Detectability and the resulting requirements for column-detector systems in capillary gas chromatography

Citation for published version (APA):

DOI:
10.1002/jhrc.1240111204

Document status and date:
Published: 01/01/1988

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 15. Mar. 2020
Detectability and the Resulting Requirements for Column-Detector Systems in Capillary Gas Chromatography

Th. Noij*, J. A. Rijks, A. J. Van Es, and C. A. Cramers
Eindhoven University of Technology, Lab. Instrumental Analysis, P. O. Box 513, 5600 MB Eindhoven, The Netherlands.

Key Words:
Capillary gas chromatography
Column-detector systems
Detectability

Summary
Expressions for the minimum detectable amount \( Q_D \) and the minimum analyte concentration \( C_0 \) as functions of the chromatographic parameters are derived for both mass and concentration sensitive detectors. The effects of pressure drop, column inner diameter, and film thickness are given.

The minimum analyte concentration for mass flow sensitive detectors, \( C_0^{m} \), can be reduced considerably by selecting the carrier gas velocity well above its optimum value (related to \( H_{\text{min}} \)), however, at the cost of long columns and long analysis times. For \( Q_D \), the improvements can be neglected, and so the analysis can best be performed at \( u_{\text{opt}} \).

When the flow rate in the detector, \( F_D \), is equal to the column flow rate \( F_C \), the maximum permissible detector volume of concentration sensitive detectors is proportional to \( d_C^2 \) up to \( d_C^2 \), and so narrow bore columns require detectors of extremely small volume. Make-up gas has to be added when the actual volume is too large, thus worsening the detectability. Another approach, vacuum operation of the detector cell, appears to be very attractive. On the other hand, when wide bore columns are used in combination with small volume concentration sensitive detectors, very small values of \( Q_D^c \) and \( C_0^c \) are obtainable when the abundant carrier gas can be removed before entering the detector cell.

Digital noise filtering can further reduce the obtainable \( Q_D \) and \( C_0 \) values, especially for broad peaks and thus for wide bore columns.

1 Introduction
Since the introduction of gas-liquid chromatography by James and Martin in 1952 [1], column technology has constituted a major field of activity in gas chromatographic research. In the past decade tremendous progress has been made in improving the quality and applicability of fused silica capillary gas chromatographic columns up to their present day performance [2-4]. Important new developments include the introduction of narrow bore as well as very wide bore WCOT columns (i.d. < 100 \( \mu \)m [5-8] and i.d. > 500 \( \mu \)m [9-12] respectively) and the preparation of capillary columns with stable, very thick films of stationary phases (up to 10 \( \mu \)m [13-17]).

It can be derived from the Goly-Giddings equation that the speed of analysis and the separation efficiency are both favored by decreasing the column inner diameter [18]. An early example of an ultra-fast analysis was presented by Desty and co-workers, who separated several organic compounds within a few seconds on a 35 \( \mu \)m inner diameter column of 120 cm length [19]. Schutjes presented a highly efficient gas chromatographic separation by analyzing a natural gas condensate using a 95 m length of a 65 \( \mu \)m i.d. capillary column, having a theoretical plate number of 10^6 [20]. An analysis time of nearly six hours was required.

The increased plate number per unit of column length results in extremely narrow peaks: peak widths of 0.2-1 second are common for 50 \( \mu \)m i.d. capillary columns of 5-10 m length. Consequently, narrow bore capillary GC makes high demands on the injection technique, the detector electronics, and the data acquisition sampling rate. Besides efficiency and analysis time, the minimum amount that can still be detected \( (Q_D) \) is favored as well, since narrow peaks result in a better signal-to-noise ratio. However, the sample volume \( V_{\text{inj}} \) that can be injected onto narrow bore columns is much smaller.

Capillary columns with thick films of stationary phases are advantageously used for the analysis of volatile compounds as the solute capacity ratios are increased without the need of sub-ambient oven temperatures. Moreover, large film thicknesses allow the introduction of larger sample volumes, thus decreasing the minimum analyte concentration, \( C_0 \). On the other hand the separation efficiency is reduced due to a larger minimum plate height.
Recently, comparative studies on the performance of capillary columns having various diameters and film thicknesses have been published by Ettre and co-workers [21-23]. Misunderstandings and shortcomings of the theoretical aspects of narrow bore and thick film columns have led to erroneous conclusions concerning the detectability of trace compounds.

Two papers by the present authors [24,25] gave a theoretical treatment of the relationships between column characteristics, chromographic parameters, and detectability, for both mass flow sensitive and concentration sensitive detectors. In this paper some of the results will be briefly summarized, and others discussed:

- non-optimal chromatographic conditions
- the effect of detector dead volume
- vacuum outlet conditions
- the influence of noise filtering.

2 Theory

2.1 Detection Limits in Gas Chromatography

In chromatography much confusion exists about the expressions used to define detector characteristics. For convenience some of the detector parameters are re-defined below.

When the detector is operated within its linear dynamic range, the detector sensitivity, $S$, for a mass flow sensitive ($S^m$) and a concentration sensitive detector ($S^c$), respectively, assuming a Gaussian shaped profile with a standard deviation, $\sigma_b$, is given by:

$$S^m = \sqrt{\frac{2\pi}{Q_i}} \frac{R_{\text{max}}}{\sigma_t} \sigma_t \quad (1)$$

$$S^c = \sqrt{\frac{2\pi}{Q_i}} \frac{R_{\text{max}}}{\sigma_{F_d}} \sigma_{F_d} \quad (2)$$

where $Q_i$ is the injected amount, $R_{\text{max}}$ is the peak height, and $F_d$ is the detector gas flow rate.

The minimum detectable amount, i.e. the lowest quantity of a solute that can be detected using a given column/detector system, follows from eq. (1) and (2):

$$Q_{\text{min}}^m = \sqrt{\frac{2\pi}{S}} \frac{4R_n}{\sigma_t} \quad (3)$$

$$Q_{\text{min}}^c = \sqrt{\frac{2\pi}{S}} \frac{4R_n}{\sigma_{F_d}} \quad (4)$$

where $R_n$ is the detector noise.

The ratio $R_n/S$ is a detector characteristic independent of the GC column, whereas $\sigma_t$ is determined by the chromatographic parameters, and eventually extra-column contributions.

Solute amounts less than $Q_{\text{min}}$ will give a signal that cannot be distinguished from detector noise with sufficient reliability. The factor of 4 is arbitrarily selected and is determined by the demands on the analytical precision [26].

The solute concentration in the sample related to $Q_{\text{min}}$ is called the minimum analyte concentration [27], $C_0$, and is given by:

$$C_0 = \frac{Q_{\text{min}}}{V_{\text{inj}}} \quad (5)$$

Both the minimum detectable amount and the maximum sample volume, $V_{\text{inj}}$, are determined by the column parameters, and so $C_0$ is no longer proportional to $Q_{\text{min}}$. Solute concentrations as low as $C_0$ can be determined by the given chromatographic system. For the analysis of actual solute concentrations below $C_0$, sample pre-concentration techniques have to be applied.

A survey of several GC detectors and their main characteristics based on literature data [28,29] is presented in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Det.</th>
<th>Type</th>
<th>$S$</th>
<th>$R_n$</th>
<th>$Q_{\text{min}}^2$</th>
<th>LDR$^3$</th>
<th>F$^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCD</td>
<td>c</td>
<td>$10^4$ Vml/g</td>
<td>$10^{-5}$ V</td>
<td>$10^{-9}$ g</td>
<td>$10^4$</td>
<td>~ 1</td>
</tr>
<tr>
<td>FID</td>
<td>m</td>
<td>$10^{-2}$ As/g</td>
<td>$10^{-14}$ A</td>
<td>$10^{-12}$ g</td>
<td>$10^6$</td>
<td>~ 1</td>
</tr>
<tr>
<td>ECD</td>
<td>c</td>
<td>$10^{15}$ Hz mll/g</td>
<td>$10$ Hz</td>
<td>$10^{-14}$ As</td>
<td>$10^4$</td>
<td>$10^7$</td>
</tr>
<tr>
<td>TID</td>
<td>m</td>
<td>$10$ As/g</td>
<td>$10^{-12}$ A</td>
<td>$10^{-13}$ As</td>
<td>$10^4$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>FPD</td>
<td>m</td>
<td>$10^5$ As/g</td>
<td>$10^{-11}$ A</td>
<td>$10^{-13}$ As</td>
<td>$10^4$</td>
<td>$10^5$</td>
</tr>
<tr>
<td>PID</td>
<td>c</td>
<td>$1$ Aml/g</td>
<td>$10^{-13}$ A</td>
<td>$10^{-15}$ A</td>
<td>$10^7$</td>
<td>1-100</td>
</tr>
</tbody>
</table>

1) Mass flow sensitive (m) or concentration sensitive (c).
2) For $\sigma_t = 0.4s$ and $F_d = 60$ ml/min.
3) Linear dynamic range
4) Selectivity relative to n-hydrocarbons.
   a) For aldrin in the constant current mode of operation.
   b) Nitrogen mode.
   c) Phosphorous mode.
   d) For benzene.

2.2 Basic Relationships and Definitions

In the theoretical concept presented here, it is assumed that the chromatographic process is performed isothermally at the optimum carrier gas velocity.

The concept of normalized chromatographic conditions: The main criterion for selecting the proper chromatographic conditions is the separation of a critical pair of compounds. The separation depends upon plate number,
Detectability in Capillary GC

capacity ratios (k), and the selectivity of the stationary phase (\( \alpha \)). The plate number required to obtain a resolution \( R_s \) can be expressed as:

\[
N_t = \frac{16 R_s^2}{k} \frac{1+k}{k} \frac{\alpha}{\alpha-1}^2
\]  

(6)

Once the stationary phase and the GC oven temperature have been selected a definite plate number is required to meet a certain peak resolution demand.

In the comparison of columns of different diameter and/or film thickness the chromatographic conditions are normalized assuming a fixed actual plate number, required to separate a "critical pair". In [24,25] the authors presented an extensive, theoretical treatment on the effect of column inner diameter and film thickness on the minimum detectable amount, \( Q_0 \), and the minimum analyte concentration, \( C_0 \).

By differentiation of the Golay-Giddings plate height equation of capillary columns, using Poiseuille-Hagen flow characteristics, equations were derived for \( Q_0 \) and \( C_0 \). This resulted in explicit expressions, under optimal chromatographic conditions, for both mass and concentration sensitive detectors. The results account for the influence of the pressure ratio (P) of column inlet to outlet and include the effect of capacity ratio k, input band volume, required plate number, etc. The main conclusions are summarized below [30].

2.3 Thin Film Columns

The minimal detectable amount \( Q_0 \) as a function of the column diameter is shown in Figure 1 for a mass sensitive (FID) and a concentration sensitive detector (TCD). The ratio of the standard deviation of the injection band, \( \sigma_i \), to the column standard deviation \( \sigma_c \), \( \sigma_i/\sigma_c \) is defined as b.

Figure 1 indicates that for extremely narrow bore columns a TCD is capable of detecting smaller quantities than a FID, provided that no extra make-up gas is required. Of course this only holds for concentration sensitive detectors with very small internal volumes. The intersection is determined by the detector characteristics as well as by the chromatographic parameters.

The small \( Q_0 \) values observed for narrow bore columns have often been misinterpreted as narrow bore columns should be used in trace analysis. However, the allowed injection volume \( V_{\text{inj}} \) is favorable for large diameter columns.

The combined effect for the minimum analyte concentration shows that for a mass flow sensitive detector \( C_0 \) is inversely proportional to \( d_c \), whereas for a concentration sensitive detector \( C_0 \) is independent of \( d_c \) (cf. Figure 2). This means that unless a sample pre-concentration technique is employed, diluted samples can best be analyzed

Figure 1
Influence of the column inner diameter (\( d_c \)) on the minimum detectable amount (\( Q_0 \)) for a FID and a TCD.
\( R_s = 1.84; \alpha = 1.030; k = 4; N_t = 10^5; b = 0.1 \).
FID: \( R_n/S = 10^{-12} \) g/s; TCD: \( R_n/S = 10^{-9} \) g/ml.

Figure 2
Influence of the column inner diameter (\( d_c \)) on the minimum analyte concentration (\( C_0 \)) for a FID and a TCD.
\( R_s = 1.84; \alpha = 1.030; k = 4; N_t = 10^5; b = 0.1 \).
FID: \( R_n/S = 10^{-12} \) g/s; TCD: \( R_n/S = 10^{-9} \) g/ml.
using a wide bore column in combination with a FID. However, it should be noted that a large column inner diameter has the drawback of long analysis times, since the retention time \( t_R \) increases proportionally with \( d_i^2 \) [20].

As can be seen from Figure 2, concentration sensitive detectors are preferred to obtain the lowest \( C_0 \) value when narrow bore columns are employed. For the specified conditions this holds for columns with an inner diameter smaller than 14 μm. In order to obtain full benefit of the sensitivity of the GC systems, the injection band width should be 10-50% of the peak width caused by the chromatographic process \((b = 0.1 - 0.5)\).

### 2.4 Thick Film Columns

By increasing the film thickness \( d_f \) for a given column, two options occur: (1) increasing \( d_f \) at constant temperature and hence increased capacity ratio, or (2) simultaneously increasing \( d_f \) and the column temperature in order to keep \( k \) constant. Whatever approach is selected, most of the parameters describing \( Q_0 \) and \( C_0 \) are affected. Moreover, the actual plate number required to establish a certain peak resolution also changes, both on changing the capacity ratio as well as on changing the temperature which affects the relative retention \( \alpha \).

On increasing the stationary phase film thickness, most of the parameters describing \( Q_0 \) and \( C_0 \) are influenced [25]. In the concept of a fixed demand on peak resolution, optimum film thicknesses exist for \( Q_0^{\text{opt}} \) and \( C_0^{\text{opt}} \) (for the option of constant temperature) as well as for \( C_0^{\text{C}} \) (for the option of constant capacity ratio). For a concentration sensitive detector, the minimum analyte concentration \( (C_0^{\text{C}}) \) is not affected by the film thickness.

The gain in \( Q_0 \) or \( C_0 \) at the optimum film thickness is only moderate compared to the values calculated for a thin film column. Therefore, it can be concluded that in the general practice of chromatography, the most beneficial \( Q_0 \) and \( C_0 \) values are obtained on thin film columns.

Thick film columns should only be used to increase the capacity ratio of volatile compounds up to values in between 0.5 and 1.5. In this range of \( k \), \( Q_0 \) is minimized for both detector types.

For the practical use of capillary columns it is very advantageous to employ on-column solute focusing techniques like cold-trapping, the solvent effect, or stationary phase gradient focusing. The minimum analyte concentration will be much smaller as the sample volume can be very large, whereas the re-injection band width is still very small.

An important conclusion is that in most situations thin film columns have to be preferred over thick film columns in trace analysis, if a minimum value of \( C_0 \) or \( Q_0 \) is the goal. The following sections will deal with thin film columns.

**Effect of detector flow rates other than \( F_d \):** So far, it was assumed that the detector flow rate is equal to the column flow rate, i.e. \( F_d = F_c \). In the practice of chromatography, however, this will seldomly be true as make-up gas is usually added to the detector in order to improve the sensitivity (FID), as quench gas (ECD) or to eliminate peak distortion by the detector cell void volume (TCD).

For a properly connected detector the solute mass flow rate is not affected by the make-up gas flow rate, and consequently it is not a critical parameter for mass flow sensitive detectors. However, the solute concentration in the detector cell is altered, and so the make-up gas drastically influences the response of concentration sensitive detectors.

When make-up gas is added to give a fixed detector flow rate independent of column parameters, concentration sensitive detectors behave like pseudo mass flow sensitive detectors with the corresponding influence of \( d_o \) on \( Q_0 \) and \( C_0 \). In the daily practice of chromatography this will often be the case. On the other hand, when detector gas flow is proportional to the column flow, i.e. \( F_d \propto F_c \), the original relationships for \( Q_0^{\text{opt}} \) and \( C_0^{\text{opt}} \) remain unchanged, except for an additional proportionality factor.

To limit peak-distortion due to the detector void volume, in many situations make-up gas has to be used. The total detector flow rate can best be related to the detector cell volume \( (V_d) \) to give a certain value of the volumetric time constant \( \tau_v \), defined by:

\[
\tau_v = \frac{V_d}{F_d}
\]  

(7)

Allowing a fixed relative distortion of the peak shape, \( \tau_v \) should be proportional to the width of the eluting peak. *E.g.* for \( \tau_v < 0.1 \tau_t \), the actual detector response exceeds 99.5% of its maximum value, while the retention time shift is less than 0.1 \( \tau_t \) [31]. For \( \tau_v = 0.1 \tau_t \) eq. (7) can be rewritten as:

\[
F_{d, \text{eq}} = \frac{V_d}{0.1 \tau_t}
\]  

(8)

For the pre-assumption that the detector flow rate is equal to the column flow rate, the maximum permissible detector volume reads:

\[
V_{d, \text{max}} = 0.1 \tau_t F_c
\]  

(9)

The relationship between the maximum permissible detector volume and the column inner diameter for the proportionality factor \( g = \tau_v/\tau_t = 0.1 \) is shown in Figure 3 [30]. When the actual detector volume is larger than \( V_{d, \text{max}} \), make-up gas has to be added to satisfy eq. (8). Contrarily, for detector volumes smaller than \( V_{d, \text{max}} \), the detector cell is flushed with a surplus of carrier gas. If it were technically possible, selective post-column removal of abundant
Detectability in Capillary GC

Reduction of the detector time constant of a TCD by vacuum operation: By reducing the actual detector pressure ($P_{\text{det}}$), the volumetric flow rate through the detector is increased by a factor $P_{\text{atm}}/P_{\text{det}}$ when $P_{\text{atm}}$ is the ambient atmospheric pressure, e.g. a factor of 100 if $P_{\text{det}}$ is set at 0.01 bar. For TCD’s the reduction of the cell pressure also results in an increased signal to noise ratio; the basis of this effect was already described in [32].

Furthermore, for a given plate number, vacuum column outlet operation results in an increased optimal velocity and thus shorter analysis times [33]. This beneficial effect is most pronounced for short and/or wide bore columns.

An example of the combined beneficial effects of small diameter columns, small detector volume (TCD) and the application of vacuum is given in Figure 4.

Effect of carrier gas velocities other than optimum: The theoretical relationships presented proceed on the assumption of gas chromatography performed at the optimum carrier gas velocity. At higher velocities the analysis time is reduced, but simultaneously the column plate number will decrease due to a larger plate height. In order to restore the ensuing loss in peak resolution a longer
carrier gas by e.g. a jet separator or a membrane could be very advantageous in this respect. By so doing, the solute concentration in the detector cell is increased, while the peak shape remains unaffected. Some calculated examples are given in Table 2, where $Q_0^c$ and $C_0^c$ are tabulated for different detector flow options. The benefits of low volume detector cells in combination with wide bore columns and post-column carrier gas removal is obvious.

![Figure 3](image-url)

**Figure 3**

*Influence of the column inner diameter ($d_i$) on the maximum permissible detector volume ($V_d$) for concentration sensitive detectors, when $F_d = F_c$, $k = 4; N_i = 10^5; \tau = 0.1$ (data). The points a, b, c, d and a', b', c', d' refer to the detector flow options of Table 2 for 50 µm respectively 320 µm i.d. columns. For column/detector combinations left of the solid line, make-up gas should be added while right of the solid line, abundant carrier gas can be removed.*

**Table 2**

<table>
<thead>
<tr>
<th>Option</th>
<th>$Q_0^c$ (pg)</th>
<th>$Q_0^c$ (ng/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 µm</td>
<td>320 µm</td>
</tr>
<tr>
<td>a) $F_d = \text{constant (30 ml/min)}$</td>
<td>865$^1$</td>
<td>8550$^1$</td>
</tr>
<tr>
<td>b) $F_d = F_c$</td>
<td>6.6</td>
<td>419</td>
</tr>
<tr>
<td>c) $F_d = F_{d,req}; V_d = 10 \mu l$</td>
<td>1000$^1$</td>
<td>1000$^1$</td>
</tr>
<tr>
<td>d) $F_d = F_{d,req}; V_d = 1.5 \text{nl}$</td>
<td>0.15$^2$</td>
<td>0.15$^2$</td>
</tr>
</tbody>
</table>

1) Make-up gas is added.
2) Selective post-column removal of abundant carrier gas.

![Figure 4](image-url)

**Figure 4**

*Chromatogram of a 10 µm i.d. column with TCD detection. Column: L = 1.5 m, stationary phase: cross-linked OV-17, phase ratio: 80, T = 30ºC, carrier gas He, 50 bar. Sample: gasoline headspace introduced by cold trap/thermosorption. Detector: micro-TCD (cell volume 1.5 nl), outlet pressure: 0.07 bar.*
column has to be selected, thus re-establishing the original plate number. However, this opposes the decreased analysis time. It can be concluded that the speed of analysis will be improved as long as the increased carrier gas velocity overrules the required column length increment. Besides the retention time, \( Q_0 \) and \( C_0 \) are affected as well.

The results of an extensive theoretical treatment [30] are summarized in Figures 5 and 6. In these figures \( \nu \) represents the ratio of the actual and the optimum carrier gas velocities at column outlet conditions:

\[
\nu = \frac{u_{0,\text{actual}}}{u_{0,\text{opt}}}
\]  

(10)

Figure 5
Effect of the carrier gas velocity on \( Q^m_0 \) for 50 \( \mu \)m i.d. and 320 \( \mu \)m i.d. columns. \( \nu = u_{0,\text{actual}}/u_{0,\text{opt}} \).

\( R_s = 1.84; \alpha = 1.030; k = 4; N_t = 10^5 \). FID: \( R_s/S = 10^{-12} \) g/s.

Figure 6
Effect of the carrier gas velocity on \( Q^c_0 \) for 50 \( \mu \)m i.d. and 320 \( \mu \)m i.d. columns. \( \nu = u_{0,\text{actual}}/u_{0,\text{opt}} \).

\( R_s = 1.84; \alpha = 1.030; k = 4; N_t = 10^5 \). TCD: \( R_s/S = 10^{-9} \) g/ml.

Figure 7
Simulation of noise reduction with fast Fourier filtering.
A. Gaussian peak (\( \nu_1 = 25 \) points) with white noise (total: 1024 points).
B. Fourier transformed signal (1024 points). Filter: matched Gaussian, \( \nu_2 = 25 \) points.
C. Back transformed filtered signal.
D. Plot of relative noise level versus \( 1/\sqrt{\nu_1} \) \( \nu_1 \) ranging from 2 to 125 points.)
In order to minimize $t_R$ and $Q_0^m$, it may seem advantageous to increase the carrier gas velocity up to values well above $u_{o, opt}$. Nevertheless, it is shown by the plots of Figure 5 that the gain is only moderate, even for wide bore columns. $Q_0$ has its minimum at or slightly below $v = 1$ with a maximum achievable improvement of only 8% (cf. Figure 6). So for minimum $Q_o$ values for both detector types, the analyses can best be performed at $u_{o, opt}$. $C_o'$ is not affected by an increase of $v$.

On the other hand, $C_o'^n$ can be considerably reduced at very high carrier gas velocities, however, at the cost of extremely long columns and correspondingly long analysis times. In practice, values larger than $v = 5$ are not recommendable. For $v = 5$ and $P = 1$, $t_R$ and $C_o'^n$ are reduced to 52% while the column length should be increased by a factor of 2.6.

**Influence of noise filtering:** By digital filtering of so called “white noise” using a matched filter, it can be shown that for a Gaussian shaped peak the reduced noise level ($R_n'$) is inversely proportional to the square root of the peak width $\alpha t$:

$$R_n' \sim \frac{1}{\sqrt{\alpha t}}$$  \hspace{1cm} (11)

To illustrate this relationship the filtering of different peak widths was simulated with Fourier filtering. Consider a Gaussian shaped peak (peak width $\alpha t$) with white noise. The process of Fourier filtering is represented in Figure 7. The signal in the time domain is transformed to the frequency domain by Fast Fourier Transform. Here it can be multiplied with a filter which preserves the main part of the desired signal and eliminates a large part of the noise frequencies. Back transformation provides the filtered signal.

Because the width of the transformed peak in the frequency domain is proportional to $1/\alpha t$, the width of the matched filter is also proportional to $1/\alpha t$ (a Gaussian filter shape was chosen for the simulation). Plotting the noise level of the filtered signal versus $1/\sqrt{\alpha t}$ provides a straight line as was predicted by eq. (11). The peak width itself is proportional to $t_R$ and with the preceding theory, it follows that for noise filtering:

$$R_n' \sim \frac{1}{d_c}$$ \hspace{1cm} for $P = 1$  \hspace{1cm} (12)

$$R_n' \sim \frac{1}{\sqrt{d_c}}$$ \hspace{1cm} for $P >> 1$  \hspace{1cm} (13)

Thus the signal-to-noise ratio can be substantially improved, especially for wide bore columns. The effect of noise filtering on $C_o$ vs $d_c$ is shown in Figure 8. $C_o'^n$ is reduced even further by wide bore columns, while now also $C_o'$ is favored by large $d_c$ values. Contrarily, the adverse effect of a large column inner diameter on $Q_o$ cannot be neutralized by noise filtering, although the dependence is also reduced by a factor of $\sqrt{d_c}$ up to $d_c$.

**Acknowledgment**

Ir. J. van Velzen's contribution to this paper, the study of the effect of reducing TCD's pressures is greatly appreciated. Mrs. Denise Tjallena is kindly acknowledged for her accuracy in handling this manuscript.

**References**


Analysis of Volatile Organic Chemicals in Aqueous Samples by Purge/GC with Selective Water Removal

J. W. Cochran*
Northrop Services, Inc., R. S. Kerr Environmental Research Laboratory, P. O. Box 1198, Ada, OK 74820, USA

J. M. Henson
United States Environmental Protection Agency, R. S. Kerr Environmental Research Laboratory, P. O. Box 1198, Ada, OK 74820, USA

Key Words:
Capillary chromatography
Purge GC
Volatile organic chemicals

Summary
A gas chromatographic method for volatile organic chemicals in which an aqueous sample is purged directly to a cryogenically cooled, fused silica column uses a Nafton tube drier between the purge vessel and GC column. The Nafton strips water from the gas stream during the purge step while allowing volatile halocarbons and aromatics to continue to the GC column. Examples of this technique are presented on 0.53 mm and 0.25 mm fused silica columns coated with a variety of stationary phases.

1 Introduction
The United States Environmental Protection Agency has mandated or recommended maximum contaminant levels for 16 volatile organic chemicals in drinking water and requires community water systems to monitor for 50 volatile contaminants [1]. These chemicals frequently exist at ppb or ppt levels and are not always easily analyzed by packed column gas chromatography (GC). Capillary GC