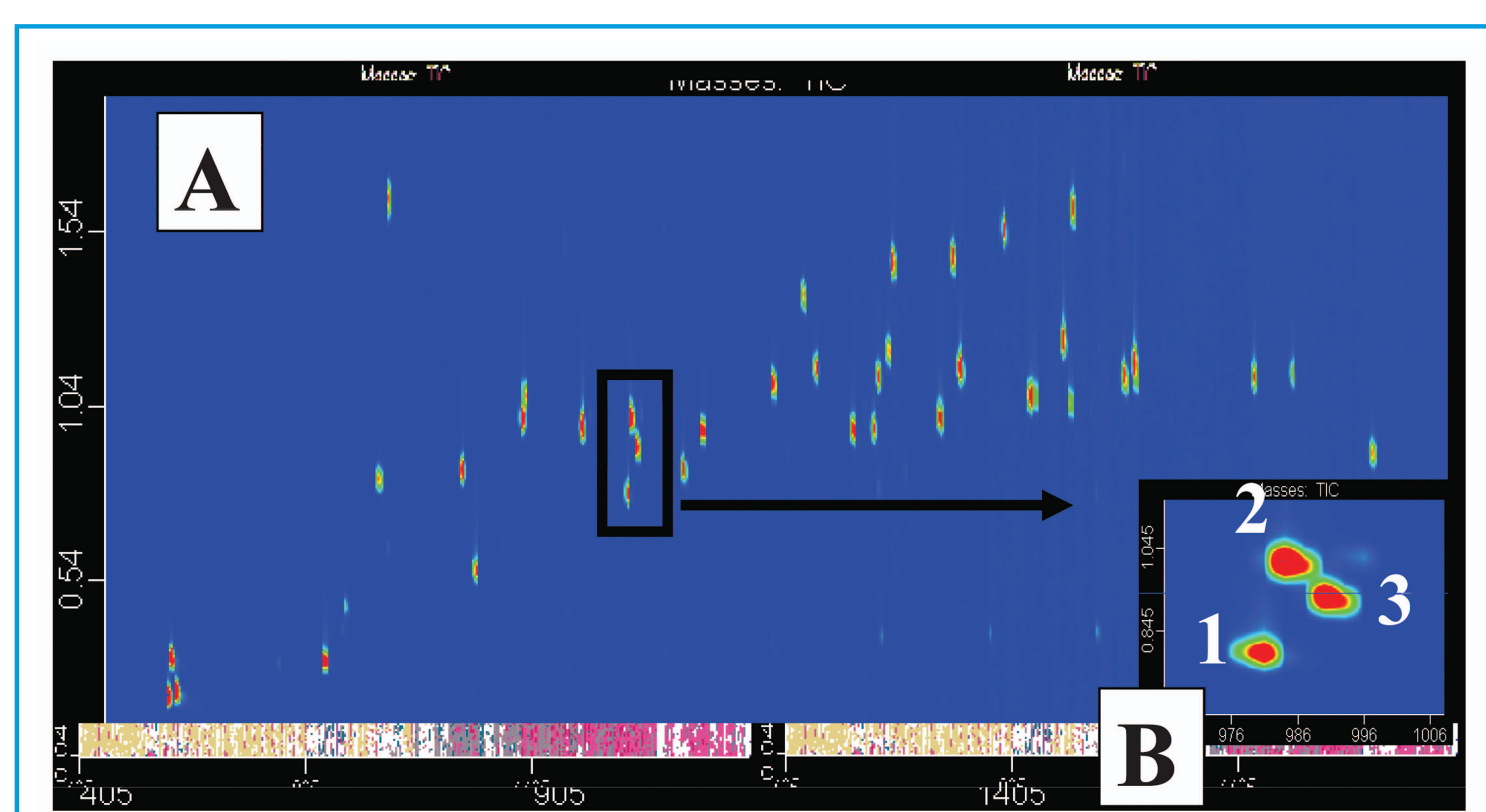


Figure 2: (A) Contour plot obtained by GC x GC-TOF MS analysis of mixed solvent standard at concentration 100 ng/mL of OCP and PCB mixture. Zoomed part of PCB elution region showing separation of target analytes (PCBs) from each other and OCPs. (B) Example of separation: shown analytes are PCB 28 (1), δ-HCH (2) and heptachlor (3).

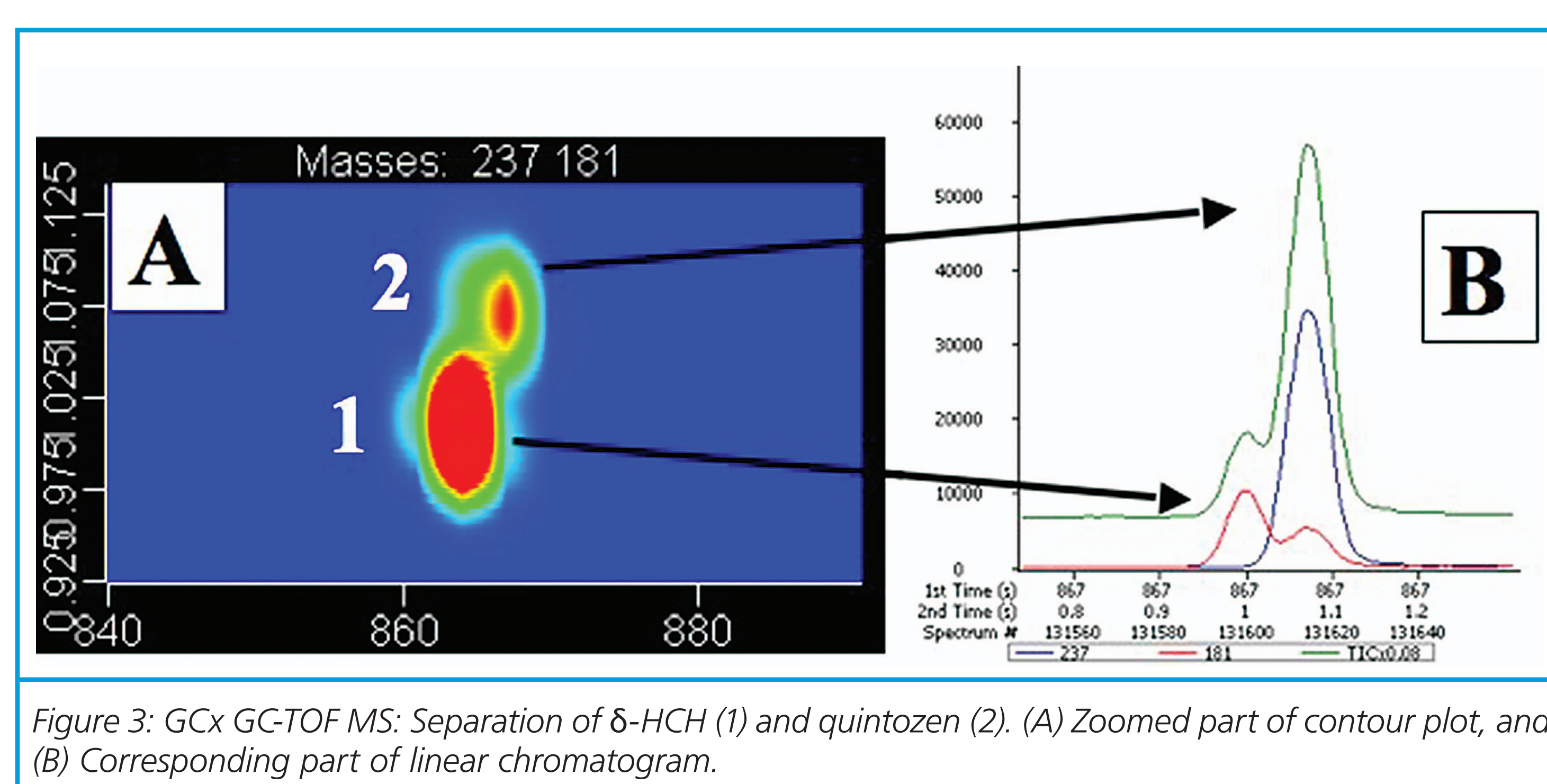


Figure 3: GCx GC-TOF MS. Separation of δ-HCH (1) and quintozen (2). (A) Zoomed part of contour plot, and (B) Corresponding part of linear chromatogram.

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