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THERMAL PEAK SPLITTING IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

Thermal peak splitting occurs under certain operating conditions when capillary columns with low thermal mass are used. The characteristic "christmas-tree" shape of the chromatographic peak is due to column temperature fluctuations.

Steady temperature gradients do not produce peak splitting, as shown by our experimental data. Our experimental data also show that the electronic temperature regulation is not responsible for these fluctuations. They arise from an uneven air flow pattern inside the oven. This type of problem is common to all gas chromatography ovens designed according to conventional concepts.

It has been found that the most sensitive part of the column is its end. A cold spot inside the detector base body can mask the phenomenon, but reduces the efficiency of the system.

A simple model was used to explain how these fluctuations produce the splitting of the chromatographic peaks. The maximum acceptable temperature fluctuation was estimated according to rough theoretical calculations. The use of a special column cage allows the column thermal mass to be adjusted without reducing the ability to follow high temperature-programming rates.

An ultimate solution to this problem is presented in the shape of a new column oven, designed to ensure the temperature stability required by capillary columns of low-thermal mass.

INTRODUCTION

One process frequently responsible for peak splitting in capillary gas chromatography (GC) is the "flooding effect"¹⁻⁸. We prefer to consider the partial solvent effect⁹⁻¹¹ as a source of peak distortion rather than peak splitting. The other process is thermal peak splitting¹² which has been observed in many laboratories where various capillaries of low thermal mass are used. De Jong¹³ developed a simple, ingenious technique for detecting this effect, consisting of recording continuously the detector response to heptane, which is mixed with the carrier gas before it enters the capillary column. The rapid temperature variation inside the oven produces a proportional noise-type response on the recorder, as it modifies the distribution of heptane between the stationary and mobile phases.

Schomburg¹⁴ recently mentioned the "christmas-tree effect" and offered a cor-

rect explanation of the mechanism. It may be supposed that recently proposed instruments with a complex "oven-in-an-oven" configuration¹⁵⁻¹⁸ were developed with the intention (although never clearly stated) of overcoming, at least partially, the thermal peak splitting problem. However, this complex configuration does not seem to be the final solution, because additional modifications of the oven have been introduced recently.

EXPERIMENTAL

The objects of the experiments were to identify the thermal origin of the christmas tree-type peak splitting, the source of the thermal disturbances in the column area, the contribution of different parts of the column to this effect and the influence of the detector base body temperature profile. Possible solutions for the elimination of thermal peak splitting are also discussed.

In addition to experiments performed with our instruments, some were also repeated with other commercial gas chromatographs. Our experiments demonstrated that this type of problem is common to all GC ovens designed according to conventional concepts. In some instances, the phenomenon is partly masked by a cold outlet or excessive peak filtering and smoothing before the chromatogram is plotted. However, if the outlet is properly heated and the detector signal is recorded on a strip-chart or galvanometric recorder at high chart speeds, the phenomenon becomes evident.

Thermal origin of peak splitting

In order to ascertain the thermal origin of this phenomenon we first tested thin-walled glass capillaries (0.36 mm I.D. and 0.46 mm O.D.), and encountered the same problem. Some simple experiments provided additional proof of its thermal origin. For example, we performed the same analysis with a fused-silica column, first installed normally in the gas chromatograph and then fully immersed in a thermostatted water-bath placed inside the oven. The chromatograms reported in Fig. 1

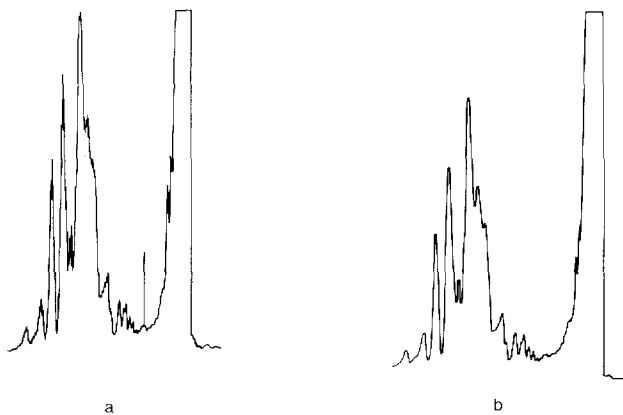


Fig. 1. Illustration of the thermal origin of the "christmas-tree" peak shape. Peak shape of C_{10} alcohols on a 10-m SP-2100 fused-silica column at 45°C. The column was (a) normally installed and (b) immersed in a water-bath. Strip-chart recorder, chart speed 2 cm/min.

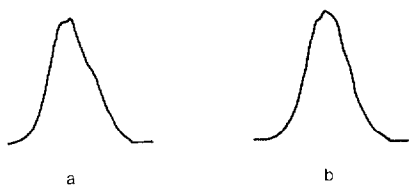


Fig. 2. Illustration that electronic temperature control does not contribute to peak splitting. Peak shapes of 10 ng of tetracosane ($C_{24}H_{50}$) injected into a 20-m, OV-1 fused-silica column maintained at $193^{\circ}C$. The oven resistance heater was feed (a) with a.c. current under the control of the electronic temperature regulator and (b) with d.c. current by applying a stabilized voltage of 90 V. Strip-chart recorder, chart speed 30 cm/min.

show that, when the column is immersed in the water-bath, normal peaks are obtained.

Source of the thermal disturbances in the column area

Electronic temperature control. The frequency of the detector signal variations producing the christmas-tree peak shape suggested that the electronic temperature control is not responsible for this effect. In fact, the variations in the heater temperature due to the pulsed current supply are averaged by the low thermal capacity of the air and the long distance covered by the air flow before it enters the column area.

In order to prove this assumption, we compared the peak shapes of the same compound obtained with large temperature variations of the oven heater due to the pulsed action of the thermoregulator, and with a constant heater temperature, obtained through a d.c. supply to the resistor.

If the electronic control had been responsible for peak splitting, the column should have generated a normally shaped peak when the temperature of the resistance heater was kept constant (d.c. supply). As christmas-tree peaks were found in both instances (Fig. 2), we discounted any influence of the electronic temperature control.

Steady temperature gradients in the column area. Simple theoretical considerations strongly suggested that the christmas-tree effect is due to temperature fluctuations and not to a steady temperature gradient in the column area. However, in order to eliminate any doubt, we studied the results obtained under conditions of a strong thermal gradient, artificially created in the column area. In order to avoid any influence of temperature fluctuations, the fused-silica column was inserted in a fibre-glass sleeve before mounting it on its cage (J&W type). A limited part of the column was wrapped with a heating ribbon in order to create a temperature gradient (see Fig. 3). The temperature of this "forced heated zone" was controlled by an autotransformer and measured by a thermocouple.

The shape of the peaks obtained with and without a forced temperature gradient were the same and did not exhibit any peak splitting (Fig. 3).

Uneven air-flow pattern inside the oven. We assumed that cold and hot air currents could be responsible for temperature fluctuations, if they alternately penetrated the column area. The simplest way to verify this assumption was to switch off the fan motor for a certain period of time and to observe the results.

At high oven temperatures, the column cools rapidly when the fan is stopped. This produces a band broadening of the non-eluted components and, therefore, peak splitting is masked.

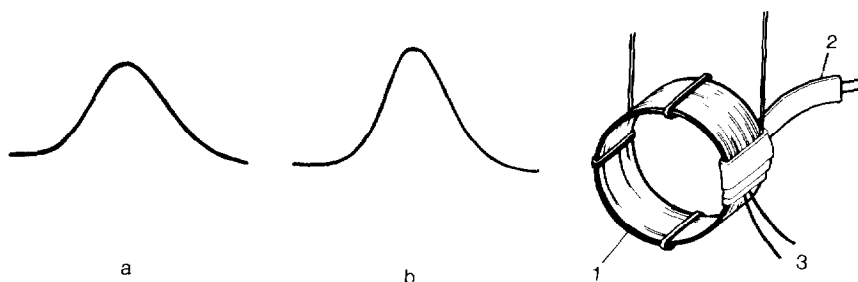


Fig. 3. Illustration that steady temperature gradients in the column area do not produce christmas-tree-type peak splitting. Peak shapes of 15 ng of dodecane ($C_{12}H_{26}$) injected into a 25-m OV-1 fused-silica column maintained at $85^{\circ}C$, (a) without forced thermal gradient, (b) with a "forced heated zone" about 6 cm long (measured on the cage circumference), maintained at $185^{\circ}C$. Galvanometric recording, chart speed, 25 mm/sec. 1 = Column; 2 = heating ribbon; 3 = thermocouple.

The experiment can be performed successfully with volatile components at oven temperatures not far from the ambient ones. As expected, peak splitting disappeared when the fan was stopped (Fig. 4).

Contribution of different parts of the column to thermal peak splitting

The peak splitting process takes place over the full length of the column, but its last portion is the most sensitive. By covering the last 10 cm with a glass sleeve and leaving the remainder of the column uncovered or by covering the entire column with the exception of the last 10 cm, split peaks were obtained. This was due to the large temperature fluctuations in the neighbourhood of the hot detector base body and to the absence of the "smoothing effects" in the short remaining part of the column (see *Mechanism of thermal peak splitting*). The temperature fluctuations and,

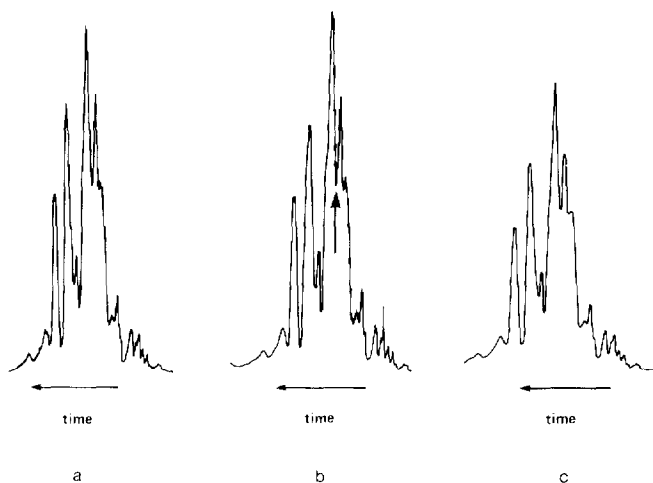


Fig. 4. Illustration that christmas-tree-type peak splitting is due to the uneven air flow pattern inside the oven (conventionally designed oven). Peak shapes of C_{10} alcohols analysed on a 10-m SE-52 fused-silica column at $60^{\circ}C$. The fan was (a) in motion, (b) stopped during analysis and (c) stopped before sample injection. Strip chart-recorder, chart speed 2 cm/min.

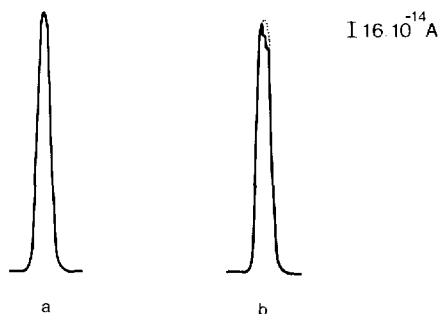


Fig. 5. Illustration that the temperature difference between the oven and the detector base body influences the peak splitting process in the last part of the column (conventionally designed oven). Peak shapes of *trans*-stilbene eluted isothermally at 150°C from a 25-m OV-1 fused-silica column. Detector base body temperature: (a) 150°C; (b) 250°C.

therefore, the peak splitting process are enhanced by a large temperature difference between the oven and the detector base body (Fig. 5).

Influence of the temperature profile along the detector base body

If the temperature profile along the detector base body shows a cold spot, this can mask the peak splitting by smoothing the band through a sequential compression-decompression process. However, it produces a supplementary band broadening for the less volatile components, resulting in a decrease in system efficiency (Fig. 6).

Such cold spots are frequently encountered when the detector base body is heated only in the region of the detection point (e.g. flame-ionization detector jet) and not over its full length.

Influence of dead volumes at the column end

A similar smoothing phenomenon can be produced by a dead volume between the column end and the detection point. Even if a large amount of make-up gas is added, such a configuration creates a mixing chamber, which produces band distortion and broadening but, at the same time, also peak smoothing.

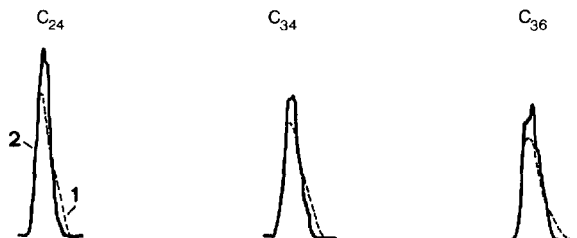


Fig. 6. Peak smoothing and broadening by a cold spot inside the detector base body. Peak shapes of tetracosane, tetratriacontane and hexatriacontane on a 30-m DB-1 fused-silica column (J&W Scientific). Temperature programme: for 45 to 335°C at 5°C/min. Detector temperature: 350°C. Solid line, normal detector base body, heated over its full length; dashed line, special detector base body, heated at 350°C only in the region of the FID jet. Strip-chart recorder, chart-speed 30 cm/min.

DISCUSSION AND THEORETICAL CONSIDERATIONS

Temperature fluctuation frequencies producing peak splitting

Temperature fluctuations generate peak splitting, because they instantaneously modify the component equilibrium between phases. In order to produce such modifications, the temperature variations outside the column must be sensed by the stationary phase. The column wall, even if it has a low mass, will average high-frequency temperature fluctuations. The frequency of temperature fluctuations that influence the partition process was roughly estimated by simultaneous galvanometric recording of the oven-temperature fluctuations in the column area and by the flame-ionization detector (FID) response to an organic tracer added to the carrier gas (De Jong method).

The "peak-to-peak" temperature variations in the column area were measured by using a low-mass thermocouple, made from 0.2-mm wire and flattened to $75\ \mu\text{m}$ on its 5-mm long measuring area. Its large surface-to-volume ratio and low mass allowed the recording of temperature fluctuations with frequencies much higher than those damaging the chromatographic equilibrium. Suitable signal filtering permitted the isolation of fluctuations with different frequency ranges. Visual comparison of the two traces suggested that thermal fluctuations with frequencies ranging from roughly 0.2 to 2 Hz are mainly responsible for change in the partition equilibrium.

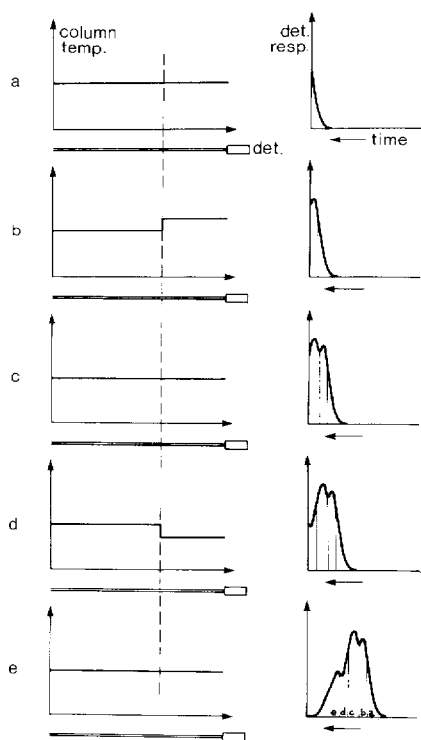


Fig. 7. Mechanism of peak splitting by temperature fluctuations in the neighbourhood of the column outlet. (a)–(e) indicate different periods of time, corresponding to certain hypothetical temperature profiles and to the relative slices of the eluted peak.

Obviously such a method is only approximate, but more elaborate correlation methods can be applied to give more precise results. However, it seems that frequencies higher than 2 Hz are generally filtered by the thermal transfer through the column wall, whereas low frequencies are discarded, owing to the limited band width of eluates in capillary GC.

Mechanism of thermal peak splitting

The thermal peak splitting process is easily understood if one considers the eluate band when it is eluted from the column. Any "damaging" temperature fluctuation in this area of the column will modify the partition equilibrium, and the component concentration in the gas phase will differ from the Gaussian profile (Fig. 7).

If temperature fluctuations arise when the component is still far from the column outlet, the band will be again deformed. We used a simple model in order to illustrate this process.

Taking into account that the eluate band can easily spread over 2–3 coils, it is understandable that fluctuations result in an instantaneous temperature increase in one zone of the band and, at the same time, in a temperature decrease in another zone (Fig. 8a).

If the eluate present in the gas phase is immobile, the disturbances will simply disappear when it returns to the average temperature. As this part of the eluate is quickly moved along by the carrier gas, a return to the average temperature does not cancel the peak distortions. However, the average temperature will produce a mass transfer between the phases in order to reach the equilibrium profile corresponding to the new situation (Fig. 8b). This mass transfer produces a smoothing effect (Fig. 8c).

During its migration in the remaining part of the column the band is subject

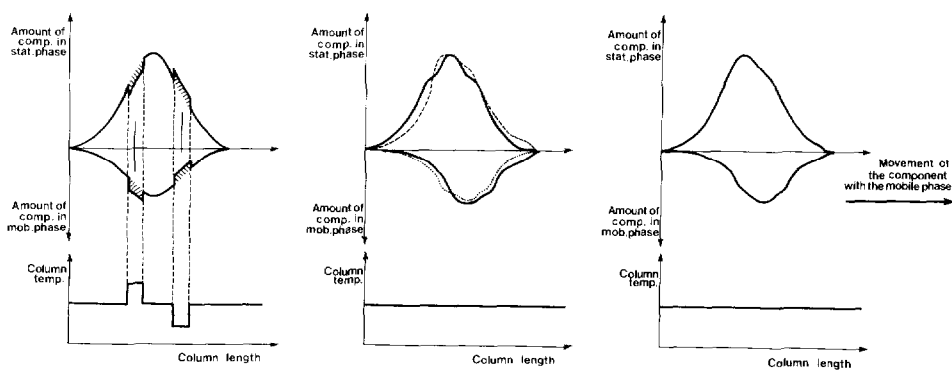


Fig. 8. A simple model, illustrating the band distortion by temperature fluctuations during eluate migration along the column. (a) Change in the amount of eluate present in each phase due to temperature variations. (b) Band profiles in the stationary and mobile phases after movement of the eluate with the mobile phase. The dotted curve represents the equilibrium profile of the eluate in the gas phase, corresponding to the portion of eluate immobilized in the stationary phase. The dashed curve represents the equilibrium profile of the eluate in the stationary phase corresponding to the portion of eluate shifted by the mobile phase. The arrows indicate the mass transfer between phases, producing a smoothing effect. (c) Smoothed equilibrium band profiles obtained after distribution of the eluate between phases and eluate migration with the mobile phase.

to a smoothing process. This is due not only to the molecular diffusion in the gas phase, but also to the repetitive distribution between phases or any other band-broadening phenomena. Of course, at the same time, the eluite band may be disturbed again by other temperature fluctuations. Because this process has a random nature, the peak shapes are not reproducible.

Theoretical considerations on thermal peak splitting

An exact theoretical treatment of the process is almost impossible and not really necessary. Such a treatment would require detailed analysis and information on random processes such as oven temperature fluctuations, as well as a detailed knowledge of the kinetics of other complex processes, such as heat transfer through the capillary column wall and the band-broadening phenomena inside and outside the column that produce the peak smoothing. Moreover, even if such an analysis were feasible, exact mathematical solutions of complex equations generated by such phenomena are unobtainable.

Therefore, our theoretical considerations are based on extremely rough approximations. They only aim to identify the parameters playing an important role in this process and, if possible, to establish very approximate mathematical expressions indicating how the amplitude of peak splitting varies with such parameters.

Relative detector signal variation, $\Delta s/s$. The amplitude of thermal peak splitting can be measured by the maximum relative detector signal variation per unit time, $\Delta s/s$, corresponding to the final peak width. Δs represents the maximum deviation of the signal, s , from the smooth Gaussian peak shape (Fig. 9). In practice, we can estimate an averaged $\Delta s/s$ value from the final peak shape. It is not always easy to measure such values, because thermal peak splitting is often accompanied by peak distortion.

The maximum relative detector signal variation, $\Delta s/s$, can easily be correlated with the variation of the capacity constant, Δk , caused by the maximum temperature fluctuation, ΔT , which produces the signal variation ($\Delta T \rightarrow \Delta k \rightarrow \Delta s$).

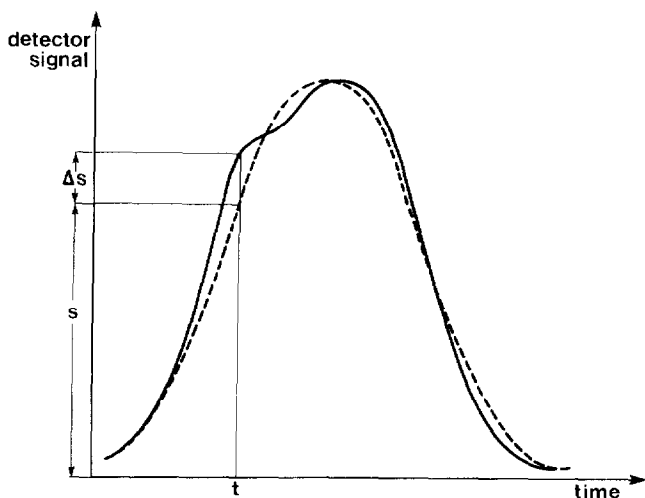


Fig. 9. Amplitude of the thermal peak splitting measured as relative variation of the detector signal, $\Delta s/s$.

For this, we assume that $\Delta s/s$ is equal to the relative variation per unit time of the amount of eluite in the carrier gas, $\Delta w_m/w_m$, inside the length Δl of the band region where the partition equilibrium was displaced by the temperature variation ΔT .

$$\frac{\Delta s}{s} = \frac{\Delta w_m}{w_m} \quad (1)$$

However,

$$\Delta k = k(T + \Delta T) - k(T) = \frac{w_s - \Delta w_m}{w_m + \Delta w_m} - \frac{w_s}{w_m} \quad (2)$$

If $\Delta T > 0$, then $\Delta k < 0$, $\Delta w_m > 0$ and $\Delta s > 0$. If $\Delta T < 0$, then $\Delta k > 0$, $\Delta w_m < 0$ and $\Delta s < 0$.

After simple algebraic transformation, we can correlate the relative detector signal variation, $\Delta s/s$, with the value of the capacity constant, k , and its variation, Δk :

$$\frac{\Delta s}{s} = - \frac{\Delta k}{1 + k + |\Delta k|} \quad (3)$$

As both k and Δk depend on the oven temperature, T , and the temperature fluctuation amplitude, ΔT , the relative detector signal variation, $\Delta s/s$, also depends on these values.

Variation of the capacity constant with temperature. In order to simplify the equation, we assume that the "25°C rule" is applicable in our case. This empirical rule states that "the capacity constant is halved when the oven temperature increases by 25°C". This leads to the following equation:

$$k(T) = k(T_0)e^{-C(T-T_0)} \quad (4)$$

where $C = 2.772 \cdot 10^{-2}$ and T_0 is the initial temperature. In fact, C is not a constant, but equal to $\Delta H_{\text{vap. sol.}}/RT^2$, and therefore depends strongly on T ($\Delta H_{\text{vap. sol.}}$ is the molar vaporization enthalpy of the eluite from the stationary phase). However, for our very rough calculations we may assume that the 25°C rule is valid.

$$\frac{dk(T)}{dT} = -k(T_0)Ce^{-C(T-T_0)} = -Ck(T) \quad (5)$$

$$\Delta k(T) = -2.77 \cdot 10^{-2} \cdot k(T) \Delta T \quad (6)$$

According to this rule a temperature variation of 1°C will produce a relative variation of the capacity constant of about 0.03 k units. This value corresponds roughly to $\Delta H_{\text{vap. sol.}}/RT_{\text{col}}^2$ obtained by setting $\Delta H_{\text{vap. sol.}} \approx 6000\text{--}7000$ cal/mole, usual values for non-polar compounds, and T_{col} (expressed in °K) around ambient.

The variation of the capacity constant with temperature is larger for higher values of the capacity constant (eqn. 6). Therefore, temperature fluctuations at low temperatures will apparently influence the partition process more than those at higher temperature. However, the amplitude of temperature fluctuations usually increases with increasing oven temperature. Moreover, the band distortions have a higher probability of being smoothed out when they occur at low temperatures.

Dependence of relative detector signal variation, $\Delta s/s$, on the capacity constant and on the amplitude of temperature fluctuations. Using the “25°C rule”, we can calculate the relative detector signal variation corresponding to a certain temperature fluctuation, ΔT , at a given oven temperature:

$$\frac{\Delta s}{s}(T, \Delta T) = - \frac{2.77 \cdot 10^{-2} k(T) \Delta T}{1 + k(T) (1 + 2.77 \cdot 10^{-2} \Delta T)} \tag{7}$$

The variation of $\Delta s/s$ with k at a constant temperature fluctuation amplitude can be estimated by setting, e.g., $\Delta T = 1^\circ\text{C}$:

$$\frac{\Delta s}{s}(T, \Delta T = 1^\circ\text{C}) = - \frac{2.77 \cdot 10^{-2} k(T)}{1 + 1.0277 k(T)} \tag{8}$$

The value of $\Delta s/s$ increases with k according to an S-shaped curve (Fig. 10) and reaches a plateau for large k values.

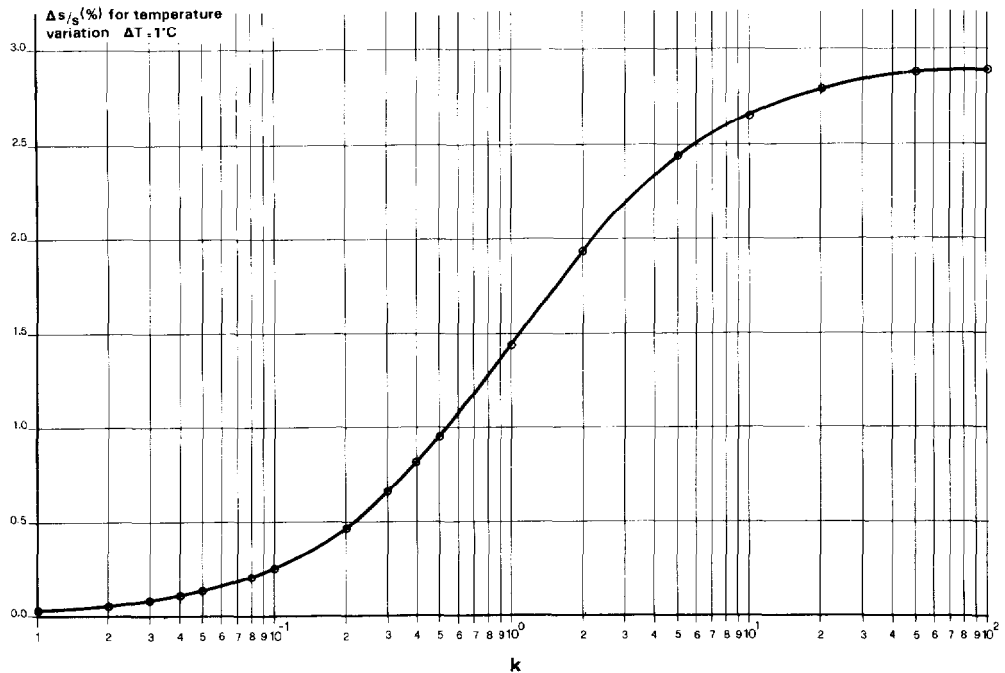


Fig. 10. Dependence of instantaneous relative detector signal variations, $\Delta s/s$, on the capacity constant value for $\Delta T = 1^\circ\text{C}$.

The value of $\Delta s/s$ corresponding to the plateau can be evaluated by the simple equation

$$\frac{\Delta s}{s} \text{ (large } k \text{ values)} \approx \frac{C\Delta T}{1 + C\Delta T} \quad (9)$$

It is found to be around 2.7% for $\Delta T = 1^\circ\text{C}$.

Variation of the amplitude of temperature fluctuations with oven temperature. It is reasonable to assume that the maximum temperature fluctuations, ΔT_{max} , are proportional to the oven temperature:

$$\Delta T_{\text{max}} = BT \quad (10)$$

where B is a constant. This hypothesis probably simulates the real situation rather well at temperatures not very close to ambient. At temperatures below 50°C , temperature fluctuations can be important owing to the opening and closing of the flap.

Average relative detector signal variation per unit time. In order to estimate the influence of such a temperature fluctuation on the relative signal variation, $\Delta s/s$, it is necessary to average this value over the column temperature:

$$\begin{aligned} \left(\frac{\Delta s}{s}\right)_T &= \frac{1}{k(T_R) - k(T_0)} \int_{k(T_0)}^{k(T_R)} \frac{\Delta s}{s} (k, \Delta k) dk \\ &= \frac{1}{T_R - T_0} \int_{T_0}^{T_R} \frac{\Delta s}{s} (T, \Delta T) dT \end{aligned} \quad (11)$$

where T_R is the retention temperature. For a correct solution, the dependence of ΔT on oven temperature and the probability of temperature fluctuations with different amplitudes at various oven temperatures must be taken into account. However, in order to simplify the mathematical treatment, we will assume as a first approximation, that ΔT is independent of oven temperature and can therefore be treated as a constant. This means in practice that, instead of using $\Delta T(T)$, the value of ΔT averaged over a range of temperatures ($\overline{\Delta T}$)_T is used in the eqn. 11:

$$\left(\frac{\Delta s}{s}\right)_T \approx \frac{1}{T_R - T_0} \int_{T_0}^{T_R} \frac{\Delta s}{s} [T, (\overline{\Delta T})_T] dT \quad (12)$$

The value of ($\overline{\Delta T}$)_T is easily found when it is assumed that ΔT is proportional to T (see eqn. 10):

$$(\overline{\Delta T})_T = \frac{1}{T_R - T_0} \int_{T_0}^{T_R} BT dT = B \cdot \frac{(T_R + T_0)}{2} \quad (13)$$

With this approximation, the relative detector signal variation per unit time averaged over a range of temperatures is given by

$$\left(\frac{\Delta s}{s}\right)_T = \frac{1}{T_R - T_0} \cdot \frac{(\overline{\Delta T})_T}{1 + C(\overline{\Delta T})_T} \cdot \ln \left\{ \frac{1 + k(T_0) [1 + C(\overline{\Delta T})_T]}{1 + k(T_R) [1 + C(\overline{\Delta T})_T]} \right\} \quad (14)$$

This equation can be further simplified by neglecting $C(\overline{\Delta T})_T$ compared with 1:

$$\left(\frac{\Delta s}{s}\right)_T = \frac{(\overline{\Delta T})_T}{T_R - T_0} \cdot \ln \left[\frac{1 + k(T_0)}{1 + k(T_R)} \right] \quad (15)$$

Maximum relative detector signal variation. Let us consider now the model of a hypothetical column, operating under isothermal and isobaric conditions at such a temperature that the migration velocity of the compound corresponds to the velocity value averaged over the range of temperatures:

$$\bar{u} = u_0 \left\{ 1 - \frac{1}{C(T_R - T_0)} \cdot \ln \left[\frac{1 + k(T_0)}{1 + k(T_R)} \right] \right\} \quad (16)$$

In this column, the relative detector signal variation, $\Delta s/s$, will be constant over the full column length. It is reasonable to identify this $\Delta s/s$ value with $(\overline{\Delta s/s})_T$, given by the eqn. 15.

We assume that the probability that the component undergoes an average temperature fluctuation $(\overline{\Delta T})$ per unit time is equal over the entire column length. In the worse case all temperature variations act in the same sense amplifying the peak distortion. Therefore, the maximum peak distortion by the oven-temperature fluctuations in terms of relative detector signal variations will be proportional to the retention time:

$$\left(\frac{\widetilde{\Delta s}}{s}\right)_{\max} = t_R \left(\frac{\Delta s}{s}\right)_T \quad (17)$$

If we return now to the real column and assume that it is operated under linear temperature programming conditions

$$T_R - T_0 = r t_R \quad (18)$$

where r is the temperature-programming rate, we find that

$$\left(\frac{\widetilde{\Delta s}}{s}\right)_{\max} = \frac{(\overline{\Delta T})_T}{r} \cdot \ln \left[\frac{1 + k(T_0)}{1 + k(T_R)} \right] = B \cdot \frac{(T_R + T_0)}{2} \cdot \ln \left[\frac{1 + k(T_0)}{1 + k(T_R)} \right] \quad (19)$$

The approximate eqn. 19 permits the estimation of the amplitude of peak distortion in terms of relative detector signal variation. Assuming that (a) the column is programmed from 50 to 300°C, (b) the "25°C rule" is applicable so that $\ln \{ [1 + k(T_0)] / [1 + k(T_R)] \}$ has values ranging from 6 to 7, (c) the temperature-programming rate is 5°C/min and (d) the average temperature fluctuation, ΔT , is 1% of the average temperature $(T_R + T_0)/2$, then $\Delta s/s$ values ranging from 2.1 to 2.5% are found by using eqn. 19. These values are, of course, unacceptable and therefore the amplitude of the temperature fluctuation must be kept below 0.1–0.2% of the oven temperature. Under these conditions, the relative detector signal variations due to the oven-temperature fluctuations are not far from the noise level.

Dependence of relative detector signal variations on temperature programming rates. Both theoretical consideration (see eqn. 19) and experimental data show that thermal peak splitting is less important at higher temperature-programming rates. This is mainly because the compound stays inside the column for a shorter time and travels more quickly in the region of higher temperatures.

In fact, at high temperature-programming rates value of k at the elution of an elute from the column, $k(T_R'')$, is much smaller than the equivalent value obtained at low programming rates, $k(T_R')$ (see Fig. 11).

The graphical representations shown in Fig. 11 also demonstrate that the average relative detector signal variation:

$$\left(\frac{\Delta s}{s} \right)_T = \frac{S}{T_R - T_0}$$

is smaller at high temperature-programming rates.

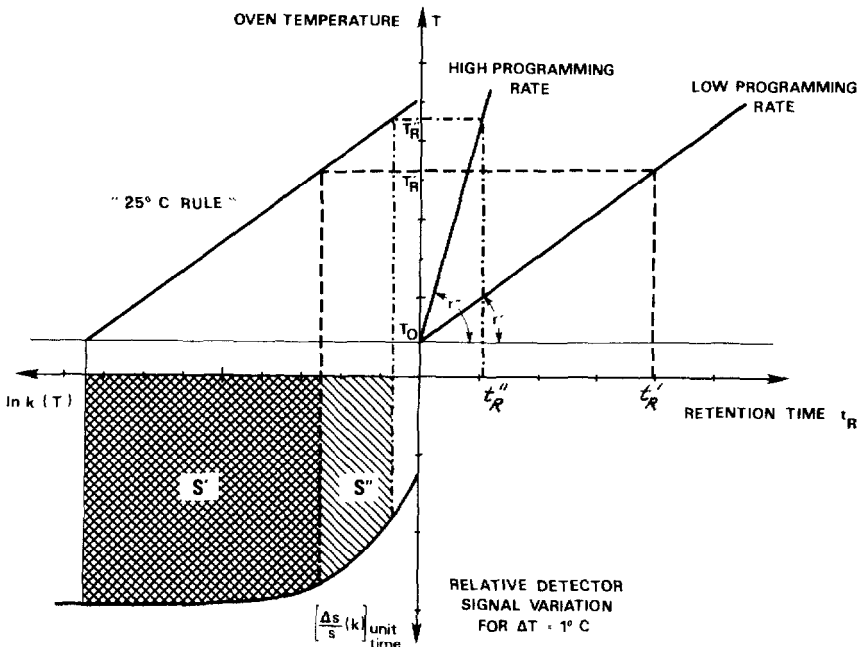


Fig. 11. Influence of temperature programming rates on relative detector signal variations, $\Delta s/s$ (variations of the capacity constant with temperature according to the "25°C rule").

Dependence of relative detector signal variations on the nature of the component.

The nature of the component influences the amplitude of the relative detector signal variations by modifying the factor $\ln \{[1 + k(T_D)]/[1 + k(T_R)]\}$ (see eqn. 19). This value increases when the evaporation enthalpy of a solute from the stationary phase increases. Therefore, for polar solutes in a moderately polar or polar stationary phase, (especially when hydrogen bonds are formed between the solute and the stationary phase molecules), peak splitting and distortions will be more important than for a non-polar solute on a non-polar stationary phase.

Thermal peak distortion and peak splitting are generally drastic for components that are not soluble in the stationary phase. In these instances, the solutes are mainly adsorbed on the stationary phase surface, and the capacity constant shows important variations with temperature.

SOLUTIONS FOR ELIMINATING THE CHRISTMAS-TREE-TYPE PEAK SPLITTING

Special column cage

The first obvious solution is to increase the thermal inertia of the flexible fused-silica or glass column, in order to make its thermal behaviour close to that of a classical glass capillary. Different solutions are possible, for example, wrapping the

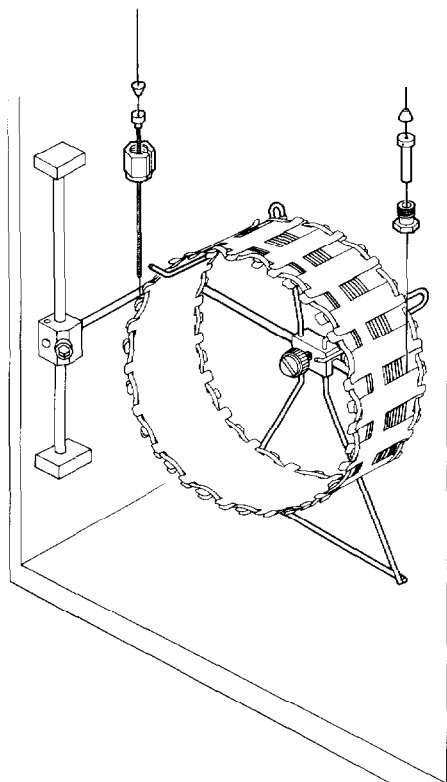


Fig. 12. Diagram of the special column cage.

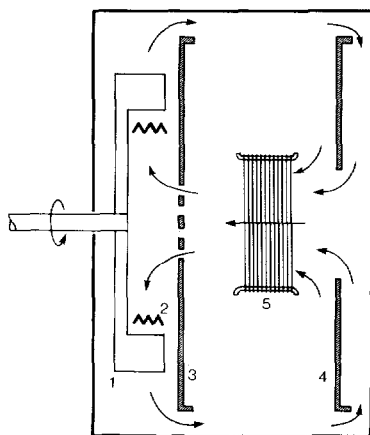


Fig. 13. Diagram of the new oven design: 1 = fan; 2 = heater; 3 and 4 = shields; 5 = column.

column in thin aluminium foil and inserting its end in a glass-fibre sleeve or inserting the entire column in the sleeve. However, these solutions are difficult to control and reproduce.

Therefore, we have designed a special column cage (Fig. 12), which allows the thermal mass of the column to be adjusted without reducing its ability to follow temperature programmes, even at rates as high as 25 or 30°C/min. When mounted in the special column cage, the peaks obtained with fused-silica columns do not show any peak splitting.

New column oven with an unconventional design

As an ultimate solution to the thermal splitting, a new column oven with an unconventional design has been developed. This design ensures that the amplitude of the temperature fluctuations in a large zone of the oven is kept below 0.05% of the actual temperature. At 250°C, the maximum peak-to-peak "temperature variations" are below 0.1°C.

The oven design and the air circulation inside the oven is illustrated in Fig. 13.

The tests performed on the new oven under various operating conditions by recording the chromatographic peaks on a galvanometric recorder or special oscilloscope show that thermal peak splitting is completely eliminated (Fig. 14).

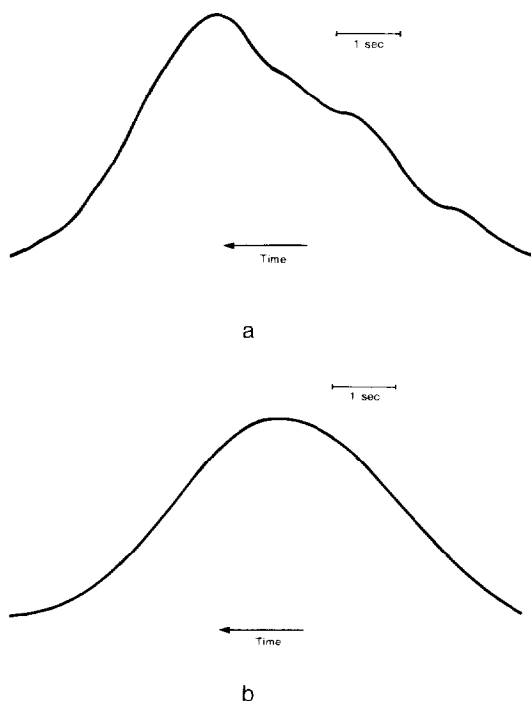


Fig. 14. Galvanometric recording of the peak shape of eicosane ($C_{20}H_{42}$), eluted from a 30-m DB-1 fused-silica column (J&W Scientific). Temperature programme: from 45 to 335°C at 5°C/min. (a) Column placed in a conventional oven; (b) column placed in the new oven.

CONCLUSIONS

Uneven air flow patterns inside the oven are responsible for thermal peak splitting. This type of problem is common to all GC ovens designed according to conventional concepts.

In some instances, the phenomenon is partly masked by a cold outlet, a dead-volume at the column end, or excessive peak filtering and smoothing before plotting. By properly heating the outlet and by recording the detector signal on a strip-chart or galvanometric recorder at high chart speeds, the phenomenon becomes evident.

A simple model and rough theoretical calculations have led to a correlation between the average relative detector signal variations, produced by column temperature fluctuations, and some key parameters: amplitude of temperature variations, temperature-programming rate and value of eluate capacity constants at initial and retention temperatures. This equation permits the approximate calculation of the maximum acceptable temperature variation.

Both theoretical and experimental results show that by keeping the temperature fluctuations around 0.05% of the actual oven temperature, peak splitting is practically eliminated. A new GC oven featuring such characteristics was developed.

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