COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY BY DUAL MSD/ECD DETECTION FOR THE DETERMINATION OF TOXAPHENE

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China (* Corresponding author, E-mail: zhengmh@rcees.ac.cn)

Introduction
Toxaphene is a complex mixture of polychlorinated bornane, camphene, and dihydrocamphene compounds, with an average chlorine content of 68–70%. Theoretically, it consists of 32,768 possible congeners. Toxaphene has been detected in a variety of environmental compartments, e.g., air, soils and sediments, even after their use was restricted. In the past, the analytical techniques used for the determination of toxaphene residues in environmental samples mostly used gas chromatography (GC) with specific detectors. In recent years, a powerful separation technique consisting of a combination of two-dimensional gas chromatography with electron-capture detection (ECD) has been used for congener-specific analysis of complex mixtures of pollutants. Several studies have reported the principles and applications of GC × GC-ECD for the analysis of halogenated compounds, including polychlorinated biphenyl (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and toxaphenes. However, the lack of selectivity of ECD considerably increases the risk of co-elution of congeners.

In this study, the more selective mass spectrometric (MS) detection was used to circumvent this limitation. The second-dimension column was connected to parallel detectors via a micro-fluidic splitting device. This method can provide total and congener-specific toxaphene results using both mass selective detection (MSD) and ECD signals from a single injection.

Materials and methods
An Agilent model 7890 gas chromatograph (Agilent Technologies, CA, USA) was used throughout this study. For the GC × GC analysis, the Agilent 7890 GC was retrofitted with a dual-jet, two-stage loop, thermal modulator ZX2 (Zoex Corporation, TX, USA). Details of the loop-modulator principle have been described elsewhere. The ZX2 thermal modulator has a 9 s modulation period, 300 ms modulation duration, 375 °C hot-jet temperature, 18 L/min cold-jet nitrogen flow rate, and 40 psi hot-jet nitrogen pressure. A low polarity column was used for the first dimension and a higher polarity was used for the second dimension. An Agilent Technologies micro-fluidic splitting device was connected to the outflow of the two-dimensional column, allowing the flow to be split (the split ratio is 1:3; this is determined by the length and diameter of the tubing connecting the splitter to the detectors) between the two detectors via short transfer capillary lines comprising 1.45 m × 0.18 mm i.d. (connected to the ECD) and 1.31 m × 0.18 mm i.d. (connected to the MSD) deactivated fused silica tubing. The oven temperature program was 120 °C (0 min), 10 °C/min to 200 °C, and 1 °C/min to 300 °C. The ECD detector was operated at 300 °C with a nitrogen make-up gas flow at 150 mL/min. The data acquisition rate of the ECD was 100 Hz. The electron ionization (EI) of the mass spectrometer was tuned and calibrated using
perfluorotributylamine (PFTBA). The source temperature and that of the GC-MS transfer line were 230 °C and 290 °C, respectively. The mass range of 100–550 Da was acquired at a data acquisition rate of 15 Hz.

Approximately 10 g of soil were extracted using a Dionex accelerated solvent extractor (ASE 350, Dionex, CA, USA). Agilent ChemStation software (Agilent Technologies, CA, USA) was used to control the GC × GC instrument and to acquire the data. The software GC Image (Zoex Corporation, Houston, TX, USA) constructs a three-dimensional image by placing the detector response on the third axis. When GC peaks are identified using their retention times, GC Image uses template pattern matching to automatically identify and characterize peaks of interest in runs of similar samples under similar conditions.

Results and discussion

Figure 1 shows a diagram of the developed MSD/ECD system. The column set chosen in this system consisted of a 30 m × 0.25 mm × 0.25μm DB-XLB fused-silica column and a 2 m × 0.10 mm × 0.1 μm BPX-50 from SGE (Darmstadt, Germany). Using MSD and ECD as dual detectors in a GC × GC system requires an appropriate split flow to both detectors; the length of the deactivated fused-silica capillary column must be optimized in order to optimize the detectors' relative sensitivities. The flow from the second column was split via a micro-fluidic device to two pieces of deactivated fused-silica capillary column, 1.50 m and 1.31 m long, which terminated at the ECD and MSD detectors, respectively, to provide simultaneous (parallel) dual detection.

![Figure 1. Schematic of the GC × GC-ECD/MSD system used in this study](image)

The collected data are analyzed and quantitated by GC × GC using specific software, i.e., GC Image. Figures 2A and 2B show two two-dimensional plots of the technical toxaphene standard obtained using the GC × GC dual-detection system.
Technical toxaphene (100 mg/L) was injected into the GC × GC. As shown in Figure 2, a high response can be obtained by the dual detectors. For high-concentration samples, this detection mode is useful for the analysis of complex samples. The MS can provide mass spectral information on the compounds, and the relative responses between the two detectors can also be used to verify peak identification.

The analysis of toxaphene in environmental samples by gas chromatography using an ECD is complicated by interferences from other halogenated hydrocarbons. Figures 3C and 3D show the two-dimensional plots of toxaphene congeners in a soil sample, obtained using a GC × GC dual-detector system.

The highlight blob has the same retention time as the congener in a standard mixture. It is obvious that the interferences and toxaphene compounds overlap, obstructing quantitative determinations. The combination of detectors in gas chromatography offers several possibilities for the routine analysis of toxaphene.

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References: