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Moving thermal gradients in gas chromatography☆

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ABSTRACT

This paper examines the separation effects of a moving thermal gradient on a chromatographic column in gas chromatography. This movement of the gradient has a focusing effect on the analyte bands, limiting band broadening in the column. Here we examine the relationship between the slope of this gradient, the velocity of the gradient and the resulting band width. Additionally we examine how transport of analytes along the column at their analyte specific constant temperatures, determined by the gradient slope and velocity, affects resolution. This examination is based primarily on a theoretical model of partitioning and transport of analyte under low concentration conditions. Preliminary predictions indicate that analytes reach near constant temperatures, relative positions and resolutions in less than 100 cm of column transport. Use of longer columns produces very little improvement in resolution for any fixed slope. Properties of the thermal gradient determine a fixed solute band width for each analyte. These widths are nearly reached within the first 40–70 cm, after which little broadening or narrowing of the bands occur. The focusing effect of the thermal gradient corrects for broad injections, reduces effects of irregular stationary phase coatings and can be used with short columns for fast analysis. Thermal gradient gas chromatographic instrumentation was constructed and used to illustrate some characteristics predicted from the theoretical results.

1. Introduction

This paper examines the effects of a moving thermal gradient along a column on the separation properties of the column in gas chromatography (TGGC). The practicing chromatographer usually has two competing concerns with regard to a GC separation: resolution and separation speed. Resolution is classically recognized as being a function of the selectivity of the column for the analytes in the sample and the efficiency of the column. It has been demonstrated in a series of papers by Blumberg and colleagues that one cannot change the environment of the column during separation to improve resolution without increasing the separation time relative to a basic separation[1] [1–4]. Consequently, isothermal methods are considered optimal for separating a relatively small number of compounds with similar retention times. When retention times are nearly identical, isothermal separations with long columns and optimum mobile phase velocities are often used to resolve analyte bands. Although such operational conditions attain good resolution, the time for separation is long and the eluting chromatographic peaks are wide.

In many practical situations where retention times cover a broad range, temperature programmed gas chromatography (TPGC) is considerably more practical than isothermal operation. Although operating under programmed temperature conditions speeds up the separation, resolution of two analyte bands with similar (finite) retention times is reduced relative to isothermal separation. One of the reasons for this is that as the temperature is increased during the separation, the partition coefficient decreases, increasing the proportion of analyte in the mobile phase. The solute band for each analyte remains essentially at the beginning of the column until the temperature of the column reaches a sufficient level, specific to the analyte, to allow the analyte to desorb into the mobile phase. Movement in the mobile phase coupled with the sorption/desorption process causes the solute band of the analyte to be transported down the column. The velocity of transport is a function of the time in the mobile phase relative to the stationary phase. As the temperature continues to increase, the efficiency of separation of

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[1] Blumberg defines a basic separation as "a separation (in conventional isothermal or temperature-programmed GC with low pressure drop) where all relevant properties of the medium, except for solute velocities, are constant while solute velocities can change in time but must be uniform."

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analytes is initially increased and then usually surpassed before they elute. Thus, although the chromatographic process takes place throughout the length of the column, the efficiency of the separation process for each analyte usually reaches an optimum at some point in the column and then decreases thereafter. These inefficiencies in the separation process are reached at different temperatures for different analytes.

A negative longitudinal moving thermal gradient in GC is an alternative to TPGC that has been known since the 1950s [5,6]. Movement of the thermal gradient at appropriate velocities can result in analytes reaching a constant temperature as they are transported at the velocity the gradient moves along the column.[2] This movement of the gradient has a focusing effect on the analyte bands, limiting band broadening in the column [7–11]. The particular constant temperature value of each transported analyte is a function of the nature of the analyte, the mobile phase velocity and the velocity of the thermal gradient. It is reasonable to expect, therefore, that the latter two can be programmed to avoid inefficiencies of the separation process in TPGC due to the higher than desirable temperatures of the analyte during transport.

Previously we have shown that the focusing property of TGGC can decrease band broadening that results from poor injection of analytes into the column relative to TPGC [10,11]. However, any other advantages of TGGC relative to TPGC regarding efficiency and analyte band resolution are not clearly known. Thus, although isothermal separations may be superior to TGGC for a range of starting temperatures,[3] TGGC may have clear advantages over isothermal operation when the sample consists of analytes with a broad range of volatilities and unknown separation temperatures.

The objectives of this work were to examine the implications of the focusing effect of the TGGC mode of separation and determine how transport of each analyte along the column affects peak width and resolution. One question investigated here is whether or not varying the gradient velocity and gradient slope independently can result in an independent control of solute band widths and resolution. This examination is based primarily on a theoretical model of partitioning and transport at low analyte concentrations and pressures. As detailed below, the TGGC method holds great promise, provided that one can control the temperature gradient and the gradient velocity to a fine degree. Preliminary results are presented in support of the theory and as a guide to the practical issues pertinent to constructing a device that can realize the expectations derived from the theoretical results.

2. Methods

2.1. Notation and definitions

Here, we assume that the model of transport of the analyte is essentially a one-dimensional model. For this model, we define the following notation:

x = coordinate (cm) of the column, starting at $x = 0$ for the beginning of the column and $x = L$ for the end of the column.
t = index of time (s), starting at $t = 0$.
v_m = velocity of the analyte in the mobile phase (cm/s). This is assumed to be the same as the bulk flow velocity and is assumed constant over time. The examples considered here are for open tubular columns and, consequently, increases in velocity at the end of column due to pressure drop are assumed to be modest. As noted below, such increases in velocity at the end of the column will have little effect on resolution but will decrease the widths of the eluting chromatographic peaks. Mobile phase velocity is held constant as temperature increases by decreasing gas pressure at the injection end to give a constant volume at the column outlet.
w = velocity of the thermal gradient through the column (cm/s).
$T_{x,t}$ = temperature (K) at point x at time t.
β = ratio of the volume of the mobile phase to the volume of the stationary phase (phase volume ratio).
R = Boltzmann gas constant.
$-b$ = slope of the thermal gradient (K/cm), where $b > 0$. Note that the slope is negative since the temperature of the column is lower at higher values of x.

In addition, we define the following for each analyte (although these values are specific for each analyte, we suppress the analyte index for notational clarity; the resulting equations are analyte specific):

y_t = location of a moving reference point at time t (cm) in the column. This reference point moves down the column at a known velocity. This velocity is a function of the properties of the analyte and the thermal gradient and, consequently, depends on the velocity of the thermal gradient.
μ_t = analyte solute band center at time t (cm), as measured from point $x = 0$.
σ_t = solute band width parameter at time t (cm). Solute band width is approximately $4\sigma_t$.
σ_p = the chromatographic peak width at elution, measured in seconds, s, where the observed chromatographic peak width will be approximately $4\sigma_p$.[4]
ΔH = enthalpy difference between analyte in the stationary phase and the mobile phase.
ΔS = entropy difference between analyte in the stationary phase and the mobile phase.
$K(T)$ = partition or distribution coefficient at temperature T, where

$$K(T) = \exp\left(\frac{\Delta H}{RT} - \frac{\Delta S}{R}\right) \tag{1}$$

$k(T)$ = retention factor

$$k(T) = \frac{K(T)}{\beta} \tag{2}$$

where β is the phase volume ratio defined above.

In implementations, we cannot separate the phase volume ratio from the effects of entropy. Thus, we will define a parameter C as

$$C = -\frac{\Delta S}{R} - \log(\beta) \tag{3}$$

[2] There are situations where the velocity of the thermal gradient is fast enough relative to the velocity of the mobile phase gas that no steady state exists. There are also situations where the thermal gradient velocity relative to the mobile phase velocity will result in little or no focusing of the analyte. See [12].

[3] Superiority of isothermal separations is readily recognized as being dependent on the column temperature. If the column temperature is too low, compounds will remain at the injection end of the column, ostensibly resident in the stationary phase. If the column temperature is too high, analytes will remain in the mobile phase and elute with the solvent peak. However, for a range of column temperatures at which isothermal separation may be operated, isothermal separations are superior. It is essential that this range of "separation temperatures" be at least approximately known prior to separation.

[4] Throughout this paper, the zone of an analyte that forms in the column during transport to the end of the column is called the "solute band." The solute band is in the column and its location, μ_t, is measured in cm from the beginning of the column. The width of the solute band, σ_t, is measured in cm. The appearance of the analyte zone in the detector as the analyte elutes from the column is called the "chromatographic peak." The retention time gives the time the chromatographic peak center reaches the end of the column and enters the detector. Both the retention time and the width of the chromatographic peak are measured in s.