DETERMINATION OF PCBs, OC PESTICIDES, CHLOROBENZENES, AND PCNs USING GCXGC-ECD

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Abstract
Analysis of halogenated organics using GCxGC-ECD can reduce analysis time and costs by decreasing the sample preparation time and the number of instruments used. The enhanced selectivity of GCxGC enables a less selective detector such as ECD to be used in the analysis of persistent environmental contaminants. Most congeners of PCBs, OCs and CBs can be separated and quantified using GCxGC-ECD. By selecting specific column combinations such as DB-17 x Rtx-PCB and DB-1 x Rtx-PCB as well as strict analytical conditions more classes of compounds (PCN, PCDE presented in this paper) can be separated and quantified. The method may potentially be used as a screening method for the determination of other compound classes, including dioxins, and dioxin-like compounds as well as new emerging contaminants in the environment.

Introduction
Organohalogenated compounds are significant environmental contaminants due to their persistence and toxicity. Compounds such as polychlorinated biphenyls (PCBs), chlorobenzenes (CBs), polychlorinated naphthalenes (PCNs), polychlorinated diphenylethers (PCDEs), and organochlorine pesticides (OCs) were identified in environmental samples and are generally known to bioaccumulate and biomagnify. PCBs, OCs, CBs, and PCNs are routinely analysed in many environmental matrices and some compounds (e.g. PCB 126, PCN 66/67) exhibit significant dioxin-like activity. Classical sample analysis may involve complex sample preparation such as extraction, clean-up and splitting of extracts into multiple fractions. This is followed by conventional gas chromatography (GC) analysis of these environmental contaminant groups in several runs.

Comprehensive two dimensional GC (GCxGC), a relatively new way to solve GC separation problems, can be successfully used for complex environmental samples. GCxGC involves a serial column configuration (employing orthogonal phases) separated by a thermal modulator. Due to the modulation process, most GCxGC peaks are very narrow, on the order of 50 to 250 ms wide, requiring a fast detector. The electron capture detector (ECD) is often used for the analysis of organohalogen compounds due to its high sensitivity for halogenated compounds. The µ-ECD detector, a modification of the classical ECD, was optimised to be used with the GCxGC system[1]. The µECD detectors have an internal volume of 30- 150µl (may still cause band broadening) and the data acquisition frequency is typically 50Hz[2]. The best results were obtained when working at the maximum flow of make-up gas (150 ml/min) and at temperatures above 300ºC[3]. A major draw back to the ECD is the lack of selectivity between halogenated compounds therefore requiring chromatographic separation in order to obtain accurate quantitative results.

Currently, the Ontario Ministry of the Environment (MOE) uses four different methods on four different instruments in order to analyse PCBs, OCs, CBs, and PCNs in environmental matrices such as biota (fish, clams), sediment, and sludge. By developing a new comprehensive multi-dimensional gas chromatography – electron capture detector (GCxGC-ECD) method presented in this paper, will enable simultaneously analysis of the compounds classes mentioned above. GCxGC increases peak capacity by applying two independent separations to a sample resulting in improved resolution of target compounds in a single analysis.

Materials and Methods
Sample preparation: Surrogate standard solution was added prior to extraction (decachlorobiphenyl and 1, 3, 5-tribromobenzene). Sediments samples were extracted using acetone and 25% mixture followed by sonication two times for 15 minutes (MOE, 2006)[4]. Before being analysed, the samples were cleaned-up with Florisil (100–200 mesh, Caledon Laboratories) and eluted with 25ml of hexane followed by 25 ml of 25% dichloromethane/hexane (MOE, 2006). The extracts are then evaporated to 1ml final volume using a Zymark Turbovap LV evaporating system (Zymark Corp., Hopkinton, MA, USA).

Standards used: PCBs as Aroclor obtained from Restek Corporation (Bellefonte, PA, USA), PCB congeners obtained from Wellington Laboratories (Guelph ON, Canada), CBs and OCs obtained from UltraScientific (North Kingstown, RI, USA), PCNs obtained from Cambridge Isotope Laboratories (Andover, MA, USA).

Analysis: The PCBs, OCs, CBs, PCDE, and PCNs standard solutions along with the sediment final extracts were analysed using a GCxGC-ECD system provided by LECO Corp (Benton Harbor MI, USA). This system is equipped with a stationary quadruple jet dual-stage modulator.

The following chromatographic column combinations were used in this research: (1) a 30m DB17, 0.25mm id, 0.15µm film thickness as the first dimension column and 1.3m Rtx-PCB, 0.18mm id, 0.18µm film thickness as second dimension and column set (2) a 30m DB1, 0.25mm id, 0.25µm film thickness as first dimension column, a 1.6m Rtx-PCB, 0.18mm id, 0.18µm film thickness as second dimension. The connections between the first dimension and second dimension columns were made using a deactivated pres-fit connector (Restek Corp.). The GCxGC-µECD conditions were as follows: for column combination (1) 1µL splitless injection in a split/splitless gooseneck, 4mm i.d liner (Restek Corp.), injector 250ºC, modulation period 4 sec to 8sec., modulator temperature offset 30ºC, Helium flow 1.0mL/min, primary oven 80ºC (2min) to 280ºC at 24ºC /min (hold 5min), secondary oven 30ºC temperature offset (315ºC final temperature), µECD at 300°C, 150mL/min argon/methane make-up gas, for column combination (2) 1µL splitless injection in a split/splitless gooseneck, 4mm i.d liner (Restek Corp.), injector 250ºC, modulation period 6 s., modulator temperature offset 30ºC, Helium flow 1.0 mL/min, hot pulse 1.0 sec., primary oven 80°C (2min) to 160°C at 10°C/min, then to 280°C at 4°C/min (hold 1 min), secondary oven 30ºC temperature offset, µECD at 300°C, 150mL/min argon/methane make-up gas.

Results and Discussion

The analyses showed that GCxGC-ECD yields good chromatographic separation of the different contaminant classes of interest. Thus, more than 100 compounds can be simultaneously separated and quantified by using this technique. In order to asses the separation of PCBs, OCs, CBs, PCDE, and PCNs, several column combinations were tested as well as different GCxGC conditions. As a result, two column combinations were selected to yield the best results for the purpose of this study: DB-17 x Rtx-PCB (column combination 1) and DB-1 x Rtx-PCB (column combination 2). In addition, different modulation times were applied to resolve the coelutions and the best results are selected for quantification.
The chromatogram presented in Figure 1 represents the 1D chromatogram of the overlaid peaks of PCB, OC, CB, PCDE and PCN standards analysed by using the column combination (1). This shows how a classical one dimensional GC-ECD analysis looked when injecting the standard mixture of the target compounds.

The target compound classes are chromatographically separated in second dimension as shown in Figure 2 when using the same column combination (1).

Figure1. 1D chromatogram – overlaid peaks of PCB, OC, CB, PCN and PCDE standards

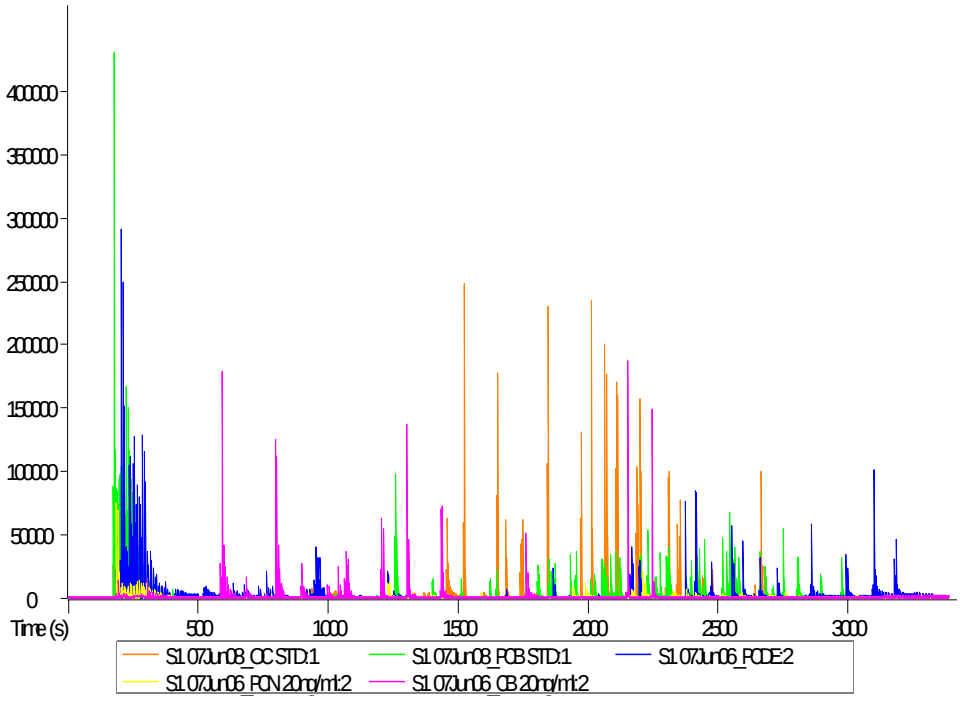
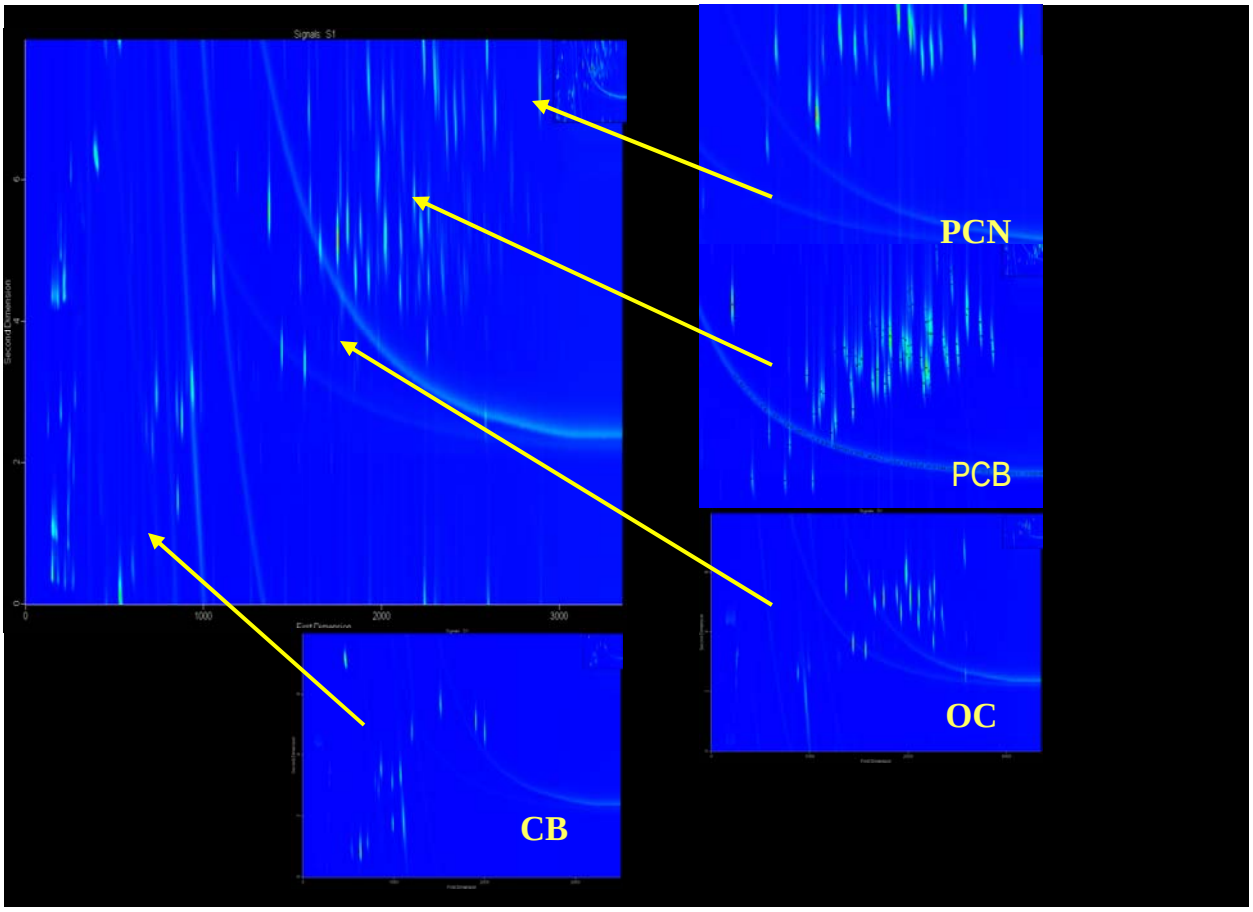


Figure 2. PCB/OC/CB/PCN standard mix – DB17xRtx-PCB



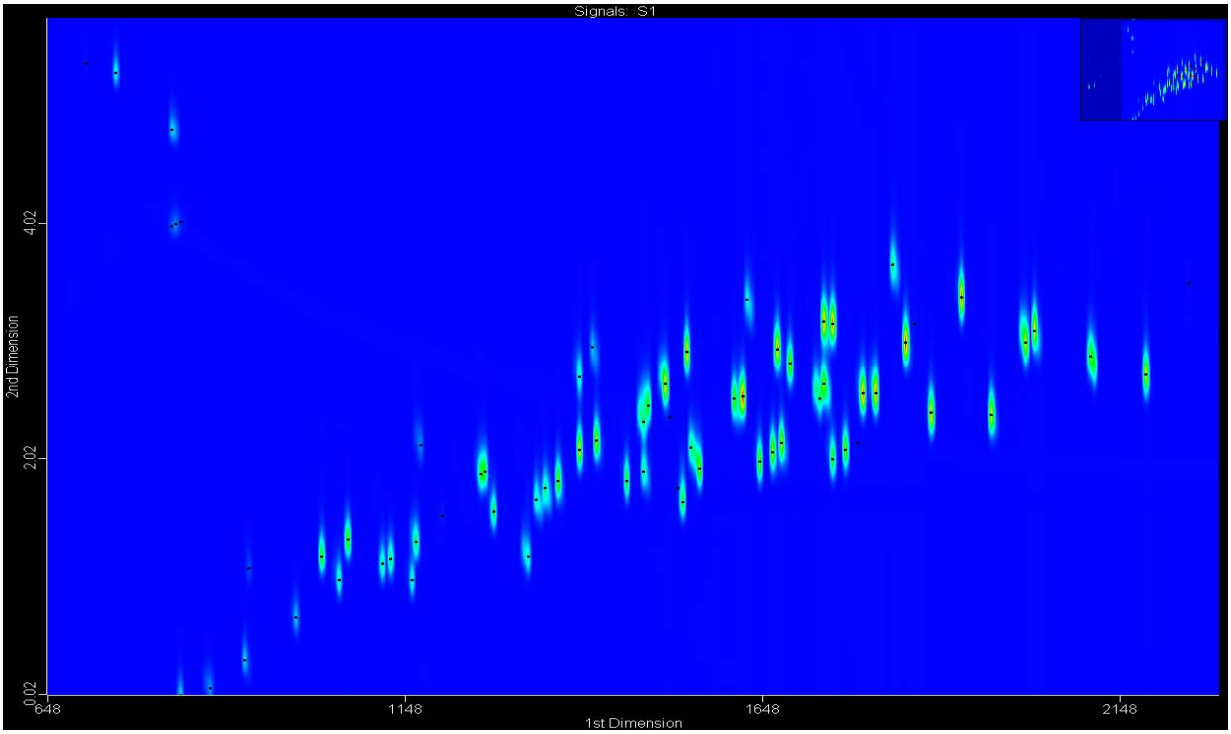
Sediments samples were extracted, cleaned-up and then analysed using column combination # 1 under the GCxGC conditions mentioned in the materials and methods section. The table below shows values for selected OCs and CBs in comparison to the classical GC-ECD method presently used by MOE[4]. The difference seen between the results for p, p'-DDE is because when using one dimensional GC some PCBs can interfere with the compound of interest while in GCxGC they are completely separated resulting in more accurate quantification.

Table 1. Comparison of results GC-ECD vs. GCxGC-ECD

Analyte Name	**GC-ECD (pg/µL)**	**GCxGC (pg/µL)**
Heptachlor	236	212
Aldrin	276	222
p,p'-DDE	409	214
Hexachloroethane	11	4
1,3,5-Tribromobenzene	19	14

For the second column combination (DB-1 x Rtx-PCB) the 12 dioxin-like PCBs (DL PCBs) are separated and their quantification can be used as a screening method for contaminated samples.

Figure 4. PCB standard – DB1xRtx-PCB



This GCxGC-ECD method can potentially replace the existing four methods for individual classes of compounds. Furthermore, the technology may potentially be used as a screening technique for non-target compounds or new emerging contaminants in environmental samples.

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