

THE USE OF AN ELECTRODELESS DISCHARGE AS A DETECTOR IN GAS CHROMATOGRAPHY

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In recent years there have been several attempts to design detectors for gas chromatography based on differences in the electrical conductance of effluent gases. A d.c. glow discharge at 900 volts between a tungsten wire and platinum disc was first used by HARLEY AND PRETORIUS¹ for identifying the constituents of petroleum ether. The method could not be used for quantitative analysis due to the rapid contamination of the electrodes. PITKETHLY² employed a neon glow lamp for differentiating the current changes due to the effluent components excited by either d.c. or oscillatory potentials. On the basis that the ionization potential of helium (24.5 V) is higher than that for most other gases, RYCE AND BRYCE³ constructed a detector in which the gases passed between a heated filament and an electrode maintained at a potential of about 18 volts. While the carrier gas helium could not be ionized at this potential, all the eluted components with lower ionization potentials gave rise to large current signals. However, this method did not lend itself to quantitative work due to the rapid poisoning of the surface of the heated filament which altered its emission characteristics.

In the meantime interest in the subject seemed to have receded due to the marked success attained with flame and radiation ionization detectors⁴⁻⁶. However, FISHER AND McCARTY⁷ developed a low pressure d.c. discharge detector where the effluent components, after a pressure drop, enter the gap of a commercial spark plug across which a glow discharge is maintained at 300 V d.c. Under these conditions the current across the gap is sensitive to changes in the composition of the gas passing through. The authors report an extremely high sensitivity of 10^{-6} $\mu\text{g/ml}$ for carbon dioxide and oxygen with nitrogen as eluant. Further, the pressure-potential-current characteristics are linear over the range of conditions studied. However each gas sample requires a critical setting of the spark gap and an optimum potential so that a steady glow is maintained without wearing out the electrodes excessively. Thus, electrode contamination, irreversible surface reactions and other "aging" effects under discharge have restricted the applicability of these detectors. We had suggested earlier⁸ that these limitations would be minimal if metallic electrodes are avoided as in a discharge in the annulus of coaxial glass tubes, sometimes referred to as an "electrodeless" discharge. We present here results of our work on the gas-solid chromatography of some of the permanent gases using such a discharge detector.

EXPERIMENTAL

Commercial nitrogen purified by passage through alkaline pyrogallol and calcium chloride (fused) is used as carrier gas. The unit permits the control of the rate of flow of the carrier gas and the injection into it of known amounts of the gas sample under analysis, the volumes of the different sections of the vacuum manifold and the capillary by-pass having been determined previously. The adsorption column consists of a 150 cm long polythene tube of 7 mm internal diameter packed with silica gel of 60–80 mesh size.

The detector is a Siemens' type all-glass discharge tube, 25 cm long with inner and outer tubes of 7 and 13 mm internal diameter, respectively. Sodium chloride solutions inside the inner and around the outer tube formed the electrodes. The tube is excited by 50 c/s potentials and the discharge current is measured by an inductively coupled moving coil galvanometer with a crystal diode (IN34) in series (Fig. 1).

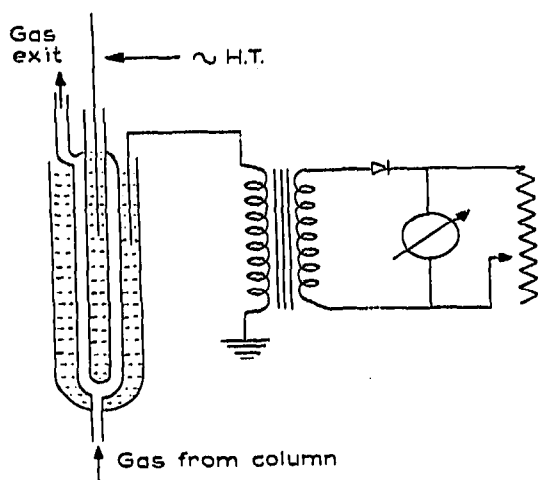


Fig. 1. Electrodeless discharge as a detector in gas chromatography.

The gas issuing from the adsorption column enters the tube at the bottom, passes through the annular discharge and finally escapes. With the carrier gas flowing at a steady rate (15 ml/min) and an exciting potential of 9 kV (r.m.s.) there is a steady discharge current (i) of the order of 1 mA. Hydrogen, oxygen and argon are injected in various amounts, both singly and in mixtures. As each component of the injected gas is eluted into the detector after its characteristic retention time, there is a sharp change in current $\pm \Delta i$, the ratio of the signal to background noise being ≥ 10 .

RESULTS AND DISCUSSION

Fig. 2 presents data for hydrogen, oxygen and argon, as also for their mixtures. From measurements of the signal size due to the gas, the lower limits of detection for each gas are determined under given operative conditions. Fig. 3 is a typical sensitivity curve obtained for oxygen.

Among the three gases studied, hydrogen and oxygen yield negative signals ($-\Delta i$) while argon gives positive signals ($+\Delta i$) (Fig. 2). Under the conditions employed the following amounts of gases have been detected unambiguously (still

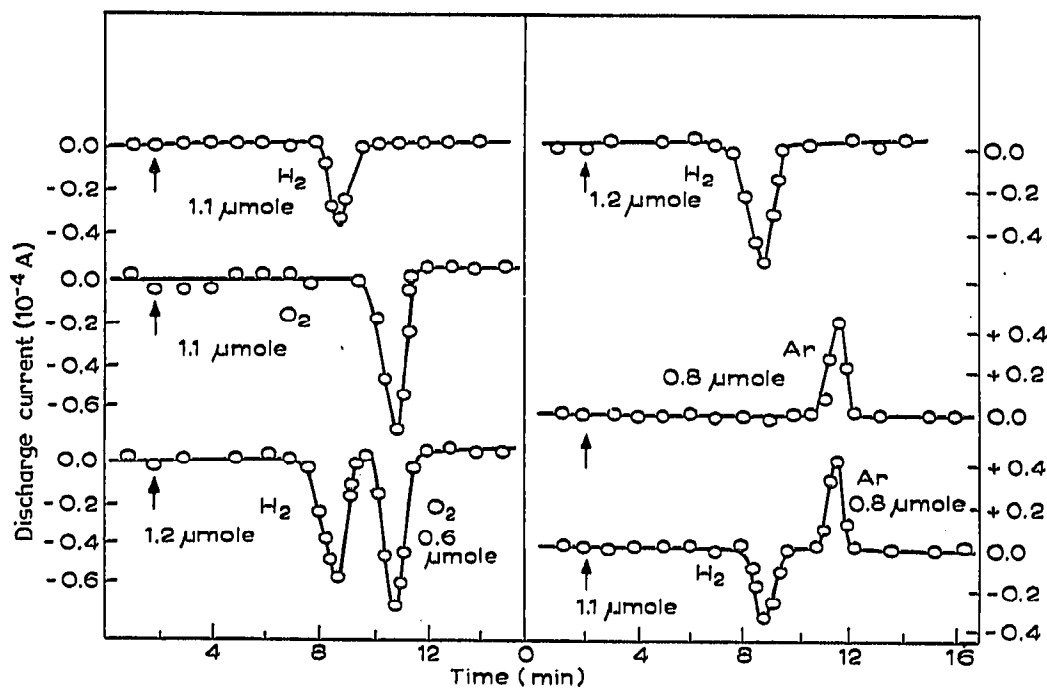


Fig. 2. Detection of hydrogen, oxygen and argon.

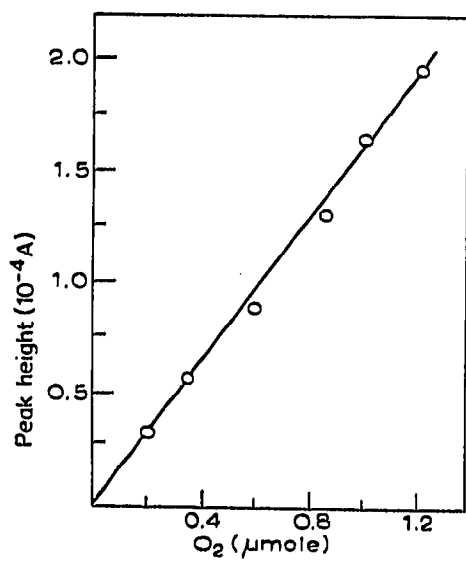


Fig. 3. Sensitivity of the detector for oxygen.

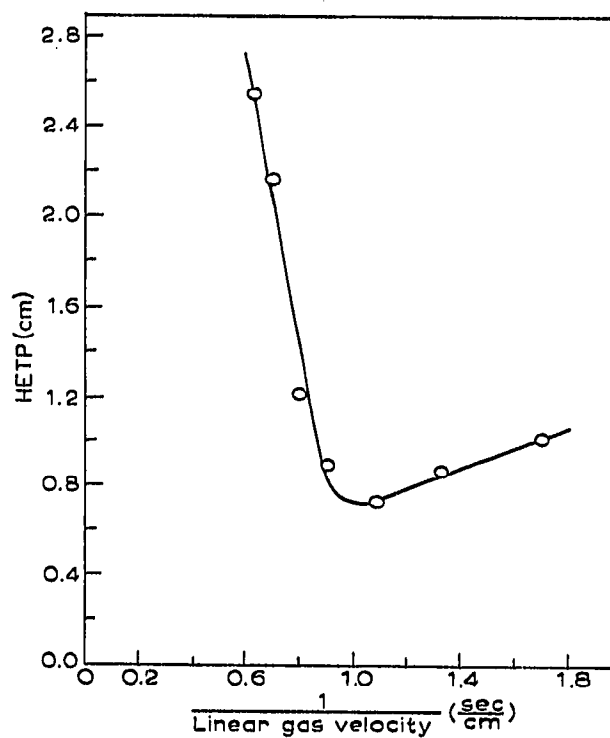


Fig. 4. Variation of HETP with linear gas velocity.

lower limits being possible); hydrogen 1.0 μ mole, oxygen 0.2 μ mole and argon 0.5 μ mole. The amounts of gases injected cover a ten-fold range and the corresponding signals show a linear variation (Fig. 3).

The height-equivalent to a theoretical plate (HETP) has also been calculated for different flow rates and Table I for oxygen is typical of the results obtained. Fig. 4 represents a plot of HETP *versus* $1/u$. The diffusion coefficient of a gas A flowing through another gas B can be computed by the van Deemter equation⁹. The value thus calculated for the diffusion coefficient of oxygen flowing through nitrogen, under the conditions of our experiments, turns out to be 0.23 cm²/sec which agrees reasonably with the value of 0.22 given in literature¹⁰ (corrected to 25°).

TABLE I

THEORETICAL PLATES FOR OXYGEN

Carrier gas: nitrogen; adsorption column: 150 cm long, 7 mm diameter, silica gel (60-80 mesh); temperature of column: 25°; voltage on detector: 9.0 kV (r.m.s.).

Linear gas velocity (cm/sec)	Retention time t (min)	Peak width at base Δt (min)	Number of theoretical plates	HETP (mm)
0.583	13.4	4.4	150	10.0
0.750	9.9	3.0	174	8.7
0.925	7.9	2.2	206	7.2
1.083	6.4	2.0	164	9.0
1.250	5.6	2.2	125	12.0
1.416	5.0	2.4	69	21.7
1.580	4.6	2.4	59	25.4

Our studies indicate that the sensitivity of the detector depends, *inter alia*, on (1) the nature of the carrier gas *vis-à-vis* the specimen gas with regard to the ionization potential, electron affinity and the presence of metastables, (2) voltage applied for excitation and (3) volume, pressure and temperature of the gas under discharge. A study of these aspects as well as an extension of the technique to the vapour phase chromatography of organic substances is in progress.

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SUMMARY

A technique has been developed for using an electric discharge without metallic electrodes as a detector in gas-solid chromatography. This has been applied successfully to the detection and separation of hydrogen, oxygen and argon present in mixtures using silica columns and nitrogen as the carrier gas. Each GSC system is characterised by the retention time t and the current response $\pm \Delta i$ over the background discharge current. The magnitude of the signal response (~ 0.1 mA/ μ mole) observed without amplification suggests that the detector employed here is free from limitations encountered in earlier discharge detectors.

REFERENCES

- 1 J. HARLEY AND V. PRETORIUS, *Nature*, 178 (1956) 1244.
- 2 R. C. PITKETHLY, *Anal. Chem.*, 30 (1958) 1309.
- 3 S. A. RYCE AND W. A. BRYCE, *Nature*, 179 (1957) 541.
- 4 I. G. MCWILLIAM AND R. A. DEWAR, *Nature*, 181 (1958) 760;
D. H. DESTY (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958, p. 142.
- 5 J. E. LOVELOCK, *J. Chromatog.*, 1 (1958) 35.
- 6 J. E. LOVELOCK, in R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 16.
- 7 E. R. FISHER AND M. McCARTY, JR., *Anal. Chem.*, 37 (1965) 1208.
- 8 H. J. ARNIKAR, T. S. RAO AND K. H. KARMARKAR, *Proc. Indian Sci. Congr.*, Part III, 1966, p. 112.
- 9 A. I. M. KEULEMANS, in C. G. VERVER (Editor), *Gas Chromatography*, Reinhold, New York 1957, p. 128.
- 10 D. E. GRAY (Editor), *American Institute of Physics Handbook*, McGraw-Hill, New York, 1957, pp. 2-212.

J. Chromatog., 26 (1967) 30-34