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COMPARISON OF OPTIMIZED GAS CHROMATOGRAPHY DETECTORS FOR PACKED AND CAPILLARY COLUMNS

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SUMMARY

A comparison of the performance of optimized gas chromatographic detectors for packed and capillary columns is described. The detectors are optimized in the sense of considering those factors which independently maximize the signal-to-noise ratio for packed and capillary columns. The difference in peak variance for these two types of columns impose different requirements for the detector time constants and flow-rates, and hence the system noise and sensitivity. The criteria for optimizing these requirements are presented and it is shown that the potential improvement in detectivity that may be obtained with capillary is not quite as great as previous authors have estimated.

INTRODUCTION

The ability of capillary gas chromatography to characterize complex samples is well established. In addition to the increased resolution offered by capillary columns, a significant improvement in detectivity is often possible. A quantitative comparison of the efficiency of packed and capillary columns is readily available in terms of the number of theoretical plates. A similar quantitative comparison is more difficult to achieve for detection limits. Yang and Cram[1] have derived expressions for "detectivity ratios" for mass flow and concentration dependent detectors. However, these ratios are better termed "maximum response ratios" because no investigation was made into the contribution of noise to the detectivity. It is well known that the instrument requirements for capillary are quite different from those for packed columns. In particular the detector time constant, defined in terms of volume and flow, as well as the electronic time constant will be different depending on whether the detection system is optimized for packed or capillary columns. It would also be expected that the detector noise would be quite different for optimized systems. Since the detectivity of a chromatographic system is a figure of merit for the signal-to-noise ratio, it is important to consider both of the latter aspects when making a comparison. For the purposes of this paper a comparison is made between the signal-to-noise ratio for a detection system optimized for a capillary column, with the signal-to-noise ratio for a detection system optimized for a packed column. The criterion used to

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establish the electronic and detector time constants is that the output response be a certain percentage of that which would be obtained with an ideal detector having negligible response time and zero volume. The concept of the electronic time constant changing so as to adapt itself to the local chromatographic conditions (*i.e.* peak width) is not simply a theoretical convenience, but is already being done to a limited extent with some modern chromatographic data systems.

DISCUSSION

Linear mass flow-rate dependent detectors

Consider a packed and capillary column with the same liquid phase and operating at the same temperature with sample mass, M, and relative retention, α. The instantaneous mass flow is given by:

$$m(t) = \frac{M}{\sqrt{2\pi}\,\sigma(t)} \exp\left[-(t - t_R)^2/2\sigma(t)^2\right] \tag{1}$$

where $\sigma(t)^2$ is the time-based variance.

The maximum mass flow is:

$$m_{max} = \frac{M}{\sqrt{2\pi}\,\sigma(t)} \tag{2}$$

Let the detectivity ratio, defined as the maximum signal-to-noise ratio between capillary and packed, be given by:

$$D = \frac{(R_{m,c}/N_c)}{(R_{m,p}/N_p)} = \frac{(R_{m,c})}{(R_{m,p})} \cdot \frac{(N_p)}{(N_c)} \tag{3}$$

where $R_{m,c}$ and N_c are the maximum response and the noise for the capillary system. The subscript, p, refers to the packed column system.

If the response ratio is defined as:

$$R = \frac{R_{m,c}}{R_{m,p}} \tag{4}$$

and the noise ratio is defined as:

$$N = \frac{N_c}{N_p} \tag{5}$$

the detectivity ratio can be expressed as:

$$D = R/N \tag{6}$$

Assuming that the detector response is linearly proportional to the mass flow-rate allows the response ratio (eqn. 4) to be expressed in terms of the maximum mass flow-rate (eqn. 2):

$$R = \frac{\sigma_p(t)}{\sigma_c(t)} \tag{7}$$

For mass flow-rate dependent detectors such as the flame ionization, nitrogen–phosphorus, and flame photometric, the detector volumes are low enough and the fuel gas flow-rates are large enough that the detector time constant is negligible[1]. Only the electronic time constant needs to be considered. If the response of the electronic amplifier behaves as a single pole filter (−20 dB/decade frequency roll off) it is readily shown[2] that the time constant, τ, required to maintain a given peak fidelity, φ, is:

$$\tau(\varphi) = \sigma(t)\left[\frac{1}{\varphi^2} - 1\right]^{1/2} \tag{8}$$

Detectors with high selectivity over hydrocarbons, such as the nitrogen–phosphorus and the flame photometric have noise characteristics that are nearly shot noise limited and are independent of the column used. The root-mean-squared current fluctuations of these detectors are then given by[3]:

$$\bar{i}_{r.m.s.} = [2Q_e i\Delta f]^{1/2} \tag{9}$$

where Q_e is the electron charge, i is the background current level, and Δf is the noise bandwidth. The noise bandwidth is related to the electronic time constant, τ, by[3]:

$$\Delta f = \frac{1}{2\pi\tau} \tag{10}$$

Thus the noise ratio (eqn. 5) is:

$$N = \frac{(i_{r.m.s.})_c}{(i_{r.m.s.})_p} \tag{11a}$$

$$= \left[\frac{\Delta f_c}{\Delta f_p}\right]^{1/2} \tag{11b}$$

$$= \left[\frac{\tau_p}{\tau_c}\right]^{1/2} \tag{11c}$$

The noise ratio is therefore:

$$N = \left[\frac{\sigma_p(t)}{\sigma_c(t)}\right]^{1/2} \tag{11d}$$

The detectivity ratio (eqn. 6) is thus:

$$D = \frac{\left[\dfrac{\sigma_p(t)}{\sigma_c(t)}\right]}{\left[\dfrac{\sigma_p(t)}{\sigma_c(t)}\right]^{1/2}} = \left[\frac{\sigma_p(t)}{\sigma_c(t)}\right]^{1/2} \tag{12a}$$

In terms of theoretical plate number this can be expressed as:

$$D = \left[\frac{t_{R,p}}{t_{R,c}}\right]^{1/2}\left[\frac{N_c}{N_p}\right]^{1/4} \tag{12b}$$

where t_R and N are the retention time and total number of theoretical plates respectively. This detectivity ratio is smaller than that estimated by Yang[1], who neglected the noise contribution, by the square root of his value. Chromatographic detectors usually have not only shot noise, which has a constant power per unit bandwidth, but also some $1/f$ noise due to mechanical vibrations and flame flicker. This noise does not increase in proportion to the electronic bandwidth. The result is that the noise ratio (eqn. 11a) is smaller than what is given by eqn. 11b. This causes the detectivity ratio to be somewhat larger than that given by eqn. 12. A more exact value for the noise ratio would require a detailed knowledge of the particular system that is used.

When comparing a flame ionization detector the background currents due to column bleed are not generally equal, as they were in the case of the previously discussed selective detectors. The noise ratio should therefore be written as:

$$N = \left(\frac{i_{\text{r.m.s.}})\ \text{c}}{i_{\text{r.m.s.}}\ \text{p}}\right) \tag{13a}$$

$$= \left[\frac{i_c\sigma_p(t)}{i_p\sigma_c(t)}\right]^{1/2} \tag{13b}$$

The detectivity ratio for a flame ionization detector is:

$$D = \left[\frac{\sigma_p(t)}{\sigma_c(t)}\right]^{1/2}\left[\frac{i_p}{i_c}\right]^{1/2} \tag{14a}$$

In terms of theoretical plate number:

$$D = \left[\frac{t_{R,p}}{t_{R,c}}\right]^{1/2} \left[\frac{N_c}{N_p}\right]^{1/2} \left[\frac{i_p}{i_p}\right]^{1/2} \tag{14b}$$

It is the last term in eqn. 14b that results in the detectivity ratio for the flame ionization detector being substantially greater than that for selective mass flow-rate dependent detectors.

Quadratic mass flow-rate dependent detectors

A flame photometric detector operating in the sulfur mode produces a response that is proportional to the square of the sulfur atom mass flow-rate, which is:

$$[m(t)]^2 = \frac{M^2}{2\pi\sigma(t)^2} \exp\left[-(t - t_R)^2/\sigma(t)^2\right] \tag{15}$$

The maximum mass flow is thus:

$$m^2_{max} = \frac{M^2}{2\pi\sigma(t)^2} \tag{16}$$

The response ratio is therefore:

$$R = \left[\frac{\sigma_p(t)}{\sigma_c(t)}\right]^2 \tag{17}$$

To determine the optimum electronic time constant, it should first be noted, from eqn. 16, that the signal to be processed by the amplifier is Gaussian, but with a variance that is one half of the time-based variance of the mass flow into the detector. This means that the optimum response time of the electronics must be smaller by $1/\sqrt{2}$ than that which would be needed for a detector that responds linearly to the mass flow. However, only the noise ratio is needed and this can be expressed the same as in eqn. 11d. The detectivity ratio for a flame photometric detector operating in the sulfur mode is:

$$D_. = \frac{\left[\frac{\sigma_p(t)}{\sigma_c(t)}\right]^2}{\left[\frac{\sigma_p(t)}{\sigma_c(t)}\right]^{1/2}} = \left[\frac{\sigma(t)}{\sigma_c(t)}\right]^{3/2} \tag{18a}$$

In terms of theoretical plate number this can be expressed as:

$$D = \left[\frac{t_{R,p}}{t_{R,c}}\right]^{3/2}\left[\frac{N_c}{N_p}\right]^{3/4} \tag{18b}$$

Again since flicker noise ($1/f$) is present to some degree in a flame photometric detector actual detectivity ratio will be somewhat larger. This result is significantly different than the results derived by Yang and Cram, who erroneously assumed the sulfur response to be proportional to the square root of the mass flow, instead of the square.

Concentration dependent detectors

The concentration at the end of the column can be given in terms of the mass flow $m(t)$ divided by the column flow at the end of the column F_0:

$$C(t)_{max} = \frac{m_{max}}{F_0} \tag{19}$$

The maximum concentration is therefore:

$$C(t)_{max} = \frac{m_{max}}{F_0} \tag{20a}$$

Substituting for m_{max} from eqn. 2 and using $jF_0 = ua$:

$$C(t)_{max} = \frac{MJ}{\sqrt{2\pi}\, au\, \sigma(t)} \tag{20b}$$

where j is the James–Martin compressibility factor, u is the linear flow-rate, and a is the effective cross-sectional area of the column. This differs slightly from the maximum concentration obtained from the distribution function derived using the volume-based variance, $\sigma(V)^2$:

$$C(V) = \frac{M}{\sqrt{2\pi}\sigma(V)} \exp\left[-(V - V_R)^2/2\sigma(V)^2\right] \tag{21}$$

where V_R is the retention volume defined by:

$$V_R = uat_R \tag{22a}$$

$$V = uat \tag{22b}$$

$$\sigma(V) = ua\sigma(t) \tag{22c}$$

The maximum concentration from eqn. 21 is:

$$C(V)_{max} = \frac{M}{\sqrt{2\pi}\,\sigma(V)} \tag{23}$$

The total sample, M, is however the same, since:

$$M = \int_{-\infty}^{\infty} C(V)\mathrm{d}V = \int_{-\infty}^{\infty} C(t)U a \mathrm{d}t \tag{24}$$

The reason that $C(V)_{max}$ differs from $C(t)_{max}$ is that the volume-based variance is related to the time-based variance by the average linear velocity (eqn. 22c). What is of interest is C_{max} at the end of the column, and this is best represented by eqn. 21b. However, this may not be the concentration in a detector which has a finite volume, V. To maintain peak fidelity it is necessary with a capillary system to add a purge gas to the detector which makes C_{max} much smaller than that given by eqn. 23c. If the total flow (column and purge) is F_t, the maximum concentration in the detector is:

$$C_{max,d} = C_{max} \frac{F_0}{F_t} \tag{25a}$$

$$= \frac{M}{\sqrt{2\pi}\,\sigma(t)\,F_t} \tag{25b}$$

The response ratio can therefore be expressed as the ratio of maximum concentrations of capillary to packed:

$$R = \left[\frac{\sigma_p(t)}{\sigma_c(t)}\right]\left[\frac{F_{t,p}}{F_{t,c}}\right] \tag{26a}$$

In terms of the number of theoretical plates:

$$R = \left[\frac{t_{R,p}}{t_{R,c}}\right]\left[\frac{N_c}{N_p}\right]^{1/2}\left[\frac{F_{t,p}}{F_{t,c}}\right] \tag{26a}$$

In terms of retention volumes:

$$R = \left[\frac{V_p}{V_c}\right]\left[\frac{N_c}{N_p}\right]^{1/2}\left[\frac{j_c}{j_p}\frac{F_{t,p}}{F_{o,p}}\frac{F_{o,c}}{F_{t,c}}\right] \tag{26c}$$

where j_c and j_p are the compressibility factors for the capillary and the packed column respectively.

Most modern concentration dependent detectors such as the thermal conductivity and the electron capture detectors have volumes small enough that no additional purge flow is needed for packed column operation, therefore, $F_{t,p} = F_{o,p}$. The ratio of compressibility factors in eqn. 27c is usually between one and two. However,

for a capillary column, the ratio of column to total detector flow will usually be between 0.1 and 0.05 depending of the choice of purge flow. Yang and Cram[1] have given an example which indicated a response ratio of 89, which was the result of neglecting the last term in eqn. 27c; this resulted in an overestimation of the ratio by approximately a factor of ten.

In order to consider the optimum total detector flow it is necessary to examine the time constant of the system. The total time constant of the detection system, τ_t, is due to both an electronic contribution, τ_e and a detector contribution, τ_d. They are related by:

$$\tau_t = [\tau_d^2 + \tau_e^2]^{1/2} \tag{27}$$

If each term in eqn. 26 contributes equally to the total time constant, then:

$$\tau_d = \tau_e = \frac{\tau_t}{\sqrt{2}} \tag{28}$$

For a given peak fidelity τ_t is related to $\sigma(t)$ by eqn. 8, therefore:

$$\tau_d = \tau_e = \frac{\sigma(t)}{\sqrt{2}}\left[\frac{1}{\varphi^2} - 1\right]^{1/2} \tag{29}$$

Thus the optimum electronic time constant is smaller than for a mass flow-rate dependent detector by $1/\sqrt{2}$. Assuming the detector volume, V, act as a mixing chamber, the detector time constant is[2]:

$$\tau_d = \frac{V}{F_t} \tag{30}$$

where F_t is the total flow through the detector, which is the sum of the column and purge flows. For a given detector volume and peak fidelity this places a requirement on the total flow:

$$F_t(\varphi) = \frac{V\sqrt{2}}{\sigma(t)}\left[\frac{1}{\varphi^2} - 1\right]^{-1/2} \tag{31}$$

The true maximum concentration in the detector can now be expressed using eqn. 25b and eqn. 31 as:

$$C(\varphi)_{max,d} = \frac{M}{2\sqrt{\pi}\,V}\left[\frac{1}{\varphi^2} - 1\right]^{1/2} \tag{32}$$

This seemingly anomalous result implies that $C_{max,d}$ is independent of the peak variance. This is because the concentration in the detector depends on the product $\sigma(t)\ F_t$, and F_t is inversely proportional to $\sigma(t)$ for an optimized detector flow. In practice however, the detector flow for a packed column is much more than the optimum required based on the detector volume; while that for a capillary is generally much less. In the latter case resolution is often sacrificed in favor of sensitivity. The detector time constant used in eqn. 30 assumes that toal mixing occurs within the detector volume. It is possible to design an electron-capture detector such that the flow through the detector volume is nearly plug-like[4]. This would reduce τ_d in eqn. 30 by $2\sqrt{3}$. The optimum flow for a capillary system would therefore be reduced, resulting in an increased response ratio as given by eqn. 26c.

The noise for a thermal conductivity detector usually has the characteristics of mostly white noise (constant noise power per unit bandwidth) which would result in a noise ratio that is the same as is given by eqn. 12d. For a pulsed electron-capture detector the noise characteristics are more difficult to estimate. Increasing the electronic bandwidth for capillary use, for both constant frequency and constant current devices, will cause an increase in noise output. This is due is part to less efficient rejection of the pulser frequency. Constant current devices will introduce additional noise due to the feedback loop that regulates the frequency. This noise will also increase with the bandwidth of the detector. In general an electron-capture detector optimized for capillary will have more noise than one which is optimized for a packed column. An additional anomaly occurs with a constant-current electron-capture detector. Because a capillary column has less bleed than a packed column, the base frequency of the detector usually is much less. The ability of the output filter to reject the pulser noise decreases with frequency, therefore more electronic noise is produced. What is often not appreciated is that the sensitivity of the electron-capture detector is proportional to the base frequency[5,6]. An electron-capture with a capillary column will appear to have a lower noise because the noise caused by the chemical background will be reduced due to the reduced response. The response to the sample will also be reduced by almost as much. The result is that for the same electronic bandwidth and sample concentration in the detector, the signal-to-noise ratio will be about the same over a rather broad range of base frequencies. At the lower base frequencies, for strongly attaching compounds, some additional sensitivity may be lost due to sample destruction by electron attachement[7]. In general it is difficult to quantify the noise sources for an electron-capture detector when used with different columns and the sensitivity decreases just discussed. In practice the response ratio (eqn. 26c) is a reasonable approximation for the expected detectivity ratio.

CONCLUSION

It has been shown that for properly optimized detection systems a capillary column will always provide better detection limits. The degree of improvement, the detectivity ratio, is generally best for a concentration dependent detector such as an electron-capture detector. The limited sample capacity of a capillary column makes it unsuitable for use with a thermal conductivity detector[8], except perhaps with SCOT columns[9]. The next best detectivity is obtained with mass flow-rate dependent de-

tectors. The flame ionization detector provides the best improvement, followed by the flame photometric detector operating in the sulfur mode, followed next by the N/P detector and a flame photometric detector operating in the phosphorus mode. It is important to recognize that the increase in detector noise that occurs in systems optimized for capillary columns partially offsets the improved peak response that is obtained. With concentration dependent detectors the use of a purge gas to maintain peak fidelity further decreases the maximum response. In normal practice however, because of the tremendous increase in column efficiency that capillary columns provide, detector flows well below the optimum can be used to improve detection limits.

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