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Tapered versus Constant Diameter Post-Column Restrictors in Capillary SFC

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Summary

A one-dimensional compressible flow model is used in the description of actual flow through ducts. This model serves well in the explanation and prediction of the characteristics towards signal distortion, noise, mass flow rate and influence on dead-time behavior of end-restrictors as used in supercritical fluid chromatography (SFC) with post-column detection. It was experimentally verified that tapered restrictors have a better performance than constant diameter restrictors at relatively low detection temperatures (200 °C).

The mass flow rate of a tapered restrictor is found to be linearly proportional to applied inlet pressure, implying the same linear dependence of the product of linear velocity and on-column density. A more than proportional rise of density will, therefore, lead to a decrease in linear velocity and *vice versa*. Since thermostat temperature fluctuations are directly translated into linear velocity variations, a very temperature stable thermostat has to be used.

As will be discussed, this complicated dead-time dependence on applied pressure has a large effect on the chromatographic results.

1 Introduction

Since the introduction of supercritical mobile phases in chromatography [1], appreciable research efforts have been devoted to instrumental aspects, applications, and the explanation of retention phenomena encountered in this particular field of chromatography known as supercritical fluid chromatography (SFC).

This paper is primarily concerned with instrumental aspects of capillary supercritical fluid chromatography using CO₂ as mobile phase and flame ionization detection. In particular, it will discuss the role of the end-restrictor as used in SFC.

Since density is one of the principal factors determining the mobility of components, the density (pressure) drop over the analytical column should, under normal operating conditions, be kept as low as possible, thus favoring the use of capillary columns. In order to minimize chromatographic band broadening, the linear velocity, *i.e.* the mass flow rate,

should be selected near its optimum value. Both the required low density drop over the column as well as the required mass flow rate imply the use of an end-restrictor in order to meet the desired chromatographic conditions.

The choice of a particular detection device imposes specific demands on the type of restrictor to be used. Due to the fact, that post-column detection takes place after decompression, which is a potential cause for signal distortion, e.g. spiking and excessive noise, post-column detection methods (FID, MS) require a more carefully chosen restrictor in comparison with on-column detection (UV-VIS, fluorescence).

A study of the flow of compressible fluids in the types of restrictors used, will allow a better understanding of the nature of some of the detection signal distortions. This topic is also of major importance in the theory and design of nebulizers as used in for instance LC-MS interfaces (Gustavsson [2]). In these cases, more emphasis is laid on the processes after the restrictor rather than during decompression.

This paper will also touch related topics, such as the relationship between linear velocity or mass flow rate and column pressure.

2 Theory of Compressible Flow in Ducts

In this section the flow of compressible fluids through ducts of variable cross sectional area (i.e. nozzles) or constant diameter pipes will be treated. This study is based on the principles of gas dynamics, which may be found in textbooks such as Daneshyar [3], Oswatitsch [4], and Owczarek [5]. A full treatment of compressible flow would involve the use of a complicated equation of state for supercritical fluids [6], which is beyond the scope of this paper.

Therefore, in order to be able to give a relatively simple description of compressible flow, a number of assumptions have to be made. Some of these assumptions are oversimplifications when applied to flow of real, i.e. non-ideal, fluids. Nevertheless, this theory will provide us with a better understanding of the flow phenomena involved.

This paper will only deal with the theory necessary to describe the flow of compressible fluids through either convergent or constant diameter ducts. The theory of compressible flow is mainly built upon four basic laws, viz. conservation of mass, Newton's second law of motion, and the first and second law of thermodynamics.

Starting from these general equations more specific equations are obtained by making a number of assumptions:

- The fluid properties are assumed to be constant over any cross section of the duct (one-dimensional approximation) and the flow is assumed to be time independent

(steady flow). This implies, that fluid properties in one-dimensional steady flow are a function of the distance, x , along the axis of the duct only;

- The fluid is a perfect gas for which $P/\rho = RT$ and the specific heats c_p and c_v are constants over the temperature range involved. In the case of supercritical CO_2 at relatively high detection temperatures (e.g. 200°C) P/ρ is nearly constant as well as c_p and c_v [6];
- The flow is assumed to be adiabatic, i.e. heat transfer through the pipe walls is assumed to be relatively small and can, therefore, be neglected.

The analysis of compressible flow made under these assumptions can be used as a model for actual flows. Furthermore, the general conclusions based upon this model are not believed to be in gross error.

2.1 Flow in a Convergent Duct

Consider the configuration shown in **Figure 1** which is a convergent duct (tapered restrictor) with the flow discharging into a region with variable back-pressure P_b .

If $P_b/P_t = 1$, the pressure throughout the duct will be constant and no flow will occur (situation 1). As soon as P_b is slightly reduced (situation 2) a subsonic flow is established with $P_e = P_b$. If P_b is reduced to lower values (situation 3), the flow remains subsonic, $P_e = P_b$, but the mass flow rate $\dot{m} = \rho v A$ increases. The mass flow rate will keep on increasing with decreasing P_b until a maximum $\dot{m}_*$ is reached as soon as the flow is accelerated to the local speed of sound in the throat of the duct (situation 4), denoted by Mach number $M = 1$ ($M = \text{flow velocity} / \text{local velocity of sound}$).

Figure 1

Compressible flow characteristics in a convergent duct.

It is a fundamental statement of fact that an initially subsonic flow can only be accelerated up to the local speed of sound in a convergent duct or duct of constant diameter for that matter.

Under the assumptions of adiabatic and frictionless flow, *i.e.* isentropic flow (valid for short nozzles with high acceleration), at that point, a critical pressure ratio $P_b/P_t = P_{*,e}/P_t$ will be attained:

$$P_{*,e}/P_t = [2/(\gamma+1)]^{[\gamma/(\gamma-1)]} \quad (1)$$

$$\text{with } \gamma = c_p/c_v \quad (2)$$

(The subscript * refers to conditions at $M = 1$)

Decreasing the value of P_b to even lower values (situation 5) will not change the pressure ratio $P_{*,e}/P_t$. Since both flow velocity as well as exit-pressure are constant under these circumstances, the mass flow rate remains at a maximum value, given by:

$$\dot{m}_* = \frac{A_* P_t}{\sqrt{(R T_t)}} \sqrt{\gamma} \frac{2}{\gamma+1} \frac{\gamma+1}{2(\gamma-1)} \quad (3)$$

Under these conditions, the flow is said to be choked.

Since the pressure upon leaving the nozzle is not equal to the backpressure, a jet will be formed in which the fluid, owing to further expansion, accelerates to a supersonic speed, which in turn may lead to the formation of shock waves. As pointed out previously, equation 3 is valid for SFC, only to a first approximation.

2.2 Flow in Constant Diameter Restrictors (Pipes)

Adiabatic flow with viscous effects for a perfect gas through constant diameter restrictors will now be considered. Viscosity is taken into account by the conventional pipe friction factor, f , defined by:

$$f = \frac{\tau}{\frac{1}{2} \rho v^2} \quad (4)$$

with τ denoting the shear stress at the wall, leading to the shear force, F_s :

$$F_s = -\frac{1}{2} \rho A v^2 4f \frac{dx}{d_c} \quad (5)$$

in which d_c denotes the column diameter and A the cross sectional area. Under laminar flow conditions, as usually encountered in SFC with postcolumn restrictors, f may be estimated by:

$$f = \frac{16}{Re} \quad (6)$$

Figure 2

Fanno curves for different mass flow rates per unit area.

From the second law of thermodynamics combined with Newton's second law of motion, it can be derived that:

$$\rho T (ds - ds_e) = \frac{1}{2} \rho v^2 4f \frac{dx}{d_c} \quad (7)$$

The term $\rho T (ds - ds_e)$ may be thought of as the loss of pressure resulting from irreversibilities, which in this case is the same as pressure loss due to friction.

Since irreversibilities, $ds > 0$, have been introduced, it will prove useful to investigate the entropy as a function of the enthalpy and mass flow rate, which results in the so-called Fanno curves (Figure 2).

Due to friction, the entropy is bound to increase with distance traveled along the pipe and will be maximal at the exit of the pipe. From the Fanno curves, it is learned that the entropy reaches an absolute maximum whenever a flow velocity corresponding to Mach number $M = 1$ is attained, which is, of course, always at the exit of the pipe.

At $M = 1$ the flow becomes choked, with the same implications as for flow through a convergent nozzle. However, in the case of pipe flow there is yet another factor to be reckoned with, *i.e.* pipe length. This is illustrated by Figure 3.

The pipe inlet is assumed to consist of a nozzle with a smallest area equal to the cross-sectional area of the pipe. The reservoir conditions and back pressure are the same in all cases considered. Only for the longest pipe (situation 4), is the pressure drop complete and the flow subsonic throughout.

If the pipe length is decreased (situation 3), sonic flow speed is attained at the outlet of the pipe and the mass flow rate increases, as will the exit pressure. The mass flow rate will reach a maximum at pipe length zero (situation 1), leaving a convergent nozzle under the assumption of isentropic flow.

Figure 3

Compressible viscous flow characteristics as a function of pipe length.

In the case of pipe flow with friction, the calculations of pressure drop, mass flow rate, etc. are of rather complex nature. Due to the scope of this paper, reference is made to the text books [3 – 5] on this subject.

2.3 Tapered versus Constant Diameter Restrictors

In this section a comparison of the pressure drop over both kinds of restrictors will be made. Consider the following experiment:

- A large reservoir (P_i, T_i) is to be equipped with the two kinds of restrictors, both discharging their flow into a region with a sufficiently low back-pressure P_b . The tapered restrictor is selected to have a throat-area, A_{nozzle} . The mass flow rate, under choked flow conditions, through this restrictor is $\dot{m}_{\text{*,nozzle}}$.
- A sufficiently long constant diameter restrictor is selected to have a cross-sectional area, A_{pipe} , with $A_{\text{pipe}} > A_{\text{nozzle}}$.
By reducing the length of this pipe, the mass flow rate is adjusted until $\dot{m}_{\text{pipe}} = \dot{m}_{\text{*,nozzle}}$.
- If a smaller cross-sectional area is chosen, less pipe length is required to restrict the mass flow rate. A trivial choice would be a pipe of length zero and a cross-sectional area equal to the nozzle throat area, i.e. a nozzle.

If both restrictors operate under choked flow conditions, the following expression for the exit pressure P_e can be derived:

$$\frac{P_{e,\text{nozzle}}}{P_{e,\text{pipe}}} = \frac{A_{\text{*,pipe}}}{A_{\text{*,nozzle}}}$$

This leads to the conclusion that pipe flow, when compared to convergent nozzle flow with the same mass flow rate, back-pressure, and reservoir conditions, has the larger pressure drop.

Since, for SFC, a low pressure drop is expected to have advantages, this suggests the use of tapered restrictors under choked flow conditions, rather than constant diameter restrictors.

3 Experimental

The supercritical fluid chromatograph was assembled from the following parts. A high pressure syringe pump (Model 601, Perkin Elmer, Norwalk, CT, USA) was modified for pressure control using a home-made controller and a pressure transducer (Model AD-1SS, Data Instruments Inc., Lexington, Mass. USA). The injection device consisted of a 60 nl internal loop Valco injection valve (Model A-3-Ni4W) with a pneumatic activator (ULCI-220V) equipped with a speed up kit (DVI) all supplied by Vici AG., Schenkon, Switzerland.

Injections were carried out with the so-called moving injection technique using a home-made injection timer device (0-0.5 [s]). Column and restrictor, connected by means of a low dead volume union (Gerstel, Mülheim, FRG), were placed in the oven of a gas chromatograph (Model F17, Perkin Elmer, Beaconsfield, England) equipped with a flame ionization detector.

Several restrictor geometries were used, viz. 5 μm i.d. O.T. fused silica (SGE, Ringwood, Victoria, Australia) varying in length between 0.3 and 0.9 meters, as well as 50 μm i.d.

fused silica (Hewlett Packard, Avondale, PA, USA) drawn out in a yellow burning methane flame. Liquified CO₂ spiked with ca. 100 ng/NI phenol was used in restrictor evaluation experiments. In other cases, research grade CO₂ (Air Products, The Netherlands) was used.

System dead-time measurements were made with methane as unretained component. Calculations of p, p, T data for CO₂ were made with the use of the equation of state proposed by *Chapela and Rowlinson* [6, 7].

4 Results and Discussion

In this section, the restrictor evaluation experiments and the dependence of dead-time on the mass flow rate will be discussed. The main objective of these experiments was to reduce detection signal distortion/noise and to verify the predictions made upon the theory of compressible flow through ducts.

Our experiments indicate that noise and distortion may share a number of causes, e.g. flow fluctuations.

4.1 Restrictor Evaluation

A common nuisance in SFC with flame ionization detection is signal distortion in the form of spiking, "christmas-tree" shaped peaks, etc. As already suggested by *Myers* [8], these distortions might originate from clusters of solute molecules entering the flame, and are obtained especially with overly large samples. This indicates loss of solubility of components during decompression over the end-restrictor (which is normally inserted through the heated block of the flame ionization detector).

One way of solving this problem is to decrease the influence of density on solubility by a sufficient increase of thermostat and detector temperature, as suggested by *Chester* [9], or thermal decomposition (pyrolysis) prior to detection [10].

Since loss of solubility is the most probable cause, another solution is to maintain the high pressure as long as possible. As discussed in this paper, this may be accomplished by using a restrictor under choked flow conditions, thus causing the pressure drop over the restrictor to be incomplete. The remaining decompression will, as a consequence, take place in the detection medium, thus diminishing the chances of detection artifacts.

Distortion may also originate from flow instability, probably caused by the restrictor being clogged up with component, leading to increased drag, causing the density to be increased and the component to regain mobility, etc. Flow fluctuations may also be caused by thermostat temperature fluctuations as will be discussed in Section 4.2.

Some of these causes will also influence the noise level. Whenever impure CO₂ enters the flame, i.e. a component is considered to be an impurity in the CO₂, all signal distortions may be looked upon as being noise. Hence a logical way to study the distortion phenomena, is to increase the impurity level of the CO₂.

CO₂ was spiked with phenol, which has a threshold pressure of approx. 8 MPa at 40° C [8]. This means that all phenol is trapped on the column, when applying a pressure below 8 MPa, and that the "true" noise level can be measured under these conditions. Increasing the pressure will cause the phenol to migrate and hence influence the detection signal.

As discussed, pressure drop increases with increasing length of a constant diameter restrictor. The noise level and frequency of spiking was noticed to increase with increasing O.T. restrictor length, e.g. for a 0.9 m restrictor the noise level was approx. 500 times larger than for the 0.3 m one, which was still at least approx. 10 times larger than the "true" noise level.

The noise level was observed to increase very rapidly with an increasing detection signal level, which is another way of saying that high sample concentrations are more liable to distortion in comparison to low sample concentrations. Changing to a tapered restrictor gave a noise level of the same order of magnitude as the "true" noise level. This tapered restrictor was inserted through the FID, so that the outlet was even with the flame tip. No detection problems due to decompression beyond the tapered restrictor exit were observed. In the cases of relatively high mass flow rates, with short constant diameter restrictors, the restrictors had to be pulled back from the flame tip in order to ensure a steady burning flame. The chromatographic implications of low mass flow rates resulting in near optimum velocity conditions, obtained by the use of sufficiently high restriction, will be the subject of a future paper.

The effects on signal distortion caused by different detection temperatures are probably component dependent. It was found that, even with a tapered restrictor, low volatile compounds eluting at moderately high pressures (>17.5 MPa) caused spiking at a detection temperature of 200° C. This spiking could be removed from the signal by raising the detection temperature, indicating that for those components the effect of temperature on vapor pressure prevails over the solubility/density effect [11]. A high enough detection temperature has, of course, to be used in order to prevent the temperature becoming subcritical due to adiabatic expansion, which incidentally may cause problems in packed columns (*Schoenmakers* [12]).

Evidence that spiking originates from clusters of solute molecules entering the flame was found in the observation that spiking reduces the bare signal level. The amount of reduction was approximately equal to the average spiking level.

4.2 Dependence of Dead Time on the Mass Flow Rate

An extremely important aspect concerning column efficiency and speed of analysis is the linear velocity, or dead-time (t_0), in dependence on the mass flow rate, which is a function of total pressure.

As already pointed out, there exists a linear relationship between the mass flow rate and total pressure for a tapered restrictor under choked flow conditions (eq. 3). Since equation 3 was derived for a perfect gas, it can not generally be applied to any kind of fluid.

However, in the case of CO_2 at sufficiently high temperatures, it can be used over a wide pressure range, since the isotherms tend to linearity under those circumstances (**Figure 4**), resembling the isotherms of an ideal gas. This

Figure 4

Calculated pressure as function of density at various temperatures for CO_2 [6, 7].

Figure 5

Measured p/t_0 as function of total pressure for a tapered restrictor. Solid line: 200 °C detection temperature; Broken line: 300 °C detection temperature.

Figure 6

Density and measured dead time as a function of total pressure for a tapered restrictor at 200 °C. Thermostat 41 °C. Column 3.0 m x 75 μm i.d.

was experimentally verified (**Figure 5**) by dead-time measurements which, in the form of p/t_0 , are proportional to the mass flow rate.

Since the product of on-column density with linear velocity corresponds to the mass flow rate, this product should also be linearly dependent on total pressure. This causes the linear velocity, or dead time, and density to be equally complex functions of pressure, as is illustrated by **Figure 6**.

Needless to say, this kind of dead-time behavior makes interpretation of pressure/density programmed chromatograms more difficult and also complicates optimization and theoretical descriptions. Different thermostat temperatures do not seem to affect the mass flow rate, but they do affect on-column density and, therefore, retention and linear velocity (**Figure 7**). As a consequence, column efficiency is affected and temperature fluctuations, i.e. velocity variations, may lead to detector signal distortion.

Figure 7

Calculated and measured (o) dead-time at 10 MPa as a function of thermostat temperature.

5 Conclusions

The one-dimensional compressible flow model predicts an incomplete pressure drop over tapered and constant diameter restrictors when operated under choked flow conditions. It also predicts a lower pressure drop for tapered restrictors when compared to constant diameter restrictors, with the same mass flow rate, temperature, and pressure. Since, in SFC, pressure drop over the restrictor may result in signal distortion, this implies the use of tapered, or similar, end-restrictors. An experimental model study confirmed the superior performance of tapered restrictors. Detection problems due to decompression beyond the tapered restrictor exit were not observed.

Experiments also showed that in order to overcome the problem of spiking due to low volatile compounds at moderately high pressures, a higher detection temperature has to be applied.

Dead-time measurements confirmed the linear relationship between the mass flow rate and applied pressure for a tapered restrictor. Since the mass flow rate is proportional to the product of linear velocity and on-column density, the linear velocity is as complex a function of pressure as is density. This may include, as is shown in this paper, a decrease in linear velocity with increasing pressure. It also implies direct translation of thermostat temperature fluctuations into linear velocity variations, which are a source for band broadening and detection signal distortion. By applying a higher thermostat temperature, causing improved linearity of the corresponding isotherm, a smoother transition of linear velocity with increasing inlet pressure is obtained.

Symbols

Letter symbols:

A	(cross-sectional) area
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
d_c	column diameter
ds	specific entropy change
ds_r	specific entropy change due to reversible heat transfer
f	pipe friction factor
F_s	shear force
M	Mach number
$\dot{m}$	mass flow rate
P	pressure

P_b	back pressure
P_e	exit pressure
P_t	Total (reservoir) pressure
R	specific gas constant
Re	Reynolds number
T	temperature
t_o	system dead time
v	flow velocity

Greek letters

γ	c_p/c_v
ρ	density
τ	component of tangential stress

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