

COMPREHENSIVE MULTI-DIMENSIONAL GAS CHROMATOGRAPHY FOR THE DETERMINATION OF COMPLEX MIXTURES OF HALOGENATED CONTAMINANTS

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Introduction

Many halogenated contaminants which occur in the aquatic environment consist of complex mixtures, often produced for industrial purposes such as polychlorinated biphenyls (PCBs), chlorinated paraffins (CPs) or polybrominated diphenyls ethers (PBDEs), sometimes as a pesticide such as toxaphene and sometimes being formed from other halogenated compounds during various processes such as polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). The method of choice for the determination of these contaminants is gas chromatography (GC), because the volatility of these compounds allows a GC determination, which is preferred because it enables the use of sensitive detection methods such as electron capture detection (ECD) or mass spectrometry (MS). The development of capillary columns¹ in GC enabled a congener-specific determination of a number of these mixtures such as PCBs, PCDDs and PCDFs. Such a congener-specific determination is preferred to a total-determination because it enables the determination of possible toxicological interesting congeners and errors due to differences between technical mixtures and the weathered and/or biotransformed mixtures in environmental samples are being avoided. Therefore, capillary GC has been used successfully in this field over the last two decades. However, more and more scientists have become aware of the limitations of single-column capillary GC for this type of determinations. Initially, discussions focused on the dimensions of the capillary column: lengths and diameters of the columns and temperature programs were optimized to obtain a better resolution. Injection on two different columns for an unambiguous determination was recommended². In some specific cases in PCB research the introduction of (heart-cut) multi-dimensional GC (MDGC) showed that even in certifications in which all participants had used two different capillary columns, some co-elutions (CB101/CB 84, CB 138/CB 163) had been overlooked^{3,4}. Therefore, the use of MDGC was recommended as an essential technique during the certification of reference materials for PCBs. MDGC was found to be particularly useful in the determination of even more complex mixtures such as toxaphene. Until now a proper separation of chlorobornane (CHB) 26 (Parlar nomenclature) from other CHBs has not been shown. In addition, due to the high number of CHB congener that can be present even in weathered or biotransformed samples, several other CHBs can also easily co-elute with others⁵. The use of MDGC offered a 100% better resolution ($R_{MDGC} = 2 R_{single-column GC}$), provided that the columns used were of a complete different character (orthogonal). However, even then not all co-elution problems are solved. For example, a clear disadvantage was the time needed for a complete separation of a number of peaks in complex mixtures. Dependent of the type of separation, up to four heart-cuts can be combined per run⁶. However, as soon as more peaks from the first column should be analyzed, more runs are required, because otherwise the peaks of the different heart-cuts start to overlap again in the second

dimension. The introduction of Comprehensive MDGC (CMDGC) finally offers the possibility of a complete separation of all peaks from the first column in the second dimension⁷. The gain in resolution is dramatic ($R_{\text{CMDGC}} = R_{\text{single-column GC}} \times R_{\text{single-column GC}}$), and, due to the two-step modulation process, there is also a dramatic gain in sensitivity. This technique has the potential to cause a similar breakthrough as the introduction of the capillary column. However, a number of technical difficulties has to be solved first.

Initial experiments focused on the use of a thermal modulator, using a piece of capillary column with conductive material on the outside through which a current was applied, causing a rapid heating of the interface⁸. The durability of the thin metal coatings used was, however, found insufficient. The use of a copper wire, coiled around the interface resulted in a good modulation, in spite of the higher thermal mass⁹. At the same time, a more elegant technique was developed by Phillips, which was based on a rotating thermal desorption modulator, a so-called slotted heater or sweeper¹⁰. A few applications of CMDGC based on this type of modulator for the determination of complex mixtures of halogenated contaminants have been developed and are shown below.

Methods

Two CMDGC set ups are available in the laboratory, one being installed in an HP 6890 GC (ZOEX, Lincoln, NE, USA), and one home-made set-up, built in a Siemens 2-8 Sichromat GC. The experiments shown here were carried out on the Siemens GC. Several parts of a prototype CMDGC of ZOEX were used in this set-up. The modulator tube which serves as the interface between the first and the second column, consists of a 0.083 m x 0.10 mm i.d. capillary column with a 3.5 μm DB-1 stationary phase (Quadrex, New Haven, CT, USA). A slotted heater periodically moves over this modulator to effect the release of compounds retained in the modulator and their transfer to the second column. A splitless injector is used and kept at 270 °C. The splitless time was 1 min. The first column was a 9.7 m x 0.18 mm DB 1 column with a film thickness of 0.40 μm (Chrompack, Bergen op Zoom, The Netherlands). The second column, installed in a separate oven, was a 1.4 or 0.8 m x 0.10 mm CP WAX-52 column (Chrompack) with a film thickness of 0.20 μm . The modulator was connected with the two columns through pieces of uncoated capillary column (0.4 mm o.d., 0.25 mm i.d.) by using Chrompack universal quick seal connectors. Two ECDs were used at a temperature of 330 °C. The carrier gas was helium at a pressure of 4.0 bar and the ECD make-up gas was nitrogen at a pressure of 3.7 bar. A motor platform was installed ca. 10 cm above the oven roof. A ceramic motor shaft driven by a stepper motor was led through a hole in the GC roof. The modulator tube was tightly stretched between a modulator platform in the first oven and a column support point in the second oven. The position of the heater was aligned to prevent contact of the heater with the modulator tube. The frequency of the slotted heater varied, but was normally set at 10 s. Control software for CMDGC (Southern Illinois University, Carbondale, IL, USA) was used to control the modulation period, the sweep speed and the pause time of the heater.

Results and Discussion

With this system it was possible to produce a number of typical CMDGC separations of PCBs and toxaphene. An example is shown in Figure 1, where the reader should realize that a black and white print does not properly bring out the quality of the separation.

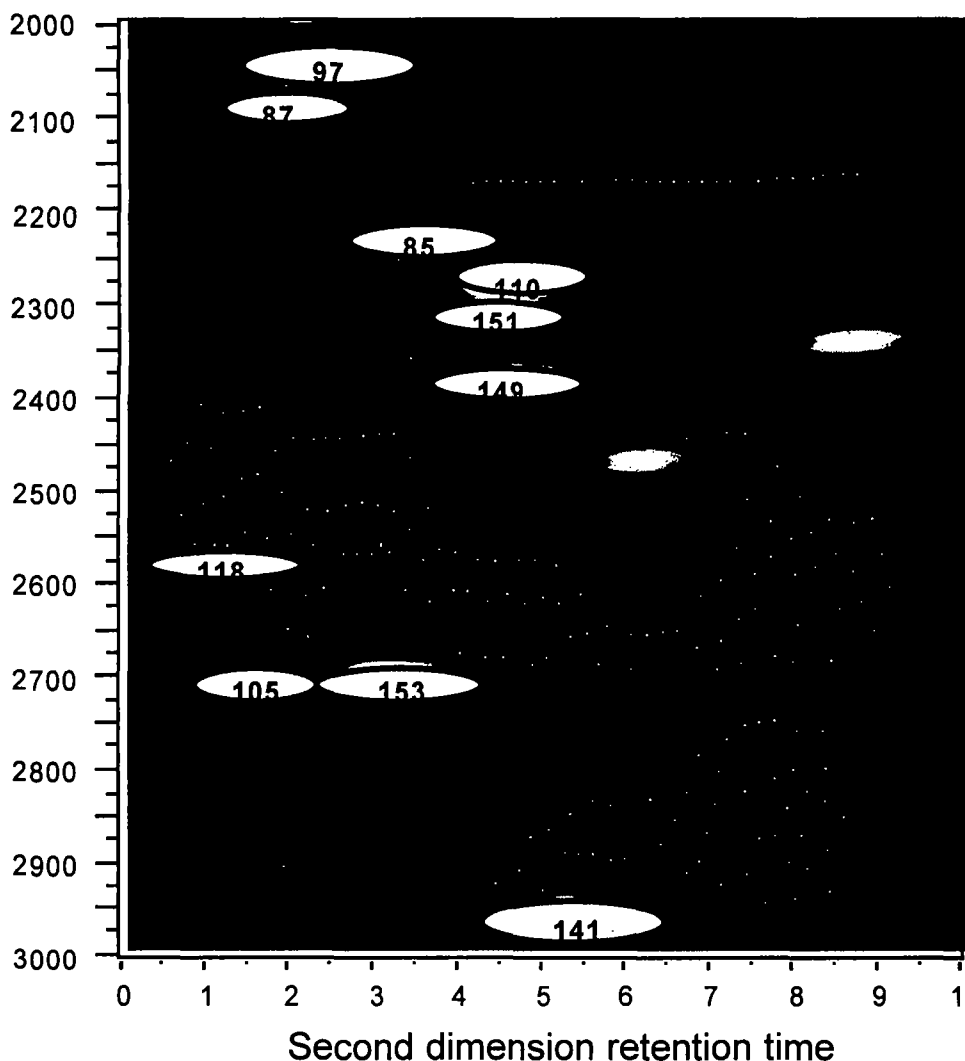


Figure 1. Detail of a CMDGC-ECD chromatogram of an Aroclor 1248 sample.

The ECDs used in this set-up were certainly not the best option. The current set-up resulted in peak widths of 1.3-1.7 s. An increase of the make-up gas from 81 to 131 ml/min did not significantly improve the peak shape. As regards peak broadening other studies have shown better results, but in all of those flame ionization detection (FID) was used while the focus was on compounds with higher vapour pressures^{11, 12}. The problem of relatively low vapour pressures is typical for this class of halogenated contaminants. Better results are expected to be obtained by using the micro-ECD of Hewlett Packard due to the much smaller cell volume of that detector.

Table 1. Repeatability of the CMDGC procedure (n=8)

CB	Injected amount (pg)	RSD (%)
28	8.5	4.3
52	7.5	4.6
101	8.9	
118	14	4.4
153	8.6	4.1
138	9.6	6.9
180	9.1	9.5

Table 2. Results of the analysis of BCR CRM 349.

CB	Concentration found (ng/g)	Certified value (ng/g)
28	44	42 ± 19
52	112	129 ± 38
101	298	348 ± 68
118	480	442 ± 103
153	830	1122 ± 234
138	964	760 ± 173
180	283	288 ± 58

The repeatability of the CMDGC set-up was tested by injecting eight times a chlorobiphenyl (CB) mixture (Table 1). The results show that very acceptable relative standard deviations (RSDs) can be obtained at that level. The quantitative aspects were tested by analyzing a certified reference material (CRM) of CBs in cod liver (CRM 349; EU, BCR, Brussels, Belgium). Five of the CB concentrations found overlapped with the certified range, while the CBs 138 and 153 were just outside that range. This result is certainly promising, given the prototype character of the set-up.

Conclusions

Comprehensive MDGC is a promising technique for the determination of halogenated contaminants. A much better resolution combined with a higher sensitivity is obtained which is expected to be very useful for the congener-specific analysis of complex mixtures such as PCBs and toxaphene. Proper optimization of the temperatures, the speed of the slotted heater and the pause time and the use of a micro-ECD may further improve the performance.

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