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Practical and theoretical aspects of designing a flame-ionization detector/mass spectrometer Deans' switch Pressure–flow relations in gas chromatograph–detector interfaces using vacuum-outlet conditions

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Abstract

In gas chromatographic (GC) practice, straightforward splitting of the column effluent over a mass spectrometry (MS) system and a flame-ionization detection (FID) system leads to unpredictable split ratios and, thus, to poor quantification. We therefore decided to implement a Deans' switch, which should allow for quantitative transfer of the column effluent to either FID or MS. Since FID works under atmospheric pressure and an MS under vacuum conditions, it is difficult to establish suitable dimensions (lengths and diameters) of the capillaries needed for a "balanced" switch. Generally, the Poiseuille equation, which describes the flow of fluids through tubes of circular cross-section, is used to this end. However, the motion of gases in small capillaries at low pressures, as is the case in GC–MS interfaces, is fundamentally different from that at near atmospheric pressures. This becomes manifest from a substantial drop of the dynamic viscosity of the gas, η , to an effective viscosity, η/F , or, in other words, the Poiseuille equation is no longer valid. Adapting the Poiseuille equation by the introduction of the correction factor, F , has been reported. In this paper F and the use of an equation for F expressed in terms of readily accessible parameters will be discussed. In addition, a successful design of a balanced FID/MS Deans' switch will be demonstrated. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Deans' switching; Pressure–flow relationships; Liquid chromatography–gas chromatography; Interfaces, FID–MS; Instrumentation

1. Introduction

In gas chromatographic (GC) practice, the identity of target analytes and unknowns is often confirmed or provisionally revealed by using mass spectrometry (MS). Subsequent quantification using MS can only be done if the identified component is available as a

standard, either in its pure form or of known purity. Unfortunately, such standards are often not available. However, because the relation between molecular structure and flame-ionization detection (FID) response is reasonably well understood [1,2], quantification of compounds of known chemical structure may be done using FID. This is one main reason why FID and MS are frequently combined in one GC set-up. Straightforward splitting of the capillary-col-

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umn effluent over FID and MS, although habitually utilized, is not recommended. The split ratio between FID and MS is usually determined by a set of fixed (capillaries inside the detector interfaces kept at constant temperature) and variable (capillaries leading to the detector interfaces at (variable) oven temperature) restrictions. This results in split ratios which can vary substantially during a temperature-programmed run and makes quantification unreliable or even erroneous [3]. In 1968 Deans developed the principle of valveless switching based on pressure balancing. The resulting devices were capable of directing effluent flows quantitatively in either one of two possible directions [4]. We therefore decided on the use of a Deans' switching device which allows for quantitative transfer of the column effluent to either FID or MS.

The calculation of the dimensions of the capillaries needed for a "balanced" switch is generally done by using the well-known Poiseuille equation. Poiseuille derived this equation while describing the flow of fluids through tubes of circular cross-section, and for situations where the diameter of the tube is large compared with the mean free pathlength in the fluid. Hence, in the case of vacuum outlet conditions, this equation may not be valid any more, and using this equation all the same, as has been suggested [5], may lead to serious deviations. Useful adaptations to the Poiseuille equation in order to fit low-pressure conditions have been reported by Knudsen [6] and Brown et al. [7]. Designing an FID/MS Deans' switch, while taking these adaptations into account, will be the subject of this paper.

2. Theory

In 1844, Poiseuille derived equations describing the flow of fluids through tubes of circular cross-section. The "Poiseuille equation", can be written as:

$$Q = \left(\frac{60\pi r^4}{16\eta L} \right) \left(\frac{p_i^2 - p_o^2}{p_o} \right) \left(\frac{p_o}{p_{\text{ref}}} \right) \left(\frac{T_{\text{ref}}}{T} \right) \quad (1)$$

where Q is the volumetric flow under reference conditions expressed in ml/min (usually as measured at the column outlet), r the radius of the tube, L the

length, η the dynamic viscosity of the gas, p_i and p_o the inlet and outlet pressures, and p_{ref} and T_{ref} the reference pressure and temperatures respectively.

If $p_o^2 < p_i^2$ (vacuum outlet conditions) this equation can be simplified to yield Eq. (2) [4]:

$$Q = \left(\frac{60\pi r^4}{16\eta L} \right) \left(\frac{p_i^2}{p_{\text{ref}}} \right) \left(\frac{T_{\text{ref}}}{T} \right) \quad (2)$$

Although this simplification seems to be mathematically correct, the underlying Poiseuille equation falls short for flows in very small capillaries at low pressures. The equation was derived based on the assumption that the velocity of the gas in contact with the walls is zero. Under low-pressure conditions, however, because of the increase in the ratio of the molecular mean free pathlength over the tube radius, the number of collisions between molecules becomes small compared to the number of collisions with the walls. In such a case the nature of the motion of the gas is termed "molecular flow" instead of "slip flow" and a factor, F , has to be introduced. Obviously, F will be unity at ordinary pressures (slip-flow conditions), but it can easily reach values up to 1000 when molecular flow becomes dominant [8]. Alternatively, one may say that in these cases the viscosity decreases to an effective viscosity, η/F . Eq. (1) then turns into:

$$Q = \left(\frac{60\pi r^4}{16\eta FL} \right) \left(\frac{p_i^2 - p_o^2}{p_o} \right) \left(\frac{p_o}{p_{\text{ref}}} \right) \left(\frac{T_{\text{ref}}}{T} \right) \quad (3)$$

Empirical relations to estimate F have been reported by Brown et al. for air in glass, copper and iron tubes [7]. They proposed the following equation:

$$F = \left[1 + 4 \left(\frac{\pi}{2} \right)^{1/2} \left(\frac{2}{f} - 1 \right) X \right] \quad (4)$$

where, as suggested by Maxwell [9], f is the fraction of gas molecules striking the walls that will be diffusely reflected, and $1-f$ the fraction that will be specularly reflected. The symbol X represents the dimensionless group:

$$X = (\eta/rp_m)(M/R_G T)^{-1/2} \quad (5)$$

where p_m is the arithmetic mean pressure $(p_i + p_o)/2$, M the molecular mass of the gas, R_G the gas constant and T the temperature. As stated above, F

becomes increasingly important when the ratio (mean free pathlength/radius of the capillary) increases and when f becomes small, i.e., when inner walls become smooth(er). The factor f must be regarded as an experimental parameter. In a survey of theories of flow at low pressures, Thomson and Owens reviewed several analytical descriptions of the transition region between the slip-flow and molecular-flow regimes [10]. They concluded that the slip theory contains the inherently erroneous assumption that the flow profile does not change as the Knudsen number (a parameter used to characterize the free molecular-flow regime, which is defined as the ratio of the mean free pathlength over characteristic container dimensions) [6] increases. They also concluded that the magnitude of the slip velocity must be regarded as an experimental unknown. They admitted that the concept of specular reflection is a good first approximation, but commented that any surface will appear “rough” to an impinging molecule, because of the vibration of wall molecules. Other descriptions, however, must also rely heavily on experimental data. Furthermore, most of the latter are designed to fit either one of the extreme conditions and there is no practical theory that describes the transition region quantitatively. As indicated above, from among the various treatments, that of Brown et al. [7] provides a correction factor, F , that can be expressed in terms of readily accessible parameters. Their equation is still being used today. Data obtained for glass capillaries give the best fit for molecular flow with $f=0.77$, and with $f=0.84$ for slip flow.

3. Experimental

Nowadays a Deans’ switch can easily be constructed using three press-fit effluent splitters as is depicted in Fig. 1. We installed such a Deans’ switch in-line in an on-line coupled size-exclusion chromatography (SEC)–GC–FID system reported in a previous paper [11] using press-fits obtained from Techrom (Purmerend, The Netherlands). The capillary column used was a 30 m×0.32 mm I.D. fused-silica coated with 0.25 μm 5% phenylmethylpolysiloxane (DB-5MS, J&W Scientific, Folsom, CA, USA). Helium was used as the

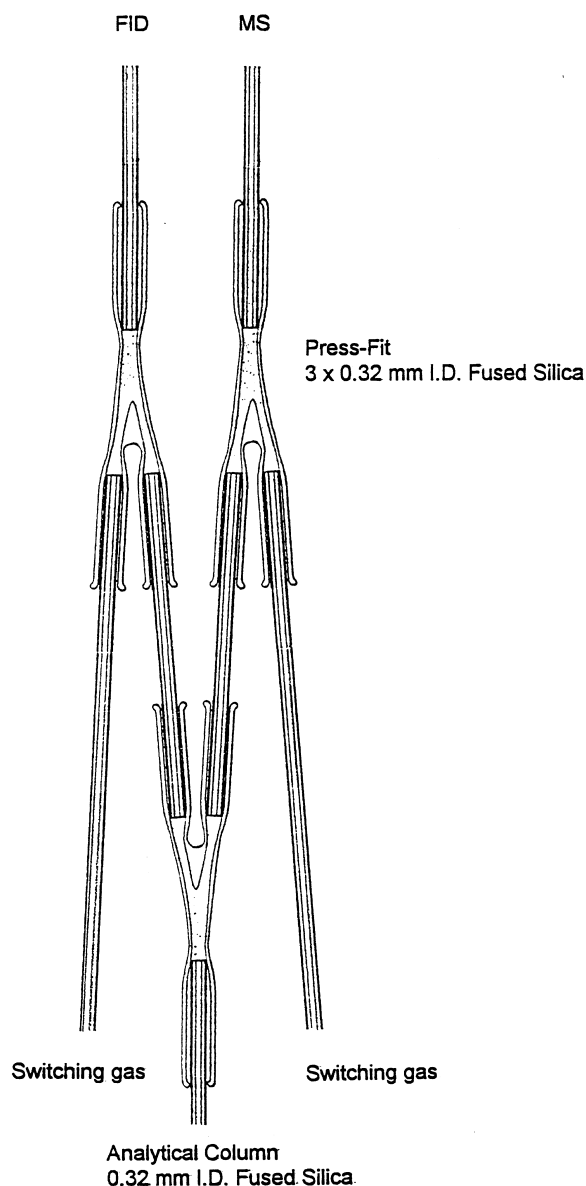


Fig. 1. Schematic of the construction of a Deans’ switch using three press-fit effluent splitters.

carrier gas. The initial oven temperature was 101°C, which was maintained for 5 min. Subsequent linear programming was done at a rate of 10 C°/min. The final temperature was 350°C, which was maintained for 20 min. The MS used was a Trio-1000 benchtop MS (Fisons, Manchester, UK) operated in the elec-

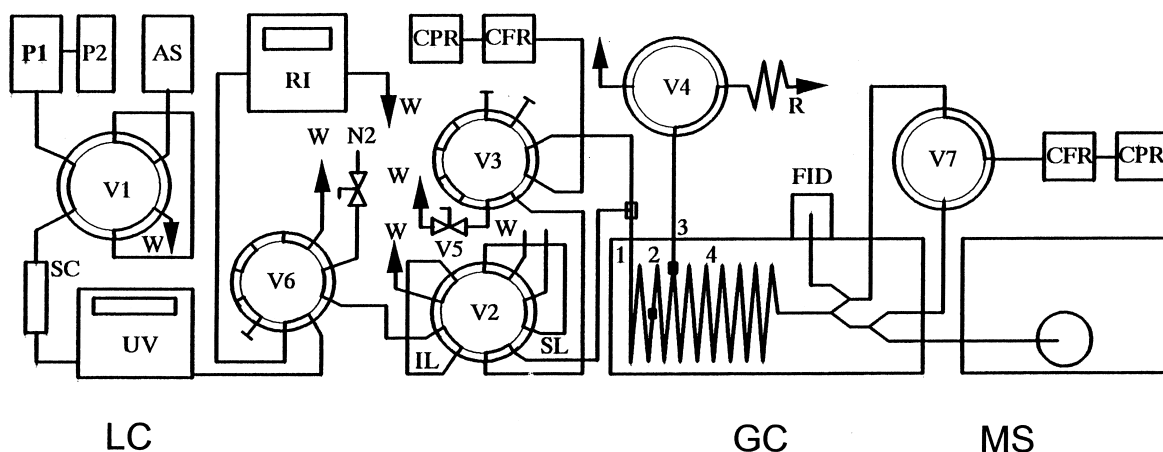


Fig. 2. Schematic diagram of the SEC-GC-FID/MS system equipped with FID/MS Deans' switching. P1 and P2, SEC pumps; AS, autosampler; V1, SEC injection valve; W, waste; SC, SEC column; UV, UV detector; V2, LC-GC transfer valve; IL, injection loop; SL, standard loop; V3, carrier-gas switching valve; CPR, constant-pressure regulator; CFR, constant-flow regulator; V4, early-vapour-exit valve; R, fused-silica restriction; V5, interface purge valve; V6, valve to circumvent mixing in the injection loop; N₂, nitrogen purge of injection loop; RI, refractive-index detector; 1, retention gap; 2, retaining precolumn; 3, early vapour exit; 4, analytical column; V7, valve to actuate the FID/MS live switch; FID, flame-ionization detector.

tron-ionization mode. A schematic diagram of the entire system is presented in Fig. 2.

The configuration surrounding the live switch is depicted in Fig. 3. From the switch one 40 cm long, 0.25 mm I.D. piece of 1,3-diphenyl-1,1,3,3-tetramethyl-disilazane (DPTMDS)-deactivated fused-silica (BGB Analytik, Rothenfluh, Switzerland) led to the FID system (Carlo Erba, Milan, Italy) which was operated at 375°C. Another piece of 0.15 mm I.D. fused-silica (SGE, Ringwood, Australia) with a total length of 64 cm led to the MS ionization source.

From this 64 cm piece, 40 cm was located within the GC-MS interface, which was kept at a constant temperature of 350°C. Switching gas (helium) was supplied to the switch by means of a high-precision flow-controller (Porter, Hatfield, PA, USA) set at 4.5 ml/min. In order to have this flow-controller operate correctly at such a low flow, a constant-pressure regulator (Carlo Erba) set at 100 kPa was mounted upstream. Actual switching was effected using a three-port Valco valve (VICI, Schenkon, Switzerland). The "balance" of the switch was measured at

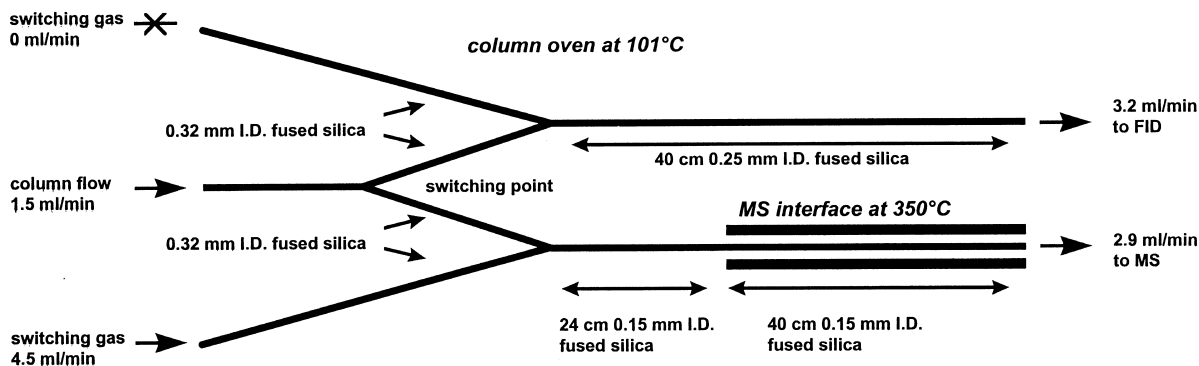


Fig. 3. Configuration surrounding the live switch as described in Section 3. Flows to FID and MS are experimental values measured at oven temperature 101°C. At oven temperature 350°C (column flow 0.7 ml/min, see Section 3) the measured flows to FID and MS were 2.6 and 2.5 ml/min respectively.

two different oven temperatures, viz. the initial (101°C) and final (350°C) temperatures of the commonly applied temperature programme [11]. Flow measurements were performed using two different flow meters (CP FP-meter and CP Flowmet II, Chrompack, Middelburg, The Netherlands). The first was attached to the flame tip of the FID system (hydrogen flow turned off!) and the second at the discharge of the MS's vacuum (pre-)pump. Special care was taken to make the latter leak-tight using silicone high-vacuum grease (medium grade, Merck, Darmstadt, Germany). Flow from the discharge of a rotary vacuum pumps suffers from short-term fluctuations. We therefore decided to use the CP Flowmet II. Because of its slow response, it proved to be insensitive to these short-term fluctuations (in contrast to the more recently introduced CP FP-meter).

The column flow was regulated by a constant-pressure/constant-flow regulator as described by Grob and Stoll [12] and was set to 1.5 ml/min at 101°C. This resulted in a column head-pressure of 66 kPa. The maximum pressure of the interface was set to 100 kPa. This pressure is too low to maintain constant flow throughout the entire temperature programme, consequently, during a temperature-programmed run the system gradually changes from constant-flow to constant-pressure conditions. A flow of 0.7 ml/min at the final temperature of 350°C was calculated using Eq. (3) with $F=1.0$ (see Section 4 below).

4. Results and discussion

In order to demonstrate the proper performance of our Deans' switch set-up, we incorporated it in an on-line liquid chromatography–GC (LC–GC) system, such as the SEC–GC system used here. This can be considered a good choice because the Deans' switch can, then, also be used for the selective venting of remaining (co-)solvent similar to the open-split interface described by Hathcock et al. [13], thus dramatically extending the operating period between consecutive cleanings of the MS ionization source. Fig. 4 shows three GC chromatograms obtained from a 500 μ l SEC fraction of a strongly aliphatic hydrocarbon mixture and demonstrates the correct operation of the Deans' switch

(i.e. the directing of the total GC column effluent either the one or the other way). Fig. 4a shows the FID trace obtained when the total effluent from the analytical column was continuously directed towards the FID. Fig. 4b shows the FID trace of a duplicate run, but now the column effluent was directed towards the MS 14.0 min after the start of the SEC–GC transfer, in other words, this was a SEC–GC–MS run with selective venting of the remaining solvent “through” the FID. Fig. 4c shows the simultaneously obtained total-ion chromatogram (10–650 u). The latter two chromatograms clearly demonstrate the complete transfer of the solvent peak via the FID route and the complete transfer of the column effluent to the MS 14.0 min after the start of the GC transfer.

Before the construction of the Deans' switch and the set-up described above, we were not aware of the serious deviations from the Poiseuille equation that can occur when calculating the performance of detector interfaces operated under vacuum-outlet conditions. In fact, we came up with the configuration described in Section 3 only after considerable trial-and-error work.

It was when we tried to rationalise the use and performance of the switch that we were confronted with large deviations. We then went looking for analytical descriptions that could be used to calculate the dimensions needed for balanced Deans' switches in the future. To assess whether the descriptions by Brown et al. [7] would meet our requirements, we submitted our Deans' switch to a series of experiments, in which both the temperature and the flow through the switch varied.

Whenever temperatures were changed, both interfaces (to FID and MS) were run at the same temperature as that of the switch. This ruled out the presence of any unpredictable temperature gradients along the length of capillaries. It also meant that the necessary calculations could be kept as simple as possible.

The helium flow supplied to the switch was varied by changing the pressure upstream of the (high-precision) Porter flow controller (cf. Section 3). Since the upstream constant-pressure regulator was provided with a pressure gauge, this was the easiest and most reliable approach to ensure reproducible flow set-points. Upstream pressures used were 100,

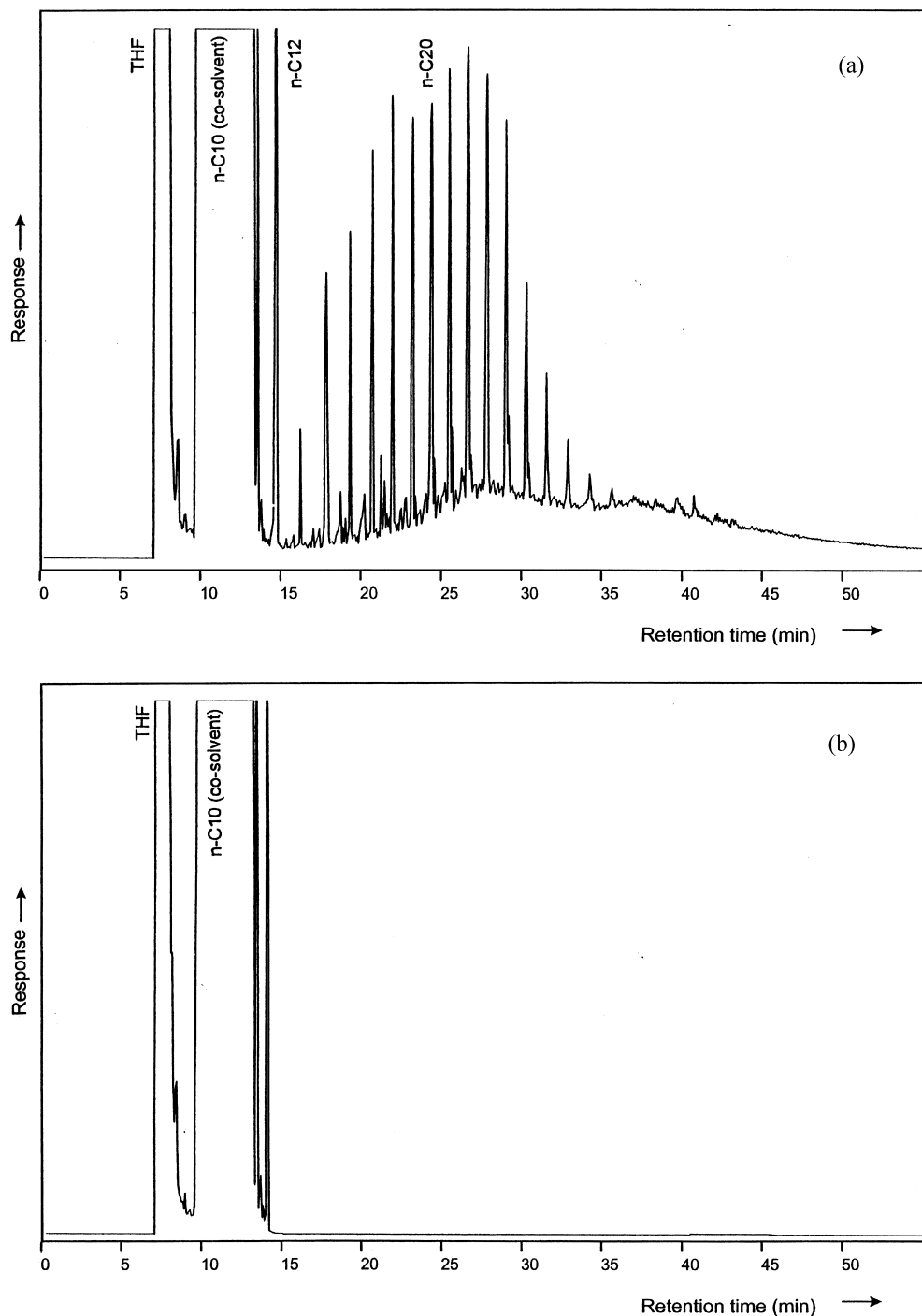


Fig. 4. (a) FID trace of a 500 μ l SEC fraction of a strongly aliphatic hydrocarbon mixture obtained when the total effluent from the analytical column was continuously directed towards the FID system. (b) FID trace of a duplicate run. The column effluent was directed towards the MS 14.0 min after the start of the SEC–GC transfer (SEC–GC–MS run with selective venting of the remaining solvent “through” the FID system). (c) Simultaneously obtained total-ion chromatogram (10–650 u). Note the complete transfer of the solvent peak via the FID route (b) and the complete transfer of the column effluent to the MS 14.0 min after the start of the SEC–GC transfer.

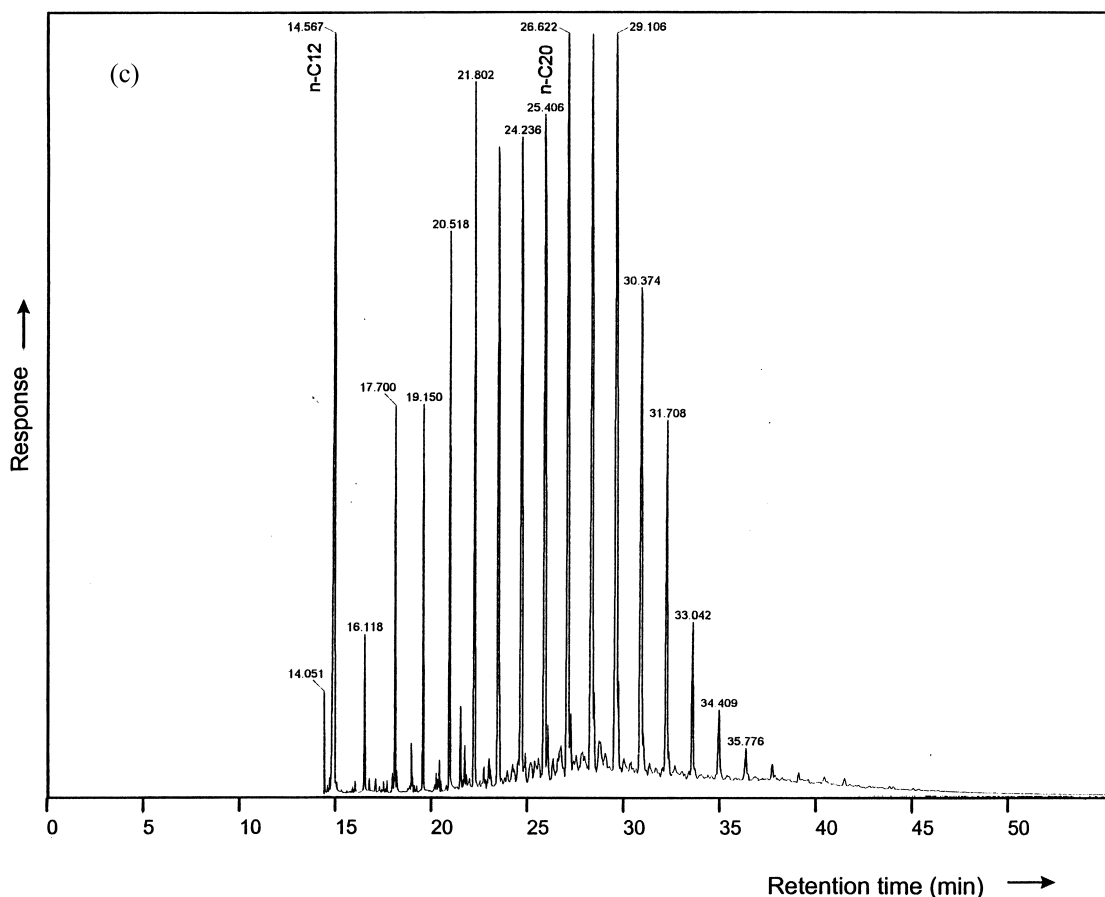


Fig. 4. (continued)

200 and 300 kPa, where 100 and 300 kPa were the limits in between which the flow-controller is guaranteed by the manufacturer to work properly.

To obtain an equation for the calculation of the (absolute) pressure, at the switching point from the flow emerging from the FID (see Fig. 3), Eq. (3) can be rewritten as Eq. (6):

$$p_i = \sqrt{\left(p_o Q \left(\frac{16\eta/FL}{60\pi r^4} \right) \left(\frac{p_{\text{ref}}}{p_o} \right) \left(\frac{T}{T_{\text{ref}}} \right) + p_o^2 \right)} \quad (6)$$

where L and r refer to the capillary leading from the switch to the FID system. In this case $F=1.0$, since the motion of the gas flowing from the switching point to the FID system may be regarded as pure slip flow. The results of the calculations and further

relevant data are summarised in Table 1. The pressures at the switching point were calculated by means of Eq. (6). Dividing the experimentally recorded flows through the MS by the flow through the MS as calculated by means of Eq. (1) (Poiseuille without correction) then yielded the experimental values of the correction factor F . From the data on calculated and experimental flows through the MS presented in Table 1, it is obvious that there are indeed large differences between theory (Poiseuille) and practice (experimental values). The former, conventional [5] approach is seen to underestimate the flow through the MS system by a factor of 2.5. Moreover the correction factor is seen to be essentially independent of the conditions (P , T , Q) used, with a mean value of 2.4 ± 0.1 . The calculated

Table 1
Summary of calculated and experimental data concerning FID/MS live switch

Temperature (°C)	Measured flow to FID (ml/min)	Pressure at switching point (kPa)	Flow to MS (ml/min)		Correction factor <i>F</i>	
			Calcd.	Expt.	According to Ref. [7]	Expt.
100	0.8	103.2	2.12	5.1	1.05	2.4
100	3.0	107.5	2.30	5.3	1.05	2.3
100	4.9	111.0	2.46	5.6	1.05	2.3
150	1.5	105.3	1.79	4.5	1.06	2.5
150	3.6	110.2	1.96	4.9	1.05	2.5
150	5.5	114.5	2.12	5.1	1.05	2.4
200	1.7	106.8	1.52	3.9	1.06	2.6
200	3.9	112.9	1.70	4.2	1.06	2.5
200	6.0	118.5	1.87	4.5	1.06	2.4
300	2.5	111.5	1.20	2.9	1.08	2.4
300	4.5	118.9	1.36	3.2	1.07	2.4
300	6.3	125.2	1.51	3.5	1.07	2.3

Conditions:

Capillary dimensions:		Viscosities of Helium according to Ref. [14]:
towards FID	40 cm × 250 μm I.D.	at 100°C: 23.2 μPa s
towards MS	64 cm × 150 μm I.D.	at 200°C: 27.4 μPa s
Ambient pressure:	101.6 kPa	at 150°C: 25.3 μPa s
Reference pressure:	101.3 kPa	at 300°C: 31.3 μPa s
MS source pressure:	4 · 10 ⁻⁶ kPa	Gas constant: 8.314 J/K mol
		Reference temperature: 25°C (298 K)
		Fraction of diffusely re- flected molecules <i>f</i> : 0.7

correction factors according to Brown et al. (Eq. (4)) obviously do not account for the observed differences.

It must be admitted that no proper model has, as yet, been found by us that accounts for the deviations observed. On the other hand, the experimental value for *F* of 2.4 established in this paper can be used safely for the construction of a balanced switch. The lengths of the capillaries (of a given diameter) can then be calculated after rewriting Eq. (3) as Eq. (7):

$$L = \left(\left(\frac{60\pi r^4}{16\eta/F} \right) \left(\frac{p_i^2 - p_o^2}{p_o} \right) \left(\frac{p_o}{p_{ref}} \right) \left(\frac{T_{ref}}{T} \right) \right) / Q \quad (7)$$

5. Conclusions

A simple Deans' switching device has been designed that allows for the full transfer of effluent from a capillary GC towards either a MS system or a detector working at atmospheric pressure such as an FID. Quantification problems that will arise when

conventional postcolumn splitting is applied during a temperature programmed run, are thereby avoided. In coupled LC–GC the same switching device can be used for the selective venting of the large amount of solvent which would otherwise cause the rapid deterioration of the ionization source of the MS.

Although no proper theoretical explanation has been found for the deviations observed between the experimental and calculated flows emerging from a detector operated under vacuum-outlet conditions, a correction factor, which is largely independent of the experimental conditions used, has been found which can be used when constructing balanced switches.

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