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NEW RESULTS WITH A FLOW-IMPEDANCE BRIDGE DETECTOR

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SUMMARY

A new version of a pneumatic analogue of the Wheatstone bridge as a gas chromatographic detector is described. The detector response is defined in terms of the viscosity difference between the carrier gas and the mixture of carrier gas and solute, and the volume of this gas mixture. A relationship is derived between the measured surface area and the amount of pure solute injected.

INTRODUCTION

In a previous paper¹ we reported the results of some preliminary experiments with a new version of a flow-impedance bridge detector for gas chromatography (GC)^{2,3}. This detector is based on the dependence of the flow resistance of a capillary on the nature of the gas. Four equal capillaries are circuited in a Wheatstone-like bridge. A flow diagram of the detector is shown in Fig. 1.

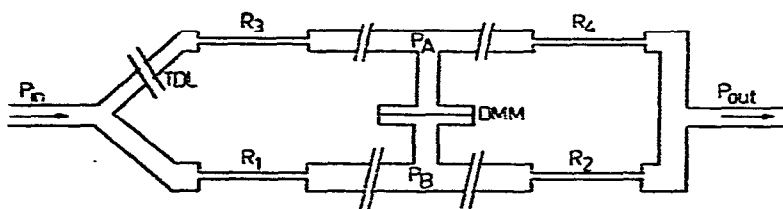


Fig. 1. Flow diagram of the detector.

R₁, R₂, R₃ and R₄ are the capillaries and P_{in} and P_{out} are the pressures at the inlet and outlet of the detector, respectively. TDL represents the time delay line and DMM the differential manometer that measures the difference between the pressures P_A and P_B. A single injection of a solute-carrier gas mixture into the flow of carrier gas through the detector results in four peaks in the output. These four peaks correspond to the passage at different times of the gas mixture through the capillaries. This shift is obtained with the time delay line. Using the experimental data collected with this prototype, a new apparatus has been developed, in the response of which

only the first of the four peaks remains. This was achieved by increasing all over the detector the effects of mixing and diffusion, except for the connection between the detector inlet and the capillary R_1 , which is made smooth in order to maintain a sharp first peak.

In this paper we describe the properties of the detector and present some results that have been obtained.

DETECTOR RESPONSE

We shall describe the response of the detector upon a single injection of a solute-carrier gas mixture, resulting in a variation of the viscosity at the inlet of the detector, as shown in Fig. 2. The time interval t_m in Fig. 2 satisfies the equation

$$t_m = \frac{V_m}{\Phi_D} \quad (1)$$

where V_m represents the volume of the gas mixture injected and Φ_D the flow-rate of

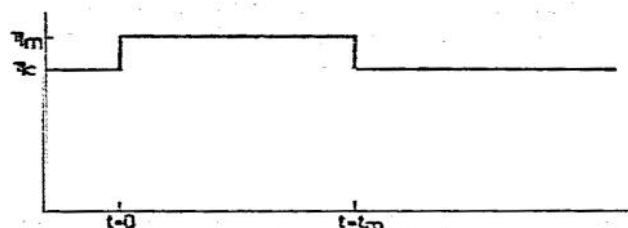


Fig. 2. Viscosity variation at the inlet of the detector as a function of time.

carrier gas through the detector. Throughout we shall restrict the discussion to those situations where four restrictions hold:

$$(i) P_{in} - P_{out} \ll P_0$$

with

$$P_0 = \frac{P_{in} + P_{out}}{2}$$

$$(ii) \eta_m - \eta_c = \eta_d \ll \eta_c$$

where η_m and η_c are the viscosities of the gas mixture and carrier gas, respectively;

(iii) the time interval t_{cap} needed for the front of the gas mixture to pass a capillary is small compared with all time intervals used in the calculations; and

(iv) the Poiseuille equation can be used in the following way:

$$\Phi_{cap} = \frac{\alpha}{\eta} \cdot P_{cap} \quad (2)$$

with $\alpha = \pi r^4 / 8l$, where Φ_{cap} is the flow through and P_{cap} the pressure drop across a capillary of radius r and length l .

In the calculations of the response we require the specifications of the differential manometer. As the two compartments of the manometer are separated by a flexible membrane, the two volumes of the compartments will be dependent on the pressure difference between them. The volumes of compartments A and B can be expressed by the equations

$$V_A = V_0 + \beta(P_A - P_B) \quad (3a)$$

$$V_B = V_0 - \beta(P_A - P_B) \quad (3b)$$

where β is the compliance of the membrane of the manometer ($\beta = \partial V/\partial P$). V_0 includes those volumes which are directly connected to the compartments.

The pressure difference, $P_A - P_B$, caused by the injection can be expressed by

$$P_A - P_B = -\frac{\eta_d}{\eta_c} \cdot \frac{P_{in} - P_{out}}{4} \cdot (1 - e^{-t/\tau}) \quad (4)$$

with

$$\tau = \frac{\eta_c V_0}{2\alpha P_0} \left(1 + \frac{2\beta P_0}{V_0}\right)$$

where $t = 0$ is the time when the front of the gas mixture arrives at the capillary R_1 . For $t > t_m$ the pressure difference $P_A - P_B$ decreases exponentially to zero. Assuming $t_m > \tau$ we can describe the detector response by (see Fig. 3)

$$P_A - P_B = -\frac{\eta_d}{\eta_c} \cdot \frac{P_{in} - P_{out}}{4} \cdot (1 - e^{-t/\tau}) \quad 0 \leq t \leq t_m \quad (5a)$$

$$P_A - P_B = -\frac{\eta_d}{\eta_c} \cdot \frac{P_{in} - P_{out}}{4} \cdot e^{-(t-t_m)/\tau} \quad t > t_m \quad (5b)$$

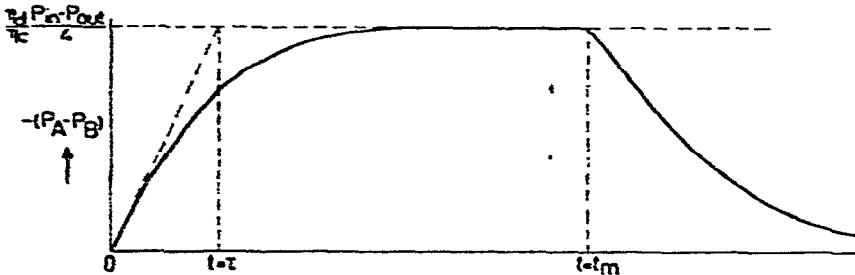


Fig. 3. Detector response on an injection, assuming $t_m > \tau$.

Another situation where we can easily calculate the detector response is characterized by $t_m \ll \tau$. We can then use the linear approximation of eqn. 5a, giving (see Fig. 4)

$$P_A - P_B = -\frac{\eta_d}{\eta_c} \cdot \frac{P_{in} - P_{out}}{4} \cdot \frac{t}{\tau} \quad 0 \leq t \leq t_m \quad (6a)$$

$$P_A - P_B = -\frac{\eta_d}{\eta_c} \cdot \frac{P_{in} - P_{out}}{4} \cdot \frac{t_m}{\tau} \cdot e^{-(t-t_m)/\tau} \quad t \geq t_m \quad (6b)$$

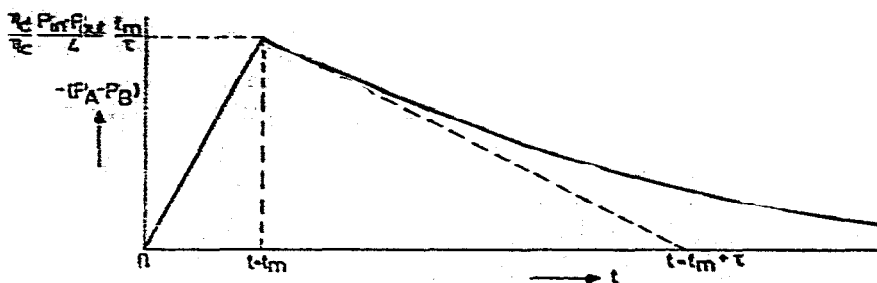


Fig. 4. Detector response on an injection, assuming $t_m \ll \tau$.

Considering Fig. 3, it will be of interest to calculate the surface area, S , of the peak. With the additional condition $t_m \gg \tau$ we shall relate this surface area to the volume, V_s , of pure solute (viscosity η_s) in the injected gas mixture. We further assume a linear relationship between η_d and the concentration of solute in the carrier gas:

$$\eta_d V_m = (\eta_s - \eta_c) V_m = (\eta_s - \eta_c) V_s \quad (7)$$

For the surface area, S , we obtain

$$S = \int_0^{\infty} (P_A - P_B) dt = (P_A - P_B) t_m = -\frac{\eta_d}{\eta_c} \cdot \frac{P_{in} - P_{ext}}{4} \cdot t_m \quad (8)$$

Making use of eqns. 1, 2 and 7, we have

$$S = -\frac{\eta_d V_m}{4\alpha} = -\frac{\eta_s - \eta_c}{4\alpha} \cdot V_s \quad (9)$$

Eqn. 9 indicates that the detector can be used for quantitative purposes. If we know the values of the viscosities η_s of the pure solute and η_c of the carrier gas at pressure P_0 , the measured value of the surface area, S , leads to the volume, V_s , that the pure solute will have at the same pressure. It should be noticed that with a non-linear relationship between the composition and viscosity of the gas mixture, corrections are necessary.

To ascertain the detection limit, ΔV_s , of the pure solute, we start with the uncertainty, ΔS , of the surface area caused by the manometer noise, ΔP :

$$\Delta S = t_m \Delta P \quad (10)$$

Using eqn. 9 and taking the signal-to-noise ratio as $S/N = 1$, we obtain

$$\Delta V_s = \frac{4\alpha}{\eta_s - \eta_c} \cdot t_m \Delta P \quad (11)$$

For the purpose of estimation, we use $t_m = \tau$ and obtain

$$\Delta V_s = \frac{2\eta_c}{\eta_s - \eta_c} \left(1 + \frac{2\beta P_0}{V_0}\right) V_0 \cdot \frac{\Delta P}{P_0} \quad (12)$$

The same result can be obtained by using eqn. 6a with $t = t_m$ and $S/N = 1$.

EXPERIMENTAL

The capillaries of the bridge are made of stainless steel with an I.D. of 0.038 cm and a length of 10.75 cm, leading to $\alpha = (4.76 \pm 0.04) 10^{-9} \text{ cm}^3$. The time delay line consists of a nylon tube with an I.D. of 0.4 cm and a length of 100 cm. This type of tube is also used to connect R_1 with R_2 and R_3 with R_4 , both connections having a length of 50 cm. As the volume of a manometer compartment is about 1 cm^3 , we have $V_0 = 7.3 \text{ cm}^3$. For the compliance of the manometer membrane we use $\beta = 1.1 10^{-2} \text{ cm}^3/\text{torr}$. P_{out} is atmospheric pressure and $P_{\text{in}} - P_{\text{out}}$ has a maximum value of 1 torr, so $P_0 = 760 \text{ torr}$. The values of the time constant, τ , of the detector are 0.44 and 0.39 sec with nitrogen and helium, respectively, as the carrier gas. Three different systems are used for injecting the solute into the flow of carrier gas (see Fig. 5):

- (i) syringe, $V_{\text{inj}} \leq 50 \mu\text{l}$ (Fig. 5a);
- (ii) injection valve, $230 \mu\text{l} \leq V_{\text{loop}} \leq 1120 \mu\text{l}$ (Fig. 5b);
- (iii) syringe in combination with a splitter (Fig. 5c); division factor $K = \Phi_D / (\Phi_D + \Phi_R)$.

All of the experiments were performed at room temperature.

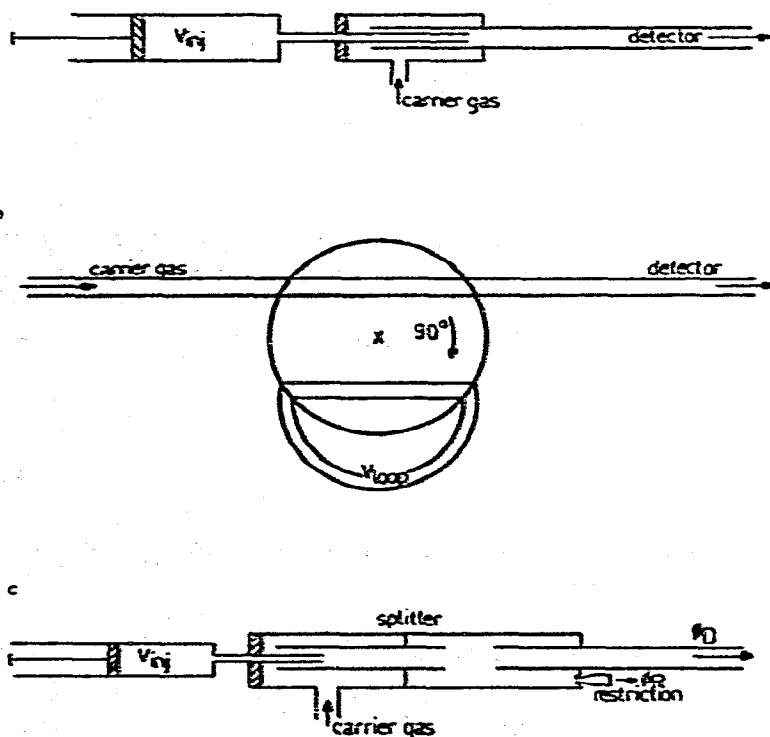


Fig. 5. Injection systems used in the experiments.

RESULTS AND DISCUSSION

Experiments were performed with nitrogen as carrier gas and oxygen as solute. This combination of gases was chosen because of the fairly linear relationship between the concentration of oxygen in nitrogen and the viscosity of the mixture⁶. Injection systems (i) and (ii) were used and directly coupled to the detector (see Fig. 6a). In Fig. 7, the measured values of the surface area under the peak are

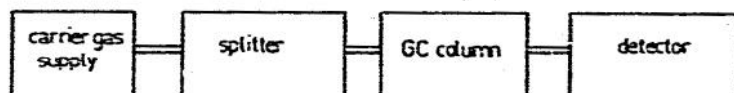
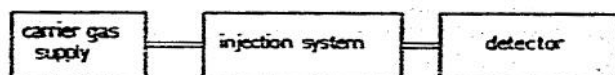


Fig. 6. Schematic illustration of the experimental arrangement.

shown as a function of the volume of oxygen injected. The volume V_0 in Fig. 7b represents the dead space of the injection valve. The slope of the lines in Fig. 7 is

$$\left(\frac{dS}{dV_s}\right)_{\text{exp}} = -(1.11 \pm 0.01) \cdot 10^{-3} \text{ torr} \cdot \text{sec}/\mu\text{l} \quad (13)$$

Calculating this slope with eqn. 9 we obtain

$$\left(\frac{dS}{dV_s}\right)_{\text{th}} = -\frac{\eta_s - \eta_c}{4\alpha} \quad (14)$$

Substitution of $\eta_s = \eta_{\text{O}_2} = (1.528 \pm 0.006) \cdot 10^{-7} \text{ torr} \cdot \text{sec}$ and $\eta_c = \eta_{\text{N}_2} = (1.322 \pm 0.006) \cdot 10^{-7} \text{ torr} \cdot \text{sec}$ leads to

$$\left(\frac{dS}{dV_s}\right)_{\text{th}} = -(1.08 \pm 0.07) \cdot 10^{-3} \text{ torr} \cdot \text{sec}/\mu\text{l} \quad (15)$$

The agreement with the experimental value is good.

To test the detector in combination with a gas chromatographic column, the arrangement shown in Fig. 6b was applied. The splitter in this arrangement enables

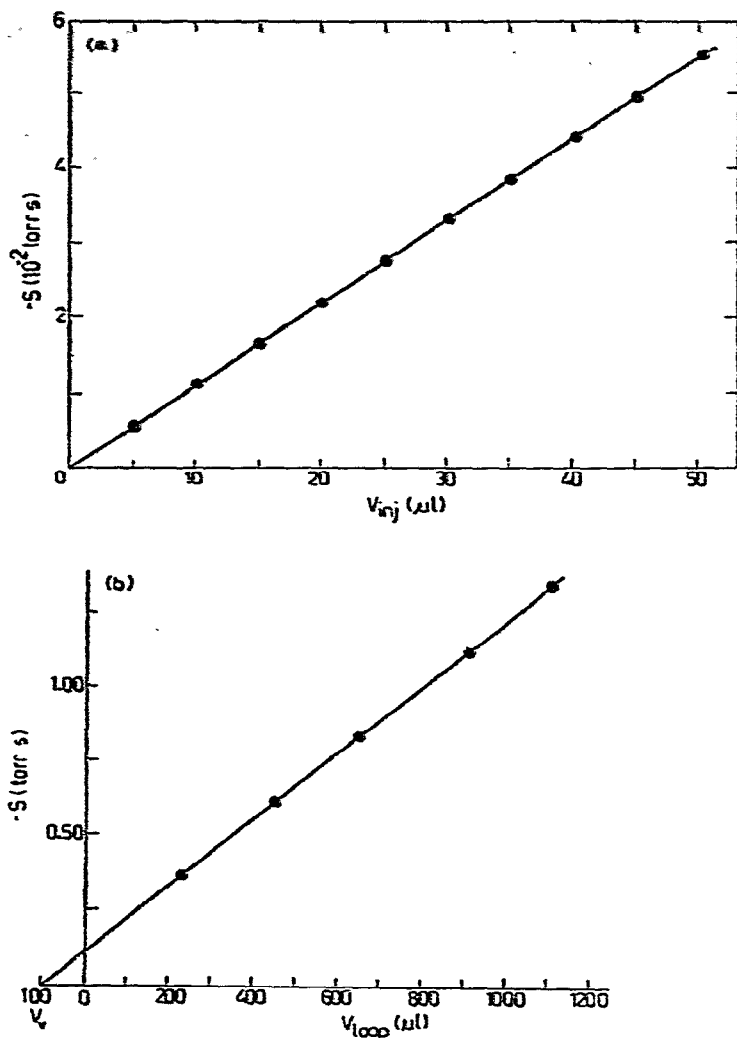


Fig. 7. Plots of the measured surface area of oxygen against the volume of oxygen injected, with nitrogen as carrier gas. $\Phi_D = 10^{-2}$ ml/sec.

us to inject the column solute volumes, V_s , that are much smaller than the syringe volumes, V_{inj} :

$$V_s = KV_{inj} \quad (16)$$

where $K \approx 10^{-2}$.

Helium was used as the carrier gas and natural gas as the solute and the GC column (50 m \times 0.02 cm I.D.) contained squalane. As this work was not concerned with optimization of the GC column but rather the exploitation of the detection principle, optimal conditions from the viewpoint of column efficiency were not sought.

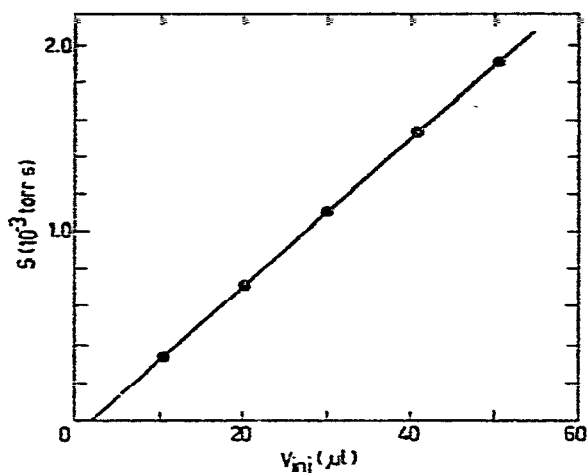


Fig. 8. Plot of surface area of natural gas against the volume injected. Conditions: helium as carrier gas; $K = 7.4 \cdot 10^{-3}$; $\Phi_D = 10^{-2}$ ml/sec.

In Fig. 8 the measured values of the surface area are plotted against the volumes of natural gas injected. The fact that the line in Fig. 8 does not pass through the origin is due to the dead space in the syringe, which has to be taken into account because of the excess pressure (2.5 atm) in the splitter. The slope of the line through the measured points satisfies the equation

$$\left(\frac{dS}{dV_{inj}} \right)_{exp} = (3.93 \pm 0.05) \cdot 10^{-5} \text{ torr} \cdot \text{sec}/\mu l \quad (17)$$

According to eqns. 9 and 16, this slope is given by

$$\left(\frac{dS}{dV_{inj}} \right)_{th} = - \frac{\eta_s - \eta_c}{4\alpha} \cdot K \quad (18)$$

where $K = 7.4 \cdot 10^{-3}$. To be able to compare this with the experimental value, we need to know the value of $\eta_s - \eta_c$. Because of the non-linear relationship between the viscosity and the concentration of natural gas in helium, we cannot use the difference between the viscosities of the pure gases. As the concentrations of natural gas that are found in the detector are below 2%, we use the linear extrapolation of the low concentration data, resulting in $\eta_s - \eta_c = - (1.06 \pm 0.03) \cdot 10^{-7}$ torr·sec. Substitution of this value in eqn. 18 leads to

$$\left(\frac{dS}{dV_{inj}} \right)_{th} = (4.1 \pm 0.2) \cdot 10^{-5} \text{ torr} \cdot \text{sec}/\mu l \quad (19)$$

This is in good agreement with the experimental value.

To estimate the experimental detection limit, ΔV_D , the measured response from an injection of $10 \mu l$ of natural gas in helium is shown in Fig. 9, which corresponds with the experiment at the lowest value of V_{inj} , as shown in Fig. 8. From Fig. 9 we can estimate the noise, ΔP , of the manometer to be 10^{-5} torr. Owing

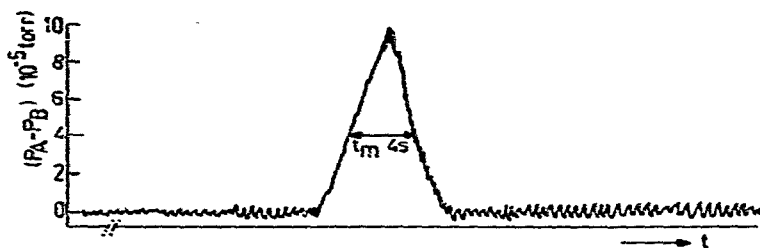


Fig. 9. Detector response on injection of $10 \mu\text{l}$ of natural gas. Conditions: helium as carrier gas; $K = 7.4 \cdot 10^{-3}$; $\Phi_D = 10^{-2}$ ml/sec.

to the splitter, only $0.08 \mu\text{l}$ of the injected volume of $10 \mu\text{l}$ reaches the detector. It can be seen in Fig. 9 that the peak is well above the noise level and that a gain of one order of magnitude is possible, giving $(\Delta V_s)_{\text{exp}} = 8 \cdot 10^{-3} \mu\text{l}$.

This value is also found when calculating ΔV_s with eqn. 11 and substitution of $t_m = 5$ sec. According to eqn. 11, smaller values of ΔV_s should be possible when using smaller values of t_m . The limit of this gain is reached as $t_m = \tau$ and satisfies, according to eqn. 12, $(V_s)_{\text{th}} = 9 \cdot 10^{-4} \mu\text{l}$.

The chromatogram shown in Fig. 10 was obtained by injecting $60 \mu\text{l}$ of a mixture containing air and hydrocarbons into a flow of helium, and using the arrangement shown in Fig. 6b.

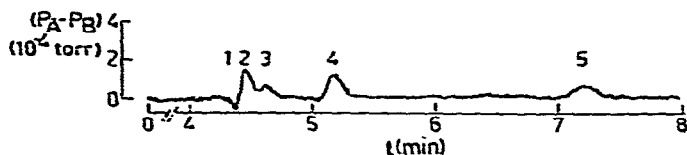


Fig. 10. Chromatogram obtained by injecting $60 \mu\text{l}$ of a mixture containing air and hydrocarbons. Conditions: helium as carrier gas; $K = 10^{-2}$; $\Phi_D = 10^{-2}$ ml/sec. Peaks: 1 = air; 2 = methane; 3 = ethane; 4 = propane; 5 = butane.

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