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Journal of Chromatography A, 1019 (2003) 65–77
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Evaluation of modulators and electron-capture detectors for comprehensive two-dimensional GC of halogenated organic compounds

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Abstract

Different cryogenic and a heated GC × GC modulator(s) were evaluated and compared for the analysis of high-boiling halogenated compounds. The cryogenic modulators investigated were: (i) the longitudinally modulated cryogenic system; (ii) the liquid-nitrogen-cooled jet modulator (KT2001); (iii) a dual-jet CO_2 modulator (made in-house); (iv) a semi-rotating cryogenic modulator (made in-house) and (v) a CO_2 loop modulator (KT2003); the heated modulator was the slotted heater system (sweeper). Each modulator was optimised with respect to analyte peak widths at half height in the second-dimension. *n*-Alkanes, chlorinated alkanes, polychlorinated biphenyls (PCBs) and fluorinated polycyclic aromatic hydrocarbons (F-PAHs) were used as test analytes. The flow rate of the coolant was found to be an important parameter, i.e. the flow rate of the gaseous nitrogen in the KT2001, and of the liquid CO_2 in the other cryogenic modulators. For the slotted heater the stroke velocity and pause time were important parameters. This modulator had a limited application range in terms of temperature due to a necessary 100 °C difference between sweeper and oven temperature. All cryogenic modulators were found to be suitable for the GC × GC analysis of high-boiling compounds, but the CO_2 modulators are to be preferred to the KT2001 due to a wider application range and slightly narrower peaks. As regards the performance of three commercially available electron-capture detectors (ECDs), the aim was to obtain narrow peak widths in GC × GC, i.e. to avoid band broadening caused by the cell volume. The most important parameters were the flow rate of the make-up gas and the detector temperature which both should be as high as possible. Comparison of analyte peak widths obtained with ECD mode and flame ionisation detection (FID) showed that all ECDs exhibited band broadening compared to the FID. The narrowest peaks were obtained with the Agilent micro-ECD, which has a cell volume of only 150 μl.

Keywords: Modulators; Electron-capture detector; Gas chromatography, comprehensive two-dimensional

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doi:10.1016/S0021-9673(03)01237-8

1. Introduction

Conventional (one-dimensional) gas chromatography (1D-GC) using modern capillary columns offers high peak capacities. However, it fails to separate all the individual constituents of very complex samples from each other and, also, from matrix constituents. With the introduction of comprehensive two-dimensional gas chromatography (GC × GC) some 10 years ago [1], a technique has become available which is especially suited for the separation and identification of organic micro-contaminants in such samples [2–4]. An essential aspect of GC × GC is the so-called modulation. It serves three main goals: (i) collecting and focusing of fractions of peaks eluting from the first-dimension column; (ii) re-injection of the collected fractions into the second-dimension column for separation and, finally, (iii) trapping of eluents from the first column during the launch of the preceding fraction. Different ways of modulating the effluent of the first column into very narrow pulses and injecting these onto the fast second column have been reported. One is to apply heat, as with the earliest modulators, the two-stage-heated modulator [1] and the sweeper system [5]. Modulation can also be achieved by cooling, as was demonstrated with the longitudinally modulated cryogenic system [6] and, more recently, with several jet-type cryogenic modulators [7–9].

Because of the extremely narrow peaks eluting in GC × GC from the short second-dimension column detection has to be very fast. In addition, the detector should not influence the peak width or shape, which means that the detector cell should be as small as possible. As the detection volume in an flame ionisation detection (FID) is limited to the flame volume, this is the detector which contributes least to band broadening [10] and, therefore, is the most popular detector for GC × GC [11,12]. More recently, time-of-flight mass spectrometers (ToF–MS) were coupled to GC × GC for the analysis of petrochemical samples [13], essential oils [14] and pesticides [15]. The use of an electron-capture detector (ECD) in fast GC was evaluated by van Ysacker [16]. He concluded that the ECD make-up flow rate is a key parameter when coupling narrow-bore columns to an ECD. The make-up flow should be sufficiently high to eliminate peak tailing caused by the large detection cell volume (450 μl). In addition, he concluded that at very high make-up flows of 400–1100 ml/min, the ECD exhibits a mass-flow, instead of a concentration-flow sensitive response, the latter being found at lower make-up flows. More recently, a new ECD with an internal volume of only 150 μl and a data acquisition rate of 50 Hz was marketed [17]. In an earlier GC × GC study it was tested using a slotted heater [18], but not with a cryogenic modulator which generates much narrower peaks [19].

Polychlorinated *p*-dibenzodioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are among the most toxic contaminants present in food and environmental samples. The trace-level determination of these compounds is expensive due to the extensive sample preparation that is often required and the legally demanded use of high-resolution mass spectrometers (HRMS). There is a clear need for methods that are less expensive and faster without compromising accuracy and/or precision. Recent developments indicate that a PCDD/Fs plus PCB analysis based on GC × GC may well be a promising alternative congener-specific method [11,18]. The gain in resolution obtained by using GC × GC instead of 1D-GC is so large, that a complete separation of all priority PCDD/Fs and PCBs from each other and from interfering sample constituents may well be possible. This would allow the use of a less expensive mass spectrometer such as a ToF–MS, instead of HRMS and, in principle, the use of ECD detection for screening purposes. These considerations have led us to extensively evaluate the performance of various types of modulators (separation) and ECDs (detection).

When performing GC × GC analyses, volatile analytes are known to be difficult to trap. At the high-temperature end of the chromatogram the opposite problem can occur, namely that re-injection is not fast enough. Therefore, six different modulators and three ECDs were tested for the analysis of high-boiling halogenated organic compounds. For performance testing, mixtures of PCBs, fluorinated polycyclic aromatic hydrocarbons (F-PAHs) and two chlorinated alkanes were used. The F-PAHs were chosen because of their novelty and their demonstrated potential as internal standards in environmental analysis [20,21]; the two chlorinated alkanes were chosen because of their similar responses in ECD and FID. The performance of the ECDs was evaluated in terms of additional band broadening.

2. Experimental

2.1. Chemicals

Three test mixtures were used: (A) a mixture of 1-fluoronaphthalene, 2-fluorofluorene, 1-fluorophenanthrene, 3-fluorofluoranthene, 1-fluoropyrene, 9-fluorobenzo(*k*)-fluoranthene (Chiron, Trondheim, Norway) at 1.5 ng/μl and C_{11}–C_{30} *n*-alkanes (except C_{16} and C_{27}) at 1 ng/μl; (B) a mixture of 1-fluoronaphthalene, 1-chlorodecane and 1-chlorododecane at 6 ng/μl and the C_{11}–C_{30} *n*-alkanes at 1 ng/μl, both in cyclohexane (Baker, Deventer, The Netherlands); and (C) PCB mix 20 (Dr. Ehrenstorfer, Augsburg, Germany), containing CBs 28, 31, 52, 77, 101, 105, 118, 126, 128, 138, 153, 156, 169, 170 and 180 at 10 ng/μl each in *iso*-octane, and further diluted to 240 pg/μl in *n*-pentane (Riedel-de Haën, Seelze, Germany).

2.2. GC conditions

Six different dual-stage modulators (i) a sweeper [5]; (ii) a longitudinally modulating cryogenic system (LMCS Everest, Chromatography Concepts, Doncaster, Australia) [6]; (iii) a liquid-nitrogen-cooled jet modulator (KT2001; ZOEX) [22]; (iv) an in-house constructed dual-jet CO_2 modulator (Vrije Universiteit) [8]; (v) an in-house made semi-rotating cryogenic modulator (with a single jet) (University of Helsinki) [23] and (vi) a CO_2 loop modulator (KT2003; ZOEX) [24] were compared on five identical HP 6890 GCs (Agilent Technologies, Palo Alto, CA, USA) equipped with a split/splitless injector (in four laboratories). In all cases, the conditions influencing the GC performance were kept identical. FID detection was used during parameter optimisation and for comparison of the modulators. The data acquisition rate of the FIDs was set to 100 Hz; they were operated at 300 °C at the following gas flow rates: hydrogen, 40 ml/min; air, 400 ml/min and make-up gas (nitrogen), 15 ml/min. The injector was kept at 280 °C with a splitless time of 1 min. The same first-dimension column, a HP-1 (26.7 m × 0.32 mm i.d., d.f. 0.25 μm; Agilent) was used in all GCs. It was coupled through a glass press-fit connector to a 46 cm (effective length) × 0.100 mm i.d. second-dimension column, which was coated with 0.1 μm BPX-50 (SGE Europe, Milton Keynes, UK). For the sweeper experiments, a slightly different column set-up was used; the first-dimension column was connected to the second-dimension column with a piece of uncoated capillary (7 cm × 0.1 mm i.d.), a modulation capillary (7 cm × 0.1 mm i.d. × 3.5 μm 100% polydimethylsiloxane film (Quadrex 007)) and another piece of uncoated capillary (14 cm × 0.1 mm i.d.). For the KT2003 the first-dimension column was coupled to the second-dimension column via a modulator loop (1.2 m × 0.1 mm i.d. uncoated capillary). For the sweeper and the KT2003 two press-fit connections were needed, while with the other modulators only one was required.

Helium (99.999% purity) was used as a carrier gas and the GCs were operated at constant pressure. The head pressure was adjusted to reach a column flow rate of 1.65 ml/min at 30 °C, and closely similar first-dimension retention times. For the sweeper this resulted in a constant pressure of 130 kPa as against 270 kPa for the KT2003 and 100 kPa for the other cryogenic modulators. The higher pressures used for the sweeper and the KT2003 were a result of the added restriction from the modulator capillary. When using the cryogenic modulators, the columns were temperature programmed from 50 °C (1 min hold) at 5 °C/min to 300 °C (10 min hold), i.e. the total run time was 61 min. In the experiments with the sweeper, the slotted heater had to be kept 100 °C above the oven temperature, and the temperature programme ended at 240 °C and was kept there for 40 min since the modulator capillary had a maximum allowable temperature of 280 °C.

2.3. Modulation

Schematics of the modulators used are shown in Fig. 1 below. For the cryogenic cooling of the modulators liquid nitrogen or liquid CO_2 (Hoekloos; technical grade) was used. Each modulator was operated under optimum conditions (as detailed in related studies) and with a modulation time of 3 s.

The *sweeper* connects the two capillary columns and has two main components: a modulator capillary (a small section of capillary column with a relatively thick stationary phase) and a rotating slotted heater (Fig. 1a). The slotted heater periodically rotates over the modulator capillary to desorb, spatially compress

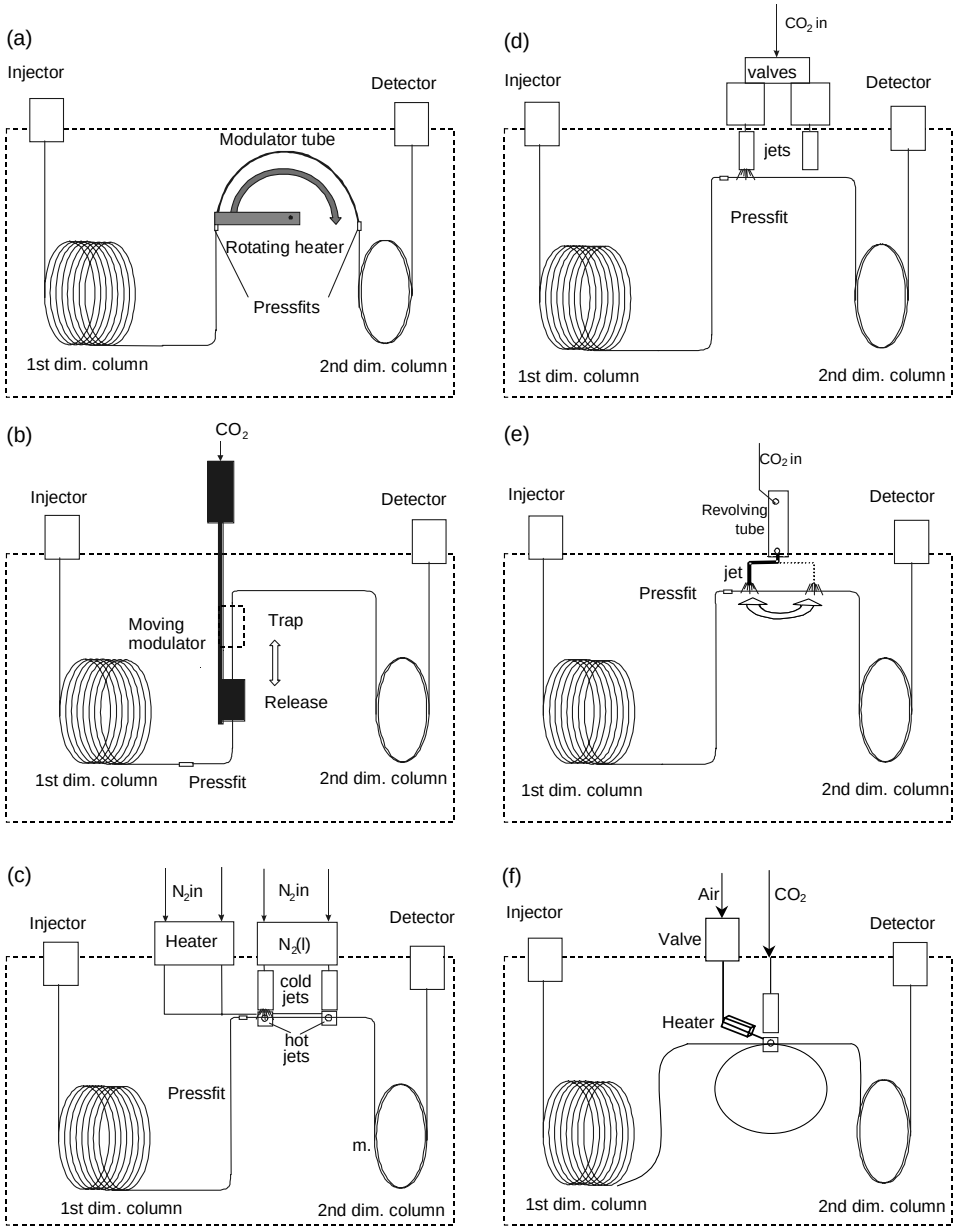

Fig. 1. Schematics of the six modulators used in this study: (a) sweeper; (b) LMCS; (c) KT2001; (d) dual-jet CO_2 modulator; (e) semi-rotating cryogenic modulator and (f) KT2003.

and release fractions of the first-dimension column eluate from the modulator capillary into the second column. The sweeper was kept 100 °C above the oven temperature; the stroke velocity was 0.20 rev/s and the pause time, 0.3 s.

The *LMCS* consists of a 3 cm long cryogenic trap positioned at the front end of the second-dimension column, and accumulates the solutes eluting from the first-dimension column (Fig. 1b). Modulation is achieved by moving the trap upstream away from the

focusing region. When the capillary is exposed to the ambient oven temperature, the trapped solutes are desorbed. The cryo-trap was adjusted to the desired temperature by using a needle valve to regulate the flow of CO_2.

The *KT2001* consists of two cold and two hot jets (all 1/8 in. o.d.), with the nozzles providing the cold jets mounted orthogonally to the hot jets (Fig. 1c). Nitrogen gas is cooled by heat exchange through copper tubing immersed in liquid nitrogen outside the GC and delivered through vacuum-insulated tubing to the cold jets, which provide two continuous jets of approximately 10 l/min of cold nitrogen gas. Remobilisation of the analytes is achieved by alternately applying short pulses of hot air (at 70 l/min). During the first 0.2 s of each modulation cycle, the 'upstream' hot jet (i.e. the one close to the GC injector) was activated. After a delay of 0.8 s, the 'downstream' hot jet was activated during 0.2 s. When the downstream hot jet gives a pulse, the analytes are injected into the second-dimension column.

The *dual-jet CO_2 modulator*, a device made in-house (Vrije Universiteit), consists of two jets and two electrically driven two-way valves (Asco, Florham Park, NJ, USA) that alternately open and close the liquid CO_2 line through two pieces of 40 mm × 0.8 mm i.d. capillary, and are coupled to the nozzles which each consist of seven 50 mm × 0.1 mm i.d. capillaries (Fig. 1d). To prevent ice formation on the outside of the jets at low oven temperatures, they are inserted in a 12 mm diameter brass socket to increase the thermal mass. The part of the second-dimension column in which the modulation takes place, is stretched and secured between two Valco (VICI, Schenkon, Switzerland) unions mounted on a bracket in order to avoid vibration of the column. The unions are mounted on two bands of 0.9 mm-thick resilient stainless steel. Their elasticity compensates for any differences in thermal expansion of the steel bracket and the fused silica column. A simple timing device that generates 24 V for valve switching controls the modulation process. The two jets were alternately switched on and off every 1.5 s.

The *semi-rotating cryogenic modulator*, a device also made in-house (University of Helsinki), consists of a single, 180° revolving CO_2 jet with a constant CO_2 flow. Modulation is effected by spraying CO_2 for 1.8 s on the upstream and 1.2 s on the downstream modulation site (Fig. 1e). The turning took about 1 ms. The outer body is made of stainless steel and constructed to fit the empty injector port of an Agilent Model 6890 GC. The CO_2 transfer line is a 0.5 mm i.d. metal tube, which is placed inside the body of the modulator and a revolving metal tube (15 mm o.d.). The nozzle (0.17 mm i.d.) is attached to the outlet of the CO_2 transfer line. To prevent ice formation and to ensure the precise spray of CO_2, an aluminium block (not shown in the picture) is attached to the nozzle. The second-dimension column is kept in place by a holder, which clamps the column between septa and is tightened by a screw in between the modulation sites to prevent it from vibrating. There is no contact of the column with metal parts due to the use of septa between the metal parts of the holder and the column. The movements of the modulator are computer controlled by means of a laboratory-written C++ program.

The *KT2003*, *CO_2 loop modulator* consists of one cold and one hot jet, with the nozzles mounted orthogonally to each other (Fig. 1f). The approach is very similar to that of the KT2001. However, instead of using two cold and two hot jets, a coil of uncoated capillary (1.2 m × 0.1 mm i.d.) is used as a modulator capillary, so that two spots, 0.6 m apart, are cooled and heated simultaneously by one set of jets where the capillary crosses itself. When the hot jet is closed, a flow of expanding CO_2 traps the analytes in both the up- and downstream spots. After a very short hot-jet pulse (ca. 200 ms), the analytes trapped in the downstream spot are injected onto the second-dimension column, and the analytes from the upstream spot are released to the modulator loop, which is long enough to hold these analytes during the hot-jet pulse before they are trapped again in the downstream spot. The cold jet consists of stainless-steel tubing (1/8 in. o.d.) squeezed at the end to create a nozzle. The tubing is placed inside a vacuumed double-wall tube to isolate it from the GC oven and focus the cold-jet stream onto the modulator loop. 1/16 in. stainless-steel tubing is coupled to a gas-sampling CO_2 bottle via a needle valve to control the expansion and, thus, the temperature of the cold jet. The hot jet consists of an aluminium tube (1/8 in. o.d.) on which a heater controlled by the AUX output of the GC is mounted. Air is used as the heating medium. The hot air stream is switched by an electronic valve controlled by an external electronic

box in which the modulation time, opening time of the valve, GC run time and modulation delay can be programmed. The modulator loop is placed inside an aluminium holder which is mounted on the cold jet.

2.4. Electron-capture detection

Three ECDs were tested with respect to band broadening in the detector and for use in fast GC and/or GC × GC analysis. A reference system was set-up using an FID as detector. Unless otherwise stated, the chromatographic conditions were the same as for the modulator test.

The performance of a μECD (Agilent Technologies), which has an internal volume of 150 μl, was compared with that of an FID on an Agilent Model 6890 GC equipped with a KT2001 for GC × GC. ECD make-up flows of 60–450 ml/min and detector temperatures of up to 320 °C were used. The electronic flow controller could achieve make-up flows of up to 150 ml/min; higher make-up flows could be obtained by adding make-up gas through a T-piece immediately in front of the ECD. Helium was used as the carrier gas at a head pressure of 100 kPa. Data were collected at 50 or 100 Hz.

A Shimadzu (Kyoto, Japan) ECD was used in GC × GC on a Shimadzu GC-2010 instrument with a dual-jet CO_2 modulator and compared to an FID mounted on the same system. This ECD has a rather large internal volume of approximately 1.5 ml. Make-up flows of 15–200 ml/min and ECD temperatures of 100–340 °C were used. Helium was used as the carrier gas at a head pressure of 100 kPa. Data were collected at 250 Hz.

As there was no modulator available at that time, the ECD from Thermo Finnigan (Rodano, Italy) was tested by means of fast GC on a Trace GC (Thermo Finnigan), using headspace split injections to create narrow peaks and a 1.2 m × 100 μm i.d. column coated with 0.100 μm DB-5. The volume of the liner was 0.25 ml. Helium was used as the carrier gas at a head pressure of 110 kPa. The Trace ECD had an internal volume of 480 μl and was kept at 300 °C. Make-up flows up to 2050 ml/min were used. The original Trace GC pressure regulator could achieve make-up flows of up to 375 ml/min; higher make-up flows could be obtained when this pressure regulator was bypassed and replaced by wider tubing and a needle valve. With this set-up, 1 μl, 1:530 split injections of the test analytes were performed. The injector was kept at 250 °C and the oven at 150 °C. The ECD measurements were compared to FID detection under the same conditions with the exception of the head pressure (55 kPa) and the split ratio (1:1000). The latter conditions result in a higher inlet flow and, consequently, a shorter hold-up time, which minimises the influence of the injector pulse on the peak width.

2.5. Data handling

Data acquisition was performed by GC × GC (version 2.0z16; Southern Illinois University, Carbondale, IL, USA/Zoex) or by HP Chemstation (Agilent). In the latter case, the raw data were exported in .csv format and then converted to ASCII matrices by use of a home-made conversion programme (Marriott, RMIT, Melbourne, Australia). Contour plots and second-dimension chromatograms were generated by Transform (version 3.4; Fortner Research LLC, Sterling, VA, USA).

3. Results and discussion

3.1. Modulators

For an honest comparison of the modulators, the retention times in the first- and second-dimension should be closely similar for all modulators. Only under these conditions can a valid statement be made regarding which modulator gives the smallest injection pulse and, consequently, contributes least to band broadening in the second-dimension. The chromatograms obtained with all modulators, were closely similar with first-dimension retention times showing a maximum difference of about 1.5 min and the second-dimension chromatograms showing differences of only up to 60 ms, i.e. in the first-dimension CB 105 eluted at 41.02–42.45 min and CB 153 at 41.12–42.50 min. In the second-dimension they were 0.21–0.27 s apart, except for with the KT2003 with which they were only 0.11 s apart.

An important difference between the heated modulator (sweeper) and the cryogenic modulators is that the latter can be used over a wider volatility range due to the fact that the refocusing effect in the sweeper interface has to take place at 100 °C above the oven

temperature, in a short section (10 cm) of a thick-coated 100 μm capillary column [25,26]. Therefore, the temperature programme had to end at 240 °C (40 min) and no comparable data could be acquired for compounds normally eluting above 240 °C (in the temperature programme). CBs 20, 31, 52 and 101 were eluted during the temperature programme, and the other CBs during the isothermal step. The late-eluting analytes, therefore, had a longer second-dimension retention time and, consequently, showed broader second-dimension peaks with the sweeper than with the cryogenic modulators. Although the slotted heater was kept 100 °C above the oven temperature, no significant bleeding of the stationary phase in the modulation capillary was observed, because the temperature inside the modulation capillary is lower than the measured temperature of the slotted heater.

Table 1 summarizes the data on peak widths at half height obtained with the various modulation interfaces. These data were collected with an FID because this detector causes the lowest extra band broadening [10]. The data clearly show that all cryogenically cooled modulators perform better than the earlier developed slotted heater except for a few high- and/or low-boiling analytes modulated with the LMCS, KT2001 or semi-rotating cryogenic modulator. The KT2001, operating on liquid nitrogen (effective temperature, −150 °C), exhibited some band broadening for compounds eluting at high retention times in the first-dimension column, e.g. F-benzo(*b*,*k*)fluoranthene and the last three CBs. This is mainly due to the high flow rates used in the cold jets. During the short time the cold jet is switched off, the warm air from the hot jet cannot heat the modulation site to a sufficiently high temperature to remobilise the collected fraction. This problem can probably be overcome by reducing the flow rate of the cooling gas, using longer hot-jet pulses and/or using a longer modulation period, but this may result in poorer peak shapes at the volatile end of the chromatogram. If a higher hot-jet temperature had been used, the re-injection would also have been more efficient and the peak widths narrower; however, the present heating cartridge and control unit did not allow a higher temperature.

The LMCS and the semi-rotating cryogenic modulators appeared to show band broadening at the lower volatility end of the application range. Obviously, the indirect cooling of the LMCS is not effective enough to trap the most volatile analytes (e.g. *n*-C_{11}, F-naphthalene and 1-chlorodecane) as efficiently as the other cryogenic modulators. Additionally, the CO_2 flow was turned on shortly before the first peaks eluted and the temperature may, therefore, not have been low enough. However, if the CO_2 flow is turned on earlier, there is an increased risk of column breakage. The band broadening for low-boiling compounds observed when using the semi-rotating cryogenic modulator may well be due to a too low CO_2 flow

Table 1
Comparison of various modulators in terms of analyte peak widths at half height (ms) for second-dimension peaks

Analyte	Elution temperature (°C)	Sweeper	LMCS	KT2001	Dual-jet CO_2 modulator	Semi-rotating cryomodulator	KT2003
n-C_{11}	118	115	105	55	50	55	30
F-naphthalene	127	105	90	60	70	125	45
1-Chlorodecane	140	120	65	45	45	80	40
1-Chlorododecane	168	95	45	45	45	70	35
n-C_{17}	199	100	45	40	40	65	30
F-phenanthrene	202	90	70	70	80	80	50
F-benzo(*b*,*k*)-fluoranthene	292	130	105	140	95	100	70
n-C_{30}	300	n.d.[a]	50	50	50	60	35
CB 28 and 31	213	85	65	70	60	70	40
CB 77	245	90	75	80	70	75	45
CB 153	255	100	65	75	65	75	40
CB 105	255	100	80	90	75	70	45
CB 180	273	120	70	120	65	75	40
CB 170	277	n.d.	85	125	70	80	45

[a] Not detected; did not elute from the column.

Table 2
Resolution of CBs 105 and 153 in the second-dimension when using different modulators

Modulator	R_s
Sweeper	1.6
LMCS	1.8
KT2001	1.3
Dual-jet CO_2 modulator	1.8
Semi-rotating cryomodulator	1.7
KT2003	1.5

as a compromise for an optimum trapping of the high-boiling compounds.

The narrowest peaks were found for the KT2003 (30–70 ms) and the dual-jet CO_2 modulator (45–95 ms).

For each modulator the second-dimension resolution of CBs 105 and 153 was calculated as this was the only pair of analytes which co-eluted in the first-dimension (Table 2). Three modulators cooled by CO_2, i.e. the LMCS, the dual-jet CO_2 modulator and the semi-rotating cryogenic modulator, showed the best resolution. Even though the second-dimension peaks were very narrow when using the KT2003, the resolution was worse than for the other CO_2 modulators because of the much higher average linear velocity through the second-dimension column. That is, separation took place at a point far from the optimum of the van Deemter curve. The resolution achieved when using the sweeper was slightly lower and the KT2001 showed the poorest result. This can be attributed to the fact that the KT2001 performs better for volatiles, while the resolution was determined for high-boiling compounds (for which this modulator showed band broadening (cf. above)).

For the analysis of high-boiling compounds such as the PCBs, all cryogenically cooled modulators behave similarly. The best overall performance, considering peak width at half height and resolution in the second-dimension, was obtained with the dual-jet CO_2 modulator.

3.1.1. Hardware requirements and application range

The *sweeper* is a circularly moving thermal modulator, which is difficult to install because major modifications of the GC are needed to make it fit. Two pairs of hands are needed for the column installation, which is tricky and easily takes several hours. The columns are held on a metal plate and are attached by a spring and glue. They are connected to each other via a modulation capillary which contains a thick film of stationary phase and four specially designed micro-press-fits. Continual circular movement makes it a non-robust and less than user-friendly system, liable to abrasion, breakage of columns and leaking problems during operation. Moreover, movement of the modulation capillary by temperature expansion necessitates adjustment every four or so runs. The sweeper is relatively easy to use for a new application, because only the stroke velocity and the pause time need to be optimised. On the other hand, because of the required thermal remobilisation of analytes, the application range for high-boiling compounds is limited by the upper temperature limit of the stationary phase in the modulation capillary. The application range covers all CBs and CDD/Fs and alkanes up to C_{30}, but requires a prolonged final step at, in the present case, 240 °C. The combined information makes it clear why the sweeper is rapidly being replaced by the cryogenic modulators. A comparison of all modulators is given in Table 3. The difficulty of exchanging a column, optimising the modulation for a new application and operating the modulator are compared on a scale ranging from, −− being very difficult or very time consuming, ++ being very easy or very fast.

The *LMCS* is a linearly moving modulator with indirect cooling. Installation is fairly easy as available holes in the GC oven can be used only minor modifications are needed. Column exchange is fairly easy, but not as simple as for the other cryogenic modulators because the column has to be threaded through a couple of narrow passages. The first-dimension column is connected to the second-dimension column by one press-fit before the trap. Modulation takes place on the second-dimension column, which is attached to the modulator by nuts and ferrules. The LMCS needs optimisation of the CO_2 flow, and, consequently, the trap temperature. Recently, Haglund et al. published a study on the effects of temperature and flow-regulated CO_2 cooling [27]. It was shown that the trap temperature has a major influence on the second-dimension peak shape and width. Due to the moving parts, the LMCS is not very robust and the GC column may break due to ice formation at high CO_2 flows and low oven temperatures. Moreover, due to friction the motor which moves the trap up and down, does not

Table 3
Comparison of characteristics of the tested modulators

Parameter	Sweeper	LMCS	KT2001	Dual-jet CO_2 modulator	Semi-rotating cryomodulator	KT2003
Column exchange	−−	+/−	+	++	+	+
Optimisation	+	++	−	++	++	+
Operation	−	+	+	+	++	++
Consumption of CO_2 (kg/h) or N_2 (l/h)	Not used	0.85	1.5–4	1.5–2	1.5–2	0.6
Application range	C_9–C_{30}	C_8–C_{40}	C_5–C_{30}	C_8–C_{30}	C_{10}–C_{30}	C_{11}–C_{30}
Weakness	Extra press-fit; moving parts	Moving parts; regular needle valve adjustment	Regular flow adjustment; column vibration	Clogging of jets; column vibration	Not adjustable during the run	Extra press-fit

always move smoothly. This may cause a very fast erratic movement of the trap and, as a result, column breakage. However, other versions of the LMCS use pneumatic control [6] or a stronger motor [28], which should give less mechanical problems. The LMCS performs well for high-boiling compounds, up to C_{40}, but is not cold enough at low oven temperatures, which results in broad peaks for early eluting analytes, in the present case, C_8–C_{15}. The LMCS has a low CO_2 consumption of only 0.85 kg/h when optimised for CB analysis.

The *KT2001* is a non-moving modulator with direct cooling by liquid nitrogen. It is installed by drilling three holes in the top of the GC oven. Proper installation of the jets is a matter of precision work. It is relatively easy to exchange the column set, as it can be threaded through a cage and secured with nuts and ferrules outside the oven; the cage is clicked in position under the jets. Unfortunately, the modulator is installed in such a way that the press-fit connection touches the back wall of the oven if the piece of second-dimension column in front of the modulator is made as short as is possible. This can cause leaks or column breakage during installation. The ferrules, which keep the column stretched, need to be checked a few times per week and re-tightened every second week. The KT2001 needs thorough optimisation, and regular re-optimisation is required because the flow settings were observed to change with time and the same read-out did not always result in the same peak shape. The most important parameters are the cold flow, the hot flow, the pulse length and the time between pulses. If the pulses are too short, typically less than 100 ms, remobilisation is not complete. Although the KT2001 uses very high gas flows (tens of l/min), the liquid nitrogen consumption is only moderate (1.5–4 l/h). Initially, the KT2001 was supplied with liquid nitrogen by letting gaseous nitrogen pass through a coil running through the whole volume of a 50 cm high container holding 7 l of liquid nitrogen. Unfortunately, with this set-up, the temperature of the nitrogen reaching the jets increased as the level of liquid nitrogen decreased. The design was, therefore, modified in-house, with the coil being held close to the bottom of the container. The temperature was now more constant and the liquid nitrogen needed refilling less frequently. The KT2001 works best for volatiles, but requires separate optimisation for each group of analytes and, consequently, has a narrower application range per run. A possibility to extend the application range during one run would be by using a programmed N_2 flow. The KT2001 is the only modulator that can be used for very volatile compounds. To quote an example, Xu et al. managed to modulate analytes as volatile as pentane [29].

The *dual-jet CO_2 modulator* is a non-moving modulator with direct cooling by CO_2. It is easily installed after drilling two small holes through the top of the GC oven. The jets are the only parts of the modulator which are inside the oven. The GC columns can easily be exchanged because only one press-fit is used, and two nuts and ferrules keep the second-dimension column in place. The nuts are tightened on a bracket, which can be pushed together to stretch the column. The stretching of the column has to be checked daily because the column can vibrate loose due to the effect of large temperature changes on the ferrules holding the column. The ferrules need weekly re-tightening. The parameters that have to be optimised are the CO_2

flow, the valve-open time, i.e. the pulse length, and the position of the jets. The position of the jets needs to be adjusted only at installation and after exchanging the jets upon clogging. The jets consist of seven capillaries each. These can become blocked by particulate matter: if three or four capillaries are blocked, modulation will be incomplete. Care should, therefore, be taken when selecting and connecting the tubing going to the jets. Fortunately, it is easy to clean the capillaries by connecting the jets to an LC pump and flushing them with acetone. The CO_2 consumption is about 1.5–2 kg/h. This is a modulator which is easy to use. In addition, the dual-jet CO_2 modulator gives the best peak shapes for analytes over the complete C_8–C_{30} application range.

The *semi-rotating cryogenic modulator* is a moving modulator with direct CO_2 cooling, with remobilisation being effected by the oven temperature. Installation is straightforward because the modulator fits on an empty injection port. The columns, which are connected by one press-fit, can easily be exchanged because they are clamped between two metal plates and septa using a single screw instead of nuts and ferrules. During the optimisation procedure, the fine-adjustment of the column position and the spray is carried out by adjusting the sector of rotation to ensure that the spray hits the column properly. Once the optimal position has been found, operation is straightforward. The CO_2 consumption is about 1.5–2 kg/h. Even though the semi-rotating cryogenic modulator has moving parts, it may well be the most robust cryogenic modulator because of the constant flow of CO_2 through one revolving jet above the column instead of one or two pulsing jets where extra time is needed to fill the valve. The system can easily be used for 2–4 weeks without any adjustment. No vibration or clogging has been observed. A disadvantage with this modulator may be that the CO_2 flow cannot be adjusted. The application range is similar to that of the other CO_2 modulators, C_{10}–C_{30}, but the performance is slightly poorer for volatiles.

The *KT2003 loop modulator* is very similar to the KT2001 but, instead of using two sets of jets, two modulation sites at the beginning and end of a coiled piece of uncoated capillary in a holder are simultaneously cooled and heated by one set of jets. Installing a column set is easy. One drawback of using the modulation coil is that it has to be glued to the holder; however, this has to be done only when exchanging the coil, which typically is once every 3 months, and not when exchanging the GC column set. There are three main parameters for optimisation: the cold-jet temperature, hot-jet temperature and valve-open time. They are inter-related and also depend on the boiling point and polarity of the target analytes. In our experience, optimisation for a new application takes about 2 days. With the KT2003 the cold- and hot-jet flows are difficult to adjust. For high-boiling compounds, the hot-jet temperature is a critical parameter because it strongly influences the remobilisation of the analytes. On the other hand, for volatiles a very low cold-jet temperature is required to avoid breakthrough. The application range of this system is from C_{11} upwards, but in the newest version gaseous nitrogen cooled by liquid nitrogen can be used instead of CO_2. Then, the application range should be the same as for the KT2001, i.e. start with pentane. The use of the modulation capillary requires two press-fit connections—one more than with the other cryogenic modulators. This can be considered a drawback because of an extra leakage source and because the dead volume of the press-fit may cause additional band broadening, which will negatively influence the second-dimension separation. However, in our experiments no such additional band broadening was observed. This is probably due to the flow at the end of the modulator capillary, which is so high that the press-fit volume does not noticeably contribute to the peak width. The use of a modulator capillary allows the entire second column to be housed in a separate second-dimension oven. This cannot be done if modulation is carried out at the front end of the second column, as is the case with the other cryogenic modulators. Actually, in principle all modulators can be used with a modulator capillary between the two GC columns. However, to the best of our knowledge, this approach has not yet been attempted. Finally, it has to be added that the KT2003 uses a CO_2 gas-sampling bottle for cooling, while all other CO_2 cryogenic modulators use liquid-sampling bottles. The use of a gas-sampling bottle results in a lower CO_2 consumption of about 0.6 kg/h.

The above discussion is summarised in Table 3. A few additional general comments are as follows. For all cryogenic modulators it is important for optimal modulation to keep the column properly stretched,

so that it cannot start to vibrate and, next, break due to the large temperature fluctuations which typically occur. All needle valves or flow controllers need occasional adjustment. One should also consider that the flow and, thus, the modulation often depend on the amount of CO_2 or N_2 left in the container. When keeping the liquid- or gas-sampling CO_2 bottles at room temperature, we found it to be impossible to use more than 50–65% of their contents. If more was used, the expansion was not sufficient to achieve the required temperature drop for modulation. However, if the CO_2 bottles were kept in a thermostated water bath at temperatures between 25 and 50 °C, their contents could be completely consumed. The optimal modulating temperature depends on the analyte and also on the wall thickness of the capillary column.

3.2. Comparison of ECDs

When assessing the suitability of ECD detection for GC × GC, one important aspect is the contribution of the cell volume of these detectors to the band broadening of the eluting peaks. To this end, for the three selected ECDs the peak widths of several chlorinated compounds were compared with those obtained by FID detection. The parameters that had to be optimised were the detector temperature and the make-up flow. The dead volume for an ECD is the complete detector cell volume [10], while for an FID it is only the volume of the flame itself, which is 10–20 μl [30].

The *Agilent μECD*, with an internal volume of 150 μl was introduced a few years ago to replace the conventional ECD with an internal volume of 1.5 ml, which was found [31] to give an excessive contribution to band broadening in GC × GC. Initially, it was assumed that part of this extra band broadening is due to the fact that the Agilent ECD can, according to its specifications, only be operated at a maximum data acquisition speed of 50 Hz. When comparative experiments were carried out by us with an FID at 50 and 100 Hz, the lower frequency was found to generally cause some 20 ms broader peak widths at half height. Subsequently—and partly contrary to the quoted specifications—the data acquisition rate of the ECD was set at 50, 100 and 200 Hz. With otherwise identical instrumental settings, these three data acquisition rates gave next to identical peak widths at half height of 336 ± 2 ms for the test analyte, CB 101. Obviously, the low data acquisition rate did not contribute to band broadening. However, it was found that the signal output of the ECD was 100 Hz, as at 200 Hz each data point was collected twice.

When second-dimension peaks of various test analytes were compared at different detector temperatures (280, 300 and 320 °C) and a make-up flow of 60 ml/min, all peaks were found to tail in the second-dimension separation, with the ECD temperature having little or no effect. Therefore, higher make-up flows were tested. At the maximum flow rate which the commercially available system can provide, 150 ml/min, peaks were some four-fold wider at the base than when using an FID. However, at half height the CB peak widths were 185–200 ms compared to 70–125 ms with FID detection (Table 4). When adding more make-up gas into the ECD via a T-piece at the detector base entrance, band broadening could be further reduced. At a total make-up flow of 450 ml/min the peaks were only two times broader at the base than with the FID, and 140–190 ms at half height (Table 4). Admittedly, at this high make-up flow the resolution of CBs 153 and 105 in the second-dimension was only 0.85 which is much less than the resolution obtained with FID detection ($R_s = 1.27$). Obviously, the ECD contributes to band broadening due to its relatively large cell volume even though it is a micro-ECD), but the extra contribution is moderate. For most applications a make-up flow of 150 ml/min was found to be sufficient. Actually, a previous study, using a HP-1 × HT-8

Table 4
Comparison of ECD and FID detection in terms of analyte peak widths at half height (ms) for second-dimension peaks

Analyte[a]	Agilent[a]			Shimadzu[a]		
	FID	$ECD_{320\,°C}$		FID	$ECD_{340\,°C}$	
		150[b]	450[b]		60[b]	200[b]
CB 28 and 31	70	190	155	125	275	270
CB 77	80	185	140	125	250	250
CB 153	75	n.m.[c]	150	105	n.m.	n.m.
CB 105	90	n.m.	165	110	n.m.	n.m.
CB 180	120	185	155	100	260	180
CB 170	125	200	190	110	275	250

[a] Parameters.
[b] Make-up flow (ml/min).
[c] Not measured due to co-elution.

column set, a sweeper and a μECD at 150 ml/min, it was possible to effect the complete separation of 90 CBs [32].

The *Shimadzu ECD*, which has internal volume of about 1.5 ml and was mounted on a Shimadzu 2010 GC which is, according to the manufacturers, especially suitable for fast GC, was tested in a similar manner as the Agilent μECD—at detector temperatures of 100–340 °C and make-up flows of 60 and 200 ml/min using the highest possible acquisition rate (250 Hz). The detector temperature showed little to no effect on analyte band broadening. However, peak tailing decreased with increasing ECD temperature but was still severe at the highest possible temperature, 340 °C. When using FID detection the CB test analytes had peak widths at half height of 105–125 ms (i.e. slightly higher than in the previous case). On the other hand, with ECD detection at 60 ml/min and 340 °C, the values were as high as 250–275 ms (Table 4) and tailing occurred through the complete second-dimension chromatogram. At higher make-up flows (200 ml/min), peak widths at half height were improved only marginally, i.e. to 180–250 ms, and tailing was also less severe. Still, the separation of CBs 105 and 153 was so poor that their resolution could not be determined. In other words, the Shimadzu ECD cannot be recommended for use in GC × GC. The large contribution to peak broadening has to be contributed to the detector volume which is closely similar to that of the conventional large-size Agilent ECD referred to above, and (also) found unsuitable for comprehensive GC.

Since no modulator was available for the set-up that had to be used, the *Trace ECD*—with an internal volume of 480 μl and kept at a detector temperature of 300 °C—was optimised by means of 1D fast GC using 1-chlorodecane and 1-chlorododecane as test analytes because of their volatility. With the original flow regulator installed on the Trace GC, a maximum make-up flow of 375 ml/min could be achieved. However, this was found not to be enough to overcome the ECD band broadening: peak widths at half height were 470–490 ms as against a mere 110–150 ms for FID. With another flow regulator, make-up flows of up to 2050 ml/min could be tested. However, even at these very high make-up flows there still was distinct additional band broadening, as evident from the measured half-height values of 180–260 ms. It should be added that when increasing the make-up flow from 375 to 2050 ml/min the sensitivity only decreased with about a factor 2. Obviously, despite its moderate cell volume, the Trace ECD cannot be recommended for fast or very fast GC operations. Our explanation may be that the cell geometry of the detector differs from that of the other two ECDs tested.

In conclusion, not unexpectedly cell volume plays a dominant, though not an exclusive, role when selecting an ECD for use in GC × GC. Even with the smallest detector commercially available today, the Agilent μECD, there still is additional band broadening compared with an FID, and some second-dimension tailing. About 10-fold difference in effective cell volume explains this result. On the other hand, if large make-up flows and high detector temperatures are applied, experimental results are fully satisfactory, both with regard to peak shapes and overall resolution and, as has been demonstrated in other studies [30,31], analyte detectability.

4. Conclusions

Quite a number of modulators for GC × GC are available today and new designs keep showing up. One main conclusion of the present study is that cryogenic modulators are clearly superior to the sweeper system where heating to high temperatures plays a critical role. Most cryomodulators perform rather well, but there are major differences with regard to user-friendliness (installation, exchange and optimisation), application range and maintenance. Overall, the dual-jet CO_2 modulator seems to perform the best, with narrow analyte peaks over the complete application range and easy installation and operation (although clogging of the jets occasionally causes some problems). From among the other modulators, the KT2003 CO_2 loop modulator, probably is the most promising: operation is straightforward, consumption of CO_2 is low, analyte peaks are narrow and with liquid nitrogen instead of CO_2, application to highly volatile analytes should be possible (see KT2001). It is interesting to add that, very recently, a single-jet CO_2 modulator has been constructed. Preliminary results are promising [33] but much more wide range testing need to be performed before final conclusions can be drawn.

The introduction of a micro-ECD detector is a major step forward in the analysis of organohalogens in GC × GC. Internal cell volumes should, typically be some 10-fold smaller than those of conventional ECDs. To avoid undue band broadening it is, even then, necessary to use high detector temperatures and very high make-up flows. Experience shows that with future versions of detectors, the range of flow rates that can be covered should be extended to approximately 1000 ml/min to create sufficient flexibility during optimisation.

Overall, one may conclude that, as far as modulation and selective detection are regarded, present-day instrumentation allows state-of-the-art analysis of a wide range of halogenated organic compounds. The continual introduction of new devices indicates that improved performance may be expected in the future.

Acknowledgements

This project was financed by the European Union, Measurements and Testing (Growth Programme) No. G6RD-CT2001-00572.

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