

**Peter Apps**Council for Scientific and  
Industrial Research (CSIR),  
Pretoria, South Africa

Original Paper

## Low cost, robust, in-house hardware for heart cutting two-dimensional gas chromatography

Natural materials are so complex that no single column can separate all of the components. Heart cutting 2-D GC (GC-GC) using a Deans switch provides maximum separation, but the requisite gas flow configurations have earned a reputation for being fiddly and time consuming to set up and tune, unless electronic gas controls and costly software are employed. A design for a vented Deans switch is presented that can be assembled in-house from standard commercial components. A vent to atmosphere replaces the balancing resistor, which solves the problem of balancing the pressures and flows, and requires no compensation for changes in gas viscosity and back-pressure during temperature programming. First and second dimension columns can both be run at optimum flow rates, even if they are of different diameters. Analyte detectability is preserved by cutting only the target fraction from the first column and transferring the whole of it to the second column. Cryotrapping the selected fraction allows cuts of any width, and transfer of analytes to the second column as sharp bands. I have applied the vented Deans switch–cold trap to the identification of flavour and fragrance compounds from South African plants and foods; cuts are very repeatable, and the detectability of trace components is enhanced. Its capabilities are demonstrated by examples from analyses of essential oils and flavour extracts.

**Keywords:** Deans switch / Flavours / GC-GC / Heart cutting / Two-dimensional

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### 1 Introduction

'Chromatography is primarily a tool for the separation of compounds. It is a failure when a separation is not realised' [1].

The need for multidimensional GC arises from the huge complexity of natural materials. The theoretical expectation that, no matter how long and narrow a capillary column is used, it is practically impossible to resolve every volatile compound in a complex mixture [2] is confirmed empirically by peak overlaps and coelutions when petrochemical or environmental samples, botanical extracts, natural flavours or fragrances, or mammalian semiochemicals are analysed by GC [3–7]. Even a 450 m column with 1.3 million effective plates generated dozens of overlapping peaks from a gasoline standard in a separation that took longer than 11.5 h [8], and resolution among only the C<sub>7</sub> hydrocarbons from crude oil cannot be achieved by any single conventional column [9].

**Correspondence:** Dr. Peter Apps, National Metrology Laboratory, CSIR, PO Box 395, Pretoria 0001, South Africa.**E-mail:** papps@csir.co.za.**Fax:** +27-12-841-2131.

The principal of multidimensional GC is straightforward and well established; a time slice of the eluate from a separation is transferred to a second column of complementary selectivity, and peaks that elute together from the first column are separated on the second one. Multidimensional GC can be implemented in two ways [7]: comprehensive GC (usually abbreviated GC × GC [10]) which is a relatively recent development [11], and heart cutting (abbreviated GC-GC) whose introduction to analytical GC precedes that of glass capillary columns [12].

While comprehensive GC is able to produce a 2-D separation for a whole chromatogram in one run, the need for a very rapid second dimension separation dictates the use of short, narrow-bore, second dimension columns with linear gas flow rates substantially above the optimum. In practise, the second dimension columns generate only about 2500 effective plates [13], and can separate 5–10 peaks [7, 14] that are so narrow that they require fast detectors and mass spectrometers [15–17], which with the present state of the art cannot provide accurate masses. In addition, and critically for flavour and fragrance work, GC-olfactometry has not been demonstrated to be possible after comprehensive separations.

In classical heart cutting, the second dimension column can be of the same length and diameter as the columns in routine use for capillary chromatography, and be operated under the same optimised conditions of temperature and flow rate. Consequently, the second dimension can generate about 150 000 plates, have a peak capacity of about 300, and be 'hyphenated' with any of the detectors that are used in 1-D capillary GC, including GC-olfactometry [18, 19], high resolution MS, and, it bears noting, GC  $\times$  GC. The power of heart cutting GC-GC has given it a wide variety of applications; [6, 17, 19–26], including high resolution preparative GC [27].

Using mechanical valves to cut fractions from the first to the second dimension [21, 28] is attractively straightforward and robust, but valves expose the sample to metal and organic polymers and have limited compatibility with the high and fluctuating temperatures used in GC [5, 17, 28], and they disturb flows and pressures [21]. These drawbacks are overcome by pressure-balanced flow switching, which was introduced to analytical GC by Deans [12]. The Deans switch is made from inert materials and has no moving parts; flow switching is accomplished solely by applying gas pressure to one side or the other of the switch using gas controls outside the GC oven. The Deans switch (sometimes referred to as a 'live switch') was commercialised in 1982 [29] and still forms the core of most commercial GC-GC configurations [30–33].

The Deans switch has an impressive track record, but its installation and adjustment can be unattractively fiddly and time consuming [17, 25, 21]. Usually a classical Deans switch is configured to switch between a first dimension detector (often referred to as a monitoring detector) and a second dimension column. Because the resistance to gas flow towards the detector is much smaller than the resistance of the second column, the flow through the switch is always biased towards the detector unless a resistor with a gas flow resistance similar to that of the second column is inserted between the switch and the detector [32, 33]. To keep the time lag between the switch and the monitoring detector as short as possible, balancing resistors are constructed from short lengths of narrow-bore tubing that have to be accurately trimmed until the volume flow rate through them matches that through the column [33]. The major drawbacks with such a configuration are that the resistor has to be altered if a second dimension column of different dimensions is installed, and that the switch is perfectly balanced at only one point during the chromatographic run because the resistance to gas flow of the second column increases as it is temperature programmed. Consequently, setting up the switch and adjusting gas flows and pressures can be unattractively time consuming [23]. The advent of electronic pneumatics and flow calculator

software facilitates switch balancing, but makes the switch's operation critically dependent on software-controlled EPC-equipped instrumentation [23, 30–33], whose high costs are restrictive for many research laboratories.

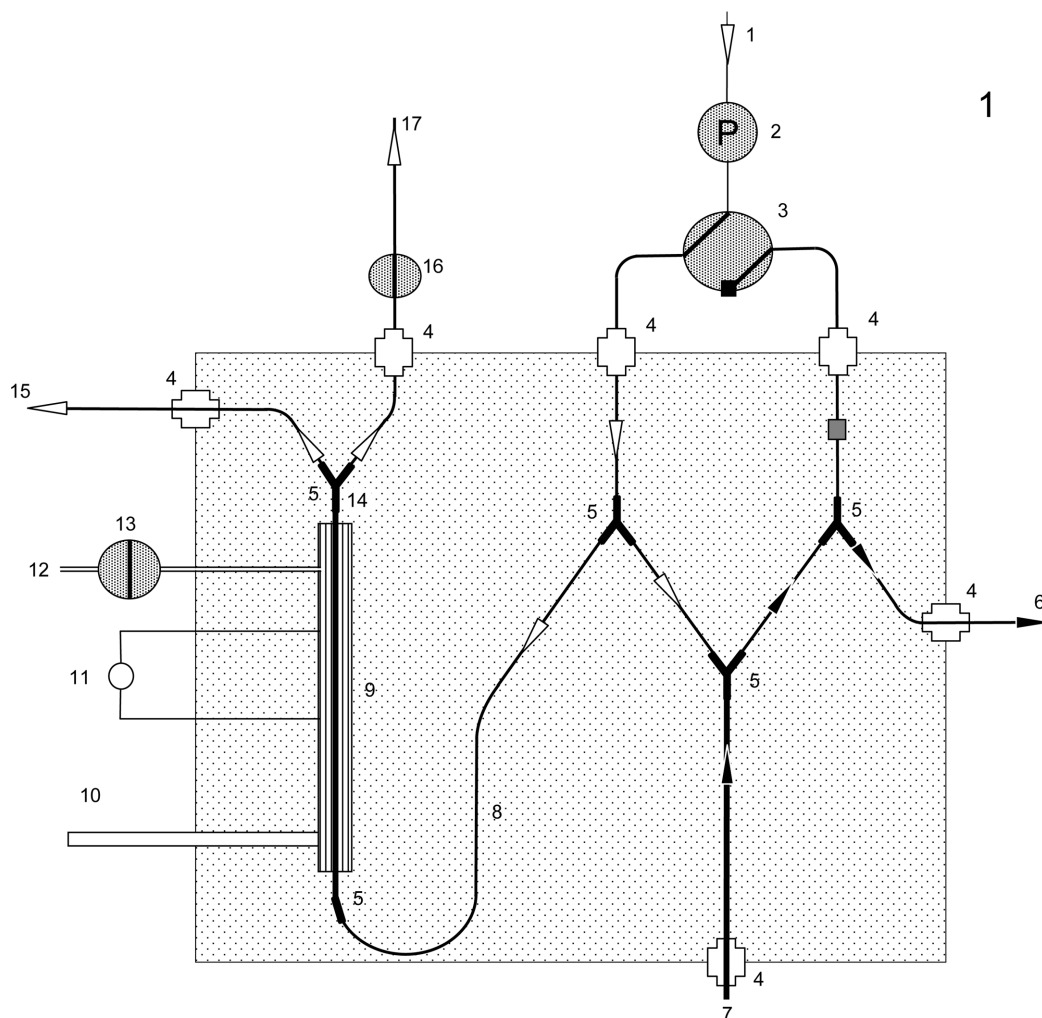
A simple change to the classical Deans switch configuration eliminates the need to use a resistor to balance the switch. A vent to atmosphere between the switch and the second dimension column eliminates the bias of the switch towards the detector, while a cold trap retains the heart cut analytes until the vent is closed and they are transferred to the second dimension column. This configuration preserves the ability of the classical Deans switch to direct all of the analytes to one or other of the detectors, thus conserving detectability, and simplifies the use of first and second dimension columns of different diameters without having to compromise optimum linear gas flow velocities through either of them.

Vented Deans switches were introduced in the mid-1980s [34–36], and a vented switch with a cold trap was at one time available from Chrompack as part of their 'MUSIC' system [37–39], but an exhaustive search of the World Wide Web and the scientific literature yielded found no currently available equivalent.

In work on identification of new flavour compounds in South African plants and indigenous foods, GC-sniffing was used to locate regions of chromatograms where intense and interesting odours eluted. MS was then employed to identify the compounds responsible. Due to the complexity of the extracts, there were always several regions of the chromatograms where interesting odours eluted but peak overlap confounded the identification of the compounds responsible.

Resolved peaks were required to provide clean spectra for reliable library searching or spectral interpretation; an ideal application for 2-D heart cutting. Because the concentration of aroma compounds in the extracts spanned at least four orders of magnitude, and many of the most intriguing odours were associated with extremely small peaks, or peaks that were completely obscured by coelutions, it was necessary to run the first dimension separations on megabore columns, and to transfer the target analytes to the second dimension column quantitatively to preserve their detectability at the second dimension detector. To meet these demands, the switch had to provide complete transfer of cuts between 530 and 320  $\mu\text{m}$  capillary columns while still allowing both columns to be run at optimum gas flow rates, and be fully compatible with flame ionisation and sniffing detection on the first and second dimensions, and MS on the second dimension.

Operational constraints dictated that the switching system be constructed at low cost from standard commercially available components, using only very basic work-



**Figure 1.** Schematic of vented switch–cold trap operation. (1) High purity carrier gas; (2) pressure regulator and gauge; (3) four-port valve; (4) 1/16-in bulkhead union; (5) press-fit connector; (6) transfer line to flame ionisation detector (and sniffer split if required) of first dimension – same length and diameter as the transfer line from the switch to the cold trap (8); (7) first dimension column (530  $\mu\text{m}$ , 30 m MeSilicone); (8) transfer line between switch and cold trap – same length and diameter as the transfer line to the FID (6); (9) cold trap with heater; (10) carbon dioxide vent; (11) low-voltage supply to trap heater controlled by a temperature controller; (12) liquid carbon dioxide supply; (13) high pressure valve; (14) short section of 530  $\mu\text{m}$  fused-silica column; (15) second dimension column running through a heated transfer line; (16) on-off valve; (17) vent to atmosphere. Open arrows denote flow of clean carrier gas, black arrows denote flow of carrier gas loaded with analytes, small shaded squares denote no gas flow. The lightly stippled area is a heated zone. Stage 1: switch to the first dimension detector before elution of the target cut from the first dimension column, analytes pass to the first dimension detector(s), carbon dioxide is closed, trap heater is off, clean gas flows to the second dimension column.

shop facilities. In addition, the switch had to be compatible with, but not dependent on, electronic pneumatic control systems, and its installation could not involve permanent changes to the GCs. Rapid installation and adjustment were mandatory since the instruments were also required for conventional single dimensional chromatography.

## 2 Materials and methods

### 2.1 Construction

A schematic of the vented switch and cold trap is given in Fig. 1.

The switch and cold trap are mounted inside a cast aluminium box of the type commonly used as shielding

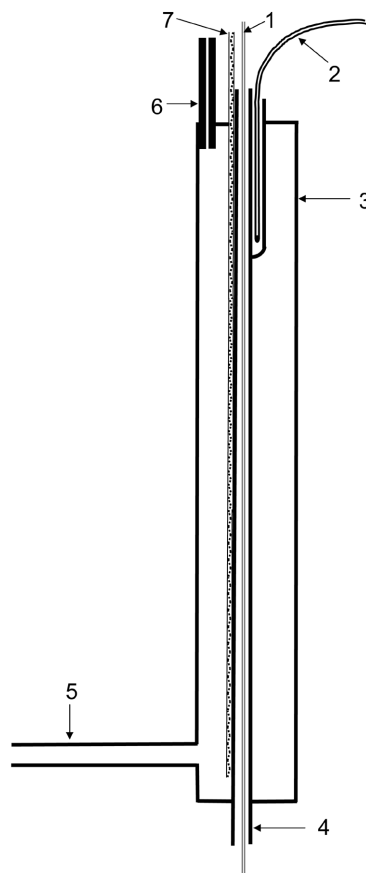
enclosures for electronics (*e.g.* RS components 282–1269 or 415–2688). The aluminium box is heated by two self-regulating heater pads (RS components 381-0119 200 W) screwed to its inside walls and is insulated externally with a layer of ceramic wool. No separate temperature controller is necessary if these self-regulating heaters are used.

All parts of the switch and cold trap that are contacted by sample are constructed from deactivated flexible fused silica (*e.g.* Supelco # 25756) connected with press-fit connectors [40] (Restek # 20486).

The switch is balanced by having the transfer line from the switch to the cold trap the same length and diameter as that from the switch to the first dimension detector (usually an FID). Depending how the switch is mounted to the GC, lengths of 30–50 cm will usually be the minimum required. Gas flows at the switch are reduced if these transfer lines have a smaller diameter than the second dimension column (*e.g.* 250  $\mu\text{m}$  if the column is 320  $\mu\text{m}$ ); the pressure to generate the optimum linear flow rate in a 25 m, 320  $\mu\text{m}$  capillary generates a volume flow approximately ten times as high in a 1 m, 250  $\mu\text{m}$  capillary).

In the cold trap, switched analytes are held on a short section of coated 530  $\mu\text{m}$  fused-silica column. For convenience I used a piece cut from the end of the first dimension column. The cold trap (Fig. 2) is a 100 mm length of 1/16 in thin-walled stainless steel tube, silver-soldered coaxially into a slightly shorter length of 1/4 in thin-walled stainless steel tube. The 1/16 in tube has a coaxial heater element (*e.g.* Thermocoax # 1NC 1.5 mm) silver-soldered along it, and at one end of the trap is a pocket for a thermocouple. Liquid carbon dioxide is fed into the annular space between the tubes through a 1/16 in narrow-bore, stainless steel tube, and out through a 1/8 in tube at the opposite end, which also serves to mount the trap to a 1/8 in bulkhead union through the wall of the aluminium enclosure. Use of a narrow-bore feed tube for the carbon dioxide is mandatory to ensure that evaporation and expansion of the carbon dioxide takes place in the trap and not in the connecting line or control valve. The flow of carbon dioxide is controlled by a shut-off high pressure needle valve (*e.g.* Supelco # 58789). The trap heater is activated by a toggle switch and its maximum temperature is controlled by feedback from a thermocouple by a temperature controller (*e.g.* RKC Instruments # REX S-100).

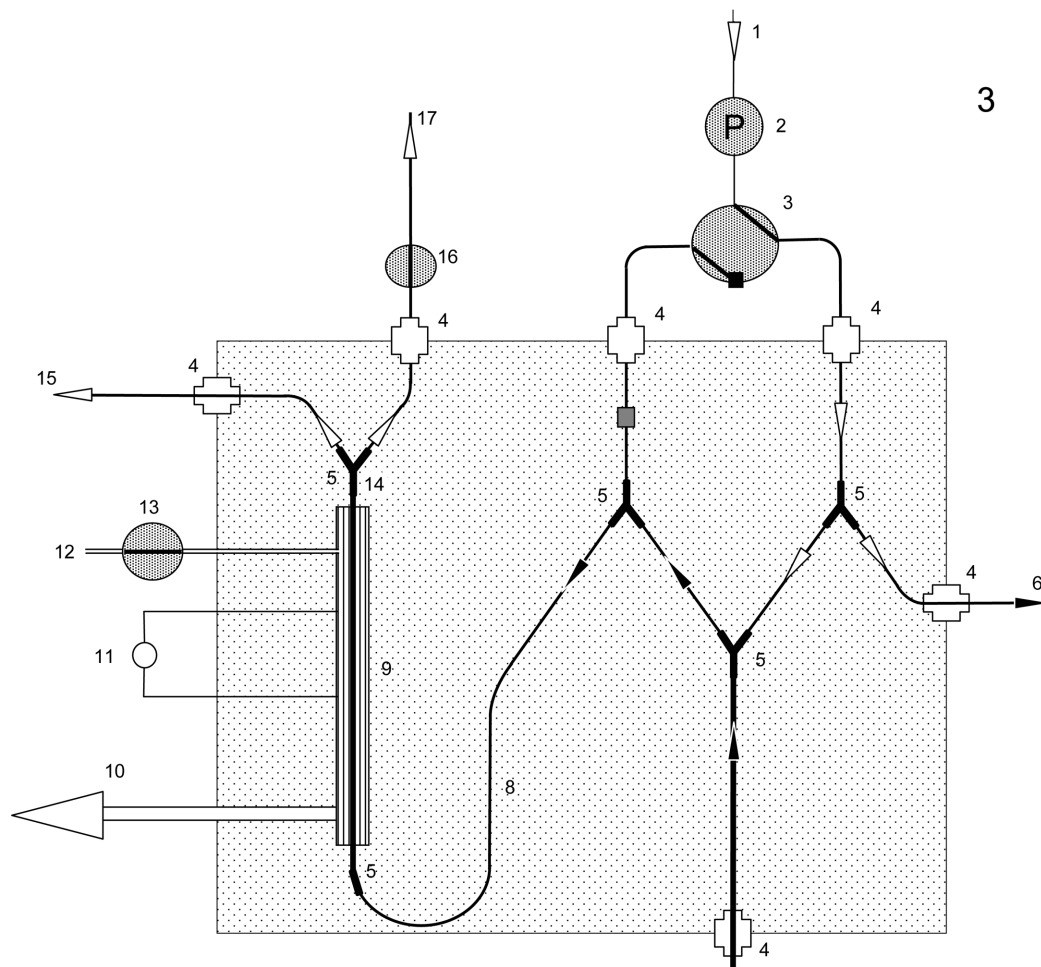
The external gas controls are connected to the silica transfer lines of the switch and cold trap via 1/16 in stainless steel tubing and 1/16 in bulkhead unions (*e.g.* Swagelok # B- or SS-100-61) mounted through the wall of the aluminium enclosure.



**Figure 2.** Schematic vertical section through the cold trap. (1) Section of 530  $\mu\text{m}$  column; (2) insulated thermocouple leads; (3) thin-walled 1/4 in stainless steel tube; (4) thin-walled 1/16 in stainless steel tube; (5) 1/8 in stainless steel tube CO<sub>2</sub> outlet; (6) thick-walled 1/16 in stainless steel tube CO<sub>2</sub> inlet; (7) coaxial heater element. For simplicity mounts and connections are not shown. All joints are silver soldered.

The first dimension column, the transfer line to the first dimension detector and the second dimension column pass straight through 1/16 in bulkheads, and are held in place with Vespel-graphite ferrules to avoid putting any mechanical stress on the press fit connectors.

The pressure at the switch is controlled by a mechanical pressure regulator (Supelco # 22816) and the switch is operated by a manual three-way valve. Clean cuts require sharp pressure changes from one side of the switch to the other, and these require the control valve and its connections to the switch to have small internal volumes. A Valco 4-port valve (# C4WE) with the pressure-regulated carrier gas supply connected to port 1, the two sides of the Deans switch to ports 2 and 4, and port 3 plugged, has proved to be suitable. The valve is mounted close to (or even on) the switch enclosure so that the connecting lines are as short as possible.



**Figure 3.** Stage 2: switch to the cold trap, analytes from the first dimension flow to the cold trap which is cooled by carbon dioxide, clean gas flows to the first dimension detector, producing a gap in the chromatogram, the vent is open.

A heated transfer line runs from the switch assembly to the oven of the second gas chromatograph. This can conveniently be constructed from 1/8 in stainless steel tubing with a coaxial heater element silver-soldered along it, controlled by a temperature controller reading from a thermocouple.

## 2.2 Installation and adjustment

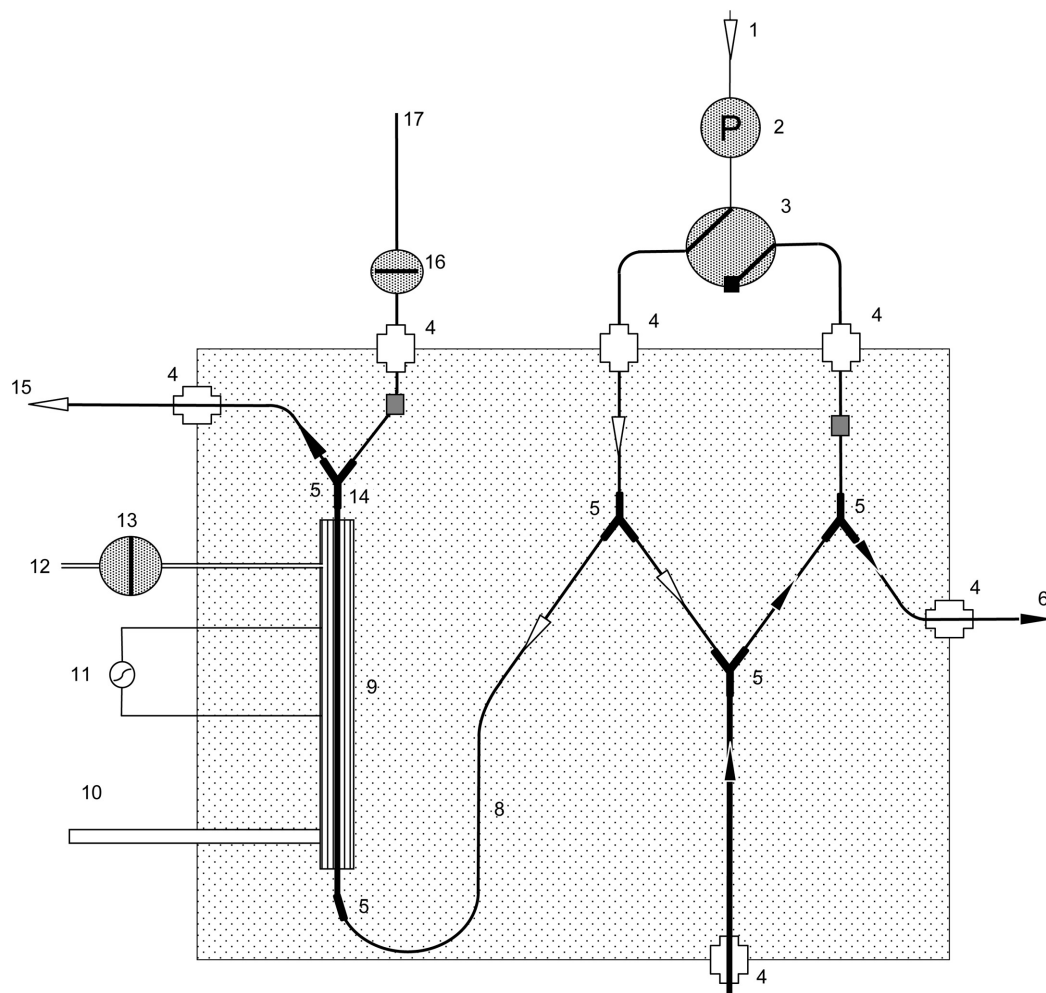
The details of mounting the switch box to the gas chromatograph will differ according to the model of instrument, the only requirements are to avoid cold spots in transfer lines and sharp bends in 530  $\mu\text{m}$  silica tubing.

The second dimension column can either be threaded through the transfer line and connected directly to the press-fit Y between the cold trap and vent, or a length of uncoated deactivated silica can be run through the transfer line and connected to the column by a straight press-fit connector in the second GC oven. When all the con-

nections have been made they should be meticulously leak-checked.

The pressure at the switch is set to deliver the required linear flow rate through the second dimension column according to tables of pressures and column dimensions or flow calculator software. The head pressure of the first column is set to deliver the required linear flow rate through that column against the back pressure at the switch. In practise, the pressure given in tables or by software can simply be added to the pressure at the switch. The linear flow can be checked by the retention time of an unretained peak at the first dimension detector.

If required, the linear flow through the second column can be checked by injecting an unretained compound with the vent closed, the switch set to the second dimension, and cold trap heating and cooling both off. The time difference between the dead time on the first dimension and the retention time of the peak at the sec-



**Figure 4.** Stage 3: switch to the first dimension detector, desorb from the trap, analytes from the first dimension separation flow to the first dimension detector, the vent is closed, the carbon dioxide is closed and the trap is heated, trapped analytes are transferred to the second dimension column.

ond dimension detector is the hold-up time in the switch, cold trap and second dimension column. To check that the switch directs all of the analytes to whichever side is selected simply inject a nonretained analyte (e. g. methane), leave the cold trap switched off, and monitor the detector on the side that is not selected.

Two vented switch systems have been installed; one between a Varian 3600 and a Varian 3400, with sniffer ports and FIDs on both dimensions, and one between a Varian 3800 with an FID and a Hewlett Packard 6890 coupled to a Hewlett Packard 5973 quadrupole mass spectrometer. Routine practise was to conduct GC-sniffing on the 3600–3400 instruments and then duplicate the separation on the 3800–6890–5973 to identify the odourous peaks.

On both systems, the first dimension column is a 30 m × 530 μm × 0.5 μm film methyl silicone (Zebron

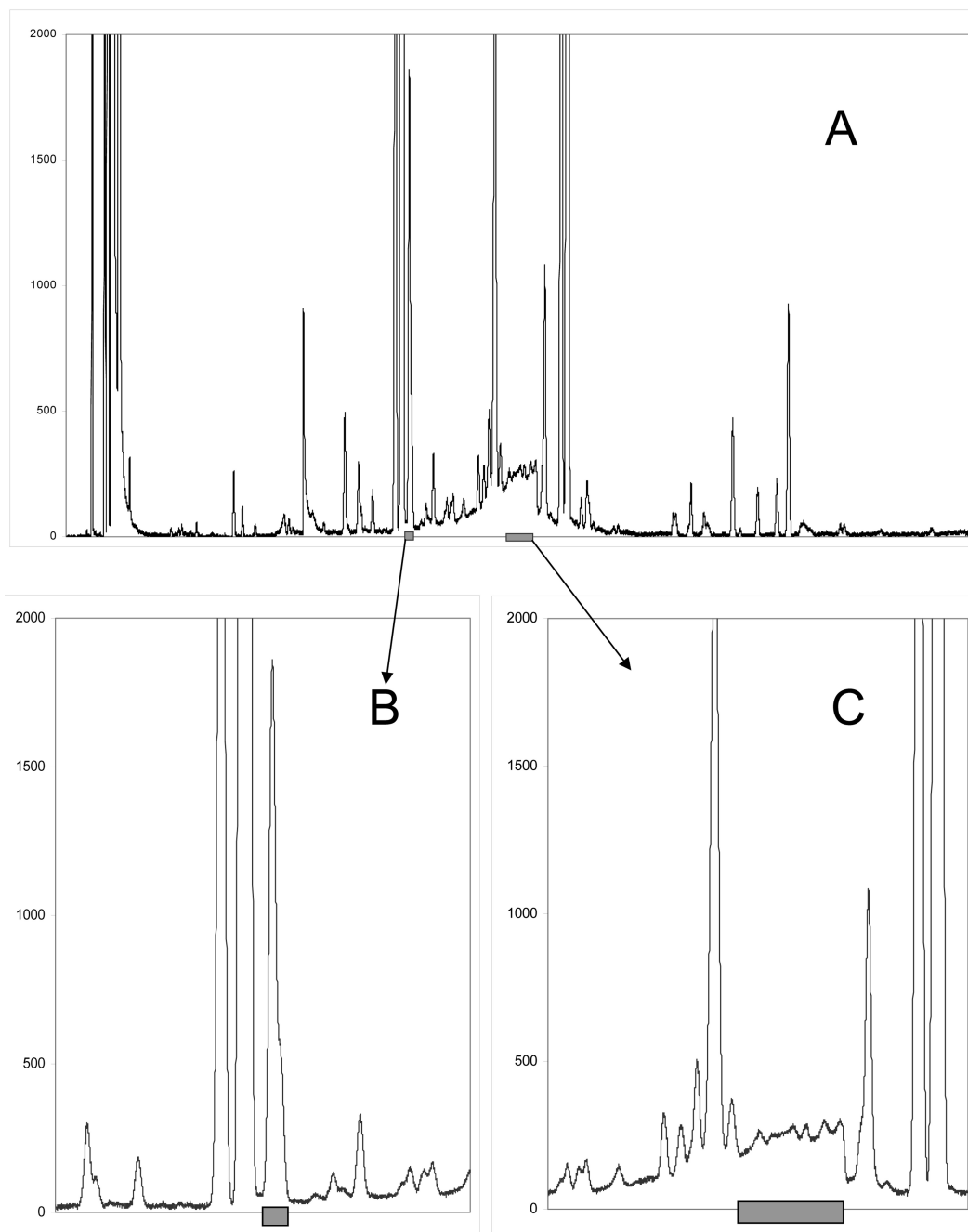
7HK-G001-17) and the second dimension column is a 30 m × 320 μm × 0.25 μm film PEG (Zebron Zbwax 7HM-G007-11). Matched columns were used in order to enable the matching of chromatograms from GC-olfactometry with those from GC-MS analyses.

In my experience, with the configuration given here, no fine tuning is required; the 10–30 mL/min flows through the switch generated by the head pressure for the second column ensure very rapid and clean cuts, and once the pressures are set for a particular pair of columns they do not need to be readjusted for changes in temperature programme.

### 2.3 Operation

Before an injection to the first dimension column, the vent is open, the carbon dioxide supply is closed, the trap





**Figure 6.** Details of the first dimension separation of tagetes oil, diluted 1:100 in hexane, 1  $\mu\text{L}$  injected splitless to a  $30\text{ m} \times 530\ \mu\text{m} \times 0.5\ \mu\text{m}$  methyl silicone column, detection by FID. (A) Complete chromatogram; (B) detail of a heart cut target with two overlapping peaks; (C) detail of a heart cut target with multiple overlapping peaks. Heart cut targets are marked by shaded rectangles.

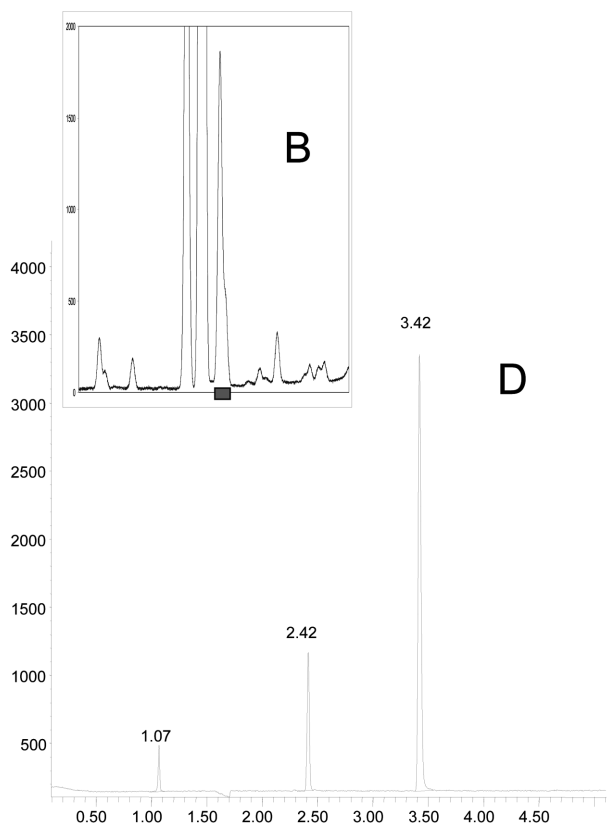
cutting; separation of an overlapping doublet into two clearly resolved, sharp, symmetrical peaks.

In order to demonstrate the repeatability of the vented switch-cold trap (and incidentally the extreme complexity of natural materials), replicate 2 min heart cuts were made from first dimension separations of tagetes essen-

tial oil, in an area of the chromatogram where all the peaks were overlapping (Figs. 6 and 8). The second dimension chromatograms are practically identical (Fig. 8E and F).

The importance of maintaining analyte detectability by complete transfer of the heart cut to the second column,



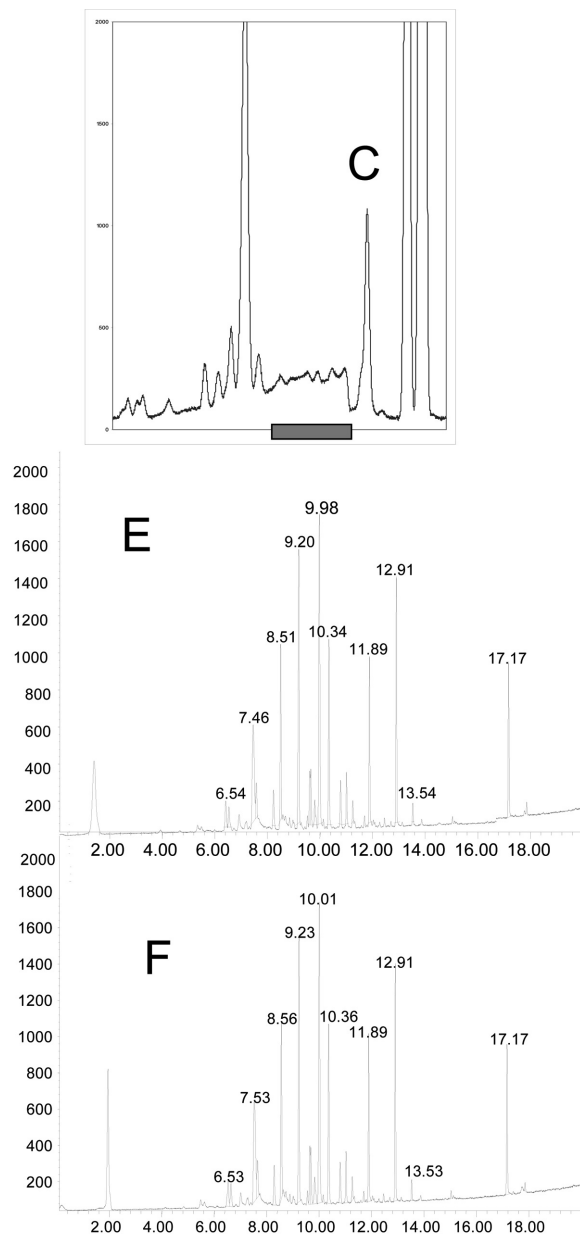


**Figure 7.** ‘Classical’ heart cutting with the vented Deans switch–cold trap to resolve two overlapping peaks. B: Detail of heart cut target in the first dimension separation on a 530  $\mu\text{m}$  methyl silicone column (Fig. 6); D: second dimension separation on a 30 m  $\times$  320  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$  PEG column. The shaded rectangle marks the heart cut target. Peak identities by MS library search; 1.07: hexane (solvent); 2.42: 3,7-dimethyl-1,3,6-octatriene (or 3,7-dimethyl-1,3,7-octatriene); 3.42: dihydrotagetone.

rather than transferring only from a split flow, or maintaining a flow of analytes to the first dimension detector, is illustrated by the peaks at 7.65 and 8.21 min in Fig. 9, which are barely five times short-term noise and approximately equal to the background signal, and yet account for the odour of the heart cut fraction.

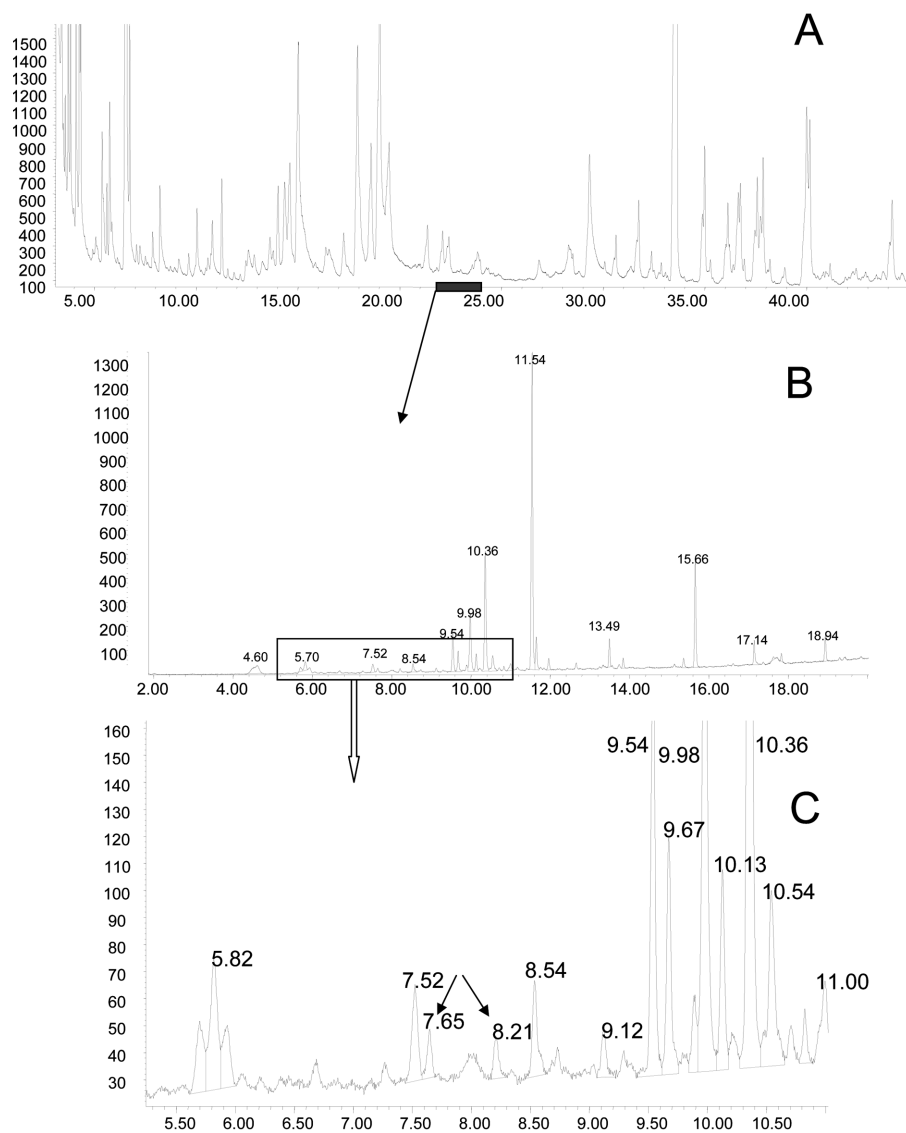
## 4 Discussion

Berg and Jonsson’s [34], Hagman and Jacobsson’s [35, 36] and Chrompack’s MUSIC [37–39] vented Deans switches operated on the same principles as the design presented here, although they all used metal compression fittings in flow lines, and Hagman and Jacobsson used needle valves as restrictors on both the vent and the transfer line to the first dimension detector. The present design takes advantage of the development of press-tight connectors [40] to build inert, low volume, zero dead volume sample flow paths. Schomburg *et al.* [29, 41] and Bertsch



**Figure 8.** Repeatability of heart cutting with the vented Deans switch–cold trap. (C) Detail of heart cut target region (shaded rectangle, Fig. 6) in the first dimension separation on a 530  $\mu\text{m}$  methyl silicone column; (E and F) replicate second dimension separations on a 30 m  $\times$  320  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$  PEG column.

[4] emphasised the need for switching systems to incorporate scavenging gas flows to flush dead volumes in connecting lines and the switch itself, and some switch designs [32, 35, 36] incorporate bypass (shunt) gas flows to flush connecting lines. Because the present switch design has very short connecting lines (<150 mm from 4-port valve to switch) carrying flows of more than 10 mL/min through press-fit connectors, fused-silica transfer



**Figure 9.** Heart cutting with the vented Deans switch–cold trap to identify trace level flavour compounds. (A) First dimension separation on a nonpolar column, the heart cut target where intense roast meat odours were detected by GC-sniffing is shown by the shaded rectangle; (B) second dimension separation on a PEG column; (C) expanded region of B to show trace components (note also the remaining complexity and peak overlap!). The arrowed peaks at 7.75 and 8.21 min are alkyl pyrazines. The cold trap was allowed to heat passively.

lines and low volume valves, there is no sign of the peak broadening or tailing that would be expected to arise from dead volumes.

Volume flows of 1–2 mL/min on the second dimension column, which give optimum linear flow velocities in 250 and 320  $\mu\text{m}$  columns, correspond to flows of 10–30 mL/min through the switch, transfer lines and cold trap which provide clean, sharp cuts and efficient trapping without excessive gas consumption and pressure pulses. The 20–30 mL/min flows through the switch sub-

stitute for the make-up gas that would normally be supplied to the first dimension detector, but have the drawback of not being compatible with direct transfer to a mass spectrometer.

The configuration presented here is fully compatible with a second dimension column of smaller internal diameter than the first dimension column. Balancing the switch with a vent instead of a restrictor accommodates the switching flow without its having to enter the second column. Because there is no need for the volume flow

rate in the second column to be higher than that in the first [32], both columns can be run at optimum linear flow rates.

The heater element on the cold trap may not be necessary; when the trap is allowed to heat passively to the temperature of the enclosure, all the peaks except for those that elute near the dead time are still sharp and symmetrical (Fig. 9). Rapid heating of cryo-traps is frequently emphasised, but it has been recognised since the early 1970s that rapid heating is required only when the column itself is at a high temperature or when the cryo-trap includes a strongly retaining stationary phase [5].

The narrowest cuts that I have transferred were 5 s wide. Such narrow cuts actually took only part of a peak from the first dimension, and were used to avoid overloading the second dimension column.

Currently, commercially available retrofit column switches (from Agilent, Gerstel and SGE) are all designed to run from programmable electronic pressure control systems as a means of reducing the sensitivity of their resistor-balanced switches to changes in flows and pressures. As a consequence, these systems cannot be fitted to older GCs that lack programmable pneumatics. Indeed, I have been unable to locate a commercial retrofit column switch that can be installed on an older instrument.

Some current 2-D systems [18] maintain a constant split at the end of the first dimension column, and transfer time slices to the second column only from this split flow, and others maintain a flow of analyte to the first dimension detector even during heart cutting [30, 31, 42]. These configurations reduce the transfer factor [10] and analyte detectability because there is a constant loss of analytes to a split, or because not all of the analyte in the time slice is transferred to the second column when some of it continues to pass to the first dimension detector. Given the extremely low concentrations at which some compounds exhibit biological activity, detectability is too valuable to be sacrificed.

This switch-cold trap configuration is not dependent on software-controlled electronic pneumatics, but it could be automated by adding remote actuators to the 4-port valve, the cryogenics valve and the trap heater. Substitution of mechanical by electronic gas controllers would allow full software control.

Although the vented switch and cold trap was developed for qualitative applications, the repeatability of its operation (Fig. 8) suggests that it might be suitable for quantitative analyses also.

The switch and cold trap configuration presented here performs as well as other published designs, and has proved itself in routine operation. It has the substantial advantage over currently available commercial systems

that it can be assembled for between a 1/5 and a 1/20 of the cost of the commercial equivalent, and it is not dependent on electronic pressure control or on a particular instrument platform.

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