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Detection Limits of Thermal Conductivity and Photoionization Detectors in High Speed Narrow Bore CGC

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Summary
Not only the required input band width and the availability of compatible instrumentation limit the reduction of column diameter but so do the column sample capacity and detector characteristics, such as volume and sensitivity. In this paper the scope and limitations of thermal conductivity and photoionization detection at atmospheric and reduced pressures for capillary gas chromatography are discussed at length.

It is shown that the sensitivity of a thermal conductivity detector is inversely proportional to the pressure. Reduction of cell volume and decrease of pressure appear equivalent with respect to minimum detectable amount and peak broadening. This results in femtogram detection limits for column diameters as low as 10 μm.

For photoionization detectors the sensitivity did not improve at reduced pressures, so that the effect of reduced pressure and addition of make-up gas on the detection limits is the same. Nevertheless, the applicability of a low volume photoionization detector (40 μl) for capillary columns with a diameter as low as 50 μm will be demonstrated by series coupled PID and FID detectors and illustrated with various applications.

1 Introduction
A substantially increased speed of analysis can be achieved by reduction of the column diameter. Unfortunately, the instrumental requirements are the more critical the smaller the internal diameter.

In recent reports [1,2] sample introduction systems capable of delivering input band widths down to 1 ms have been described. These systems are compatible with greatly reduced column diameters. On moving towards smaller column diameters, however, the sample capacity decreases faster than the minimum detectable amount. Consequently, the dynamic range of the column-detector combination, being the ratio of sample capacity and minimum detectable amount, decreases with column diameter. This seriously limits the reduction of column diameter.

The reduction in dynamic range is proportional to \( d_c^2 \) for mass flow sensitive detectors, whereas it is only proportional to \( d_c \) for concentration sensitive detectors (without make-up gas) [3]. Therefore, in principle a concentration sensitive detector becomes more and more favorable, compared to a mass flow sensitive detector, on decreasing the column diameter. Usually make-up gas has to be added in order to prevent additional peak broadening in the detector cell void volume. Contrary to mass flow sensitive detectors, the detector response of concentration sensitive detectors is drastically influenced by the use of make-up gas. As a result it follows that the full response of concentration sensitive detectors can only be preserved if the cell volume decreases proportionally to \( d_c^2 \) [4].

Recently we demonstrated the compatibility of a thermal conductivity detector with a cell volume of 1.5 nl with highly reduced column diameters [11]. In this study we show that miniaturization is not always necessary for a TCD. The full response of a TCD can also be preserved by a reduction of the detector cell pressure. This implies that relatively large volume TCD's can be made compatible for high speed analysis with narrow bore capillary columns.

For similar reasons a photoionization detector (concentration sensitive) was evaluated at reduced and atmospheric pressures. The potential of the TCD and PID for narrow bore columns will be illustrated by various applications.

2 Theory
2.1 Effect of Pressure on TCD Sensitivity
The sensitivity (S) for a concentration sensitive detector (e.g. TCD, PID) is defined as:

\[ S = A \cdot F_d/W \]  

where,

\( A \) = peak area
\( F_d \) = detector flow
\( W \) = injected sample amount
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For a TCD or a PID respectively this can also be written as:

TCD: \[ S = V/C \ [\text{Vml/g}] \]  

(2)  

PID: \[ S = I/C \ [\text{Aml/g}] \]  

(3)  

where  

\[ V = \text{TCD detector response} \ [\text{V}] \]  

\[ I = \text{PID detector response} \ [\text{A}] \]  

\[ C = \text{sample concentration} \ [\text{g/ml}] \]  

According to Wells and Simon [5] the response \( V \) (volt) of a thermal conductivity detector is given by:

\[ V = I R_o a X \left( A - \frac{\lambda_1}{\lambda_2} B \right) (T - T_w) \left( 1 + aT \right) \]  

(4)  

where,

\[ I = \text{filament current} \]  

\[ T = \text{filament temperature} \]  

\[ T_w = \text{block temperature} \]  

\[ R_o = \text{filament resistance at 0°C} \]  

\[ a = \text{temperature coefficient of resistance} \]  

\[ X = \text{molar fraction of the sample} \]  

\[ \lambda_1 = \text{thermal conductivity of carrier gas} \]  

\[ \lambda_2 = \text{thermal conductivity of sample} \]  

\[ A, B = \text{constants} \]  

The sample concentration can be written as:

\[ C = X M P_d / R T_w \]  

(5)  

where

\[ M = \text{molecular weight of the sample} \]  

\[ R = \text{gas constant} \]  

\[ P_d = \text{detector pressure} \]  

Combining eqs. (2), (4), and (5), the TCD sensitivity can be expressed as:

\[ S = I R_o a \left( \frac{R T_w}{M P_d} \right) \left( A - \frac{\lambda_1}{\lambda_2} B \right) (T - T_w) \left( 1 + aT \right) \]  

(6)  

The thermal conductivity of carrier gas and component are independent of pressure at least down to 0.1 bar [6]. Consequently the TCD sensitivity increases inversely proportional with pressure. This is in contrast with the addition of make-up gas in which the sensitivity remains constant. Therefore, the reduction of pressure seems an efficient way to decrease the detector band broadening. Some additional gain in sensitivity can be obtained because a lower TCD block temperature is allowed at reduced pressures.

The gain in analysis speed is another advantage that can be obtained at reduced outlet pressures [7]. This effect, however, is limited to columns with a relatively high permeability (wide bore or short narrow bore columns).

2.2 Detection Limits of Concentration Sensitive Detectors

The minimum detectable amount \( W_o \) for a concentration sensitive detector can be written as:

\[ W_o = \sqrt{2 \pi} \left( \frac{4 R}{S^3} \right) \sigma_c F_d \]  

(7)  

where

\[ \sigma_c = \text{standard deviation of the chromatographic peak broadening} \]  

\[ R_n = \text{noise level} \]  

\[ F_d = \text{detector flow rate} \]

Three possibilities to reduce peak broadening in the detector cell volume can be distinguished: the addition of make-up gas, reduction of detector cell volume, and reduction of detector cell pressure.

In general, the required detector flow for a fixed contribution of the detector band broadening to the total band broadening (e.g. 10 %) can be written as:

\[ F_d = \frac{V_d}{g \sigma_c} \]  

(8)  

where

\[ V_d = \text{detector cell volume} \]  

\[ g = \text{constant depending on detector cell geometry and maximum acceptable peak distortion in the detector} \]

When make-up gas is needed to fulfill eq. (8), it follows from eq. (7) that \( W_o \) remains constant when column diameter is reduced. In view of the column sample capacity, which falls proportionally to \( d_c^5 \), this is highly unfavorable for the dynamic range of the column/detector combination. Much better detection limits are achieved when the detector flow is equal to the column flow (no make-up gas). In this case a decreasing column diameter is accompanied by a reduction of \( W_o \) proportional to \( d_c^2 \). Simultaneously, the maximum permissible detector also has to decrease proportional to \( d_c^2 \) [4].

If, on the other hand, detector cell pressure is reduced, the detector band broadening will decrease comparably with the addition of make-up gas. However, as can be seen from eqs. (6) and (7), the increase in detector flow is completely compensated for by the increase in detector sensitivity (the \( F_d/S \) ratio is constant). In fact the net effect of reduced pressures on detection limits and detector band broadening is equivalent to a reduction of detector cell volume. Therefore, problems with detector miniaturization can be avoided and relatively large volume TCDs can be accepted for high speed analysis with narrow bore columns.

For the PID a detailed theoretical analysis similar to the TCD is much more complicated. Therefore, the effect of detector pressure on sensitivity and detection limits is studied experimentally.

3 Experimental

Two types of thermal conductivity detectors were used in this study. A Varian constant temperature TCD (Varian, Walnut Creek, USA) with a cell volume of 140 μl. This TCD was part of a Varian 3400 gas chromatograph. The detector electronics were specified to have time constants of 2-220 ms dependent on the selected range.

The other TCD was part of a miniaturized gas chromatograph (Micro Sensor Technology, Freemont, CA, USA) [1]. It was operated in the constant temperature mode, has a specified cell volume of 1.5 nl and a thermal time constant of 200 μs.

The low volume (40 μl) photoionization detector (HNU Systems Inc., Newton, MA, USA) with a 10.2 eV lamp was mounted on a
Carlo Erba 4160 gas chromatograph (Carlo Erba, Milam, Italy). The amplifier electronics were modified to lower the time constant from 200 to 2 ms.

During operation at reduced outlet pressures a buffer vessel was placed in between the detector and the vacuum pump to reduce pressure fluctuations. Because the PID could not be made sufficiently leak tight, it was placed in a leak tight container.

Capillary columns with diameters ranging from 320 µm to 10 µm were used with helium as carrier gas. Due to the high inlet pressures required for narrow bore columns, carrier gas was controlled with a Tescom 44-1123-24 high pressure regulator (Tescom Corp, Minn, USA).

Chromatograms were recorded with a digital storage oscilloscope (Nicolet 3091, Madison, WI, USA) capable of sampling at a maximum rate of 1 MHz or with a home-made 12 bit ADC capable of sampling at a maximum rate of 2500 Hz. Data from both systems could be transferred to a Nelson integration system (Nelson, Cupertino, CA, USA).

4 Results and Discussion

4.1 Effect of Pressure on TCD Sensitivity

The TCD sensitivity was experimentally determined according to the relation:

\[ S = \frac{A_{F_d}}{W} = \frac{A_{F_c}}{W \cdot P_d} \]  \hspace{1cm} (9)

where \( F_c \) = column flow.

In Figure 1 the measured sensitivity is plotted versus \( 1/P_d \) for both TCDs. The sensitivity of the separate TCDs was normalized at atmospheric pressure. The micro TCD was coupled with a 50 μm i.d. column, whereas with the Varian TCD the column diameter was 320 μm at pressures from 0.1-1 bar and 50 μm at pressures less than 0.1 bar.

The increase in sensitivity is in agreement with the predicted dependence on pressure in eq. (6). At low pressures (below 0.1 bar) some influence of the decrease in thermal conductivity is manifested. This is also confirmed by a small decrease in filament current at constant filament temperature.

Fortunately the noise does not increase at lower pressures. Therefore, it can be concluded that reduction of detector pressure is always better than addition of make-up gas when a lower detector band broadening is required. Compared to make-up gas, a gain up to at least a factor 200 can be obtained. In fact, this corresponds to a reduction of cell volume from 140μl to 0.7 μl (\( F_d = F_c \)). Reduction of detector pressure enables the application of relatively large volume TCD's for high speed analysis with narrow bore columns. An example of a fast separation with a 50 μm i.d. column and TCD detection at reduced pressure (cell volume 140 μl) is given in Figure 2.

Although the micro TCD already has an extremely low cell volume (1.5 nl), the dead volume at the column-detector interface becomes critical when column diameter is reduced to 10 μm. This problem can be solved by reduction of the detector pressure.

Recently we showed a separation on a 10 µm i.d. column with the micro TCD at reduced pressure [4]. Extremely small amounts can be detected with narrow bore columns, because the minimum detectable amount for a concentration sensitive detector (\( F_d = F_c \)) is proportional to \( d_c^2 \).

Using eq. (4) with \( S = 10^4 \) (V ml/g) (atmospheric) and \( R_n = 10^{-6} \) (V) (Varian or micro TCD), it follows that for the 10 μm i.d. column, a peak width at half height of 50 ms and a reduction of pressure proportional to the required detector band broadening, amounts could be detected down to about 4 fg [4].
4.2 Narrow Bore Columns with Photoionization Detection

Despite the low cell volume (40 μl) of the PID used in this study, make-up gas is required even for normal bore (0.2–0.4 mm) columns. Adjusting the make-up gas flow to an acceptable contribution of the detector to the total band broadening will result in a constant minimum detectable amount independent of the column diameter [eq. (7) and (8)].

We measured a minimum detectable amount of about 0.2 pg for aromatics. The sample capacity of, for instance, a 50 μm column with \( d_f = 0.1 \mu \text{m} \) can be estimated to be about 2 ng [8]. Therefore, the dynamic range is still sufficient for 50 μm i.d. columns in combination with the PID.

In contrast with the TCD, it was observed experimentally that the PID sensitivity did not increase at pressures down to 5 mm Hg. Therefore, for the PID the effect of decreasing the pressure on sensitivity and detection limits is equivalent to the use of make-up gas.

Because the PID is a non-destructive detector it can be coupled in series with other detectors. We made a PID-FID series connection with an uncoated deactivated transfer capillary (320 μm i.d., \( L = 0.3 \text{ m} \)) leading directly from the detector cell through the GC oven up to the flame tip of the FID. The total make-up gas flow passes through the transfer capillary, so the extra peak broadening in this capillary is always lower than in the detector cell. The applicability of the PID-FID combination for narrow bore columns (50 μm i.d.) is demonstrated in Figure 3.

4.3 Minimum Column Diameter

When column diameter is reduced sample capacity decreases faster than the minimum detectable amount, resulting in fast overloading of the column. This is illustrated in Figures 4 and 5, where some fast separations with a 10 μm i.d. column and FID detection are given.

The sample was introduced with a cold trap thermodesorption system capable of delivering an input band width as low as 1 ms [2]. It shows that overloading of the stationary phase already occurs close to the detection limit due to the highly reduced dynamic range, especially for higher capacity factors (Figure 5).

In Figure 6 the sample capacity and the minimum detectable amount for various detector types are plotted versus the column diameter. For the sample capacity the theoretical relations and experimental data of Ghijsen [8] and Jaulmes [9] are used. The minimum detectable amount was determined according to the relations of Noij et al. [3]. When the sample capacity is equal to the minimum detectable amount a further reduction of column diameter is useless. In practice the column diameter must be...
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Figure 6
Sample capacity and minimum detectable amount versus column diameter. Plate number 10^5, carrier gas He, phase ratio 200, capacity factor 5.

- A) sample capacity, allowing 10% peak asymmetry;
- B) minimum detectable amount for a FID; \( R_p/S = 10^{-12} \, \text{g/s} \);
- C) minimum detectable amount for a PID with a matched make-up gas flow; \( R_p/S = 10^{-13} \, \text{g/ml} \);
- D) minimum detectable amount for a TCD (cell volume 140 \( \mu \text{m}^3 \)) with a matched make-up gas flow; \( R_p/S = 10^{-15} \, \text{g/ml} \);
- E) minimum detectable amount for a TCD with a matched reduction in pressure; \( R_p/S = 10^{-15} \, \text{g/ml} \) (atmospheric).

well above this point because some dynamic range is needed for real world analysis and reliable quantitation. Although the lines can shift somewhat depending on variables such as plate number, phase ratio, temperature, etc. Figure 6 clearly demonstrates that reduction of column diameter is seriously limited by detector characteristics such as cell volume, sensitivity, and noise.

For example assuming a required dynamic range of 100 the minimum column diameter for a FID is about 25 \( \mu \text{m} \), whereas a TCD allows columns down to about 10 \( \mu \text{m} \).

5 Conclusions
Reduction of cell volume and of detector pressure are equivalent alternative approaches to decrease detector band broadening for thermal conductivity detectors in combination with narrow bore columns. Detection limits in the femtogram range are obtained with column diameters as low as 10 \( \mu \text{m} \).

For photoionization detection the reduction of the cell volume is more critical. The effects of reduced pressures and addition of make-up gas on detection limits are equivalent. A low dead volume photoionization detector (cell volume 40 \( \mu \text{l} \)) could be successfully applied for column diameters down to 50 \( \mu \text{m} \).

Considering the present day detectors and the required dynamic range the limit of the reduction of column diameter is about 10 \( \mu \text{m} \).

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