DETERMINATION OF PCBs, OC PESTICIDES, CHLOROBENZENES IN SLUDGE AND SEDIMENT SAMPLES BY GCxGC-ECD

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Abstract
Gas chromatographic analysis of polychlorinated biphenyls (PCB), organochlorine pesticides (OC) and chlorobenzenes (CB) is one of the most common analyses performed by environmental laboratories. Using comprehensive two-dimensional GC (GCxGC), target analytes from these different compound classes can be determined simultaneously in a single analytical run. The enhanced selectivity of GCxGC enables a less selective detector such as an electron capture detector (ECD) to be used for the analysis of a number of persistent environmental contaminants.

Introduction
Organohalogen compounds are important environmental contaminants due to their persistence and toxicity. PCBs, OCs, and CBs were identified in environmental samples and are generally known to bioaccumulate and biomagnify. Classical sample analysis may involve complex sample preparation such as extraction, clean-up and extract fractionation followed analysis on several different gas chromatography (GC) column phases. Conventional GC offers good peak capacity but it fails to separate many individual constituents in complex environmental samples. Comprehensive two-dimensional gas chromatography (GCxGC) provides significant increases in separation power, peak capacity and speed of analysis[1]. GCxGC involves a serial column configuration (i.e. DB1-Rtx-PCB presented in this paper) separated by a thermal modulator. GCxGC increases peak capacity by applying two independent separations to a sample resulting in improved resolution of target compounds in a single analysis. Due to the modulation process, most GCxGC peaks are very narrow requiring a fast detector. Time-of-flight mass spectrometers (TOFMS) are the detectors of choice because they enable mass spectral deconvolution of overlapping peaks when the fragmentation patterns are different[2]. The ECD is often used for the analysis of organohalogen compounds due to its high sensitivity for halogenated compounds. A major drawback of 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 three different methods on three different instruments in order to analyse PCBs, OCs, and CBs for sediment and sludge samples. The new comprehensive two-dimensional gas chromatography – electron capture detector (GCxGC-ECD) method presented in this paper, enables simultaneous analysis of the compounds classes of interest.

Materials and Methods
Sample preparation: A surrogate standard solution was added prior to extraction (decachlorobiphenyl and 1, 3, 5-tribromobenzene). Sediment/sludge samples were extracted using dichloromethane: hexane= 1:4 (v/v) using automated solvent extraction (ASE 200, Dionex). The extraction conditions are as follows: one cycle extraction at 100°C, heat time 5 min., purge time 90 sec., flush volume 60%. Samples extracts were cleaned-up using SPE cartridges (silica, Sep-PakTM Plus, 1g, Mega Bond Elut HFTM, Varian, Mississauga, ON, Canada) and eluted with 15ml dichloromethane: hexane= 1:4 (v/v). The extracts are then evaporated to 1ml final volume in iso-octane using a Zymark Turbovap LV (Zymark Corp., Hopkinton, MA, USA). Copper treatment is applied to all samples to remove the sulphur interferences prior to analysis.
Standards and reference materials used: PCB congeners obtained from Wellington Laboratories (Guelph ON, Canada), CBs and OCs obtained from UltraScientific (North Kingstown, RI, USA), sediments reference materials

SRM 1944 from NIST (Gaithersburg, MD, USA), sludge reference material CNS-312 from RTC (Laramie, WY, USA), 4,4'-dibromo-octa-fluoro-PCB used as internal standard for PCB congener quantification.

Analysis: The PCBs, OCs, CBs standard solutions along with the sediment/sludge final extracts were analysed using a GCxGC-ECD system provided by LECO Corp[5]. This system is equipped with a stationary quad jet dual-stage modulator. GC column combinations were: 30m DB1, 0.25mm., 0.25µm as first dimension column, and 1.6m Rtx-PCB, 0.18 id, 0.18µm film as second dimension. GCxGC-µECD conditions: 1µL splitless injection using a split/splitless injector and a 4mm i.d. gooseneck liner (Restek Corp.), injector 250ºC, modulation period 4 sec., modulator temperature offset 35ºC, helium flow 1.5 ml/min primary oven 80°C (2min) to 160°C at 10°C/min, then to 280°C at 4°C/min (hold for 5 min.) , secondary oven 35ºC temperature offset, µECD at 300°C, 150mL/min 5% argon in methane make-up gas. The run time is 45 minutes.

Results and Discussion

Results show that GCxGC-ECD is a very powerful technique providing excellent chromatographic separation of the different contaminant classes of interest. Within class separation was achieved with no coelutions for PCB and OC standards analysed separately (Figure 1, Figure 2) and only one coelution for the CB standard (Figure 3).

Figure 1. PCB congener standard – 2D orthogonal separation

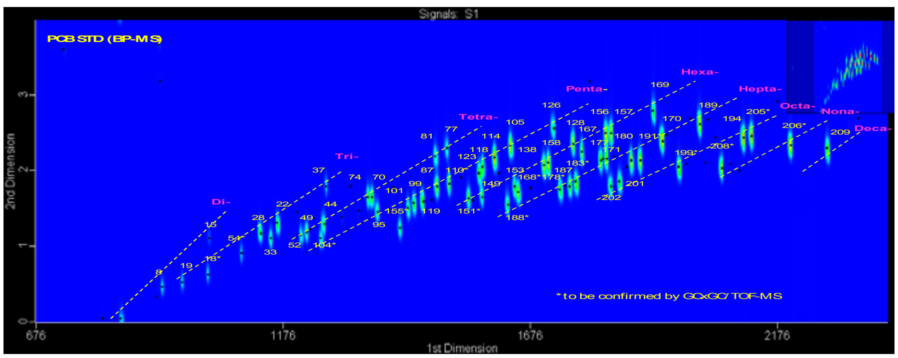
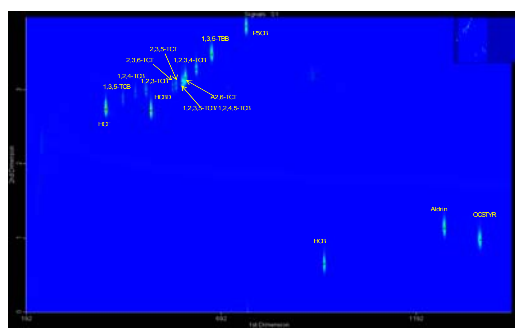


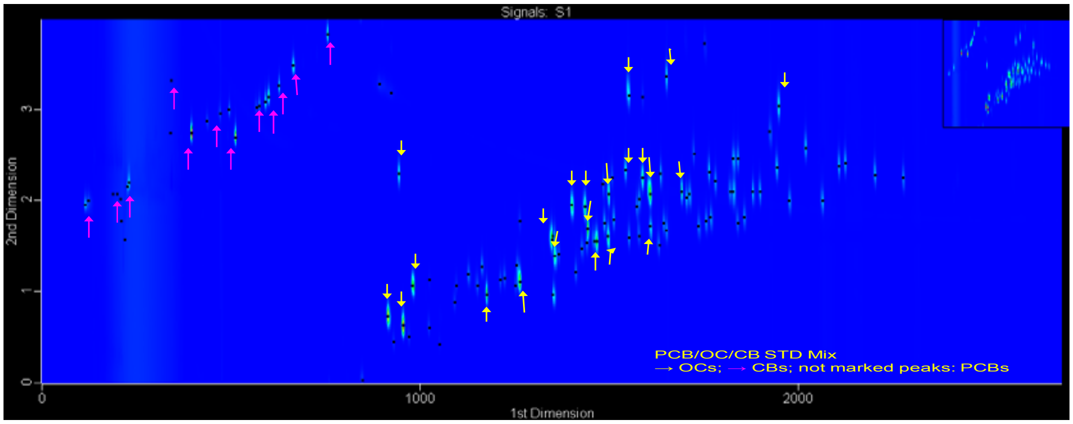
Figure 2. OC standard – 2D chromatogram

Figure 3. CB standard – 2D chromatogram



For a combined PCB/ OC/ CB standard mixture, three coelutions are present between these three classes of compounds: heptachlor-epoxide / PCB 74, cis-nonachlor / PCB 114, and PCB 171/ DMDT (Figure 4).

Figure 4. Between Class Separation by GCxGC-ECD: PCB/OC/CB mix standard solution



Reference materials for sediments and sludges

SRM1944 sediment and CNS312 sludge reference materials were extracted and prepared as described above. Table 1 and Table 2 show some representative compounds analysed by GCxGC-ECD compared with certified values.

Table 1. Sediments Reference Material SRM1944

Name	SRM1944 Expected amount (ng/ml)	SRM1944 GCxGC-ECD (n=3)
PCB 138	62.1	69.8
PCB 153	74.0	64.1
PCB 180	44.3	44.7
p,p'-DDE	86.0	69.0
p,p'-DDD	108	105
p,p'-DDT	119	115

Table 2. Sludge Reference Material CNS-312

Name	CNS312 Expected amount (µg/kg)	CNS312 S.D.	CNS312-04 GCxGC-ECD Mean (n=8)	CNS312-04 GCxGC-ECD S.D.
PCB 138	136	26.5	157	5.86
PCB 153	214	39	234	6.71
PCB 180	232	36	259	8.65
o,p'-DDT	223	93.8	222	5.13
p,p'-DDD	809	235	796	31.8
p,p'-DDE	229	45.7	197	4.92
p,p'-DDT	23.5	6.17	25.8	0.74

Environmental Significance

Sludge samples collected from a Waste Water Treatment Plant (WWTP) in Ontario were analysed by GCxGC-ECD and the results were compared to previous data from the GC-ECD analysis. While only p, p'-DDE and very low amounts of total PCBs were found by classical GC-ECD analysis, GCxGC-ECD revealed many other classes of compounds could be found in the samples. For instance, patterns of additional and unknown compounds e.g. polychlorinated alkanes (PCAs) are seen (Figures 5 to 7) and can be quantified afterwards. Thus, previously archived data can be qualitatively and quantitatively interpreted and historical trends can be determined.

Figure 5. 2D Chromatogram of the sludge sample

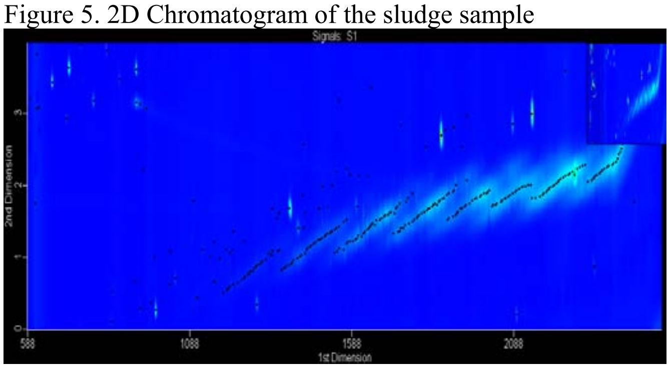


Figure 6. PCA Standard – 55.5% Chlorinated

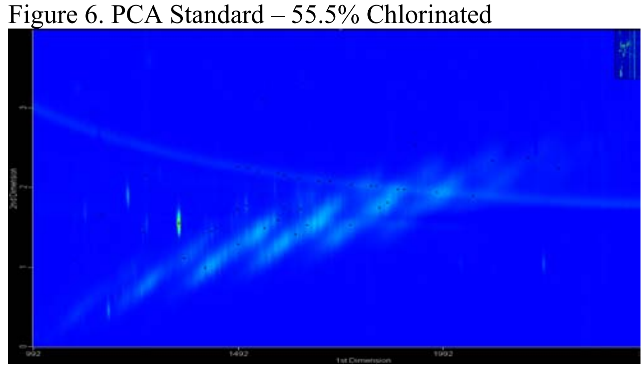
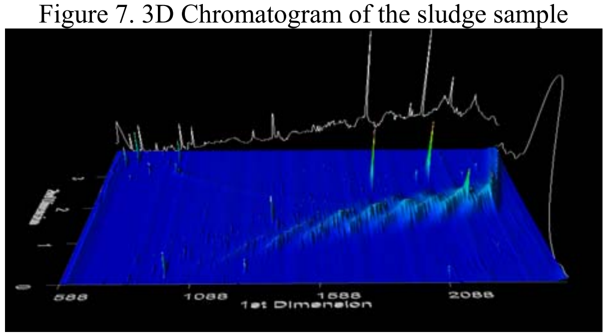


Figure 7. 3D Chromatogram of the sludge sample



Future work

Improved separation between PCBs and PCAs should be achieved for some complex matrices, such as sludges, since some of the higher chlorinated PCBs (i.e. PCB 170, PCB 180) interfere with PCA bands.

This GCxGC-ECD method can potentially replace the existing three methods for individual classes of compounds. Furthermore, the method may potentially be used as a screening method for the presence of other compound classes, including dioxins, and dioxin-like compounds as well as new emerging contaminants in the environment.

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