

## 4.2 A Brief Overview of the Theory of Flow Along GC Packed Columns and Some Practical Consequences for Measuring Atmospheric CH<sub>4</sub>, N<sub>2</sub>O, and SF<sub>6</sub>

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### Abstract

First, I present a brief and compact overview of the theory of flow along GC packed columns using: the Darcy's Law of flow through porous media, the continuity equation for the carrier gas (assuming stationary flow), and the continuity equation for the trace gas of interest with a diffusion term and a source/sink term due to the transfer of trace gas molecules between the mobile and the stationary phases (it is assumed that this transfer obeys a linear partition isotherm). Using these equations, the pressure profile, the compressibility factor, the relation between the retardation factor and the distribution constant, and the relation between plate height and diffusivity are easily obtained. Second, I present a study (new in the scientific literature) of the behaviour of two packed columns (precolumn and maincolumn) GC systems after a sample injection and the subsequent applied carrier gas pressure ramp. Finally, several features of the chromatograms for atmospheric CH<sub>4</sub> (obtained with a FID) and for N<sub>2</sub>O and SF<sub>6</sub> (obtained with an ECD) are explained using the previous formalism.

### 4.2.1 Fundamental equations for flows along GC packed columns

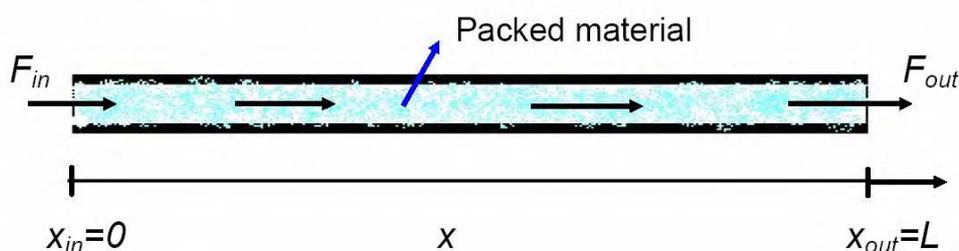


Figure 1. GC packed column scheme.

We assume *slab geometry* (quantities only depend on  $x$ : the length along the column) and *isothermal flow* (the column is inside an isothermal oven at temperature  $T_c$ ). The column, of internal cross-section  $A$  and length  $L$ , is filled with a packed grainy material, called *stationary phase* in the following. The gas flowing through the column is called *mobile phase*, and it has two components: *carrier gas* and *solutes* (trace gases of interest, which are assumed *very dilute*). The volume within the column,  $V_T$ , has two addends: the volume occupied by the packed material  $V_S$ , and the void volume  $V_M$  (intergrain plus pores-in-grains volumes). *Porosity*,  $\phi$ , is defined as  $\phi = V_M / V_T$ . *Solutes are adsorbed and desorbed by the stationary phase*.  $c_{Mi}$  is the concentration of solute  $i$  in the mobile phase,  $c_{Si}$  is the concentration of solute  $i$  in the stationary phase.

**Continuity equation for the carrier gas** flowing in stationary state (constant in  $t$ : time):

$$\rho u = \frac{\rho F}{A \phi} = \frac{\rho_{out} F_{out}}{A \phi} = \text{constant} \quad (1),$$

where  $\rho$  is the carrier density,  $u$  is the carrier average linear velocity along  $x$ ,  $F$  is the volumetric flow, and subindex *out* denotes the magnitude of a quantity at the end of the column ( $x = L$ ).

**Darcy's Law of flow through porous media** (e.g., Giddings)

$$u = - \frac{\kappa}{\phi \mu} \frac{\partial p}{\partial x} \quad (2),$$

where  $\kappa$  is the permeability of the porous media,  $p$  is the carrier pressure, and  $\mu$  is the carrier dynamic viscosity (that, for an ideal gas, depends on  $T_c$  but not on  $p$ , e.g. see section 1.7. of Batchelor).

**Ideal gas equation for the carrier gas:**

$$p = R_c \rho T_c \quad (3),$$

where  $R_c$  is the specific gas constant of the carrier.

**Continuity equation for solute  $i$  in the mobile phase with a diffusion term and a source/sink term** due to the transfer of solute molecules between the mobile and the stationary phases:

$$\frac{\partial c_{Mi}}{\partial t} + u \frac{\partial c_{Mi}}{\partial x} + c_{Mi} \frac{\partial u}{\partial x} = D_i \frac{\partial^2 c_{Mi}}{\partial x^2} - \frac{V_s}{V_M} \frac{\partial c_{Si}}{\partial t} \quad (4),$$

where  $D_i$  is the *diffusivity of solute  $i$  in the carrier gas* (which includes molecular diffusion, multipath around grains, and non-instantaneous partition among phases; and depends on  $u$ ). Note that this equation is the same than that for trace gases in the atmosphere (e.g. see equation 17.1 of Seinfeld & Pandis). Note that the expansion term (third addend on the left hand side) must be taken into account in gas (no in liquid) chromatography (however, this term is “forgotten” by some authors, e.g. eq. 2.65 of Conder & Young).

**Linear partition isotherm:**

$$c_{Si} = K_{ci} c_{Mi} \quad (5),$$

where  $K_{ci}$  is the *distribution constant* for solute  $i$  (which depends on temperature and chemical composition of the stationary phase and the solute  $i$ ).

After a straightforward integration of equation (2) using equations (1) and (3):

$$\rho(x) = \rho_{out} \sqrt{1 + B(L-x)} \quad (6),$$

$$p(x) = p_{out} \sqrt{1 + B(L-x)} \quad (7),$$

$$u(x) = u_{out} / \sqrt{1 + B(L-x)} \quad (8), \text{ with}$$

$$B = \frac{2 \mu F_{out}}{\kappa p_{out} A} \quad (9).$$

The (column) *average carrier velocity*,  $\bar{u}$ , is defined as  $\bar{u} \equiv L/t_M$ , where  $t_M$  is the *hold-up time*: the time required for the carrier to pass through the chromatographic column (e.g. Miller). Taking into account that  $t_M = \int_0^L \frac{dx}{u}$  and using equations (8), (1), and (3), it can be showed that  $\bar{u} = j u_{out}$  and therefore  $\bar{F} = j F_{out}$ , where  $\bar{F}$  is the (column) *average volumetric flow*, and  $j$  is the *compressibility factor*.

$$j = \frac{3}{2} \left[ \frac{(p_{in} / p_{out})^2 - 1}{(p_{in} / p_{out})^3 - 1} \right] \quad (10).$$

Using equation (5), equation (4) can be rewritten as:

$$\frac{\partial c_{Mi}}{\partial t} + v_i \frac{\partial c_{Mi}}{\partial x} + c_{Mi} \frac{\partial v_i}{\partial x} = \chi_i \frac{\partial^2 c_{Mi}}{\partial x^2} \quad (11)$$

where  $v_i(x) = u(x)/(1 + K_{ci} V_s/V_M)$  and  $\chi_i = D_i/(1 + K_{ci} V_s/V_M)$ . Note that  $v_i$  is the *effective advection velocity of the solute  $i$* , and it is lower as larger is  $K_{ci}$ , and therefore as larger is the fraction of solute  $i$  adsorbed by the stationary phase. Note that *equation (11) is valid even when the carrier flow is not stationary*, that is, when equation (1) does not hold.

The *retardation factor*,  $R$ , can be defined as  $R \equiv t_M/t_{Ri}$ , where  $t_{Ri}$  is the *total retention time* (e.g. Miller): the time required for the solute  $i$  to pass through the chromatographic column. Taking into account that  $t_{Ri} = \int_0^L \frac{dx}{v_i}$  and using previous equations, it can be showed that

$$R = 1/(1 + K_{ci} V_s/V_M).$$

Equation (11) only can be solved using numerical methods (out of the scope of this presentation). However, it is instructive to look at the *solution of a very simplified form of equation (11)*: there is no expansion term, and  $v_i$  and  $\chi_i$  are constants (and boundary conditions  $c_{Mi} = 0$  at  $x_i = \pm\infty$ ). For the *particular initial condition* of the form  $c_{Mi}(x, t = 0) = S\delta(x)$ , (where  $\delta$  is the Dirac delta function) which means a very narrow initial peak with the integral of concentration equal to S, the solution is (e.g. see section 17.5 of Seinfeld&Pandis):

$$c_{Mi}(x, t) = \frac{S}{\sqrt{2\pi}\sigma(t)} \exp\left[-\frac{(x - v_i t)^2}{2\sigma^2(t)}\right] \quad (12),$$

where  $\sigma^2(t) = 2\chi_i t$ . So, the peak is a Gaussian that is advected at  $v_i$  speed and has a spatial  $\sigma \propto \sqrt{t}$  (due to diffusion). For a *general initial condition*, the solution is the convolution product of solution (12) and the general initial condition (e.g. see section 5.4. of Guenther & Lee).

Plate height can be defined as  $H_i = \sigma^2(t_{Ri})/L$  (e.g. see equation 3.25. of Miller). So, using the previous equations, the following relation can be obtained:

$$H_i = \frac{2\chi_i}{v_i} = \frac{2D_i}{u} \quad (13)$$

#### 4.2.2 Transient behaviour of two packed columns GC systems after sample injection and some practical consequences for measuring atmospheric CH<sub>4</sub>, N<sub>2</sub>O, and SF<sub>6</sub>

We consider *two packed columns (precolumn and maincolumn) GC systems*. In particular, for numerical examples, we consider the new GC installed at Izaña Global GAW Station (see Gomez-Pelaez & Ramos), and chromatograms obtained with that instrument (see Figures 3 and 4 of Gomez-Pelaez & Ramos). Figure 2 of Gomez-Pelaez & Ramos shows the internal GC configuration for Inject and Backflush valve positions.

Let be  $\Delta p_{in} \equiv p_{in} - p_{out}$ . An EFC4 regulates column flow maintaining a prescribed  $\Delta p_{in}$  (using a fraction of a set maximum flow, the non used fraction is vent). To obtain the desired  $F_{out}$ , the appropriate value of  $\Delta p_{in}$  is found empirically changing  $\Delta p_{in}$  till measure the desired  $F_{out}$  with an external flowmeter. Indeed, the *external flowmeter* measures  $F_{mea}$ , which is related to  $F_{out}$  through the relation  $F_{mea} = F_{out} T_L/T_c$ , where  $T_L$  is the laboratory temperature ( $T_L = 294.4$  K and  $T_c = 353.1$  K). In the following, we present a *sketch of some preliminary results we have obtained*.

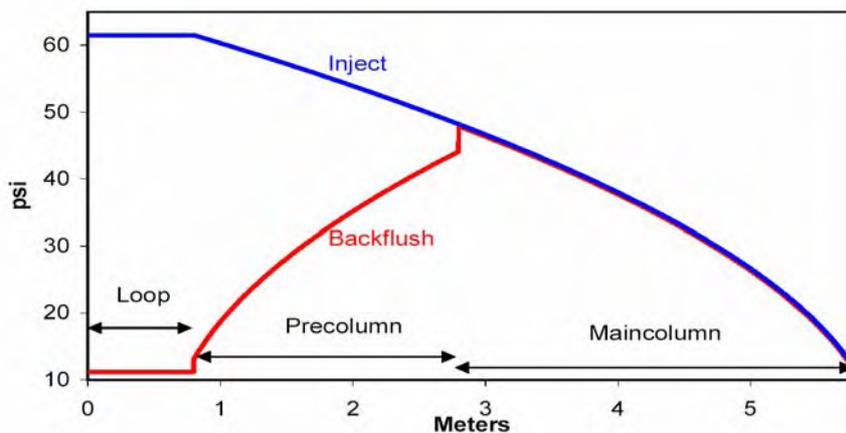


Figure 2. This graphic shows the pressure (units: psi) distribution along the sample loop, the precolumn, and the maincolumn for two valve positions: Inject (blue curve) and Backflush (red curve). It shows actual values for the ECD subsystem of the GC installed by Gomez-Pelaez & Ramos.

We neglect pressure drops along the short S.S. tubes 1/16" O.D. that connects columns and valves, except downstream of the ECD precolumn in Backflush position because there is a

tube of 8 m length, for which we compute a pressure drop of 1.9 psi (using the solution of the classical Poiseuille problem, e.g. section 6.3. of Streeter, Wylie & Bedford; using  $F_{mea} = 32.2$  ml/min, I.D.=0.8 mm, and  $\mu = 2.54 \times 10^{-5}$  N·s/m<sup>2</sup>). *The flow is laminar in all tubes, including 1/4" O.D. sample loops (Reynolds number is far below the critical one).*

Unfortunately, manufacturers of packed columns do not provide  $\phi$ ,  $\kappa$ ,  $K_{ci}(T_c)$ , nor  $D_i(u)$ . Using equation (7), we compute  $B = 5.87\text{m}^{-1}$  for the *ECD maincolumn in Backflush position* ( $L=3$  m,  $\Delta p_{in} = 37.0\text{psi}$ , and  $p_{out} = 11.2\text{psi}$ , the typical atmospheric pressure at Izaña Observatory). Using that value of  $B$ , equation (7) predicts  $\Delta p_{in} = 50.4\text{psi}$  for the *ECD pre and maincolumn in Inject position* (both columns are of the same type, and  $F_{out}$  is the same in Inject and Backflush positions;  $L=5$  m). That value is in relative good agreement with the empirical one:  $\Delta p_{in} = 50.0\text{psi}$ . Again using equation (7), we compute  $B_h = 3.03\text{m}^{-1}$  for the *FID maincolumn in Backflush position and high flow* ( $L=1.83$  m,  $\Delta p_{in} = 17.4\text{psi}$ , and  $F_{mea} = 52.4$  ml/min). For the *FID maincolumn in Backflush position and low flow* ( $F_{mea} = 30.6$  ml/min), and using  $B_i = 1.77\text{m}^{-1}$  (obtained from  $B_h$  taking into account the dependence of  $B$  on  $F_{out}$ ), equation (7) predicts  $\Delta p_{in} = 11.8\text{psi}$ . This value is in relative good agreement with the empirical one:  $\Delta p_{in} = 11.5\text{psi}$ .

Figure 2 shows *the pressure distribution along the ECD columns and loop for Inject and Backflush positions*. Curves of the same shape are valid for the carrier density, due to equations (6) and (7). Let be  $p_L$  the atmospheric pressure in the laboratory. Sample loop flushing is stopped 30 seconds before injection to allow the sample loop achieve  $p_L$  and  $T_c$ . *For achieving a stationary flow when switching from Backflush to Inject* (which needs a larger  $\Delta p_{in}$ ), a fast  $\Delta p_{in}$  ramp is set in the GC method (100 psi/min, with a set maximum flow of 500 ml/min for several seconds). So, during this *transient* (several seconds), the precolumn and the loop are filled with carrier and pressurized till achieve the pressure distribution given by the blue curve in Figure 2. *During this transient, equation (11) is still valid, and the sample is compressed and introduced in the precolumn. However, it can happen that only part of the sample is introduced in the precolumn during the transient, and the part that remains in the loop suffers a different diffusion than the part inside of the precolumn, producing an asymmetric peak.* To discriminate between both cases, it is useful to compute the amount of carrier volume,  $Vol$ , at  $p_L$  and  $T_c$ , that is contained in each column for each valve position. It can be showed that:

$$Vol = \frac{R_c T_c}{p_L} \int_0^L A \phi \rho(x) dx = \frac{2 p_{out} A \phi}{3 p_L B} \left[ \left( \frac{p_{in}}{p_{out}} \right)^3 - 1 \right] \quad (14)$$

For our GC, we compute:

Vol(ml)	Maincolumn	Precol-Inject	Precol-Back	Available in Precol	Loop
ECD	19.7	20.8	12.4	8.4	10
FID	10.2	10.9	5.5	5.4	10

So, almost all the content (one half) of the sample loop is introduced in the precolumn during the transient for the ECD (FID). *This can explain why N<sub>2</sub>O peak is symmetric whereas CH<sub>4</sub> is asymmetric.* Note that the high asymmetry on the top of the CH<sub>4</sub> peak does not seem produced by a non-linear isotherm. For simplicity, we neglect the small volumes of the short S.S. tubes 1/16" O.D. that connect columns. It can be showed that *for a given  $L_p + L_m$  (precolumn and maincolumn lengths), the maximum available volume in the precolumn happens when  $L_p = L_m$ .* When switching from Inject to Backflush, there is an excess of carrier gas in the precolumn (equal to the previous defect) that is vented in a few seconds. So, it can be showed that *for having an effective backflush,*

it is necessary to have in the precolumn a larger integrated flow (in time) in the backflush direction than in the direct direction (it holds in our system).

It can be showed (computing and comparing hold-up time and O<sub>2</sub> retention time) that between arrows c (switch from Inject to Backflush) and d on left panel of Figure 3 of Gomez-Pelaez & Ramos, what is detected in the ECD is the O<sub>2</sub> present in the maincolumn (very weak tail). Abrupt decrease d happens when there is no more O<sub>2</sub> inside the maincolumn.

Finally, we point out that changes in  $p_L$  do not only change the moles of sample collected in the loop, but also change the mass flow  $F_{out} \rho_{out}$ . It can be showed that if  $\Delta p_{in}$  is kept constant, it holds

$$\frac{d(F_{out} \rho_{out})}{F_{out} \rho_{out}} = \frac{2}{BL} \frac{\Delta p_{in}}{p_{out}} \frac{dp_{out}}{p_{out}} \quad (15),$$

where  $d$  indicates a small increment of the quantity. For our ECD maincolumn in Backflush position, a 1% relative change in  $p_L$  produces a 0.37% relative change in mass flow.

## References

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