

# Response characteristics and operating limits of thermal conductivity detectors at reduced pressure in capillary gas chromatography

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## ABSTRACT

The response characteristics of thermal conductivity detectors (TCDs) at reduced pressure, especially in the pressure range 0.2–25 Torr, was studied systematically. It was found that there existed an operational pressure limit ( $P_{\min}$ ) below which the gas flow in the detector cell was no longer laminar and the detector response became pressure dependent. In addition, the noise level increased exponentially as the pressure decreased below  $P_{\min}$ . When the detector was operated at pressures above  $P_{\min}$ , both the responses and relative responses of the TCD were constant for a given concentration of a sample.  $P_{\min}$  as a function of temperature, cell structure and carrier gas properties was interpreted theoretically and verified experimentally. Using this technique, coupling of capillary columns directly with a conventional TCD without make-up gas was realized while maintaining the efficiency of the capillary columns and the concentration sensitivity of the detector.

## INTRODUCTION

The thermal conductivity detector (TCD) has enjoyed great popularity in packed column gas chromatography since the 1950s. Apart from its simple construction, sturdiness, lack of destruction of samples and ease of operation, this detector has a universal nature and the same relative response towards different classes of components of similar molecular size, regardless the differences in their chemical properties. This is different from ionization detectors. Another important feature of the TCD is that it is concentration sensitive, which implies that the minimum detectable concentration with the TCD is independent of the column diameter when the detector cell volume is small enough to be neglected. As capillary columns have replaced

conventional packed columns in almost all gas chromatographic analyses, the combination of the advantages of the TCD with those of capillary columns has significant practical importance.

The main obstacle that prevents the coupling of capillary columns with TCDs has been the stringent requirements on the detector cell volume in capillary gas chromatography. The maximum permissible detector cell volume ( $V_{d,\max}$ ) for a 530  $\mu\text{m}$  I.D. wide-bore capillary column is less than 10  $\mu\text{l}$ , which is far below the cell volume of a conventional TCD. For use with smaller diameter columns, the required condition is even more severe, as  $V_{d,\max}$  is proportional to of the column inner diameter to the power 2–3. One solution to this problem is to add make-up gas to the TCD in order to increase the total gas flow through the cell, but this has the drawbacks of dilution of the column eluent, resulting in a decrease in sensitivity and a reduction in the working range of the column–detector system [1].

Reduction of the cell volume is another solution

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adopted by several groups [2–4]. The 3.5- $\mu\text{l}$  micro-TCD from Hewlett-Packard (Avondale, PA, USA) meets the requirement of capillary columns with I.D.  $\geq 390 \mu\text{m}$ . Make-up gas has to be added when using smaller diameter columns. A TCD fabricated on a silica wafer [2] offers a 1.5-nl cell volume, and can match  $\geq 50 \mu\text{m}$  I.D. capillary columns theoretically. The coupling of a micro-detector with capillary columns of various diameters is difficult as the dead volume of the connection is much larger than the cell volume itself, unless the capillary column and the TCD are fabricated on one silicon wafer. Adding make-up gas in the connecting part can eliminate the effect of the dead volume, but at the same time dilutes the eluent. The dilution becomes more severe when a narrow-bore capillary column is used because the flow ratio of the make-up gas to the eluent is rather high.

A third solution is to reduce the cell pressure. The effective cell volume is reduced by a factor  $P_0/P$ , where  $P_0$  and  $P$  are the atmospheric pressure and cell pressure, respectively. Actually, the use of a TCD at reduced pressure was first reported in 1963 [5] for other purposes. The first successful work on the vacuum operation of a TCD to couple with a capillary column was reported by Shirmmeister [6], and there have been further publications on this subject since then [7–10]. However, there are misunderstandings about the influence of the cell pressure on the detector responses in the low-pressure range, and there is no report of studies of the effect of cell pressure on the detector relative response, noise level and stability of operation and, in particular, the operating limits of the cell pressure. There is also a lack of study of the response characteristics as the pressure under intermediate flow conditions.

In this work, the relationships between cell pressure and the above-mentioned factors were studied systematically. The limit of the operating pressure of a TCD as a function of carrier gas properties and cell structure was determined and interpreted theoretically, and was verified experimentally. The influence of cell pressure on the relative response for molecules with different molecular weights and diameters was also studied.

## THEORY

The ideal flow conditions inside the TCD cell are

laminar, the thermal conductivity of a gas then being independent of pressure [11]. The noise level of a TCD is low and insensitive to pressure changes. As the pressure decreases, the flow pattern changes from laminar to intermediate and then to molecular. The boundaries between these different flows is defined by the value of the Knudsen number, *i.e.*,

$$D/\lambda > 110 \quad \text{laminar flow} \quad (1)$$

$$1 < D/\lambda < 110 \quad \text{intermediate flow} \quad (2)$$

$$D/\lambda < 1 \quad \text{molecular flow} \quad (3)$$

where  $\lambda$  is the mean free path of the gas molecules and  $D$  is the diameter of the tube with sufficient length. In the TCD, the filament is placed in the centre axis of the cylindrical cell and the  $D$  term in above equations is replaced by the radius ( $R$ ) of the cell. As the cell length is short, the above definition is only an approximation.

In the range of intermediate flow, an irregular flow pattern occurs and the degree of irregularity depends on the ratio  $D/\lambda$ . The thermal conductivity of the gas becomes poorer and pressure dependent under these conditions, resulting in higher noise levels and a higher filament temperature when the TCD is operated in the constant-current or constant-voltage mode. The main source of the detector noise comes from the irregular flow when other conditions are fixed, and the noise level is proportional to the degree of irregularity of the flow pattern. In the range of molecular flow, the flow pattern becomes random and the noise level reaches a maximum.

Because the TCD is designed to operate under laminar flow conditions, the lowest cell pressure that can be used in TCD operation is limited by inequality 1. Substituting  $\lambda = 2.33 \cdot 10^{-20} T/(P\phi^2)$  (cm) into inequality 1, we obtain the desired equation,

$$P_{\min} = 2.56 \cdot 10^{-18} T/(R\phi^2) \text{ (Torr)} \quad (4)$$

where  $\phi$  is the molecular diameter of the carrier gas  $R$  is the radius of the TCD cell, and  $T$  is the wall temperature of the cell (K). For a TCD of fixed cell volume, the lower is  $P_{\min}$  the smaller is  $V_e$ , which is what we require.

From eqn. 4, we know that there are three ways to reduce  $P_{\min}$ : (i) using a low operating temperature  $T$ , which is limited by the volatility of the sam-

ple and the column temperature; (ii) increasing the cell radius  $R$ , which also increases the cell physical volume ( $V_o$ ), and the decrease in  $P_{\min}$  cannot compensate for the increase in  $V_e$ ; in fact,  $V_e$  can be reduced efficiently by using a smaller cell radius; and (iii) using a carrier gas of larger molecule size; unfortunately, the optimum carrier gas velocity is also reduced when a large-molecule carrier gas is used, and columns under these conditions require a smaller  $V_{d,\max}$ .

When hydrogen is used as the carrier gas,  $\phi = 2.75 \cdot 10^{-8}$  cm, we have

$$P_{\min} = 3.39 \cdot 10^{-3} T/R \text{ (Torr)} \quad (5)$$

The effective cell volume ( $V_e$ ) therefore cannot be reduced arbitrarily because  $P_{\min}$  sets the lowest limit. As a result, the minimum effective volume  $V_{e,\min}$  is

$$V_{e,\min} = V_o P_{\min}/P_o \quad (6)$$

Only columns for which the maximum permissible detector volume  $V_{d,\max}$  meets the condition  $V_{d,\max} \geq V_{e,\min}$  are suitable for coupling with a TCD without make-up gas. The peak shape will be distorted when using columns with  $V_{d,\max} < V_{e,\min}$ .

## EXPERIMENTAL

A Type 102G gas chromatograph from Shanghai Analytical Instruments (Shanghai, China) was fitted with a common capillary inlet system and a six-port gas sampling valve, which was connected between the carrier gas line and the injection port. Two types of TCD were used. Type I was a four-element flow-through TCD with two cells of total volume  $600 \mu\text{l}$  and  $S = 6000$  from Sichuan Analytical Instruments (Sichuan, China), and type II was a laboratory-made two-element flow-through TCD with a cell volume of  $300 \mu\text{l}$  and  $S = 1500$  [ $S$  is the response of a TCD for a given substance at a given concentration, *i.e.*,  $S = \text{mV}/(\text{mg}/\text{ml})$ , at a noise level  $\leq 20 \mu\text{V}$ ]. The diameters of both types of cells were 3.60 mm. The outlet of the TCD cells was enlarged to 2.0 mm I.D. and was connected via 2.0 mm I.D. copper tubes to a vacuum line through a needle valve, which was used to adjust the cell pressure. A U-tube manometer, connected with the TCD outlet, was used to measure the operating pressure. The cell pressure was then calculated by

using eqns. 3.26 and 3.52 in ref. 11. The accuracy of temperature control of the TCD body was kept at  $\pm 0.01^\circ\text{C}$ .

Cross-linked fused-silica capillary columns were used: (a)  $30 \text{ m} \times 0.25 \text{ mm}$  I.D. SE-30, film thickness  $0.2 \mu\text{m}$ ; and (b)  $14 \text{ m} \times 0.53 \text{ mm}$  I.D. SE-30, film thickness  $1.0 \mu\text{m}$ . A  $15 \text{ cm} \times 50 \mu\text{m}$  I.D. fused-silica tube was used as a restrictor between the analytical column and the TCD to eliminate the effect of low pressure on the column performance and to maintain the mass flow-rate of the carrier gas constant. An empty silica tube with an inside diameter and length identical with those of the analytical column was used on the reference side. Other columns were also used in the examples of applications, and are described in the figure legends.

The carrier gas was high-purity hydrogen (minimum concentration 99.995%). Standard samples were all of analytical-reagent grade. Chromatograms were recorded on a CDMC-2A integrator (Shanghai Research Institute of Computer Technology, Shanghai, China).

## RESULTS AND DISCUSSION

The concept of  $P_{\min}$  is very important for both the design and operation of TCDs. Theoretically, we expected that the detector performance would change drastically when  $P$  varied from  $P > P_{\min}$  to  $P \leq P_{\min}$ . This assumption was examined experimentally in the following way.

### Noise level $V_n$

The influence of the cell pressure ( $P$ ) on the  $V_n$  value of the TCD was studied in the constant-voltage and constant-current modes. For better comparison, the filament bridge current ( $I$ ) was adjusted to about 100 mA at 30 Torr for both operational modes. As the  $\lambda$  value, and hence  $P_{\min}$ , is temperature dependent, the measurement was carried out at two given TCD body temperatures, 60 and  $170^\circ\text{C}$ . The resulting of  $V_n$  versus  $P$  plot in the constant-voltage mode is shown in Fig. 1. The noise remained at a very low level when  $P$  was higher than 15 Torr.  $V_n$  began to increase slowly as  $P$  decreased, and then there was a sharp increase in  $V_n$  at  $P < P_{\min}$ , which was the turning point of the curve. Fig. 2 shows the  $V_n$ - $P$  relationship in the constant-current mode. The turning point of the curve, for

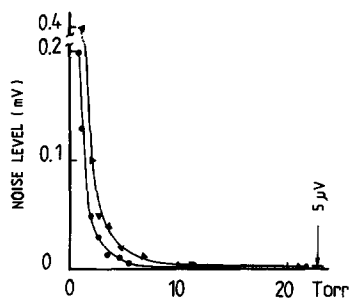


Fig. 1. Plots of detector noise level vs. detector cell pressure for TCD Type I in the constant-voltage mode. TCD body temperature: ● = 60°C; ▲ = 170°C.

the same TCD body temperature, is the same as in Fig. 1, but the change in  $V_n$  was more abrupt. Measurement of the filament resistance indicated that the filament temperature increased near and below  $P_{\min}$  for both operational modes, but was higher for the constant-current mode. The filament temperature in the constant-current mode is shown in Fig. 3A and B for reference. In the theoretical discussion, we expected that  $V_n$  would change drastically near the region of intermediate flow, *i.e.*,  $R/\lambda \leq 110$  or  $P \leq P_{\min}$ . Substituting the experimental conditions of  $R = 0.18$  cm and  $MW(H_2) = 2$  into inequality 5, we found that  $P_{\min}(60^\circ\text{C})$  was 6.3 Torr and  $P_{\min}(170^\circ\text{C})$  was 8.3 Torr. The values agreed well with the experimental results.

Substituting the above  $P_{\min}$  values into eqn. 6, we obtained the values of  $V_{e,\min}$  for the type II TCD, *i.e.*,  $V_{e,\min}(60^\circ\text{C}) \approx 2.5 \mu\text{l}$  and  $V_{e,\min}(170^\circ\text{C}) \approx 3.3 \mu\text{l}$ . The corresponding  $V_{e,\min}$  values were double these for the type I TCD.

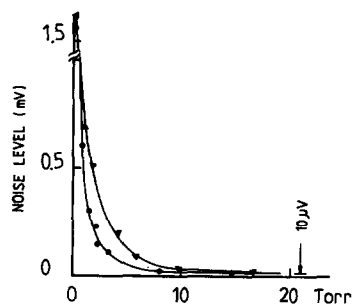


Fig. 2. Plots of the noise level vs. detector cell pressure for TCD type II in the constant-current mode. Body temperature: ● = 60°C; ▲ = 170°C.

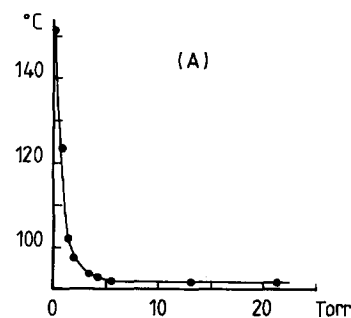
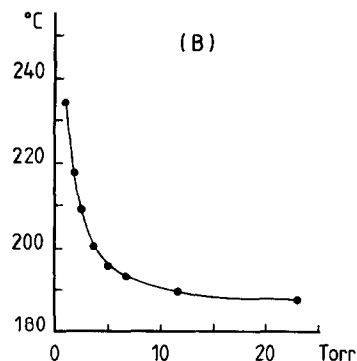


Fig. 3. Relationship between filament temperature and cell pressure in the constant-current mode. TCD type II; body temperature, (A) 60°C and (B) 170°C.

### Responses

The detector response for nitrogen was investigated over a wide pressure range from 550 down to 0.5 Torr. A fixed-volume valve sampling was used in conjunction with fixed split injection after the valve. A constant flow of make-up gas was added to the detector in the pressure range 550–30 Torr, in order to reduce the peak distortion and to keep the mass flow through the detector cell constant. This measure ensured the integration of the concentration profile unchanged for a given amount of sample. A stable detector response for nitrogen was observed in this pressure range, as shown in Fig. 4A. This was in good agreement with theory.

At pressures around and below 30 Torr, no make-up gas was used. The change in column outlet pressure is negligible compared with the column inlet pressure (above 1100 Torr). Further, as the main pressure drop is on the restrictor, the mass flow-rate of carrier gas through the column, and then through the detector cell, was constant at a given

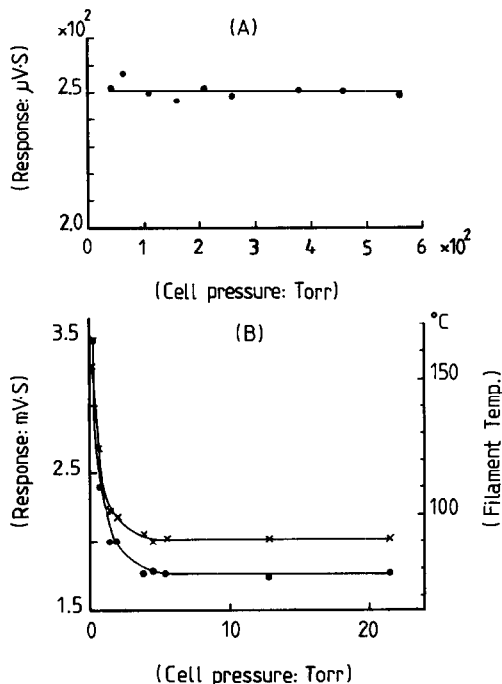


Fig. 4. (A) Detector response to nitrogen. TCD type I, 25°C. Bridge current, 50 mA. Column A, make-up gas flow-rate 25 ml/min. Sample size, 50  $\mu\text{l}$  of pure nitrogen; splitting ratio, 1:100. (B) (●) Plot of the detector response to nitrogen vs. cell pressure and (x) plot of filament temperature at different cell pressures. TCD type I, 60°C, constant-voltage mode. Column B. Sample size, 20  $\mu\text{l}$ ; splitting ratio 1:40.

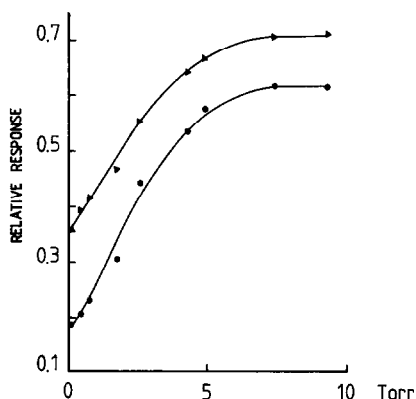


Fig. 5. Plot of detector relative response vs. cell pressure. ▲ = Propane; ● = isobutane. TCD type II, 30°C. Sample, mixture of nitrogen, propane and isobutane. Other conditions as in Fig. 4B.

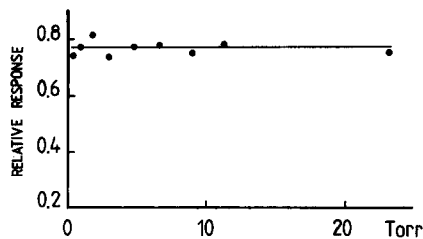


Fig. 6. Plot of detector relative response to  $\text{CCl}_4$  vs. cell pressure. The response is relative to that of nitrogen. TCD, type II, 170°C. Column B. Headspace sampling.

column temperature. Subsequent measurements were all carried out under these conditions.

The response for nitrogen from 22 to 0.5 Torr is demonstrated in Fig. 4B. The response was constant at cell pressures  $P > P_{\text{min}}$ , and increased at  $P \leq P_{\text{min}}$ . The increase in detector response was caused mainly by the increase in filament temperature. Because the noise level increased faster than the response (see Fig. 1), the signal-to-noise ratio was poorer at  $P \leq P_{\text{min}}$ .

The detector responses, relative to nitrogen, for propane and isobutane are shown in Fig. 5. The responses of the sample were pressure dependent until the cell pressure was higher than 7 Torr, which is slightly above  $P_{\text{min}}$ . Another interesting compound was tetrachloromethane ( $\text{CCl}_4$ ). The response of  $\text{CCl}_4$  relative to nitrogen is illustrated in Fig. 6. Because of its fairly constant relative response,  $\text{CCl}_4$  was chosen as the reference com-

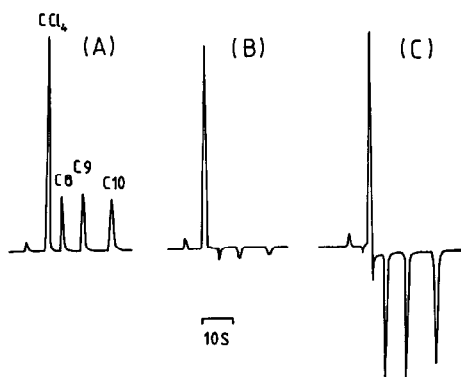


Fig. 7. Detector response to  $\text{CCl}_4$ ,  $n\text{-C}_8\text{H}_{18}$ ,  $n\text{-C}_9\text{H}_{20}$  and  $n\text{-C}_{10}\text{H}_{22}$  at three cell pressures: (A) 3.8, (B) 1.8 and (C) 0.5 Torr. TCD, type II, 170°C. Column B. Sample size, 0.2  $\mu\text{l}$ ; splitting ratio, 1:40.

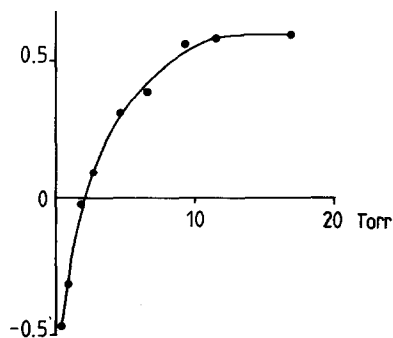


Fig. 8. Plot of detector relative response to  $n\text{-C}_9\text{H}_{20}$  vs. cell pressure. The response is relative to that of  $\text{CCl}_4$ . Other conditions as in Fig. 7.

pound for liquid samples. The high molecular weight ( $\text{MW} = 152$ ) and smaller molecular diameter of  $\text{CCl}_4$  compared with propane and isobutane, suggested that the cross-sectional area of the molecule is the dominant factor in thermal conductance under intermediate flow conditions.

The situation became more complex with samples of larger molecular size. The chromatograms of a four-compound mixture, obtained at three different  $P$  values, are depicted in Fig. 7. The negative peak phenomenon led us study the responses of the compounds more carefully. The example given in Fig. 8 shows the change in the response toward  $n$ -nonane around the intermediate flow region. Note that the response of  $n$ -nonane became zero at 2.0 Torr, then negative at lower pressures. The response became constant at pressures higher than 9.0 Torr. This result demonstrated again that the detector response was normal and stable only at cell pressures higher than  $P_{\min}$ . For convenience, we chose  $1.2P_{\min}$  as the practical pressure limit.

A comparison of the detector relative responses for various compounds at normal pressure (760 Torr) and at 15 Torr is shown in Table I. Peak area

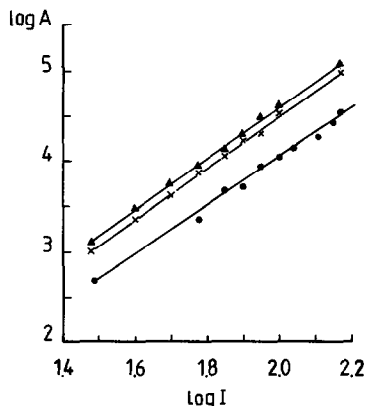


Fig. 9. Detector response ( $A$ ) vs. filament current ( $I$ ). TCD, type II,  $25^\circ\text{C}$ , constant-current mode. Sample, nitrogen. ● = Atmospheric pressure, column  $2\text{ m} \times 2\text{ mm}$  I.D., 60-80 mesh Carbo-sieve B; × = 8 Torr, column A; ▲ = 2 Torr, column A.

( $A$ ) was used in the measurement. The values were correlated with benzene for easy comparison with other published data. The relative responses of the TCD at normal pressure can be used directly in situations with reduced pressure, as long as  $P \geq 1.2P_{\min}$ .

The response (peak area,  $A$ )–filament current ( $I$ ) relationship was also studied using nitrogen as the sample. The lines in Fig. 9, obtained at three different pressures, were parallel to each other. This shows that the relationship  $A = kI^y$  applies and the pressure has no influence on  $y$ . The value of  $y$  is determined by the slope of the  $\log A$  vs.  $\log I$  plot, which was 3.14 in the example.

#### Detection limit

Two detection limits can be given for a detector, the minimum detectable concentration ( $Q_c$ ) and the minimum detectable amount ( $Q_m$ ). At cell pressures higher than  $1.2P_{\min}$ ,  $Q_c$  was constant because the response and the noise level were unchanged in this

TABLE I

RELATIVE RESPONSES OF SELECTED COMPOUNDS AT DIFFERENT PRESSURES

Pressure	$\text{CO}_2$	$\text{CH}_4$	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_4$	$\text{C}_3\text{H}_8$	$\text{C}_3\text{H}_6$	$i\text{-C}_4\text{H}_{10}$	$n\text{-C}_4\text{H}_{10}$	$n\text{-C}_8\text{H}_{18}$	$n\text{-C}_9\text{H}_{20}$	$n\text{-C}_{10}\text{H}_{22}$
15 Torr	1.52	2.01	1.43	1.56	1.24	1.23	1.01	0.97	0.70	0.72	0.71
Normal	1.62	2.04	1.43	1.54	1.23	1.23	1.03	1.00	0.71	0.72	0.71

TABLE II

## THE DETECTOR RESPONSE TO ISOBUTANE AT DIFFERENT CONCENTRATIONS

Measurements were carried out on column B, carrier gas velocity 30 cm/s, column temperature 25°C, sample size 1 ml, splitting ratio 1:150, detector temperature 68°C, detector cell pressure 7.6 Torr, filament bridge current 150 mA, constant-voltage mode. The baseline noise was 0.005 mV.

Concentration (%)	60	6	0.6	0.06	0.006
Response (mV)	540	51	4.4	0.44	0.032

pressure range. Factors affecting  $Q_c$  at reduced pressure are the same as at normal pressure, as discussed thoroughly in 1960s [12]. However, the influence of cell pressure on  $Q_m$  was substantial.  $Q_m$ , the amount of sample of concentration  $Q_c$  entering the TCD cell in unit time, is given by

$$Q_m = Q_c F_d \quad (7)$$

where  $F_d$  was the gas flow-rate through the detector cell.

When the column is coupled directly to the detector without make-up gas,  $F_d = \pi r^2 u P$ , where  $u$  is the linear velocity of the carrier gas at the column outlet and  $r$  is the radius of the column. Substituting  $F_d$  in

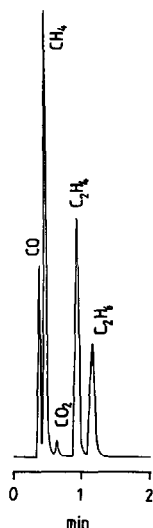


Fig. 10. Chromatogram of the residual gases from an oil refinery plant. TCD, type I, 15 Torr, 120°C. Column, 2 m × 0.46 mm I.D., 60–80 mesh Porapak QS, 50°C. Sample size, 50 μl; splitting ratio, 1:100.

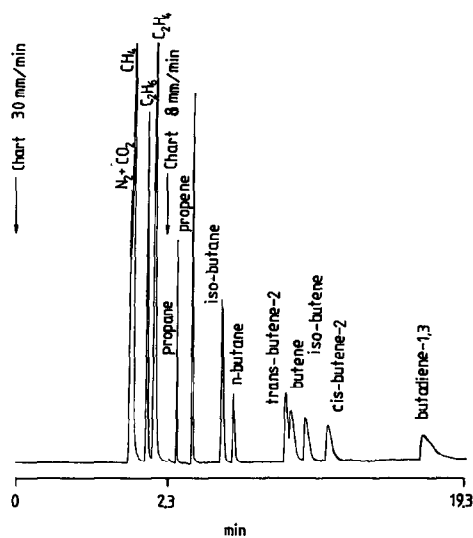


Fig. 11. Analysis of the gas mixture produced in the cracking process in a crude oil refinery. Column, 44 m × 0.46 mm I.D. coated with  $\gamma$ -alumina, 50°C. Others conditions as in Fig. 10.

eqn. 6, we have  $Q_m = \pi Q_c u r^2 P$ . When  $u$  and  $P$  are constant, then

$$Q_m \propto r^2 \quad (8)$$

This means that the smaller the detector cell volume, the lower is  $Q_m$ .



Fig. 12. Chromatogram of a gasoline. TCD, type II, 68°C, 15 Torr. Column B, 68°C. Sample size, 0.1 μl; splitting ratio, 1:50.

The constant  $Q_c$  characteristic of the TCD opened the way to use smaller diameter columns while maintaining the practical sensitivity for a given sample concentration, as long as  $V_{d,max} \leq V_{e,min}$ .

The above discussion was concentrated on the detector itself. The detection limit of column–detector systems has been treated extensively by Noij and co-workers [1,8].

The dynamic range of the TCD at reduced pressure was determined experimentally. Isobutane mixed with hydrogen was used as the sample. Different concentrations of isobutane were prepared by step dilution. Two gas-tight glass syringes of volume 100 ml and 10 ml, were used for the sample mixing and dilution. The syringe was flushed with hydrogen three times before preparing a given concentration of sample. The experimental result, shown in Table II, indicated that the linear range of the response was about four orders of magnitude, and the minimum detectable concentration  $Q_c$  was around 0.01%, at reduced pressure. Both of these characteristics were the same as at normal pressure. The deviation of the data in Table II was caused mainly by the error in the sample concentration.

#### Examples of application

A gas mixture, which had been analysed on a conventional packed column with a TCD of 600- $\mu$ l cell volume, was analysed on a micro-packed capillary column with the same detector operated at 15

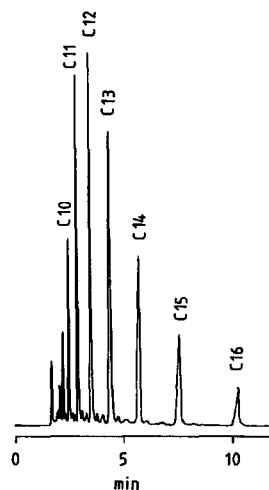


Fig. 13. Analysis of an alcohol mixture. TCD, type II, 15 Torr, 160°C. Column B, 160°C. Other conditions as in Fig. 12.

Torr. The chromatogram is illustrated in Fig. 10; the analysis time was halved and the sample volume injected on to the column was 0.5  $\mu$ l. The effective volume  $V_e$  of the detector at 15 Torr was 11.8  $\mu$ l, much smaller than 600  $\mu$ l but still too large even for the 0.48 mm I.D. column used. As a result, the peaks in Fig. 10 show some extra tailing.

The analysis of the gas mixture released from the cranking process in a oil refinery plant was performed on a PLOT column coated with alumina; the chromatogram is shown in Fig. 11. The TCD cannot be replaced with a flame ionization detector (FID) because the samples contained both hydrocarbons and permanent gases such as nitrogen and carbon dioxide.

The following two samples were analysed using a TCD with a cell volume of 300  $\mu$ l operated at 15 Torr.  $V_e$  of the detector was about 6  $\mu$ l, which is smaller than  $V_{d,max}$  (ca. 6.6  $\mu$ l) of the 0.53 mm I.D. capillary column. The chromatogram of the first fraction of gasoline was shown in Fig. 12, in which the peak shape is satisfactory. The analysis of a higher boiling sample, the raw material for making

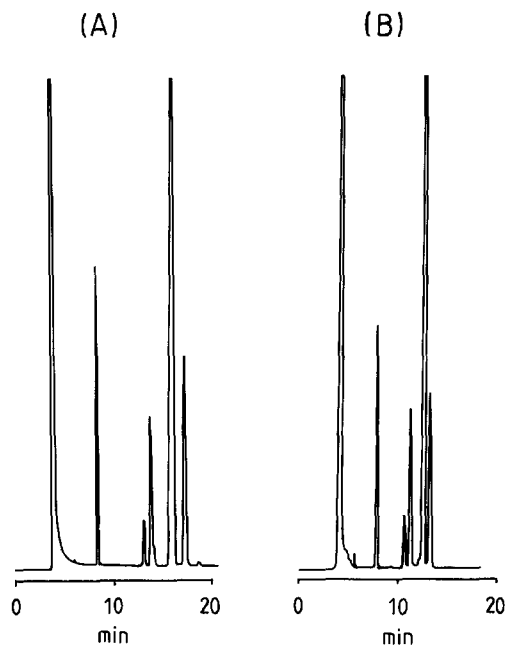


Fig. 14. Comparison of FID and TCD. Sample, esterified evening primrose oil. (A) FID: column, 20 m  $\times$  0.25 mm I.D., PEG-20M, 190°C. (B) TCD: column, 26 m  $\times$  0.46 mm I.D., PEG-20M, 226°C. TCD, type II, 18 Torr, 226°C.



an anti-freeze agent, is illustrated in Fig. 13. The main components of the sample were C<sub>10</sub>–C<sub>16</sub> alcohols.

A comparison of the TCD and FID for the analysis of esterified evening primrose oil is demonstrated in Fig. 14A and B, respectively. The chromatograms were almost identical. As the  $V_{d,max}$  of a 20 m × 0.25 mm I.D. column is about 1.5  $\mu$ l, we had to use a larger diameter column to couple with the TCD ( $V_e \approx 6 \mu$ l).

The wide range of operating temperature of the TCD and the variety of columns used in the five examples demonstrated that capillary columns coupled with TCDs can be used to analyse a broad range of samples. Because the TCD is operated at reduced pressure, the detector can be operated at the same temperature as the column without the problem of sample deposition. In addition, the optimum linear velocity of the carrier gas was much faster at a reduced outlet pressure [13], which will benefit faster analyses.

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