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Journal of Chromatography A, 919 (2001) 127–132

JOURNAL OF CHROMATOGRAPHY A

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Simple, non-moving modulation interface for comprehensive two-dimensional gas chromatography

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Received 22 January 2001; received in revised form 13 March 2001; accepted 21 March 2001

Abstract

A simple, non-moving dual-stage CO_2 jet modulator is described, which cools two short sections of the front end of the second-dimension column of a comprehensive two-dimensional gas chromatograph. A stream of expanding CO_2 is sprayed directly onto this capillary column to trap small fractions eluting from the first-dimension column. Remobilization of the trapped analytes is performed by direct heating by the GC oven air. Installation, maintenance and control of the modulator is simple. Focusing and remobilization of the fractions is a very efficient process, as the bandwidths of the re-injected pulses are less than 10 ms. As a result, alkane peaks eluting from the second-dimension column have peakwidths at the baseline of only 120 ms.

Keywords: Instrumentation; Interfaces, GC×GC; Gas chromatography, comprehensive two-dimensional; Alkanes

1. Introduction

In the last decade multidimensional approaches in chromatography have become increasingly popular as a means to enhance selectivity and/or resolution. The coupling of liquid chromatography to gas chromatography (LC–GC) [1], but also the coupling of two different GC columns (GC–GC) are well-known examples. With the GC–GC systems most procedures are based on the use of heartcut techniques [2]. Still, despite the superior separation possibilities so created, only a limited number of laboratories routinely use GC–GC. One reason for this lack of interest is that the technique reputedly is complex in setting up and maintenance. In addition, GC–GC does not provide the dramatic increase in peak separation power of true coupled-column techniques. Since, because of overridingly important time constraints, GC–GC can only be applied to one, or a few, selected fractions of a first-dimension separation (the heartcuts), only a small portion of the peak capacity that can theoretically be achieved, is exploited. The recently introduced alternative, comprehensive two-dimensional gas chromatography (GC×GC), on the other hand, fully exploits this peak capacity.

1.1. Modulators

As is the case with any multidimensional tech-

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0021-9673/01/$ – see front matter
PII: S0021-9673(01)00785-3

nique, the interface between the dimensions is of crucial importance for the proper performance of the system. Although there are, in principle, two techniques for modulation, viz. valve [3] and thermal modulation, only the latter is considered to be really comprehensive and will be discussed in this paper. Since thermal modulation in a capillary column interface can be performed by both heating and cooling, there are two alternatives.

(i) *Heated modulators*. Heated modulators use a thick-film modulation capillary to trap subsequent fractions containing the eluting analytes from the first column by means of phase-ratio focusing. After trapping, heat is applied to thermally desorb the analytes from the thick-film stationary phase and re-inject the narrow chemical pulses into the second column. Fig. 1 presents this phase-ratio focusing and thermal desorption process as a self-explanatory four-step procedure. The first paper on GC×GC, by Liu and Phillips [4] used this approach with a dual-stage metal-coated capillary as modulation capillary, which was resistively heated to desorb the trapped analytes. Although impressive results were reported, this thermal desorption system was found not to be sufficiently robust for prolonged use. An improved and more sophisticated heated desorption system was designed and made commercially available by Ledford et al. [5]. With their mechanical so-called sweeper modulator various interesting GC×GC applications were reported, mainly concerning the separations of complex petroleum samples [6–9] or organochlorine mixtures [10].

(ii) *Cooled modulators*. Cooled modulators, with cooling generally achieved by cryogenic means, do not use a modulation capillary. Instead, they trap and focus the analyte-containing fractions as they elute from the first column on the front end of the second column itself. The best example is the so-called longitudinally modulated cryogenic system (LMCS) [11]. After the liquid CO_2-cooled modulator has started moving, the surrounding GC-oven air ensures rapid heating and, thus, rapid remobilization of the trapped analytes prior to their re-injection. The cryogenic trap, focus and re-injection process is schematically presented in Fig. 2.

Apart from the mechanical differences between the heated and cooled modulators, there are also differences with regard to their applicability. In the heated modulators an increase in temperature of at least 100°C is necessary to remobilize the analytes from the thick-film capillary that holds the retained fraction [12]. The maximum temperature to which

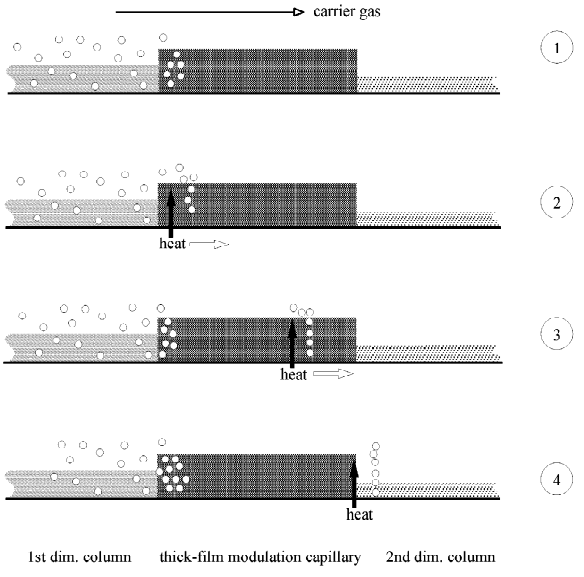

Fig. 1. Four-step schematic of the heated modulation process. 1=Trapping of solutes; 2=remobilization of solutes; 3=continuous refocusing of solutes and trapping of next fraction; 4=release of solutes, i.e. re-injection.

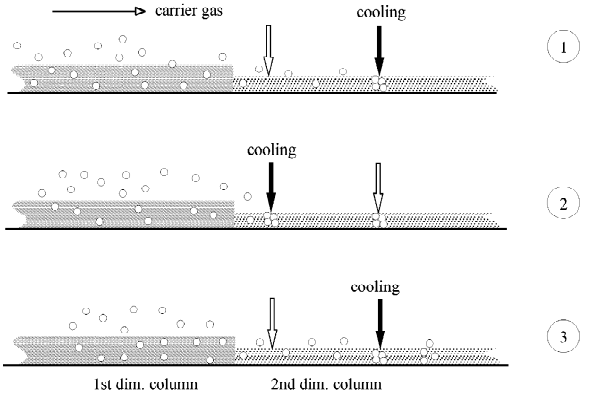

Fig. 2. Three-step schematic of the cryogenic modulation process. 1=Trapping of solutes; 2=release of solutes; 3=separation and next trapping. Open arrow: cooling off, filled arrow: cooling on.

this capillary can be heated, i.e. the maximum allowable temperature of its stationary phase, determines the maximum operating temperature of the system. With the cooled modulator systems (which do not feature an interface capillary), on the other hand, the maximum allowable temperature is determined by the two stationary phases themselves and is, therefore, some 100°C higher. The common characteristic of the thermal modulators presented until now, is that they use a heating/cooling device that moves uncomfortably close to the narrow-bore capillary. Even if very precise (and rather tedious) tuning of these devices is performed, breakage of the tiny and fragile 100-μm capillaries occurs all too frequently. Ledford having become aware of this shortcoming of moving modulators, recently reported on a two-stage liquid nitrogen/heated air jet modulator, which does not contain any moving parts [13]. Actually, this is an elegant adaptation of his earlier single-jet-cooled heated modulator that was incorporated in the sweeper system [14]. A continuous stream of cold gas, cooled by liquid nitrogen, cools a short section of the front end of the second column for trapping/focusing of the analytes eluting from the first column. Two heated-gas jets alternately heat parts of this section to remobilize the analytes as very narrow chemical pulses for re-injection. The cooled sections of the second column can reach temperatures as low as −190°C, which enables the modulation of compounds with retention factors as low as methane.

Although the modulator is very robust and modulation is performed very satisfactorily, the extra heating that is needed to remobilize trapped fractions, possesses a limitation to the maximum column temperature of the system. Moreover, liquid nitrogen is not easily available in all laboratories and needs bulky insulation when transported through tubing. Pressurised liquid CO_2, on the other hand, is a more convenient and easy-to-handle coolant, which has recently been used by us for that purpose in a simple homemade moving modulator to directly cool a column section for trapping [15]. This paper describes the design and performance of a non-moving dual-stage liquid CO_2 jet modulator. It confirms that there is no real need to use the heated-gas jets: one can rely on the GC-oven air instead, as has also been demonstrated in the LMCS approach.

2. Experimental

2.1. GC conditions

The gas chromatograph was a Hewlett-Packard HP6890 (Agilent, Palo Alto, CA, USA) with a split/splitless injector and a flame ionization detection (FID) system capable of producing a digital signal at a sampling rate of 200 Hz. The 30 m×0.32 mm I.D. first-dimension column was coated with 0.25 μm HP1. It was coupled through a press-fit connector to the 1.0 m×0.10 mm I.D. second column, which was coated with 0.1 μm BPX50 (SGE Europe, Milton Keynes, UK). Carrier gas was set to 1.0 ml/min through a column head pressure of 170 kPa helium. The columns were temperature programmed from 50°C (4 min isothermal) to 300°C at 2°C/min. Fig. 3 presents a schematic of the GC×GC system.

2.2. Data handling

A Hewlett-Packard Chemstation performed the data acquisition. The data files were exported in .csv format and subsequently converted to ASCII matrices by means of a laboratory-written conversion programme (Ph. Marriott, RMIT, Melbourne, Australia). Contour plots and second-dimension chromatograms of these matrices were generated through Neosys Transform (Creaso, Apeldoorn, Netherlands).

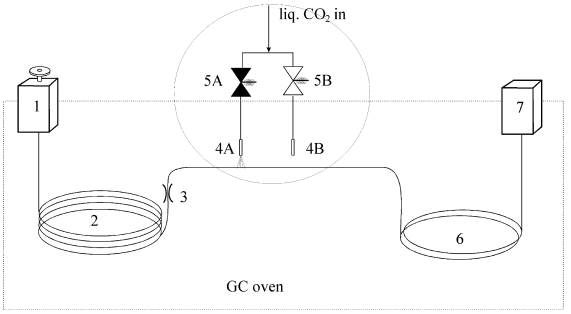

Fig. 3. GC×GC system with dual-stage CO_2 jet modulators (the encircled zone is expanded in Fig. 4). 1=Injector; 2=first column; 3=column connection; 4A=CO_2 nozzle A; 4B=CO_2 nozzle B; 5A=CO_2 valve A; 5B=CO_2 nozzle B; 6=second column; 7=detector.

3. Results and discussion

3.1. CO_2-cooled jet modulator

The dual-stage CO_2 jet modulator is, in fact, the counterpart of the earlier developed on-column two-stage heated modulator of Liu and Phillips [4]. In that system two separate parts of the capillary that hold the retained and focused fraction, respectively, were directly — and alternately — heated in order to remobilize the fractions for re-injection. In the dual-stage CO_2 jet modulator, two parts of the capillary are directly and alternately cooled in order to trap and focus each subsequent fraction (Figs. 3, 4A and B), which is, next, remobilized by the heat from the surrounding oven air.

The CO_2 jets consist of two electrical-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 are 50 mm×0.5 mm I.D. capillaries (Fig. 4). In order to force as much CO_2 from the outlet of the nozzles to touch the column, the outlets were made into 0.04 mm wide and 3 mm long slits running parallel to the capillary. To prevent ice formation on the outside of the jets at oven temperatures below about 100°C, they were inserted in a 12 mm diameter brass socket to increase the heat capacity.

As the liquid CO_2 expands at the outlet of the nozzles, the throttling process cools the exiting gas through the Joule–Thompson effect. Since this gas is sprayed directly onto the second column at the prevailing flow, this column quickly cools down to about 100°C below the oven temperature. Closing the valve will immediately stop the cooling, and the surrounding air from the GC oven will heat up the short cooled section of the capillary of about 10 mm instantaneously to oven temperature. According to Kinghorn and Marriott [16], who calculated the time required to heat a capillary column from cryogenic to oven temperatures, this time is only 13 ms for a conventional 100 μm I.D. column (15 μm polyimide and 80 μm fused-silica walls).

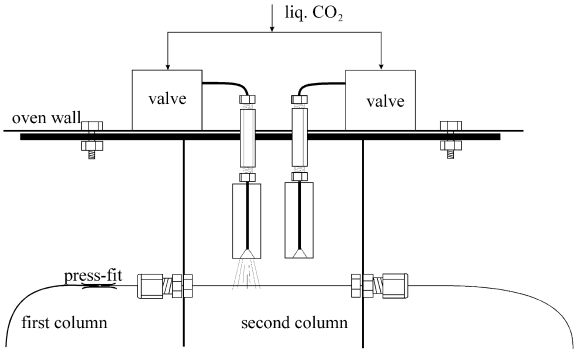

Fig. 4. Blow-up of the bracket containing the CO_2 valves and jets of Fig. 3.

The part of the second-dimension column in which the modulation takes place, is stretched and secured between two Valco (VICI, Schenkon, Schwitzerland) unions mounted on the bracket. Tight stretching is necessary in order to avoid vibration of the column caused by the rather high flow of cold CO_2 that is sprayed onto the column. The unions are mounted onto two bands of 0.9 mm thick resilient 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 the 24 d.c. voltages for valve switching controls the modulation process. Modulation times as short as 0.1 s have successfully been achieved.

3.2. Performance of the modulator

The main functions of the modulator are two-fold: trapping of small fractions of the effluent of the first column as narrow pulses, and re-injection of these pulses into the (remaining) part of the second column. To assess the performance of the modulator, it is sufficient to calculate the bandwidth of these pulses.

In general the first column used in GC×GC contains a non-polar stationary phase, and separation occurs via temperature programming. Retention on this phase is inversely proportional to the product of vapour pressure of the pure component (p_i^0) and the activity coefficient of the analyte in the stationary phase at infinite dilution (γ_i^∞). The retention factor ($k_{e,i}$) at the time (temperature) of elution then is:

$$k_{e,i} \div \frac{1}{p_i^0(T_e)\gamma_i^\infty} \quad (1)$$

where T_e is the elution temperature [17]. Ideally, i.e. in the absence of molecular interactions (and entropic effects), all analytes will have an activity coefficient of unity. When using a linear temperature programme, the $k_{e,i}$values at the moment of elution will be roughly equal. With all γ_i^∞ values also approximately equal (about unity), this implies that all solutes co-eluting from the first-dimension column will have approximately equal vapour pressures. This will influence the bandwidth of the remobilized pulse. Analytes having the same vapour pressure, and being exposed to the same temperature inside the column, will behave very similar, and will be remobilized simultaneously. Thus, once the fractions are focused into narrow pulses in the cooling cycle, they will remain narrow on remobilization very easily.

The overall band broadening (σ_t) is determined by the sum of the variances of injection, detection and chromatographic effects:

$$\sigma_t^2 = \sigma_i^2 + \sigma_c^2 + \sigma_d^2 \quad (2)$$

If negligible contribution to band broadening by the volume and electronics of the detector (σ_d) is assumed, the injection bandwidth (σ_i) can be calculated from the bandwidth of a second-dimension peak by subtracting the chromatographic band broadening (σ_c). The latter can be calculated from:

$$\sigma_c^2 = \frac{t_{R_i}^2}{N} \quad (3)$$

where t_{R_i} is the second-dimension retention time of the peak being considered and N the plate number. For N we used the theoretical plate number as supplied by the column manufacturer, which is about 8000 for an alkane with a retention factor of $k' = 1$ on a 1.0 m×100 μm I.D. column.

3.3. Modulation performance

A separation of C_8–C_{18} *n*-alkanes was performed to collect the required data. The modulation frequency was set at 0.25 Hz, which is equivalent to 2 s for the trapping, and 2 s for the release time. Actually, a 1 s trapping and 3 s release time was found to produce the same result. A typical result is shown in Fig. 5.

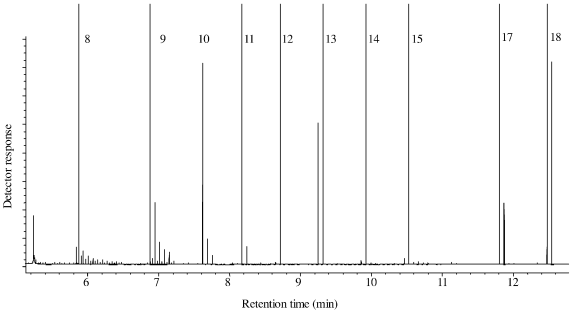

Fig. 5. GC×GC separation of C_8–C_{18} *n*-alkanes (denoted 8–18) with the dual-stage CO_2 jet modulator. (The intensity of the modulated *n*-alkane peaks do not represent a gaussian distribution, since the modulation is performed randomly throughout a first-dimension peak).

Calculations were carried out as outlined above. One example is shown in Fig. 6, viz. for the modulated peaks of *n*-C_{14}, with the insert allowing the peakwidth to be read more easily. The peakwidths were found to be $\sigma_t = 30 \pm 5$ ms, which is better than previously reported second-dimension peaks [6,10,19]. The injection bandwidth was calculated, by extrapolation to $k' = 0$ [18], to be $\sigma_i < 10$ ms, which is better than the injection bandwidths of the sweeper, which are typically $\sigma_i = 60$ ms (calculated from [5,6]) and the cryo-modulator of Marriott et al., which are 20–50 ms [20]. In other words, the present modulator performs according to expectations.

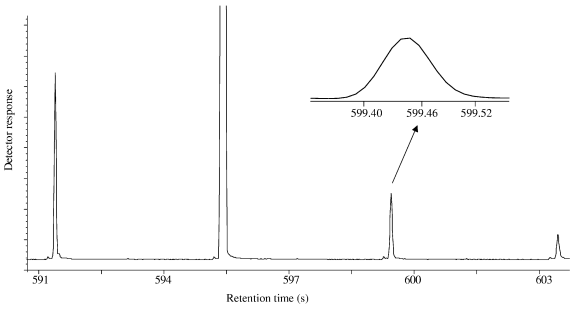

Fig. 6. Expansion of Fig. 5. Modulated *n*-C_{14} peaks. Insert shows the exact peakwidth. (The very small peak preceding each main *n*-alkane peak is probably a dimethyl-siloxane artifact, originating from septum or stationary phase), and now visible because of the enhanced sensitivity of GC×GC).

4. Conclusions

The dual-stage CO_2 jet modulator is a simple device, which is easy to install and maintain. Running costs are low and liquid CO_2 is readily available. Control of the modulator is performed by alternately switching two valves. Since there are no moving parts, which is a main difference with most other modulators discussed in the literature, damage to the (second-dimension) column will occur in exceptional cases only. The ability of the set-up to focus the trapped first-dimension fractions as narrow pulses is as good as, or even better than, that of these other modulators. On-going work is aimed at using the present set-up for a variety of applications. These will also include use of the modulator as a means of focusing the input band from the injection in order to facilitate the use of narrow-bore capillary columns. Enhancing analyte detectability by placing the modulator just in front of the detector, will also be attempted (cf. [21]).

Acknowledgements

Dik van Iperen of our workshop is kindly acknowledged for the technical discussions and advice concerning the construction of the nozzles. The authors wish to thank SGE Europe for providing the second-dimension column as used in this study.

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