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## Development of a thermal desorption modulator for gas chromatography

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### Abstract

The separation space in gas chromatography can be enhanced dramatically by the comprehensive coupling of two independent separation dimensions. An interface between the two columns must accumulate analytes eluting from the first dimension, focus them and at the appropriate moment transfer them to the head of the second column. A thermal desorption modulator can be used for this purpose. It consists of a capillary in a relatively cold zone which effects trapping and focusing of the analytes. A current through a conductive material on the outside of the capillary provides rapid heating and consequently a fast transfer of the analytes to the second column. Several conductive materials were applied using different techniques and their performance was evaluated. The durability of thin metal coatings was found insufficient. The use of a wire coiled around the capillary was more robust and its temperature response appeared to be fast enough, despite the higher thermal mass. The effect of voltage and heating time on the thermal desorption was studied and various temperature estimations were made. Large-volume on-column re-injection and semi-comprehensive multidimensional gas chromatography of chlorobiphenyls are shown as examples.

**Keywords:** Thermal desorption modulators; Instrumentation; Multidimensional gas chromatography; Large volume injections; Chlorobiphenyls; Polychlorinated biphenyls

### 1. Introduction

The use of more than one dimension of separation in gas chromatography (GC) is often necessary when highly complex samples, such as petroleum products or complex mixtures of environmental contaminants, have to be separated. It is possible to use heart-cut techniques, in which only a relatively small portion of the first separation is transferred to a different type

of secondary column for further separation [1]. Several heart-cuts can be introduced onto the second column, but the number of heart-cuts (per run) is limited because peaks from one cut may interfere with those of another. This will result in the partial loss of the resolution already obtained [2]. The analysis of an entire sample requires sequential injections and heart-cuts and, consequently, takes a lot of time [3,4]. On the other hand, by collecting the complete set of secondary chromatograms, it is possible to construct the complete two-dimensional chromatogram.

The speed of the second separation determines the

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minimum introduction time between heart-cuts. The width of the heart-cuts should not exceed the peak width of the first dimension, otherwise part of the possible two-dimensional peak capacity will be sacrificed. If the second separation can be performed fast enough, it is possible to separate a continual series of short heart-cuts in a single analysis. A method capable of doing that is called comprehensive multidimensional GC (MDGC) [5]. The interface which connects two GC columns “comprehensively”, must accumulate the eluate from the first column for a certain period while the first separation proceeds. After collecting this portion, it must be injected as a narrow plug into the second column. The performance of the interface must be reproducible and non-discriminatory with regard to analyte properties [6].

Liu and Phillips [7] have developed a thermal desorption modulator (TDM) for this purpose. Part of the outside surface of a capillary column is covered with an electrically conductive paint. The capillary is installed between the first and second column, in a cold zone outside the GC oven. Analytes eluting from the first column experience a strong retention in the relatively cold TDM and are, consequently, focused in a small zone. By applying a current pulse through the conductive layer at the appropriate moment, the TDM can be heated very rapidly. This causes the analytes to leave the stationary phase, after which the carrier gas transfers them to the head of the second column. The successful use of the TDM depends on its low thermal mass which allows rapid temperature changes resulting in sharp injection plugs. An improved type of interfacing used by Phillips and Xu consists of two stages: the sample is first trapped in the first part and, then again, in the second part of the modulator [8]. This two-step process ensures extra peak focusing.

TDMs similar to the above have been used for other applications such as multiplex GC [9], on-column sample introduction [10], a combination of large-volume introduction and signal averaging [11] and for high-speed GC in which the whole column temperature is modulated [12]. Other groups have used resistive heating for temperature programmable (PTV) injectors [13] and for on-column cold trap re-injection [14–16]. In these techniques the thermal mass of the interface is large and a large energy

input is therefore necessary. Another consequence of the high thermal mass is a relatively slow cooling process. However, in the applications reported a fast cooling down is not as important as in comprehensive MDGC. The advantage of these interfaces is that they are more robust.

The heating period of a TDM —which should, of course, be as short as is possible— must at least be as long as the time it takes for the trapped analytes to be transferred out of it. When a TDM is heated to a temperature at which all analytes are in the vapour phase, the minimum heating period depends on the linear gas velocity and the length of the TDM. This minimum period can be decreased without changing the performance of the first-dimensional separation, by introducing extra carrier gas just in front of the TDM or by decreasing the internal diameter of the TDM.

In this paper the construction and optimisation of a TDM is reported. Because of the required fast TDM temperature changes, proper selection of the electrically conductive materials applied on the outside of capillary columns was found to be of primary importance. Several ways to connect the TDM to the electronic circuit were evaluated. A pulsed heating method was derived to avoid too high temperatures during prolonged heating periods. The influence of different parameters such as voltage, pulse length and pulse interval which affect the TDM temperature and the length of the heating time, were studied. Various approaches were used to estimate the TDM temperature. Large-volume on-column re-injection and semi-comprehensive MDGC of chlorobiphenyls (CBs) were used to demonstrate the practicality of the TDM-based approach.

## 2. Experimental

### 2.1. Materials and chemicals

Iso octane (nanograde) and CBs (98–99% purity, congener numbering according to Ref. [17]) and technical polychlorinated biphenyl (PCB) mixtures Aroclor 1254 (Monsanto, St. Louis, MO, USA) were obtained from Promochem (Wesel, Germany). Copper tubing (3.2 mm O.D.×2.1 mm I.D.) and polyimide were purchased from Chrompack (Middelburg,

Netherlands). Solder (Sn–Pb, 6:4) was obtained from a local electronics shop.

## 2.2. TDM construction

The various TDMs were prepared from 30-cm pieces of 0.22 and 0.10 mm I.D. capillary columns with 0.51 and 0.12  $\mu\text{m}$  thick CP-Sil 8 CB-type stationary phase films (5% phenyl 95% methyl polysiloxane), respectively, from Chrompack. A thin electrically conductive layer of Electro-kit, an acrylic-resin-based coating containing metallic silver (Perfecta International, Goes, Netherlands) was deposited on the outside of several capillary columns. A uniform layer of conductive material is necessary to obtain the same heating at every point of the TDM. This was done by painting them with a small brush or by slowly pulling the columns through a paint bath and drying at 423 K. The coating was diluted with a small amount of acetone (technical grade, Chemproha, Haarlem, Netherlands). If necessary, several layers were applied until a resistance of 0.5–1.0  $\Omega\text{ cm}^{-1}$  was obtained.

Pure metal was deposited on capillary columns (30 cm) through metal evaporation by “Joule heating” using an Universal Coating System L 560 (Leybold, Köln, Germany). Silver (No. BD 481 178-T) and aluminium (No. 261549) were obtained from Balzers (Balzers, Liechtenstein); they were both 99.99% pure. During metal evaporation the vacuum chamber was held at 5 nbar and the columns were rotated at a frequency of 0.5 Hz. A layer of 200–400 nm was deposited at 1.0–2.0  $\text{nm s}^{-1}$ , resulting in a resistance of 6.0–1.0  $\Omega\text{ cm}^{-1}$ . Copper wire (0.05 and 0.08 mm diameter) obtained from Poppe (Venlo, Netherlands), was coiled tightly on the outside of capillary columns, to ensure optimal contact. The spacing between the coils was 0.05 mm, which was inspected through a microscope during preparation. The obtained resistance was 0.2–0.1  $\Omega\text{ cm}^{-1}$ .

## 2.3. GC equipment

A Sichromat 2-8 gas chromatograph with two independently controlled ovens and a  $^{63}\text{Ni}$  electron-capture detection (ECD) system (Siemens, Karlsruhe, Germany) was used for all experiments.

The TDMs were led into and from the ovens via laboratory-made throughputs. Mountings for the electrical connectors to the TDM were situated just beneath the throughputs in the GC ovens. The experimental set-up is shown in Fig. 1. The first column was a 2.0  $\text{m} \times 0.25\text{ mm}$  I.D. methyl-deactivated wall-coated open tubular (WCOT) fused-silica retention gap (Chrompack) or a 24  $\text{m} \times 0.20\text{ mm}$  I.D., 0.15  $\mu\text{m}$  SB-Smectic (Lee Scientific, Salt Lake City, UT, USA) fused-silica column. A 11.7  $\text{m} \times 0.24\text{ mm}$  I.D., 0.44  $\mu\text{m}$  CP-Sil 8 CB (Chrompack), a 8.0  $\text{m} \times 0.10\text{ mm}$  I.D., 0.12  $\mu\text{m}$  CP-Sil 8 CB column (Chrompack) or a 5.3  $\text{m} \times 0.20\text{ mm}$  I.D., 0.33  $\mu\text{m}$  Ultra 2 (5% phenyl 95% methyl polysiloxane, Hewlett-Packard, Portland, OR, USA) column were used as second column. The columns and TDMs were connected using universal quick seal connectors (Chrompack). Injector and detector temperatures were 543 and 573 K, respectively. Nitrogen (99.999% pure, HoekLoos, Schiedam, Netherlands) was used as carrier gas and make-up gas for ECD (48  $\text{ml min}^{-1}$ ). Splitless injections of 0.2 to 1.0  $\mu\text{l}$  of iso octane-diluted standards were used. The splitless time was 1.0 min and the injector septa were purchased from Interscience (Breda, Netherlands).

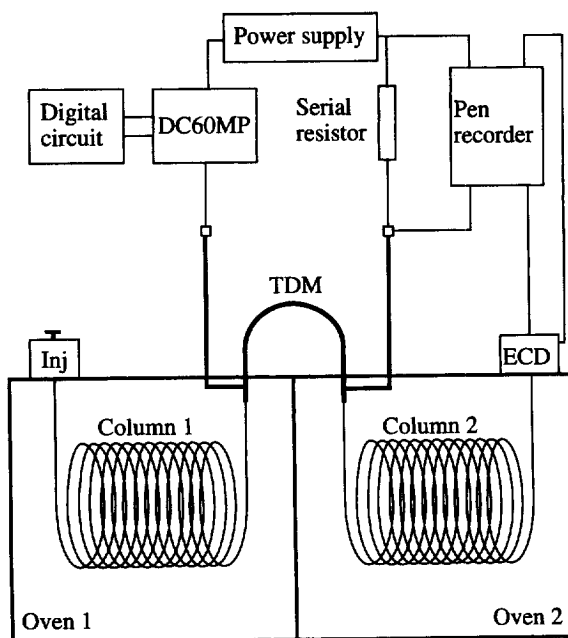


Fig. 1. Schematic experimental set-up, for details see Section 2.4.

Single-column GC was performed isothermally with an AutoSystem gas chromatograph (Perkin Elmer, Norwalk, CT, USA) equipped with a  $^{63}\text{Ni}$  ECD system at 648 K. 0.5  $\mu\text{l}$  samples were introduced splitless; the injector temperature was 543 K. Nitrogen was used as make-up gas and hydrogen (99.999% pure, HoekLoos) as carrier gas. A 50 m $\times$ 0.15 mm I.D., 0.30  $\mu\text{m}$  CP-Sil 8 CB column (Chrompack) was used, the column inlet pressure being 3.0 bar.

All data were acquired using an ICW-800 (CPU 386) computer (Getronics Computer Products, Amsterdam, Netherlands) and Maxima 820 Chromatography Software (Milford, MA, USA). For the visualisation of semi-comprehensive chromatograms the data were further handled on a Macintosh Performa 475 computer (Apple Computer, Cupertino, CA, USA) with Microsoft Excel 4.0 (Microsoft, Redmond, WA, USA).

#### 2.4. Electronic circuit for heating of TDM

The resistance of a metallic conductor increases with its temperature, i.e., during the application of electric heating. The temperature resistivity coefficients of metals typically have a value of about  $4 \cdot 10^{-3} \text{ K}^{-1}$ , which means that the resistance increases 2-fold when the temperature increases by ca. 250 K. If a constant voltage supply is used, the applied electric power will decrease considerably during the heating period because it is inversely proportional to the resistance. The opposite happens if a constant current supply is used: the applied power now is proportional to the resistance and increases during the heating, which effects an accelerated increase of the temperature. The latter situation may lead to unacceptably high temperatures and, possibly, the burning of the TDM. A constant voltage supply is preferred, although the initial power then has to be chosen relatively high to maintain a high temperature during the whole heating period.

A schematic view of the electronic circuit used in the experiments is included in Fig. 1. A variable D 050-10 (0–50 V, 0–10 A, Delta Electronica, Zierikzee, Netherlands) power supply is used to supply the heating current through a DC60MP optically coupled relay (Opto22, Huntington Beach,

CA, USA) to the TDM. A laboratory-made CMOS-based digital circuit was used to control the exactly timed on and off signals to the DC60MP. To compensate for the current decrease caused by the increasing resistance during heating, a resistor (4.7  $\Omega$ , 50 W; RS Components, Corby, UK) was connected in series with the TDM. The energy dissipated in the TDM becomes more stable during the heating period because of this serial resistor (see Fig. 2). One channel of a BD 111/112 dual channel pen recorder (Kipp and Zonen, Delft, Netherlands) was used to monitor the voltage drop across the serial resistor, the other channel was used to monitor the ECD response in parallel.

### 3. Results and discussion

#### 3.1. Electrical connectors to the TDM

The electronic circuit must be connected to the TDM by connectors which are located inside the GC ovens to avoid cold spots. The first approach was to simply pinch the coated capillary between two small metal plates (Fig. 3A) by small springs. The connecting surface was very small and as a consequence the transition resistance was relatively high. Because of that, a large amount of heat is dissipated in this region; this may well lead to the burning of the conductive material or even the whole TDM. In many instances this effect was indeed observed. Another problem is the possibility of damaging the conductive coating during installation between the metal plates. A low-resistance contact with the TDM can be made by using graphite ferrules which are pressed between two unions (Fig. 3B). In this case the connection was more robust, but abrasion of the conductive layer during installation was still a problem. A third method to attach the connectors to the TDM was by putting the TDM through a short copper tube (e.g., 15 mm) and pasting the tube to the connector with a small amount of polyimide. After drying at 423 K in the GC oven, the space between the capillary and the inner wall of the tube was filled with solder at 573 K while a stream of nitrogen purged the capillary. Very robust and easily installable connectors were obtained with this procedure

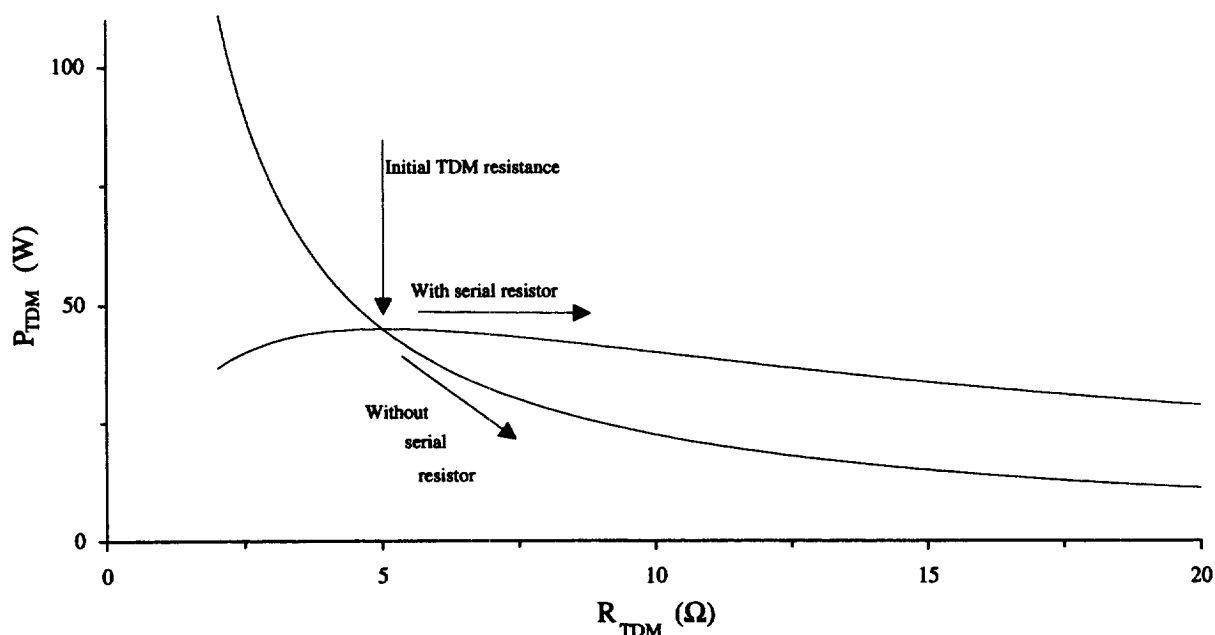


Fig. 2. Calculated plot of the power dissipated in the TDM ( $P_{\text{TDM}}$ ) vs. the resistance of the TDM ( $R_{\text{TDM}}$ ) with and without a serial resistor (5  $\Omega$ ).

(Fig. 3C). The copper tube was connected to the electronic circuit using crocodile clips.

### 3.2. Pulsed heating

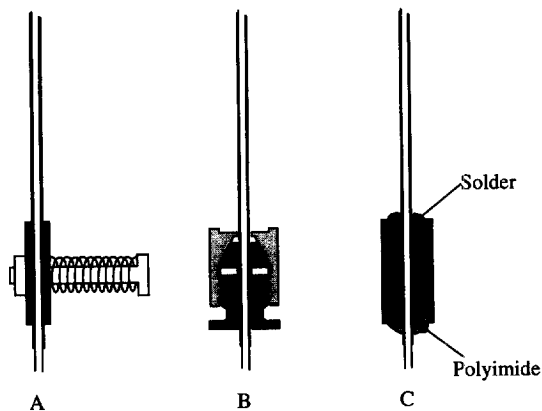


Fig. 3. Schematic view of three attachments of electrical connectors to the TDM: (A) coated capillary pressed between two plates by a small spring, (B) graphite ferrule pressed between two unions and (C) capillary pasted in a piece of copper tubing using polyimide space between capillary and inner wall of the tubing filled with solder.

In Fig. 4 a simulated temperature curve of a TDM during constant heating is proposed. The trapped analytes are considered to be in the vapour phase for temperatures above the lower horizontal dotted line; that is, they can then be transferred to the second column by the carrier gas. Using a set-up with a 2.0 m retention gap, a TDM and an 11.7 m second column and a column inlet pressure of 2.5 bar, the minimum time to transfer analytes through the TDM was estimated to be 3 s. Shortening of this period by further increasing the linear gas velocity caused insufficient resolution in the second column and leakage of the quick seal connectors. When the electrical heating pulse has to be as long as 3 s, the TDM temperature will reach the upper dotted horizontal line, which represents the (unknown) temperature at which the conductive material, or even the capillary itself, is burned. It should be noted

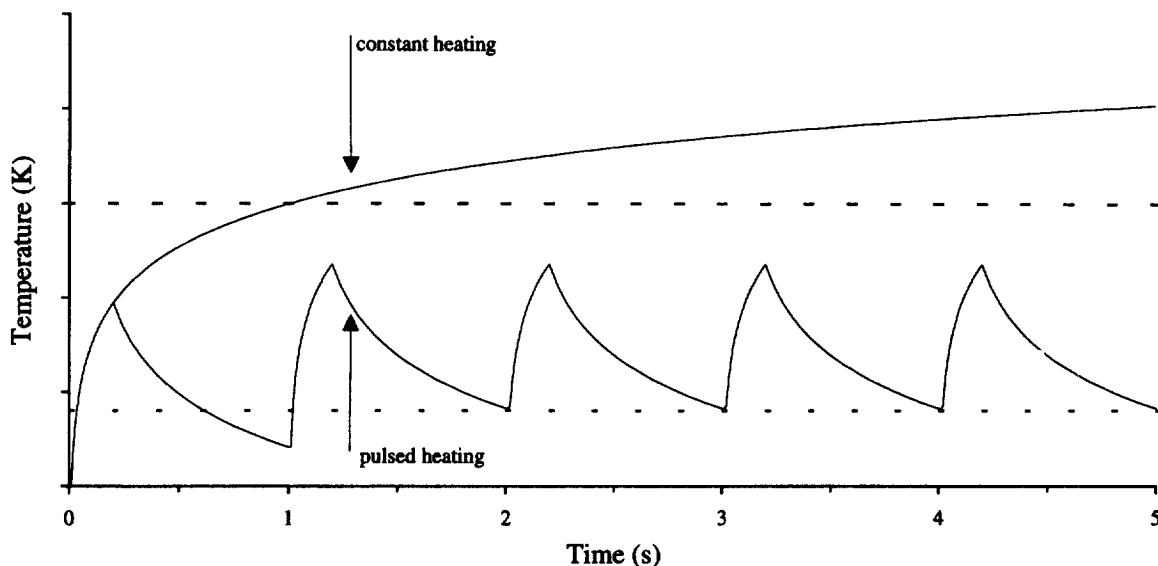


Fig. 4. Simulated temperature curve of a TDM during constant heating and pulsed heating. Lower dotted line represents the temperature at which the analytes are in the vapour phase, upper dotted line is the temperature at which the conductive material is destructed.

that the temperature of the conductive coating on the outside of the TDM will be much higher than the temperature inside the modulator. To prevent the TDM from reaching too high temperatures, pulsed heating is used (Fig. 4). The temperature at which an analyte is completely in the vapour phase can be higher than the lower dotted line in Fig. 4. In that situation there are periods during which the analyte travels with a lower velocity than of the carrier gas and, consequently, a longer heating period will be required to move the analyte out of the TDM. The parameters which affect temperature increase are the applied voltage and the TDM resistance. The length of a pulse and the time between pulses also influence the length of the heating period. These parameters are discussed below.

### 3.3. Application of conductive material on the TDM

A set-up with a retention gap, a painted TDM and a 11.7 m×0.24 mm I.D. second column coupled in series was used to test the TDMs. The TDMs were subjected to pulses up to 350 ms (power supply voltage,  $V_{\text{tot}}$ , was set at 26 V). In all cases heating of the TDM was observed, but it was not possible to

transfer the trapped test analyte (CB 28) to the second column. When more energy was applied to the TDMs, the coating became burned in places leaving a black non-conductive region on the capillary surface. The paint used consists of metal particles in an organic binder matrix which makes it necessary to apply a relatively thick layer. High temperatures cause charring of the binder material, resulting in an increased resistance which raises the temperature even more during the next pulse until the spot burns out. The use of paints without an organic binder result in a pure metallic film, which is more robust [18]. Unfortunately, painting a TDM is a very precise task which requires great skill and patience.

Metal can also be precipitated on the capillary by metal evaporation. With this technique metal is evaporated from a heated crucible and deposited on the material above it. Spots with an equal distance to the crucible are covered with the same amount of metal. In principle, it is possible to use a wide range of metals for this purpose. Important parameters are the electrical resistivity, temperature resistivity coefficient, thermal conductivity, specific heat and linear expansion coefficient of the metal. A high electrical resistivity enables the use of a thicker

layer. However, too high a value causes the total thermal mass to increase, which is not favourable. The temperature resistivity coefficient should be as low as possible to limit the current and energy changes during heating. The thermal conductivity must be high and the specific heat of the metal must be low for a fast temperature response of the TDM. The linear expansion coefficient of the metal and the capillary should be in the same range to prevent the conductive layer from breaking off because of different expansion rates. The most suitable metals are gold and silver; copper and aluminium are good alternatives. Another, even more important parameter, is the attachment between the metal and the polyimide surface of the capillary. However, data on metal attachment to polyimide are not available and the selection was therefore based on the general experience that silver, chromium and aluminium attach strongly to similar materials. Silver and aluminium were therefore selected for deposition studies and several TDMs were covered with thin layers of these metals. It was found to be important to rotate the capillaries during metal deposition, which results in a more durable layer. TDMs (30 cm) with a resistance of 30–35  $\Omega$  were obtained in this way. Visual inspection showed an improved homogeneity of the conductive layer compared with the painted TDMs (Fig. 5A and B). Indeed, it was possible to apply more energy to these TDMs. Unfortunately, despite the better characteristics the trapped CB 28 could not be desorbed, and when even more energy was applied these pure metal coatings also burned out.

An alternative to using a thin conductive layer is the use of a metal wire coiled directly around the capillary. A wire has a higher thermal mass, which will result in a slower temperature response and a smaller contact surface. Furthermore, a reasonably high resistance is less easily obtained. However, since the conductive layers are easily damaged, wire-coiled TDMs were used to examine the parameters affecting the TDM operation. The resistance of wire-coiled TDMs depends on the metal selected, the thickness of the wire, the diameter of the capillary column and the length of the wire, which depends on the distance between coils. Copper was chosen because it was readily available and because it is a good choice according to the above considerations,

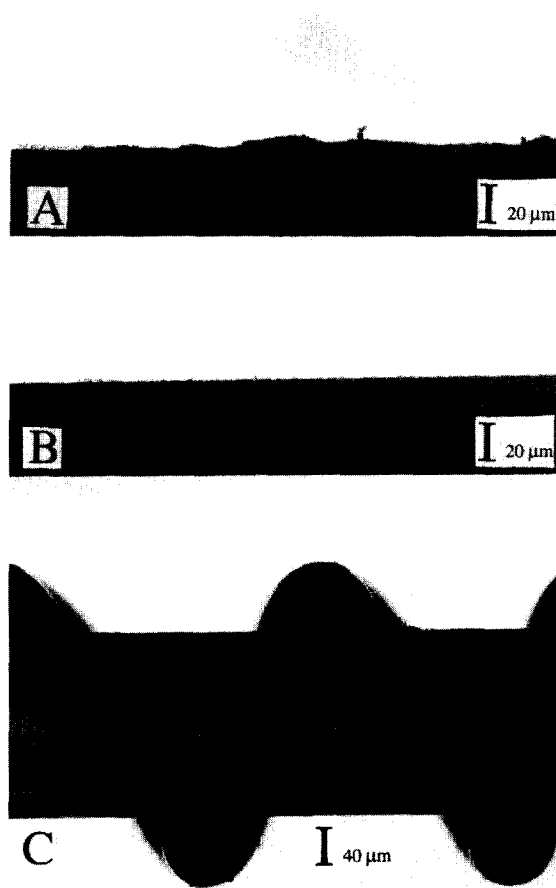


Fig. 5. Application of conductive material on TDMs: (A) conductive paint, (B) pure silver by means of metal evaporation and (C) copper wire-coiled.

which are, except for the attachment to polyimide, valid for wires too. The wire was coiled tightly around the capillaries to facilitate heat transport. Direct contact of the coils was, of course, avoided (this also accelerates cooling) (Fig. 5C). The resistance of copper wire-coiled TDMs was constant along the length of the capillary ( $0.11 \pm 0.01 \Omega \text{ cm}^{-1}$ ) and reproducible between several TDMs (R.S.D.=6%,  $n=5$ ). With a copper wire-coiled TDM (set-up with a 2.0 m retention gap and a 5.3 m Ultra 2 second column) it was possible to apply sufficient energy to desorb trapped analytes. A whole range of CBs, up to CB 206, one of the strongest retained CBs on a Sil 8 type stationary phase [19], could now be transferred. As an example, Fig. 6 shows the desorption

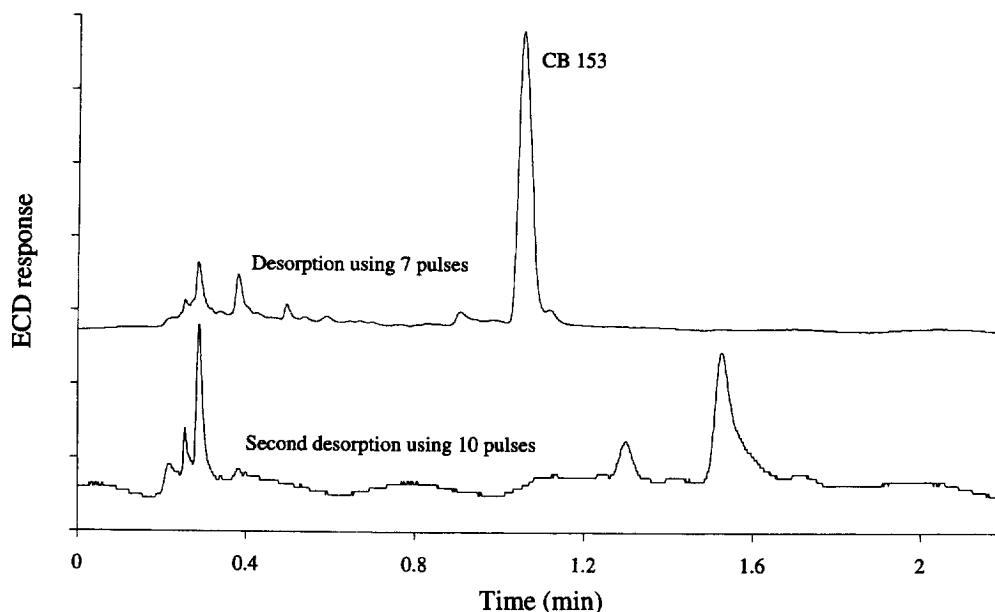


Fig. 6. Desorption of CB 153 from a TDM using 7 successive pulses (upper trace, attenuation 4) followed by a second desorption using 10 successive pulses (lower trace, attenuation 1). Copper wire-coiled TDM: 25 cm $\times$ 0.10 mm I.D., 0.12  $\mu$ m CP-Sil 8 CB, 2.6  $\Omega$ . Power supply at 17 V, pulse length 300 ms, pulse interval 400 ms. Second column 5.3 m $\times$ 0.20 mm I.D., 0.33  $\mu$ m Ultra 2 at 513 K isothermal. Column outlet flow 2.0 ml min $^{-1}$  at 298 K.

of CB 153 and a second desorption of the TDM using a longer heating period. The trace of the second desorption shows that the first desorption was sufficient to desorb CB 153 and that more strongly retained analytes or impurities need a longer heating period to be eluted from the TDM. The early peaks observed in both traces are presumably due to low-molecular-mass analytes formed during heating of the TDM by slight destruction of its stationary phase. Desorption of trapped impurities present in the carrier gas (e.g., from the injector septum or the stationary phase of the first column) is another possibility. The early peaks were found to increase when increasing the period between successive desorptions which favours the latter explanation.

All further experiments were performed using copper-wire-coiled TDMs.

### 3.4. Temperature of the TDM

The relation between the temperature of the TDM and the amount of energy which must be applied cannot easily be calculated because it depends on a

number of variables which are neither known nor constant during the heating period. An equation which allows the calculation of the temperature of an electrically heated trap (TDM) was given by Van Es et al. [14]. However, in their equation the heat loss during the heating period is neglected and the thermal conductivity is not taken into account. In addition, it is difficult to calculate the heat capacity of a TDM because it consists of various materials. Actually, Van Es et al. [14] calculated a significantly higher temperature than they found experimentally. In other words, it probably is more convenient to measure the temperature experimentally.

The TDM temperature can in principle be measured by inserting a low-mass thermocouple in the capillary [14,20]. Such a thermocouple should, however, be very small (O.D. $\ll$ 100  $\mu$ m) and have a fast response. Thermocouples which meet these requirements are expensive and not readily available. Additionally, the carrier gas flow will be partly obstructed by the thermocouple, which makes comparison with the normal situation difficult. Another approach is temperature measurement via the in-



frared radiation from the TDM. However, the area which commercial infrared temperature sensors cover is large compared to the TDM surface. Consequently, the measurement will not be free from interferences because it is difficult to shield the TDM, which is just above the GC oven, from heat-dissipating sources.

Alternatively, the use of the temperature resistance dependency of the TDM can be used to estimate its temperature [15]. The changing voltage drop across the (constant-resistance) serial resistor gives an indication of the TDM temperature change via the changing resistance of the TDM. A TDM (5.0  $\Omega$  at 298 K) was placed in the GC oven and the voltage drop across the serial resistor,  $V_{SR}$ , was measured at different temperatures. Pulses of 300 ms were used and the power supply,  $V_{tot}$ , was set at 20 V. A slightly curved relationship between the voltage drop and the reciprocal temperature was found:

$$V_{SR} = 4514 T_{TDM}^{-1} + 2.45 \quad (1)$$

$$R^2 = 0.992, 318\text{--}493 \text{ K}, n = 13$$

This agrees with the theory which, for a limited temperature range, predicts a linear relation between resistance and the temperature:

$$R_{(T_2)} = R_{(T_1)} [1 + \alpha(T_2 - T_1)] \quad (2)$$

where  $R_{(T_1)}$  and  $R_{(T_2)}$  are the resistance at temperatures  $T_1$  and  $T_2$ , respectively, and  $\alpha$  is the temperature resistivity coefficient. The voltage drop across the serial resistor can be expressed by:

$$V_{SR} = V_{tot} R_{SR} / (R_{SR} + R_{TDM}) \quad (3)$$

where  $R_{SR}$  and  $R_{TDM}$  are the resistances of the serial resistor and the TDM, respectively.

Series of pulses ( $V_{tot} = 20$  V, pulse length = 300 ms) with different intervals were applied to the TDM (5.0  $\Omega$  at 298 K). When the intervals between pulses became smaller than 1.7 s, the voltage drop across the serial resistor during the first pulse was larger than those of the second and next pulses. Obviously, for the later pulses, the interval time becomes too short to cool to the initial temperature and as a consequence the resistance is higher than at the start of the first pulse. A further decrease of the interval time causes a further decrease of  $V_{SR}$  during the second and next pulses. A plot of  $V_{SR}$  against the

interval time (data not shown) has the hyperbolic shape expected for a cooling curve. Using Eq. (1) the temperature of the TDM can be calculated from  $V_{SR}$ . Plotting these temperatures against the interval time results in the cooling curve obtained after a pulse (Fig. 7). Extrapolating this curve to a zero interval time results in an estimated TDM temperature of  $464 \pm 5$  K at the end of the first pulse of the series. This means a temperature increase of ca. 145 K during a pulse.

If the relation between the retention of an analyte and the isothermal column temperature is known, it can be used to determine the mean column temperature from the analyte retention. By neglecting gas compressibility effects and expressing the retention as time per column unit of length, the relation can be used to estimate the temperature of a column of different length. This approach was used for the temperature estimation of a TDM. The number of pulses ( $V_{tot} = 17$  V, pulse length 320 ms and pulse interval 380 ms) necessary for complete desorption of CB 138 from a 30 cm  $\times$  0.10 mm I.D. TDM (3.7  $\Omega$ ) was found to be 22–23 which corresponds with a retention of 51.3–53.7 s  $m^{-1}$ . The second column was of the same type as the TDM but had a length of 8.0 m. The relation between the retention of CB 138 at different temperatures was measured by perform-

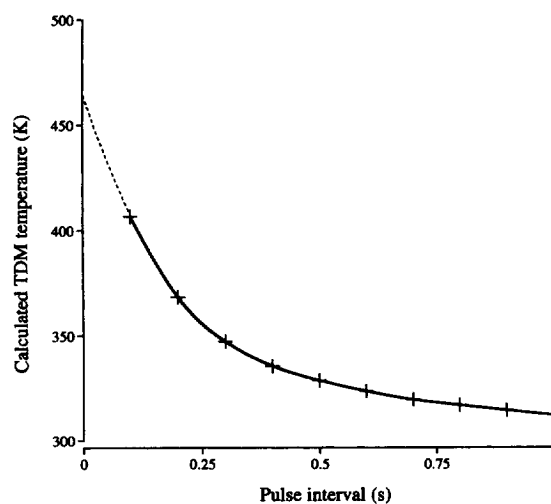


Fig. 7. Calculated temperature from the voltage drop change across the serial resistor for the second and next pulses of a series vs. the pulse interval.

ing several desorptions of CB 138 with the second column held at different isothermal temperatures (543–453 K,  $n=8$ ). By using this relation and the retention of CB 138 in the TDM a mean TDM temperature of  $487 \pm 5$  K was calculated. This is a rough calculation because of the assumptions made and the imprecision of the measurements. Still, this temperature is rather close to the temperature calculated for the end of the first pulse, despite the fact that they were obtained with different TDMs.

Once the temperature of a TDM is known, it is possible to estimate the number of pulses necessary to remove other analytes if the temperature–retention relation of the TDM is known. A sufficiently high temperature of the TDM is important because it enables the analytes to be transferred to the second column as a narrow plug.

### 3.5. Isothermal behaviour of the TDM

If the TDM temperature is not high enough, different heating periods are required for the desorption of different analytes. For a range of thirteen CBs the minimum number of successive pulses ( $V_{\text{tot}} = 17$  V, pulse length 320 ms and pulse interval 380 ms) was determined using individual CB standards and the same experimental set-up as in Section 3.4. The relative number of required pulses —i.e., pulses for CB  $x$ /pulses for CB 138— was plotted against relative retention data taken from the literature and isothermal data obtained at 533 K, which were all obtained for the same type of stationary phase as the TDM (Fig. 8). The correlation between the TDM data and the isothermal data is rather satisfactory ( $R^2=0.955$ ). This shows that the mean TDM temperature is constant during the desorption period. Next to that, the figure shows that non-isothermal retention data are not very useful for a comparison of columns. The retention energy differences between compounds are obscured by temperature programming and because of that, these data can not be used to predict retention in a TDM.

Relative retention data of the CB test set from the TDM and those obtained isothermally at 443–533 K were plotted against relative isothermal retention data obtained at 533 K. In Table 1 the characteristics of these curves are given. A slope higher than unity is obtained when the temperature is lower than that

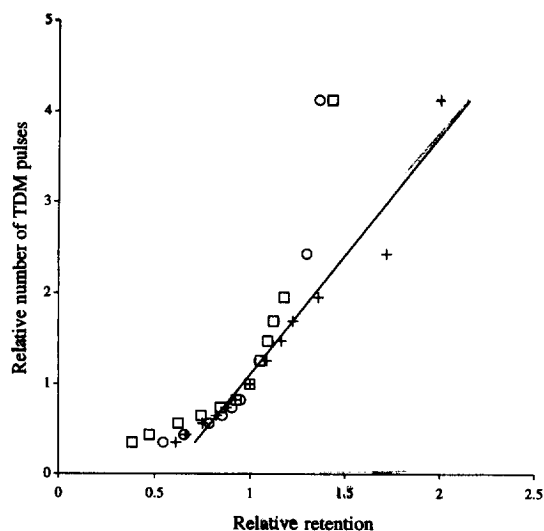


Fig. 8. Relative number of pulses (to that of CB 138) necessary for the desorption of CB congeners plotted against the relative retention data (relative to that of CB 138) from literature: (○) linear temperature programme from Ref. [19], (□) step temperature programme from Ref. [22] and (+) experimental isothermal data at 533 K.

of the data against which the plot is made. A linear relation ( $R^2=0.996$ ) was found between the isothermal temperature and the slope:

$$T_{\text{iso}} = 583 - 51.8 \times (\text{slope}) \text{ (K)} \quad (4)$$

The TDM temperature calculated using this relation was  $454 \pm 2$  K. This is a somewhat lower temperature than those calculated above ( $464 \pm 5$  and  $487 \pm 5$  K). However, the former of these is the temperature at the end of a pulse instead of a mean

Table 1

Characteristics of the curves obtained when plotting TDM-obtained and isothermally obtained relative retention data against relative retention data obtained at 533 K; all data relative to CB 138

Temperature (K)	Intercept	Slope	$R^2$	No. of CBs used
$T_{\text{TDM}}$	-1.377	2.493	0.955	13
443	-1.688	2.630	0.952	24
463	-1.365	2.382	0.996	26
483	-0.866	1.888	0.994	27
503	-0.512	1.522	0.998	27
533	0	1	1	29

temperature during the whole desorption step and was obtained with a slightly different TDM. The latter temperature was obtained from the retention data of one test CB and not with the relative retention of a whole set, as in the final approach. This final approach is preferred because it uses relative retention data and, by that, corrects for effects such as gas compressibility.

### 3.6. Parameters affecting the desorption

The parameters which affect the TDM temperature are the resistance, the voltage drop across the TDM, the pulse length and the pulse interval. The effect of the last three parameters was studied using a set-up with a 2.0 m retention gap, a 30 cm × 0.10 mm I.D. TDM (3.3 Ω) and a 8.0 × 0.10 mm I.D. second column. The power supply was set at 16 V and 300 ms pulses were used with a 600 ms interval time. For the desorption of CB 28, 30 pulses were necessary. With a pulse interval of 500 ms, this number decreased to 23 pulses, and with 400 ms, to 14 pulses. When the interval time decreases, the TDM cannot cool to its initial temperature and, consequently, the mean temperature during the heating period will be higher. In a subsequent series of experiments, the cycle time, i.e., the pulse length plus the pulse interval, was held constant at 700 ms. Now, with this constant cycle time the pulse length was varied and the minimum number of pulses necessary for desorption of CB 28 determined (Fig. 9a). The effect of an increased pulse length is enhanced by a shorter (cooling) interval between pulses: the 40-ms increase of the pulse length is seen to decrease the number of pulses required from 18 to 11.

Finally, at a constant pulse length (320 ms) and cycle time (700 ms), the voltage of the power supply was varied and the minimum number of pulses for the desorption of CBs 28, 138 and 206 determined. The shape of the curves of Fig. 9b can partly be explained by the amount of dissipated energy which is proportional to the square of the voltage. In addition the migration speed of the analytes is limited by the speed of the carrier gas. As can be seen from Fig. 9b, if the voltage is high enough, the minimum heating time to desorb all analytes will be 7–8 pulses. However, to prevent the TDM from

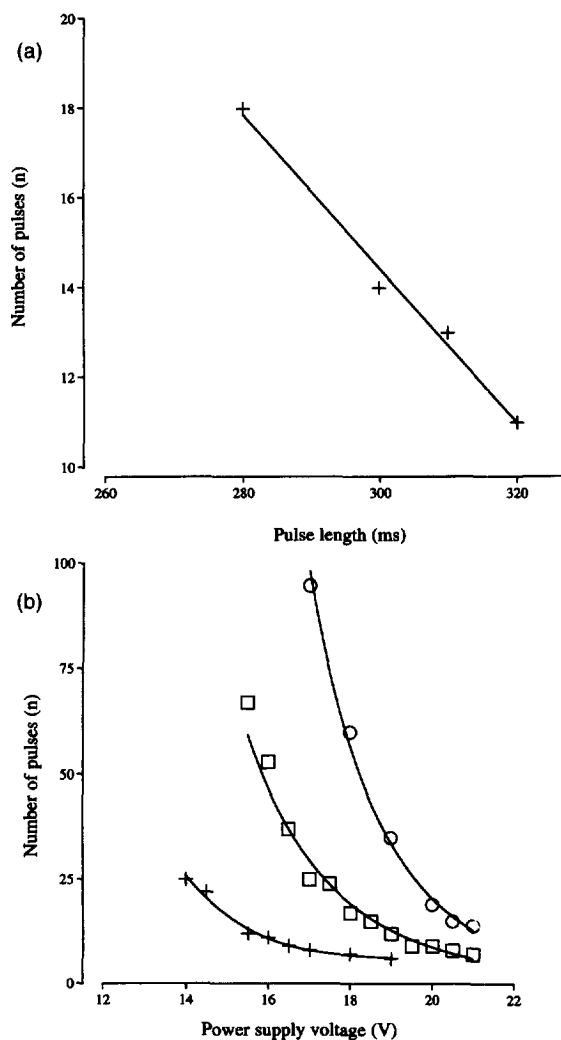


Fig. 9. Number of pulses necessary to desorb CBs (+) 28, (□) 138 and (○) 206 from a copper wire-coiled 30 cm × 0.10 mm I.D., 0.12 μm CP-Sil 8 CB TDM (3.3 Ω), cycle time 700 ms: (a) using different pulse lengths, power supply at 16 V and (b) using different power supply voltages, pulse length 320 ms.

burning, a lower voltage (21 V) was chosen with a longer heating time (10 pulses).

### 3.7. Application of wire-coiled TDMs

In the previous sections, the performance of the wire-coiled TDM and the parameters effecting analyte desorption have been discussed. The pulsed heating technique results in an isothermal behaviour

during desorption. All test CBs could be transferred to the second column by using ten successive pulses. The TDM could be used for at least five months of constant operation. Below, the possibility to perform several injections and enrich the analytes in the TDM before re-injection as a narrow plug onto the second column and the use of the TDM to interface two different columns to obtain a multidimensional separation are shown as practical examples.

### 3.7.1. Large-volume introduction using a TDM as on-column re-injection device

The TDM temperature just above the roof of the GC oven (ca. 330 K) was sufficiently high to let the bulk of the iso octane in which the CBs used as analytes were dissolved, pass through. By carrying out a series of successive injections, analytes can be enriched in the TDM and their detection limits improved. The danger of not too strongly trapped analytes being swept from the TDM or spread over a broad zone inside the TDM by the large amount of

solvent from the later injections could be avoided by cooling especially the first part of the TDM by a focused stream of pressurised air. An example of ten successive 1.0  $\mu\text{l}$  injections of a CB mixture at concentrations of 0.3–1.3  $\text{ng ml}^{-1}$  is given in Fig. 10. The separation was not too good because of the restricted length of the second column, 8.0 m. The GC–ECD chromatogram is collected at a high sensitivity to make detection possible. The trace starts with a huge peak which is not due to the solvent but to other rather volatile substances in the solvent. The trace also contains a few unknown peaks caused by impurities present in the iso octane. The TDM obviously will enrich the analytes of interest as well as the impurities. Therefore, large-volume introduction demands high-purity solvents to avoid blank problems.

The on-column sample introduction is useful because it introduces the (enriched) sample as a narrow plug after solvent elimination. Admittedly, large-volume introduction can also be performed by

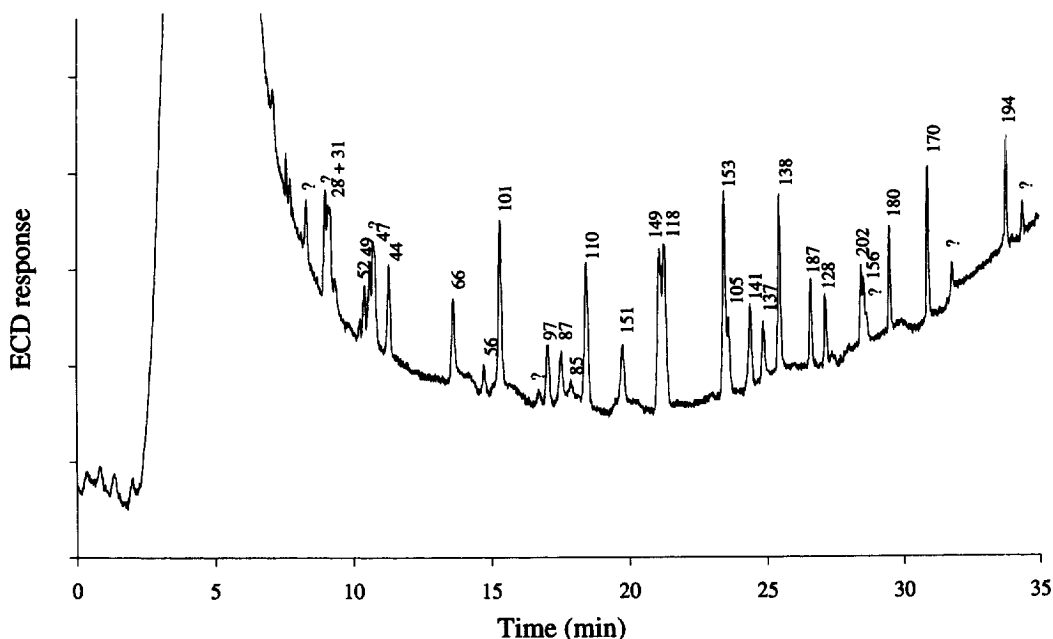


Fig. 10. GC–ECD chromatogram obtained after ten successive 1.0  $\mu\text{l}$  injections of a mixture containing several CBs (number according to Ref. [17]) at 0.3–1.3  $\text{ng ml}^{-1}$  in iso octane on set-up with a 2.0 m  $\times$  0.25 mm I.D. retention gap, a TDM as in Fig. 9 and a 8.0 m  $\times$  0.10 mm I.D., 0.12  $\mu\text{m}$  CP-Sil 8 CB column. Desorption using ten successive pulses; pulse length 320 ms, cycle time 700 ms and power supply at 21 V. The first oven was held at 543 K. Temperature programme of the second column started at start of desorption: 2 min at 343 K, 30  $\text{K min}^{-1}$  to 453 K, 11 min, 5  $\text{K min}^{-1}$  to 543 K, 10 min.

other means, e.g., with a PTV, which does not require the successive introduction of small volumes. However, the advantage of the TDM is its small size and low cost. Besides, the present experiment was intended as a first test of the practicality of this TDM approach.

### 3.7.2. Semi-comprehensive MDGC

In comprehensive MDGC the two separation dimensions must be as different as is possible to obtain maximum separation power [21]. By plotting the relative retentions of the compounds of interest on different column combinations against each other it is possible to select a useful combination for MDGC. This was done by De Boer et al. [22] for 51 CBs on seven columns with different stationary phases. Although the plots were obtained with non-isothermal retention data, they were used to select the combination of a smectic polysiloxane liquid crystal and a slightly polar 5% phenyl 95% polysiloxane stationary phase. A 24 cm × 0.10 mm TDM (2.7 Ω) was installed between a 24 m SB-Smectic and a 5.3 m Ultra 2 column as first and second separation columns, respectively. The smectic column was used as the first dimension because it cannot be used at high temperatures. Consequently, highly retained analytes will elute as rather broad peaks, which will have a negative influence on the analyte detectability. This problem is eliminated by the presence of the TDM which refocuses these peaks before introducing them on the head of the second column.

For the comprehensive coupling of two columns, the TDM must sample the first column at least every theoretical peak width and transfer the analytes to the second column for separation. However, in the present system the second separation is rather slower than in other systems presented in the literature [8]. It was not possible to increase the speed of the second separation much further without sacrificing part of the resolution of the first separation and also because leaking of the quick-seal connectors occurred. Another reason for the relatively low separation speed was the use of an ECD, which has a sampling rate which is small compared to that of a flame ionization detector. Therefore, it is necessary to use a relatively slow temperature programme (e.g., 1 K min<sup>-1</sup>) in order to obtain relatively broad

eluting peaks from the first column. The TDM collects material for 3 min after which it is desorbed by a series of electrical pulses. The GC-ECD chromatogram consists of a continuous series of 3-min chromatograms. By dividing this chromatogram into 3-min portions and placing these traces side by side it is possible to construct a two-dimensional chromatogram. Examples are given in Figs. 11 and 12 which show part of a two-dimensional chromatogram of the non-ortho CBs 77, 126 and 169 and a two-dimensional chromatogram of a technical PCB mixture, Aroclor 1254, respectively. Every trace starts with a few minor peaks (cf. Fig. 6). After about 60 min, large peaks start to appear which are most probably caused by bleeding of the first column followed by (discontinuous) TDM transfer to the second column. The two figures demonstrate that in this approach only one analysis is required to separate a whole sample into two dimensions, where in conventional heart-cut MDGC many runs would be required to do this [5].

In the examples shown, the second separation was fast enough to avoid excessive peak broadening while preserving the separation in the second dimension. However, the present system does not yet sample the first column frequently enough to be really comprehensive we therefore prefer to call it semi-comprehensive MDGC. For the rest, the smectic column used has the disadvantage of major bleed: the peaks caused by this effect occupy a lot of space in the secondary chromatograms. Replacing the first column by a more stable one will probably make a higher modulation frequency possible.

## 4. Conclusions

Thin painted coatings on TDMs cannot withstand the high temperatures and the large amount of energy needed to desorb trapped analytes. It was possible to apply more energy to pure aluminium- and silver-plated TDMs but this still was not enough to desorb trapped analytes. The main advantage of a thin metal on-column coating is a fast temperature response. However, such TDMs are quite fragile and small imperfections sooner or later cause the loss of the modulation capability. Metal-lined capillaries are

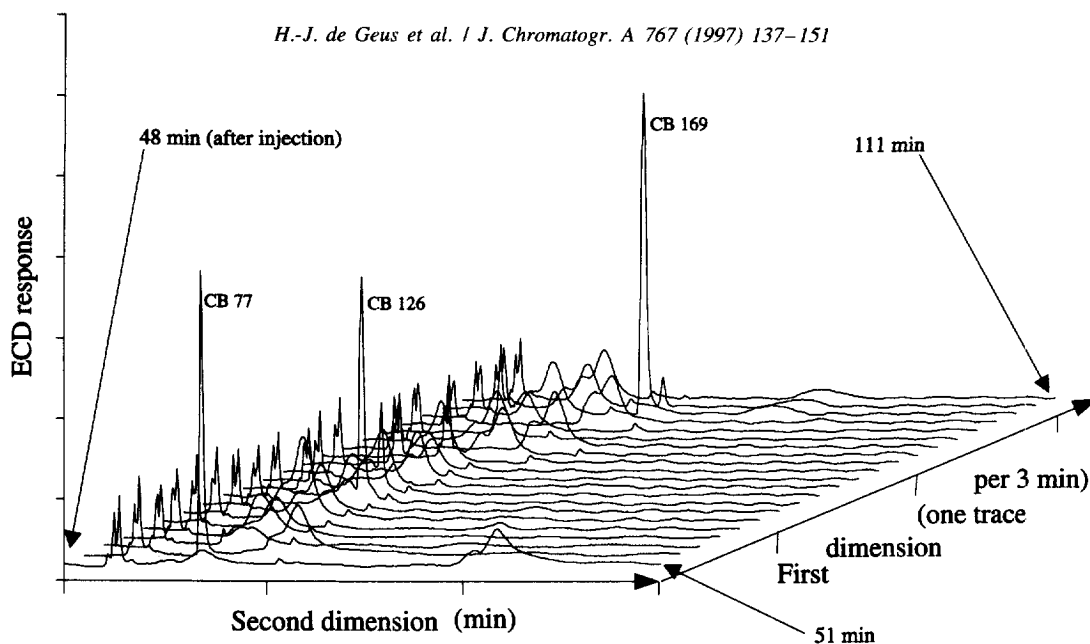


Fig. 11. GC-ECD chromatogram obtained after 1.0  $\mu\text{l}$  injection of mixture containing CBs 77, 126 and 169 (numbers according to Ref. [17]) at 20–40  $\text{ng ml}^{-1}$  in iso octane on set-up with a 24  $\text{m} \times 0.20 \text{ mm}$  I.D., 0.15  $\mu\text{m}$  SB-Smectic first column 0.25 mm I.D. retention gap, a 24  $\text{cm} \times 0.10 \text{ mm}$  I.D., 0.12  $\mu\text{m}$  CP-Sil 8 CB TDM (2.7  $\Omega$ ) and a 5.3  $\text{m} \times 0.20 \text{ mm}$  I.D., 0.33  $\mu\text{m}$  Ultra 2 second column. The TDM was desorbed every 3.0 min using 10 successive pulses, pulse length 300 ms, cycle time 700 ms and power supply at 18 V. Temperature programme of the first column: 1 min at 363 K, 30  $\text{K min}^{-1}$  to 433 K, 1 min, 1  $\text{K min}^{-1}$  to 473 K, 80 min. Temperature programme of the second column: 4.33 min at 433 K, 1  $\text{K min}^{-1}$  to 453 K, 3  $\text{K min}^{-1}$  to 533 K, 70 min. The obtained chromatogram was divided into 3-min traces which were plotted next to each other from 48 min up to 111 min.

more robust, but they have a large thermal mass and a relatively large amount of electrical energy is needed for heating. Metal tubes should not be used as TDMs because many analytes will react on the metal surface. The present study shows that copper-wire-coiled TDMs are a good and rather robust alternative which can be used to interface two different GC columns to give a multidimensional separation.

The use of pulsed, instead of constant, heating eliminates the problem of too high a temperature during the heating period. This technique results in an isothermal desorption behaviour. Increasing the voltage drop across the TDM leads to a higher temperature and a decrease of the required heating period. The effect of the pulse length and pulse interval on the TDM heating was also demonstrated. Several temperature estimations were made which all resulted in a TDM temperature of ca. 460 K during the desorption. However, in the further experiments the desorption parameters were adjusted to make the desorption of all test CBs possible within 7 s, which

obviously means a higher TDM temperature. Actually, for optimisation of the TDM performance it is not necessary to know its exact temperature.

The applicability of the TDM is shown for large-volume injection and semi-comprehensive MDGC. The temperature response of the TDM is probably fast enough for true comprehensive MDGC. Their small size makes it possible to use several TDMs in one set-up. For example a combination of on-column sample introduction, comprehensively coupling different columns and signal averaging before detection. In a further study the minimum sample frequency of the TDM and methods to speed up the second separation will be examined. Replacing the first column by a more stable one than the smectic used in this study will probably make a higher modulation frequency possible. The use of columns with different internal diameters, the introduction of extra carrier gas just in front of the TDM and the use of a two-stage TDM are additional possibilities to increase the speed of the second separation, while maintaining the resolution in the first separation.

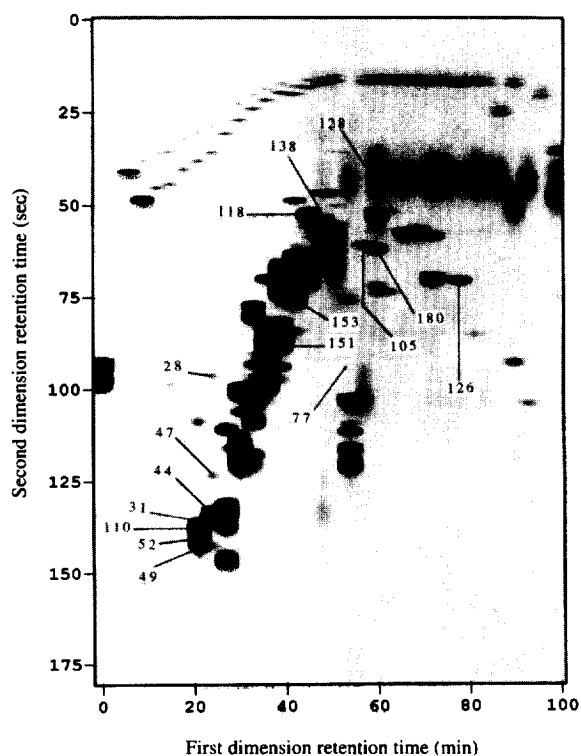


Fig. 12. GC-ECD chromatogram obtained after a 1.0  $\mu\text{l}$  injection of Aroclor 1254 ( $21 \mu\text{g ml}^{-1}$  in iso octane) in the system of Fig. 11, using the same conditions. The 3-min portions were now plotted in a plane, the black spots indicating points at which analytes elute. The positions at which some relevant CB congeners elute are indicated.

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### References

- [1] J.C. Duinker, D.E. Schulz and G. Petrick, *Anal. Chem.*, 60 (1988) 478–482.
- [2] J. de Boer, Q.T. Dao, P.G. Wester, S. Bøwadt and U.A.Th. Brinkman, *Anal. Chim. Acta*, 300 (1995) 155–165.
- [3] B.M. Gordon, M.S. Uhrig, M.F. Borgerding, H.L. Chung, W.M. Coleman III, J.F. Elder Jr., J.A. Giles, D.S. Moore, C.E. Rix and E.L. White, *J. Chromatogr. Sci.*, 26 (1988) 174–180.
- [4] J. de Boer and H.-J. de Geus, *Proc. 15th Int. Symp. Chlorinated Dioxins and Related Compounds*, Edmonton, August 21–25, 1995, Vol. 26, pp. 345–350.
- [5] H.-J. de Geus, J. de Boer and U.A.Th. Brinkman, *Trends Anal. Chem.*, 15 (1996) 398–408.
- [6] Z. Liu, S.R. Sirimanne, D.G. Patterson Jr., L.L. Needham and J.B. Phillips, *Anal. Chem.*, 66 (1994) 3086–3092.
- [7] Z. Liu and J.B. Phillips, *J. Chromatogr. Sci.*, 29 (1991) 227–231.
- [8] J.B. Phillips and J. Xu, *J. Chromatogr. A*, 703 (1995) 327–334.
- [9] J.B. Phillips, D. Luu, J.B. Pawliszyn and G.C. Carle, *Anal. Chem.*, 57 (1985) 2779–2787.
- [10] Z. Liu and J.B. Phillips, *J. Microcolumn Sep.*, 1 (1989) 159–162.
- [11] Z. Liu and J.B. Phillips, *J. Microcolumn Sep.*, 2 (1990) 33–40.
- [12] V. Jain and J.B. Phillips, *J. Chromatogr. Sci.*, 33 (1995) 55–59.
- [13] H.G.J. Mol, H.-G.M. Janssen, C.A. Cramers, J.J. Vreuls and U.A.Th. Brinkman, *J. Chromatogr. A*, 703 (1995) 277–307.
- [14] A. van Es, J. Janssen, C. Cramers and J. Rijks, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 852–857.
- [15] S.R. Springston, *J. Chromatogr.*, 517 (1990) 67–75.
- [16] C.L. Rankin and R.D. Sacks, *J. Chromatogr. Sci.*, 32 (1994) 7–13.
- [17] K. Ballschmiter, R. Bacher, A. Mennel, R. Fischer, U. Riehle and M. Swerev, *J. High Resolut. Chromatogr.*, 15 (1992) 260–270.
- [18] J.B. Phillips, personal communication, June 20, 1996.
- [19] M.D. Mullin, C.M. Pochini, S. McCrindle, M. Romkes, S.H. Safe and L.M. Safe, *Environ. Sci. Technol.*, 18 (1984) 468–476.
- [20] T. Górecki and J. Pawliszyn, *Proc. 18th Int. Symp. Capillary Chromatography*, Riva del Garda, May 20–24, 1996, Vol. III, pp. 1634–1642.
- [21] C.J. Venkatramani, J. Xu and J.B. Phillips, *Anal. Chem.*, 68 (1996) 1486–1492.
- [22] J. de Boer, Q.T. Dao and R. van Dortmund, *J. High Resolut. Chromatogr.*, 15 (1992) 249–255.