

CHROM. 10,030

PROPERTIES OF THE FLOW-IMPEDANCE BRIDGE DETECTOR

JOSEF NOVÁK and JAROSLAV JANÁK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

(Received February 16th, 1977)

SUMMARY

A pneumatic analogue of the Wheatstone bridge as a gas chromatographic detector is described. The detector response is defined in terms of the resistances of the bridge flow-impedance elements and the concentration of the solute in the column effluent. Conditions are discussed under which the flow disturbances due to viscosity changes within the column can be eliminated.

INTRODUCTION

Changes in the composition of a fluid passing at a given velocity through a flow-impedance element may result in changes in the pressure drop across the element. The possibility of utilizing this phenomenon for detecting gas chromatographic (GC) fractions was first shown by Griffiths *et al.*¹ in 1952. Later we described a flow-impedance bridge as a GC detector^{2,3}, which was applied successfully to the detection of metal vapours separated by GC at temperatures up to 1100°^{4,5}. Recently, a paper describing a more sophisticated version of this detector appeared⁶, in which the authors expressed doubts about whether the arrangement suggested earlier by us^{2,3} could compensate for the effects of the flow variations due to the viscosity changes of the gas in the column when a chromatographic fraction is passing through it. They also demonstrated these effects by an example.

In this paper, we specify the properties of the flow-impedance bridge detector and present some results of our earlier measurements⁷ with it.

ARRANGEMENT OF A CHROMATOGRAPH WITH THE FLOW-IMPEDANCE BRIDGE DETECTOR

A flow diagram of the equipment is shown in Fig. 1. The variable resistor R_v serves to control the flow-rates of the carrier gas through the column (v_c) and through the bridge proper ($v_{1,2}$ and $v_{3,4}$). The series resistor R_s functions as a source of flow; thus, if the pneumatic resistance of R_s is substantially greater than that of the column, the flow-rate of the gas leaving the column is virtually independent of the changes in the impedance of the latter. Under these circumstances, the presence of the solutes in the column does not cause any appreciable flow disturbances. R_1 , R_2 , R_3 and R_4

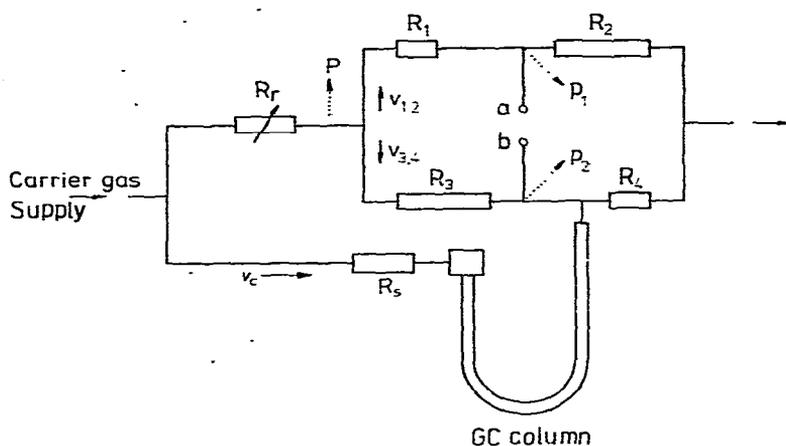


Fig. 1. Flow diagram of a gas chromatograph with the flow-impedance bridge detector.

are the flow-impedance elements constituting the bridge, R_4 being the sensor proper. The response of the detector to the eluates is measured as a change in the difference between the excess pressures p_2 and p_1 . P is the excess pressure at the inlet of the bridge. By setting the ratio $v_c/(v_{1,2} + v_{3,4})$ appropriately, the bridge can be balanced out.

DETECTOR RESPONSE

Employing the notation R_1, R_2 , etc., also for the pneumatic resistances of the respective elements of the bridge, p_2 and p_1 can be expressed by

$$p_2 = R_4 \cdot \frac{P + R_3 v_c}{R_3 + R_4} \quad (1)$$

and

$$p_1 = P \cdot \frac{R_2}{R_1 + R_2} \quad (2)$$

and for v_c with the bridge being balanced out we have

$$v_c^* = P \cdot \frac{R_2 R_3 - R_1 R_4}{R_3 R_4 (R_1 + R_2)} \quad (3)$$

where the asterisk indicates that the equation applies to the special case when $p_2 = p_1$.

Denoting the out-of-balance response by \mathcal{R}_0 , the response to the solute-carrier gas mixture by \mathcal{R}_{i0} and the net response to solute i by \mathcal{R}_i , we can write

$$\mathcal{R}_0 = p_{2,0} - p_1$$

$$\mathcal{R}_{i0} = p_{2,i0} - p_1$$

and

$$\mathcal{R}_i = \mathcal{R}_{i0} - \mathcal{R}_0 = p_{2,i0} - p_{2,0} \quad (4)$$

where $p_{2,0}$ and $p_{2,i0}$ are the values of p_2 measured when the sensor (R_4) is being passed through by the carrier gas alone and by the mixture of solute and carrier gas, respectively. Hence, with regard to eqns. 1, 2 and 4, \mathcal{R}_i can be expressed as

$$\mathcal{R}_i = (P + R_3 v_c) \left(\frac{R_{4,i0}}{R_3 + R_{4,i0}} - \frac{R_{4,0}}{R_3 + R_{4,0}} \right) \quad (5)$$

where $R_{4,i0}$ and $R_{4,0}$ are the flow impedances of the sensor R_4 in the situations specified with $p_{2,i0}$ and $p_{2,0}$, respectively. If $R_{4,i0} - R_{4,0} \ll R_{4,0}$, eqn. 5 can be simplified to

$$\mathcal{R}_i = R_3 \cdot \frac{P + R_3 v_c}{(R_3 + R_{4,0})^2} (R_{4,i0} - R_{4,0}) \quad (6)$$

and for a balanced-out bridge (cf., eqn. 3) the response (\mathcal{R}_i^*) is

$$\mathcal{R}_i^* = \frac{PR_2 R_3 (R_{4,i0} - R_{4,0})}{R_{4,0} (R_3 + R_{4,0}) (R_1 + R_2)} \quad (7)$$

Provided that the measuring resistor is a capillary, we can write, according to the Poiseuille equation:

$$R_{4,i0} - R_{4,0} = R_{4,0} (\eta_{i0} - \eta_0) / \eta_0 \quad (8)$$

where η_{i0} and η_0 are the dynamic viscosities of the solute-carrier gas mixture and of the carrier gas alone, respectively. Further, η_{i0} is given by⁸

$$\eta_{i0} = \frac{\eta_0}{1 + A_{i0} \cdot \frac{y_i}{1 - y_i}} + \frac{\eta_i}{1 + A_{0i} \cdot \frac{1 - y_i}{y_i}} \quad (9)$$

where η_i and y_i are the viscosity of pure gaseous solute and the molar fraction of the solute in the mixture being detected, and A_{i0} is given by

$$A_{i0} = 1.055 \left(\frac{\sigma_i + \sigma_0}{2\sigma_0} \right)^2 \left(\frac{2M_i}{M_i + M_0} \right)^{\frac{1}{2}}$$

where σ_i , σ_0 , M_i , and M_0 are the molecular collision diameters and the molecular weights of the gaseous solute and of the carrier gas, respectively; A_{0i} is obtained by replacing σ_0 in the denominator and M_i in the numerator of the right-hand side with σ_i and M_0 , respectively. For low solute concentrations and narrow concentration limits, eqn. 9 can be simplified to⁹

$$\eta_{i0} = \eta_0 + \left(\frac{\eta_i}{A_{0i}} - \eta_0 A_{i0} \right) y_i \quad (10)$$

Combining eqns. 6 and 7 with 8 and 10, we obtain for \mathcal{R}_i and \mathcal{R}_i^*

$$\mathcal{R}_i = \frac{R_3 R_{4,0} (P + R_3 v_c)}{(R_3 + R_{4,0})^2 \eta_0} \left(\frac{\eta_i}{A_{0i}} - \eta_0 A_{i0} \right) y_i \quad (11)$$

and

$$\mathcal{R}_i^* = \frac{PR_2 R_3}{(R_3 + R_{4,0})(R_1 + R_2) \eta_0} \left(\frac{\eta_i}{A_{0i}} - \eta_0 A_{i0} \right) y_i \quad (12)$$

The relative molar response, RMR , defined as $(d\mathcal{R}_i/dy_i)/(d\mathcal{R}_r/dy_r)$, is given by

$$RMR_{ir} = \frac{(\eta_i/A_{0i}) - \eta_0 A_{i0}}{(\eta_r/A_{0r}) - \eta_0 A_{r0}} \quad (13)$$

where r denotes a reference compound.

With orifice plates as flow-impedance elements in the bridge, the device would respond to changes in the density of the fluid⁴. In this instance, the response is described by eqns. 11 and 12 with the term $[(\eta_i/A_{0i}) - \eta_0 A_{i0}]/\eta_0$ being replaced with $(d_i - d_0)/d_0$, where d_i and d_0 are the densities of pure gaseous solute and of the carrier gas, respectively. The relative molar response is then given by

$$RMR_{ir} = \frac{d_i - d_0}{d_r - d_0} \quad (14)$$

This relationship is identical with that applying to the gas-density detector¹⁰; the densities in eqn. 14 can obviously be replaced with the corresponding molecular weights.

EXPERIMENTAL

The flow-impedance elements of the bridge were made of thick-walled (polarographic) glass capillaries with the resistances $R_1 = R_4 = R$ and $R_2 = R_3 = 2R$, R being 100 mmHg·sec/ml with hydrogen at 20°. All of the capillaries had the same inner diameter, *i.e.*, the lengths of the capillaries were $L_1 = L_4 = L$ and $L_2 = L_3 = 2L$, L being about 3 cm. In this instance, the response of the equilibrated bridge is given by (*cf.*, eqns. 3 and 12)

$$\mathcal{R}_i^* = \frac{P}{3\eta_0} \left(\frac{\eta_i}{A_{0i}} - \eta_0 A_{i0} \right) y_i$$

with

$$v_c^* = P/2R$$

The capillaries were sealed in an epoxy-resin block in which all the necessary conduits were drilled out prior to assembling the detector. The carrier gas was hydrogen. Both the column and the detector were at room temperature. The resistance of R_3 was about 3 times that of the column. The excess pressure P was 100 mmHg. Under these

circumstances, the flow-rates $v_{2,}$, $v_{1,2}$ and $v_{3,4}$ were 1.35, 0.9 and 0.45 ml/sec, respectively, with the bridge being balanced out. The response proper was sensed with a low-volume (capillary) differential U-tube manometer connected at positions a and b (cf. Fig. 1) in the bridge. The manometer was filled with dinonyl phthalate. The GC columns were 50×0.7 cm I.D., containing low-resistance (30-60 mesh) packings of molecular sieve 5A and 20% squalane on Sterchamol.

RESULTS AND DISCUSSION

The chromatograms were obtained by reading at 5-sec intervals the difference in the levels of the liquid in the U-tube manometer and plotting these values against time. Fig. 2 shows a chromatogram obtained by injecting 1 ml of air, chromatographed on the molecular-sieve column. The linearity of the detector response is shown by the plots of the heights of the peaks of oxygen and nitrogen against the

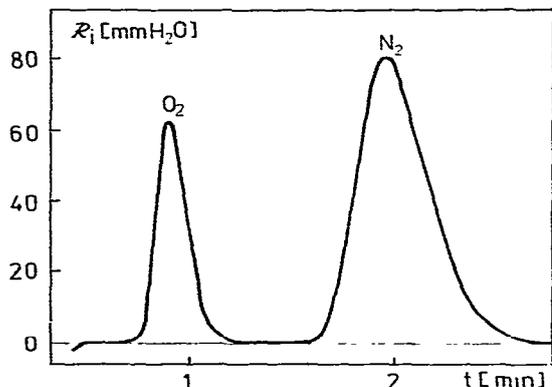


Fig. 2. Chromatogram of oxygen and nitrogen. Conditions: 1 ml of air, molecular sieve 5A column, hydrogen carrier gas, room temperature.

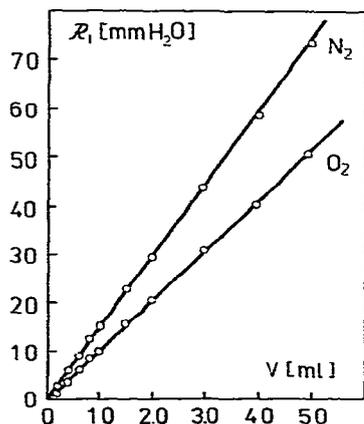


Fig. 3. Plots of the peak heights of oxygen and nitrogen against the volume of air injected. Conditions: molecular sieve 5A column, hydrogen carrier gas, room temperature.

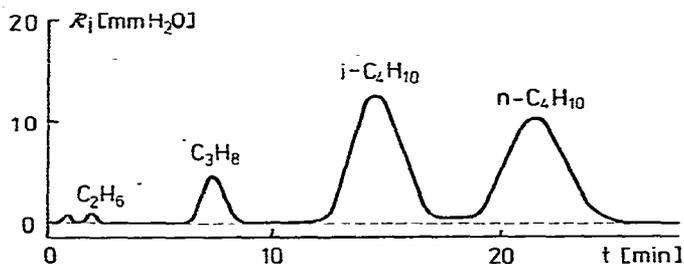


Fig. 4. Chromatogram of a mixture of hydrocarbons. Conditions: 2.5 ml of a propane-butane mixture, squalane column, hydrogen carrier gas, room temperature.

volumes of air injected in Fig. 3. The chromatogram in Fig. 4 was obtained by injecting 2.5 ml of a propane-butane mixture, employing the squalane column.

The concern over the possibility of flow disturbances due to changes in the viscosity of the gas within the column⁶ is justified. These disturbances would manifest themselves fully when employing a source of a constant excess pressure at the column inlet. However, when a fixed mass flow of the carrier gas is provided at the column inlet, the viscosity changes will produce changes in the excess pressure between the outlet of the source of flow and the column inlet while the flow-rate at the column outlet will be virtually constant, except for some transitory variations due to gas compressibility, which disappear soon after injecting the sample. The chromatograms in Figs. 2 and 4 show that the flow perturbations due to the presence of chromatographic zones in the column are virtually suppressed by the arrangement described here.

REFERENCES

- 1 J. H. Griffiths, D. James and C. S. G. Phillips, *Analyst (London)*, 77 (1952) 897.
- 2 J. Janák and J. Novák, in H. G. Struppe and H. P. Angelé (Editors), *Gas-Chromatographie 1963*, Akademie-Verlag, Berlin, 1964, p. 99.
- 3 J. Novák and J. Janák, *Czech. Pat.*, 114, 605 (May 15th, 1965); *U.S. Pat.*, 3, 354, 696 (Nov. 28th, 1967).
- 4 V. G. Guglya, A. D. Gol'den, A. A. Datskevich and A. A. Zhukhovitskii, *Zavod. Lab.*, 33 (1967) 1142.
- 5 D. N. Sokolov and N. A. Vakin, *Zavod. Lab.*, 36 (1970) 1314; D. N. Sokolov, *J. Chromatogr.*, 47 (1970) 320.
- 6 R. Annino, J. Curren, Jr., R. Kalinowski, E. Karas, R. Lindquist and R. Prescott, *J. Chromatogr.*, 126 (1976) 301.
- 7 J. Novák, *Thesis*, Technical University, Prague, 1965.
- 8 J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1965, p. 533.
- 9 J. Novák, *Quantitative Analysis by Gas Chromatography*, Marcel Dekker, New York, 1975, p. 30.
- 10 A. J. P. Martin and A. T. James, *Biochem. J.*, 63 (1956) 138.