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Design and use of a thermal conductivity detector at reduced pressure for temperature-programmed capillary gas chromatography

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ABSTRACT

Based on a systematic study of the response characteristics of a thermal conductivity detector (TCD) at reduced pressure, a newly designed TCD was constructed and evaluated for use in temperature-programmed capillary gas chromatography. The effective cell volume is as low as 1.3 μl (physical volume 100 μl), and there is no dead corner along the sensing path. Capillary columns of I.D. $\geq$0.25 mm can couple directly with the TCD without a make-up gas. The detector response time is less than 0.1 s, the linear dynamic range is about four orders of magnitude and the detection limit is about 10 ppm (v/v) for octadecane. In the split injection mode, a simple configuration of the capillary inlet system offers a constant carrier gas flow-rate through the column with temperature-programmed operation. Practical examples are given that demonstrate the applicability of this detector and the system.

INTRODUCTION

The advantages of capillary columns over packed columns in the analysis of volatile compounds has led to renewed interest in the thermal conductivity detector (TCD). Although the TCD is well defined [1,2] and is among the most commonly used detectors in packed column gas chromatography, there is still much work to be done in order to apply it in capillary GC. The basic requirements are: (i) reducing the effective cell volume (V_e) of TCD to a few microlitres while maintaining its sensitivity and linear dynamic range; (ii) keeping the baseline of the detector output stable during a temperature-programmed analysis; (iii) maintaining the carrier gas flow constant during temperature programming (TP). This is essential for concentration-sensitive detectors in quantitative analysis.

It is known that the effective cell volume can be reduced substantially when a TCD is operated at low pressure, *i.e.*, $V_e = V_0 P/P_0$, where V_0 is the physical volume of the cell and P and P_0 are the cell pressure and atmospheric pressure, respectively [3,4].

In a previous study on the response characteristics of a TCD at reduced pressure, we found that an operating pressure limit (P_{min}) exists for a TCD [5]. When the operating pressure P is lower than P_{min}, both the absolute response and the relative response of the detector are pressure dependent, and the noise level increases exponentially as the pressure decreases. At $P > P_{min}$, the detector response is stable and insensitive to pressure, and the relative response factors measured at normal pressure can be used directly at lower pressures. An analytical equation was deduced in that study showing the relationship between P_{min} and the cell radius R, cell body temperature T and the molecule cross-section ϕ of carrier gas used, *i.e.*, $P_{min}(\text{Pa}) = 3.41 \cdot 10^{-6} T/$

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($R\phi^2$). These findings prompted us to design and construct a TCD [6] that has superior performance to the conventional TCD.

The intention of this study was to design and evaluate a new TCD, operated at reduced pressure, for use with capillary columns. The detector should meet the above requirements (i) and (ii), and should be as sturdy as a conventional TCD. Further, requirements (iii) has to be fulfilled in order to gain wider applicability.

EXPERIMENTAL

A ShangFen 1102 gas chromatograph (Shanghai Analytical Instrumentation, Shanghai, China) was used. The original TCD was replaced with the new designed detector as shown in Fig. 1. There are two heating blocks in the detector body, one surrounding the TCD cell and the other placed between the TCD cell and the oven. The second one is used for preheating the gases that flow through the detector. This measure ensured that the baseline of the TCD output was stable during the temperature programming of the oven. The capillary inlet system was modified (Fig. 2), a short piece of empty fused-silica tubing being used as the split restrictor, and was placed in the same oven as the analytical column. The splitting ratio was adjusted by changing the length of the restrictor. This configuration, together with the constant-flow controllers originally mounted on the chromatograph, provides a constant gas flow through both the analytical side and the reference side in temperature-programmed analysis. It also keeps the splitting ratio constant during temperature

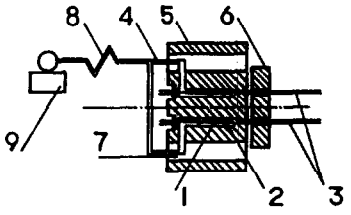

Fig. 1. Schematic diagram of detector system operating at reduced pressure [7]. 1 = Filament; 2 = TCD cell; 3 = inlet; 4 = outlet; 5 = heating block 1; 6 = heating block 2; 7 = heat-insulating material; 8 = restrictor; 9 = vacuum pump.

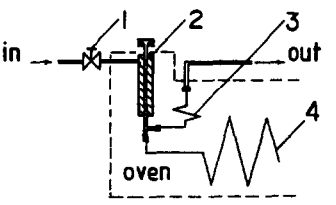

Fig. 2. Schematic diagram of split injection system allowing constant flow through both the analytical column and the reference column with temperature programming. 1 = Constant flow controller; 2 = split injector; 3 = short piece of empty capillary tubing; 4 = analytical column. The reference side is the same as above.

programming. The splitting ratio was about 1:50 in all experiments.

The fused-silica capillary columns used were (A) 50 m × 0.25 mm I.D. OV-101; (B) 25 m × 0.32 mm I.D. cross-linked PEG-20M and (C) 25 m × 0.25 mm I.D. cross-linked OV-1.

High-purity hydrogen (minimum concentration 99.999%) was used as the carrier gas.

RESULTS AND DISCUSSION

Design considerations for the TCD cell

The physical volume of the detector cell was 100 μl. It was designed to operate at pressures in the range 140–540 Pa for use with capillary columns. It can also be used at normal pressure with packed columns. To reduce the flow disturbances both at the gas inlet and outlet region within the cell, we took the following measures: the inlet gas flow was along the axis of the cell, and hence the filament; the hole of the outlet had the same diameter as the cell; and the position of the hole was at the end part of the filament support. Hence there was no dead corner and no abrupt change of gas flow along the sensing path. The noise level of the detector was only one quarter of that of the conventional type [5]. The minimum detectable concentration with this detector was 10 ppm for n-C_{16} and n-C_{18} at a TCD body temperature of 200°C and a bridge current of 120 mA, as was shown in Fig. 3.

The pressure P of the TCD cell has to be kept at $P \geq 1.2P_{min}$. To meet this criterion, a restrictor was placed between the outlet of the cell and the vacuum line. In principle, P should be as low

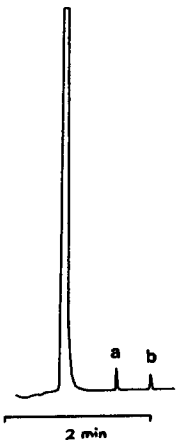

Fig. 3. Test for sensitivity of the detector. Sample: (a) n-C_{16} and (b) n-C_{18} in octane, 30 ppm (v/v) for each. TCD, 200°C, 120 mA; column, 30 m × 0.32 mm I.D. cross-linked SE-54 at 140°C.

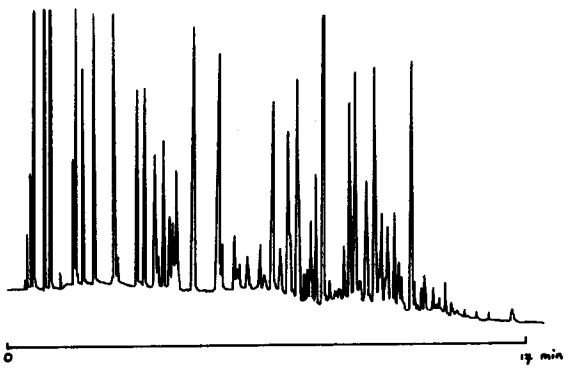

Fig. 4. Chromatogram of naphtha on column A. Initial temperature 50°C, maintained for 2 min, then programmed to 140°C at 2°C/min. TCD temperature, 200°C.

as possible in order to reduce V_e, and the restrictor should be adjustable, such as with a vacuum needle valve, to control the cell pressure when using a column with a different diameter or on changing the flow-rate. A pressure gauge is also needed to indicate the cell pressure [5]. This measure will increase the complexity for both instrumentation and operation. We simplified the pressure control by using only one fixed restrictor, which just met $P = 1.2P_{min}$ at a column I.D. of 0.25 mm. When larger diameter columns are used, P and hence V_e will increase. However, the maximum permissible detector volume $V_{d,max}$ is proportional to $(\text{I.D.})^n$, where $n = 2–3$ [8], so the increase in V_e is slower than that of $V_{d,max}$, *i.e.*, $V_e \leq V_{d,max}$ for columns with I.D. ≥ 0.25 mm.

Baseline drift during TP

As the two filaments of the TCD were not identical, two factors can influence the baseline drift in TP operation: the change in inlet gas temperature caused by the oven temperature programming, and the change in carrier gas flow-rate because of the temperature dependence of the viscosity of gases. The heating block 2 in Fig. 1 was used to compensate for the first factor, and the constant flow control system was used not only for quantitative analysis but also for stabilizing the baseline. Fig. 4 demonstrates the temperature-programmed analysis of a naphtha sample using this detector. The drift of the baseline is very small, in contrast to the constant inlet pressure mode, where the baseline shows a *ca.* 1 mV drift under the same TP conditions. The first two peaks in Fig. 4 are air and water peaks (the identities of the two peaks were established by GC–MS), which are undetectable with flame ionization detection (FID). The column inlet pressure showed a >80% increase when the column temperature raised from 50 to 140°C.

Accuracy of quantitative analysis with TP

For concentration-sensitive detectors, there is an additional requirement for flow control in TP operation. Normally it is very difficult to maintain a constant flow control to within *ca.* 1 ml/min, so we used the strategy of keeping the splitting ratio constant and controlling the total mass flow (shown in Fig. 2). The influence of this control on the accuracy of quantitative analysis was examined with a series of n-alkane mixtures analysed using both isothermal and TP operation. The results of the area percentage reports from the integrator and their elution temperatures (T_r) calculated from their elution times are given in Table I. The differences in the results of the isothermal and TP runs are caused mainly by the change in carrier gas flow-rate, which depends on the quality of the constant mass flow controller. The error was within 1% in the test, but when constant inlet pressure control is used the error can exceed 50% in the same TP operation.

TABLE I

PERCENTAGE PEAK AREAS (A) AND THE ELUTION TEMPERATURES (T_r) OF n-ALKANES MEASURED UNDER ISOTHERMAL (150°C) AND TP CONDITIONS (80°C FOR 2 min, THEN PROGRAMMED TO 160°C AT 8°C/min)

n-Alkane	A		T_r (°C)
	Isothermal	TP	
n-C_{10}	16.3	16.2	123.1
n-C_{11}	12.5	12.3	136.7
n-C_{12}	15.3	15.1	150.2
n-C_{13}	33.0	33.2	160.0
n-C_{14}	22.9	23.2	160.0

Examples of application

The chromatogram shown in Fig. 4 is for a real sample analysis. Because of the universal response characteristics of the TCD, the water content in naphtha was also determined in a single run.

The analysis of esterified evening primrose oil was carried out under isothermal conditions, and the resulting chromatogram is shown in Fig. 5. The same sample was also analysed under the same column conditions but using FID (chromatogram not shown), and the peak area of γ-linolenic acid was 6.5% lower than that obtained with the TCD because of the relatively low response factor of this compound in FID. The TCD response factors for molecules having similar cross-sections are the same, which benefits quantitative analysis, particularly when pure standard samples are not available.

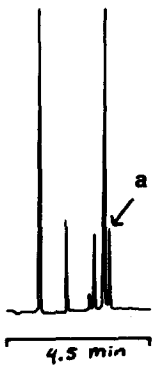

Fig. 5. Analysis of evening primrose oil on column B at 210°C. TCD temperature, 250°C. a = γ-linolenic acid.

Fig. 6. Chromatogram of C_4 mixture used as lighter fuel. Column C at 50°C.

Fig. 6 shows the rapid analysis of a gas mixture containing air, isobutane, n-butane and butene. This experiment was used to test the response speed of the detector. Note the time scale in the chromatogram.

The last example examined was a synthetic essential oil. It was originally analysed with FID and GC–MS. The components in the sample contained O, N and rings, but the exact positions of some functional groups were not known and several standards were unavailable in our laboratory. The relative response factors were set to unity for all of the components, based on the consideration that the molecular mass of all the components exceeded 240. This sample was then analysed with the TCD (Fig. 7). Unexpectedly,

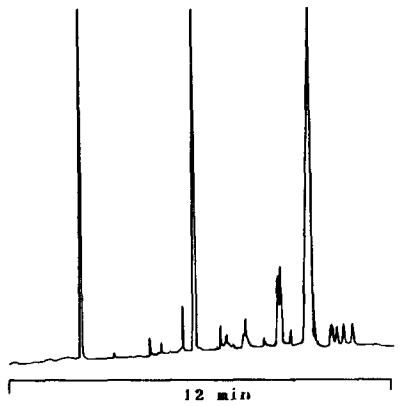

Fig. 7. Quantitative analysis of synthetic essential oil on column A with TCD detection. Column temperature, 200°C; detector temperature, 220°C; bridge current, 150 mA.

the quantitative results were different from the former data. We believe the accuracy of the latter analysis was better for this sample, for reasons explained above for the second example.

More important applications of this detector system are the quantitative analysis of natural gas and other gas mixtures containing inorganic gases. This aspect is under study.

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