A SOLID ELECTROLYTE DETECTOR FOR THE DETERMINATION OF TRACE AMOUNTS OF OXYGEN IN THE PRESENCE OF ARGON AND OTHER GASES

J. B. CLEGG*

Morganite Research and Development Ltd., Battersea, London S.W.11 (Great Britain)

(Received June 15th, 1970)

SUMMARY

A simple high-temperature electrochemical detector is described which is specific for oxygen gas. This feature enables the analysis of trace amounts of oxygen in argon to be carried out with the chromatographic column at normal temperatures. The response for oxygen is quantitative and exactly obeys the Nernst electrochemical equation. Other gases which react with oxygen at high temperatures, *e.g.* hydrogen and methane, give signals of opposite polarity to oxygen. The stability of the detector is dependent on the type of electrical connections to the sensing head. The use of a conductive reaction cement has been found to give connections which give a stable output with low electrical noise.

INTRODUCTION

The determination of trace amounts of oxygen, *ca.* 10^{-6} ml at s.t.p., in argon by gas–solid chromatography presents a number of difficulties. The two gases have almost identical retention times on columns of Linde 5A molecular sieve at room temperature[1] and on porous polymer packings, such as Porapak Q. Separation can easily be achieved when both gases are present in similar concentrations or as minor components, by cooling the column to $-72°$[2,3]. When oxygen is present as a trace component, the analysis is only possible when the column parameters are carefully optimised. However, chromatographic columns operating under these conditions give rise to characteristically long retention times and broad based peaks.

Indirect methods have been described in the literature in which hydrogen is used as carrier gas and oxygen in the sample is catalytically converted into water and separated by the usual chromatographic techniques[4–6]. Such methods, with thermal conductivity detectors, have sensitivities of the order of 10^{-4} ml oxygen.

Column materials which are specific for oxygen and give separation at room temperature, such as fire-brick impregnated with bull's blood, have been investigated[7]; but as materials containing haemoglobin are unstable, the column life is limited.

---

* Present address: Mullard Research Laboratories, Redhill, Surrey, Great Britain.

Because of the lack of suitable column materials, detectors which are specific for oxygen have been reported. PHILLIPS *et al.* described a redesigned Hersch oxygen cell for the determination of oxygen in argon without complete separation and reported a limit of detection of 1×10^{-5} ml oxygen[8]. LITTLEWOOD *et al.* described an oxygen reaction coulometer incorporating a similar detection system for measuring changes in oxygen content caused by the introduction of combustible material[9].

High-temperature galvanic cells have been investigated for measuring the partial pressure of oxygen in hot gases[10,11]. These cells consist basically of a solid electrolyte containing oxygen vacancies, *e.g.* zirconia stabilized with calcium oxide, with electrodes in contact with opposite faces of the ceramic. The theoretical open circuit potential between the electrodes is related to the ratio of the oxygen partial pressures p_1/p_2 at the two electrodes by the Nernst equation:

$$E = \frac{RT}{nF} \ln \frac{p_1}{p_2} \tag{1}$$

where

E = e.m.f. developed by the cell, V
T = temperature of the electrodes, °K
R = the universal gas constant
F = Faraday's constant
n = number of electrons transferred in the electrode process (4, for electrode reactions involving 1 gmole of oxygen).

The logarithmic dependence makes it possible to measure very small quantities of oxygen, and gases which react with oxygen at high temperatures.

This paper describes such a cell which has been developed in this laboratory for use as a specific detector for determining trace amounts of oxygen, hydrogen and methane in argon and other inert or non-reactive gases.

APPARATUS

The detector (Fig. 1) consists of a cylindrical tube, closed at one end, of impervious zirconium oxide stabilized with calcium oxide mounted into an aluminium block which carries inlet and outlet connections for the carrier gas. Two platinum electrodes are held in contact with the closed end by means of a ceramic reaction cement made from a mixture of orthophosphoric acid (0.4 ml, 25% v/v) and powdered stabilized zirconia (100 mesh, 2 g). (The cement is applied to the end of the tube with the electrodes in position and the arrangement slowly heated to 1100°C.) Purified helium carrier gas is fed into the zirconia tube through an alumina tube carrying the inner platinum electrode. The tube assembly is totally enclosed by a silica tube which carries the reference gas, either air or helium. The sensing head of the detector is heated by a wire-wound tube furnace at 1050°C. Electrical interference from the furnace is prevented by electrostatically screening the silica tube with platinum foil held at earth potential. Standing voltages developed between the electrodes are backed off with a simple potentiometer circuit and the out-of-balance signal is recorded with a potentiometric recorder (20 mV f.s.d.).

The detector is built into a glass and stainless steel chromatograph which incorporates a purification train, comprising molecular sieves, titanium sponge and
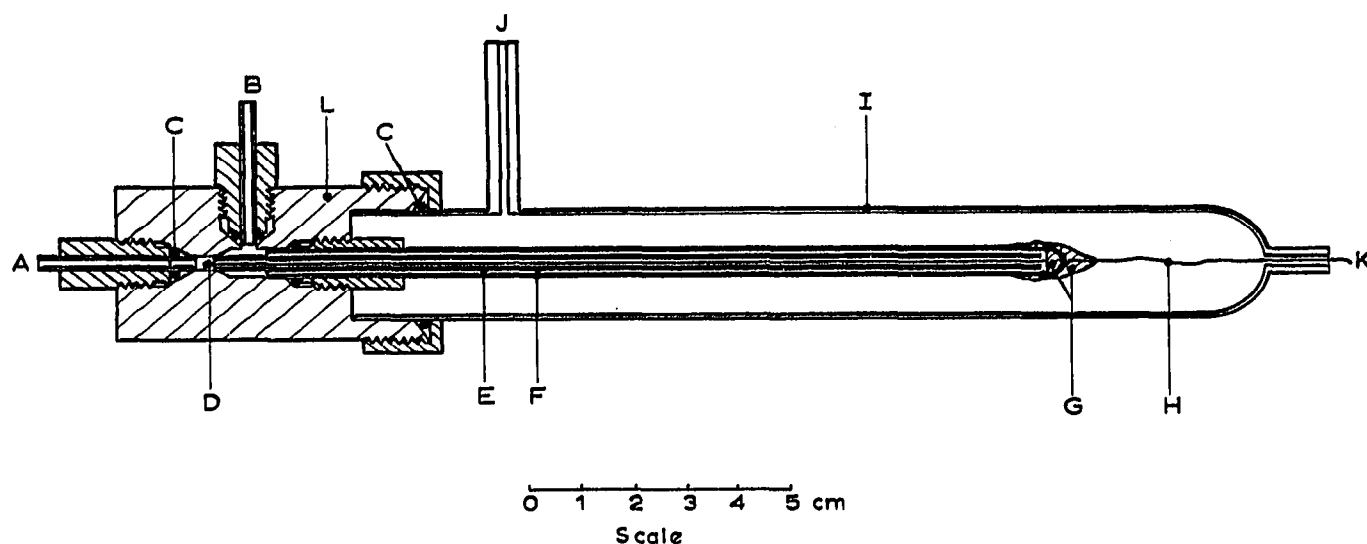
Fig. 1. Diagram of the oxygen detector. A = Carrier gas inlet; B = carrier gas outlet; C = silicone rubber O-rings; D = inner platinum electrode; E = alumina tube; F = zirconia-lime sheath; G = ceramic reaction cement; H = outer platinum electrode; I = silica tube and platinum foil; J = reference gas inlet, helium or air; K = reference gas outlet; L = aluminium block at earth potential.

"Hopcalite" columns with a sampling and low-pressure standardizing system similar to the one described by BERRY[12]. The chromatographic column consists of a coiled stainless steel tube (120 cm × 4 mm I.D.) containing 40–50 mesh molecular sieve 5A which has been activated at 350°C *in situ* for 24 h. The column is electrically heated and normally operates at 65°C.

RESULTS AND DISCUSSION

Dependence of standing voltage on flow of carrier gas, with air as reference gas

The results plotted in Fig. 2 show that the standing voltage tends to a maximum of 330 to 340 mV. The Nernst equation indicates that the voltage should be independent of flow rate provided that the partial pressure of oxygen in the carrier gas does not alter and the temperature of the electrodes remains constant. This discrepancy is due to a slight porosity of the electrolyte at high temperatures with the consequent
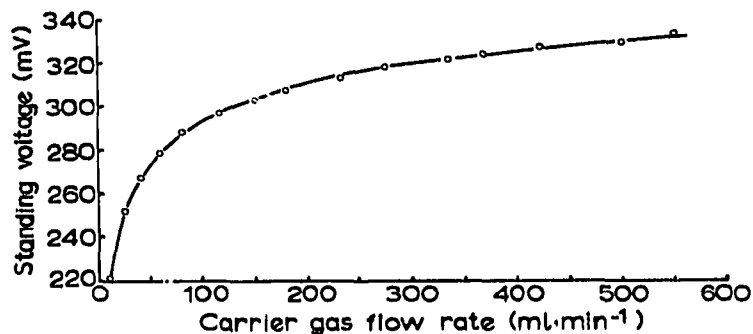

Fig. 2. Effect of carrier gas flow rate on the standing voltage with air as reference gas. Detector temperature, 1050°C.

diffusion of molecular oxygen from air into the carrier gas. The following treatment enables errors caused by the use of slightly pervious tubes to be calculated together with an accurate measurement of the partial pressure of oxygen in the ingoing carrier gas.

Diffusion of molecular oxygen through the electrolyte is primarily governed by the difference in partial pressures of oxygen inside and outside the tube. This is essentially constant provided that the partial pressure of oxygen in the carrier gas does not exceed 10^{-2} atm and thus the leak rate of molecular oxygen will be constant. If the carrier gas, at 1 atm pressure, flowing at V ml·min^{-1} contains v ml of oxygen per ml and if the leak rate of oxygen is u ml·min^{-1} then:

$$p_{O_2} = \frac{u}{V} + v \tag{2}$$

where p_{O_2} is the partial pressure of oxygen in the carrier gas as measured by the detector.

The validity of this equation is shown by the straight-line graph when p_{O_2} is plotted against $1/V$ (Fig. 3). From the slope and intercept, the measured leak rate is 6.9×10^{-4} ml oxygen per min and the concentration of oxygen in the carrier gas with no leakage is 5×10^{-7} ml O_2 per ml of carrier gas. Hence by determining the partial pressures of oxygen in the carrier gas at a number of different flow rates the leak rate of oxygen through the electrolyte, or through any other part of the system, can be obtained together with an accurate value for the partial pressure of oxygen in the ingoing carrier gas.

As a result of this variation of voltage with flow, the chromatographic column must be sufficiently long to prevent any pressure pulses caused by the introduction of the sample from interfering with the response of the detector.
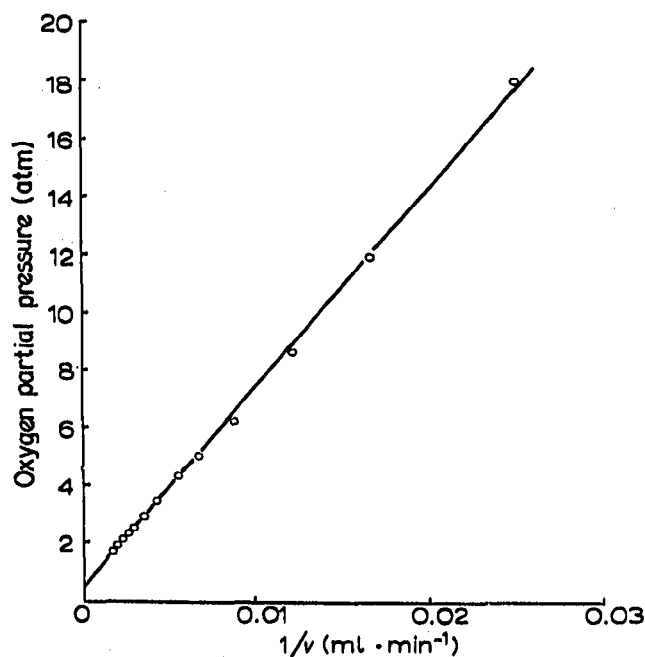

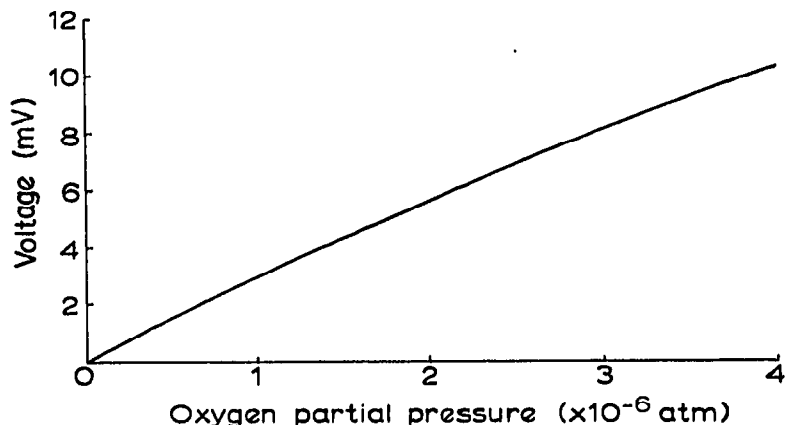Fig. 3. Oxygen partial pressure of carrier gas as a function of flow rate.

Fig. 4. Theoretical detector response for oxygen with rectangular peaks. Carrier gas p_{O_2}, 9.2 × 10⁻⁶ atm; detector temperature, 1050°C; reference gas, air.

Detector response

Due to the exact relationship between voltage and oxygen partial pressure (eqn. 1), it is possible to calculate the oxygen response of the detector. Consider a small quantity of oxygen, injected at reduced pressure, which remains as a discrete volume as it passes through the detector, then the expected peak height response, based on rectangular shaped peaks, would be as shown in Fig. 4, for the given conditions. The graph is not linear due to the logarithmic nature of the Nernst equation, but it does provide an acceptably linear part over the lower range, *i.e.* up to 3 × 10⁻⁶ atm. However, when a gaseous mixture containing oxygen is injected into a chromatographic system, dilution with the carrier gas occurs and therefore the detector response will be lower than that given by the theoretical curve. As the flow rate of the carrier gas and the oxygen peak elution time are known for this system (70 ml·min⁻¹, 19 sec), the reduced oxygen partial pressure of the injected gas can be calculated. Assuming that the detector signal is proportional to the oxygen partial pressure (true for pressures ≤ 3 × 10⁻⁶ atm) and triangular peaks of constant width are produced, then the theoretical response can be recalculated. Fig. 5 shows that excellent agreement is
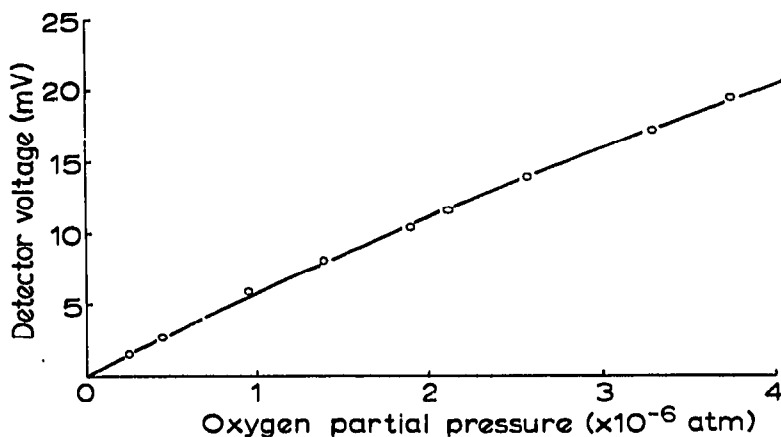

Fig. 5. Response curve for oxygen with triangular peaks. —, Theoretical curve; ○, experimental data.
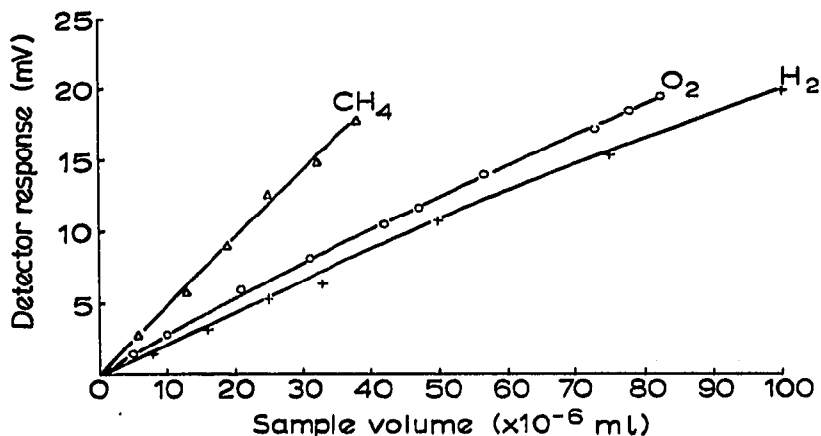
Fig. 6. Response for hydrogen, oxygen and methane with air as reference gas. The polarity of the oxygen signal has been reversed. Detector temperature, 1050°C; flow rate, 70 ml·min⁻¹.

obtained between the predicted response curve and the practical measurements (taken from oxygen data in Fig. 6).

Gas samples containing hydrogen and methane give signals of opposite polarity to oxygen, when they are eluted through the detector (Fig. 6). In this case these gases react with oxygen present in the carrier gas to produce a lowering of oxygen partial pressure. The sensitivity is greater for methane than hydrogen because both carbon and hydrogen atoms in methane are capable of reacting with oxygen.

Inert and unreactive gases such as argon and nitrogen do not produce signals and consequently the analysis of oxygen in argon can be carried out with the column operating at normal temperature and without separation. Calibration of the system when the components are not resolved is however rather more complicated. Argon samples which have a lower oxygen partial pressure than the carrier gas give signals of opposite polarity to that of the oxygen calibrating gas. For the case where the argon sample (1.1 ml) contains negligible oxygen, *i.e.* two orders of magnitude lower than the carrier gas, the maximum peak height signal would be expected to be ≈ 2.6 mV for the standard operating conditions. This corresponds to a negative error signal of
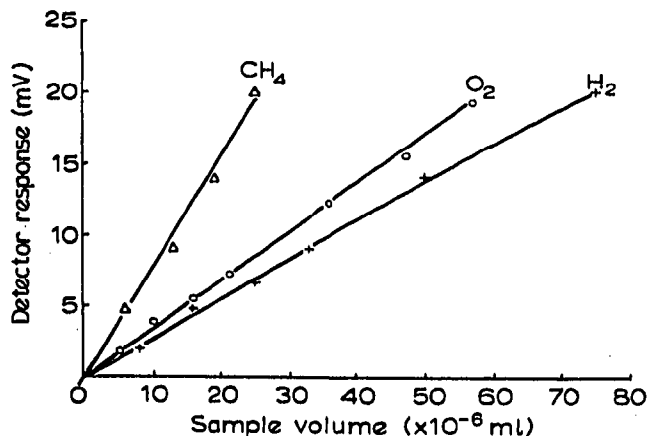

Fig. 7. Response for hydrogen, oxygen and methane with helium as reference gas. The polarity of the oxygen signal has been reversed. Detector temperature, 1050°C; flow rate, 70 ml·min⁻¹.

$\approx 1 \times 10^{-5}$ ml oxygen for argon samples having oxygen partial pressures equal to or greater than the carrier gas.

The sensitivity of the detector is governed by the oxygen partial pressure of the carrier gas and it has been shown that this is increased as the carrier gas flows through the detector due to diffusion of molecular oxygen. This can easily be reduced to negligible quantities by using pure helium carrier gas as reference. With this condition, the detector standing voltage only amounts to several mV and it is unaffected by temperature fluctuations. Assuming that the detector now operates with the carrier gas at its limiting purity, 5×10^{-7} atm oxygen, the oxygen sensitivity would be expected to be approximately ten times greater. Fig. 7 shows that the observed increase in sensitivity is a factor of two and suggests that leaks were occurring in the pipe-work prior to the detector. The required partial pressure of oxygen in the ingoing carrier gas to give this sensitivity is 4.5×10^{-6} atm.

The noise level of the detector operating in this mode is 0.2 mV, peak to peak, and the base-line drift is better than 0.4 mV $\cdot$ h^{-1}. These parameters are primarily governed by the purity of the carrier gas and the nature of the ohmic contacts at the sensing end of the solid electrolyte. The use of the ceramic reaction cement, which is conductive at high temperatures and forms a rigid contact between the electrodes and electrolyte, has been found to give good electrical stability. The cement is formulated to give sufficient through porosity to permit ready access of gas to the gas-electrolyte interface and is in addition capable of electrical conduction by transport of the oxide ion.

The minimum detectable volumes, corresponding to a signal/noise ratio of one, are: hydrogen 7×10^{-7} ml, oxygen 6×10^{-7} ml and methane 3×10^{-7} ml. The
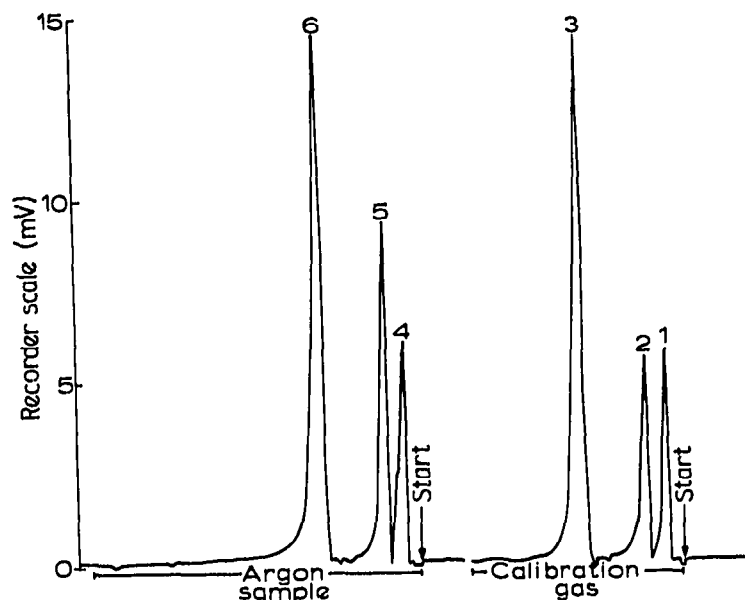

Fig. 8. Chromatogram of a 1.1-ml sample of argon and a calibration gas containing hydrogen, oxygen and methane. For the oxygen peaks the polarity of the signal has been reversed. Detector temperature, 1050°C; flow rate, 70 ml·min^{-1}; chart speed, 30 in.·h^{-1}; column, molecular sieve 5A at 65°C; reference gas helium. 1 = Hydrogen, 20 × 10^{-6} ml s.t.p.; 2 = oxygen, 16 × 10^{-6} ml s.t.p.; 3 = methane, 19 × 10^{-6} ml s.t.p.; 4 = hydrogen, 20 × 10^{-6} ml s.t.p.; 5 = oxygen, 35 × 10^{-6} ml s.t.p.; 6 = methane, 19 × 10^{-6} ml s.t.p.

chromatogram (Fig. 8) of a 1.1-ml sample of argon illustrates the sensitivity of the detector and the noise level at low concentrations.

REFERENCES

1 M. T. LILBURN, *Talanta*, 14 (1967) 1029.
2 E. W. LARD AND R. C. HORN, *Anal. Chem.*, 32 (1960) 878.
3 O. L. HOLLIS, *Anal. Chem.*, 38 (1966) 309.
4 K. ABEL, *Anal. Chem.*, 36 (1964) 953.
5 J. W. SWINNERTON, V. J. LINNENBOM AND C. H. CHEEK, *Anal. Chem.*, 36 (1964) 1669.
6 E. J. HAVLENA AND K. A. HUTCHINSON, *J. Gas Chromatog.*, 6 (1968) 419.
7 A. A. ZHUKHOVITSKIĬ, N. M. TURKEL'TAUB AND A. F. SHLYAKHOV, *Khim. i Tekhnol. Topliv i Masel*, 6 (1962) 7.
8 T. R. PHILLIPS, E. G. JOHNSON AND H. WOODWARD, *Anal. Chem.*, 36 (1964) 450.
9 A. B. LITTLEWOOD, G. BURTON AND W. A. WISEMAN, in A. B. LITTLEWOOD (Editor), *Gas Chromatography 1966*, Institute of Petroleum, London and Elsevier, Amsterdam, 1967, p. 193.
10 J. WEISSBART AND R. RUKA, *Rev. Sci. Instr.*, 32 (1961) 593.
11 R. E. BATES AND R. LITTLEWOOD, *Internal B.I.S.R.A. Publ.*, No. 211 (1963).
12 R. BERRY, in M. VAN SWAAY (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 321.