

Note

Response of electron-capture detector to hydrogen, oxygen, nitrogen, carbon dioxide, nitric oxide and nitrous oxide

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The major character of the electron-capture detector (ECD) is its great selectivity based on the electron absorption coefficients of the compounds which pass through the detector. Nitrous oxide has been shown to have a high electron absorption coefficient at temperatures around 300°C. This initiated the development of a very sensitive method for the measurement of N₂O by ECD³. Recently, Thijsse⁴ and Simmonds⁵ have shown that the ECD can be used for a sensitive measurement of CO₂ as well as N₂O. Moreover, work by Phillips *et al.*⁶ and Simmonds⁵ indicates that the selectivity of the ECD can be modified by the appropriate choice of detector temperature and carrier gas composition. This may be of great practical value, since in many cases of biological and atmospheric research concentrations of single compounds in gas samples vary by several orders of magnitude. We have used an ECD for the measurement of O₂, CO₂, NO and N₂O in biological experiments and report here the response of this detector to H₂, O₂, N₂, CO₂, NO and N₂O.

EXPERIMENTAL

A closed system with a total volume of 131 ml was used for all calibration experiments (Fig. 1). By means of a membrane pump (Neptune Dyna, Scientific Products, McGraw Park, IL, U.S.A.) the gas was circulated through a flow meter (Matheson, Joliet, IL, U.S.A.), a serum bottle with rubber septum (Bellco, Vineland, NJ, U.S.A.) and the sampling loop (Carle, Anaheim, CA, U.S.A.) of a gas chromatograph (Perkin-Elmer, Norwalk, CT, U.S.A.). The system could be flushed with argon or air from a gas tank. Stainless-steel tubing (1/8 in.) and Gyrolok fittings (Hoke, Cresskill, NJ, U.S.A.) were used for tubing and connections. For calibration, known

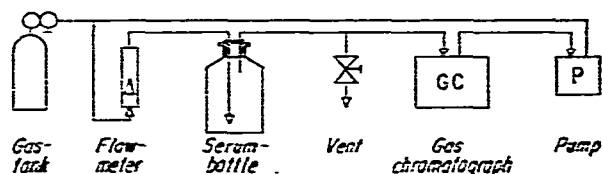


Fig. 1. Closed system used for calibrations and biological experiments.

amounts of a gas were injected by syringe through the septum into the serum bottle. After sufficient mixing time a sample of the gas mixture of known composition was injected by means of a sampling valve (0.1-ml loop) into the dual column gas chromatograph (Fig. 2). After separation in column I the components could either be passed to the detector or vented by a four-way valve (Carle). When in vent configuration the carrier gas stream of column II was led through the detector. Both columns could further be used for the analysis of gas samples injected through a conventional septum port. Specifications and operating conditions of the gas chromatograph used for all experiments are given in Table I. The detector signal was integrated by a Supergrater-I (Columbia Scientific Industries, Austin, TX, U.S.A.) and recorded by a 10-in. linear recorder (Beckman, Fullerton, CA, U.S.A.).

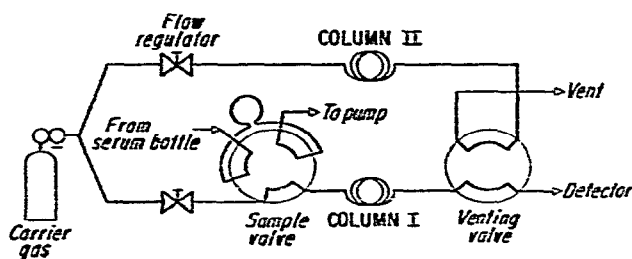


Fig. 2. Dual column gas chromatograph with sampling valve and venting valve.

TABLE I

SPECIFICATIONS AND OPERATING CONDITIONS OF GAS CHROMATOGRAPH

Model	Perkin-Elmer 910
Columns	1.8 m \times 1/8 in. O.D., stainless steel, Porapak Q, 50-80 mesh or molecular sieve 5A
Detector	Dual ^{63}Ni electron-capture detector; pulse voltage, 55 V; width, 250 nsec; standing current setting, 3.0 mA; temperature, 300°C
Carrier gas	95% Ar, 5% CH ₄ , or 94% Ar, 5% CH ₄ , 1% O ₂ ; flow-rate, 15 ml/min
Temperatures	Injector, 60 °C; column, 55 °C; interface 70 °C
Sampling valve	Carle No. 5518, 0.1-ml sampling loop
Venting valve	Carle No. 5511

Besides being used for calibration experiments, the closed system was adapted to studies of microbial denitrification in various ecosystems. Studies with pure cultures of denitrifiers were performed in a 125-ml flask with septum-stopped sidearm and magnetic stirrer^{7,8}. For the biological experiments the venting valve was especially useful, since water vapor was always present, and acetylene was often added. Venting of these two compounds allowed shorter sampling intervals and guaranteed a stable baseline.

RESULTS

Fig. 3 shows a chromatogram obtained on a Porapak Q column during a denitrification experiment with digested sludge. In order to prevent interference of CO_2 with the detection of N_2O (ref. 9) the operating conditions of the gas chromatograph were optimized for a complete separation of those two gases. The extreme selectivity of the ECD is illustrated by a comparison between the signals of CO_2 and N_2O : the CO_2 -peak represents a partial pressure of 2.6 kPa, whereas the partial pressure of N_2O was only 5.0 Pa.

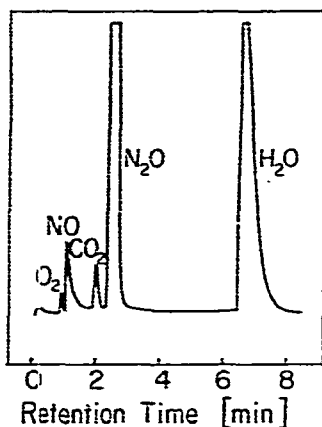


Fig. 3. Separation of gases on Porapak Q and detection with ECD. Carrier gas: 95% Ar, 5% CH_4 . Attenuation 16. Partial pressures in Ar-atmosphere: O_2 , 34.5 Pa; NO , 0.8 Pa; CO_2 , 2.60 kPa; N_2O , 5.0 Pa; H_2O , 3.17 kPa.

The ECD was most sensitive to N_2O and NO . Fig. 4 shows the response of both nitrogen oxides up to the highest tested partial pressure of 10 Pa. Below 2.5 Pa both calibration curves had a slightly steeper slope than above this value. Calibration curves for O_2 and CO_2 are shown in Fig. 5. The detector response to

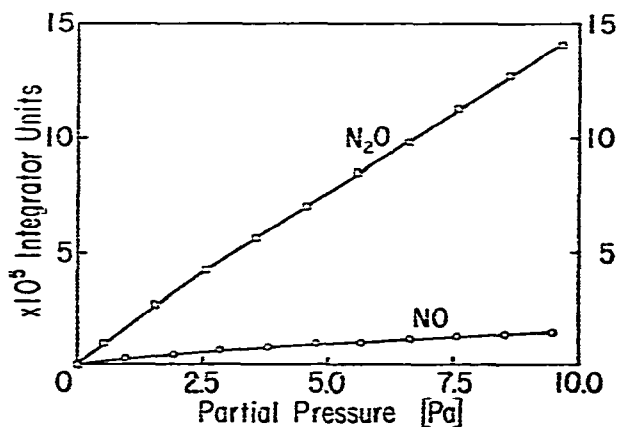


Fig. 4. Calibration curves for N_2O and NO on Porapak Q.

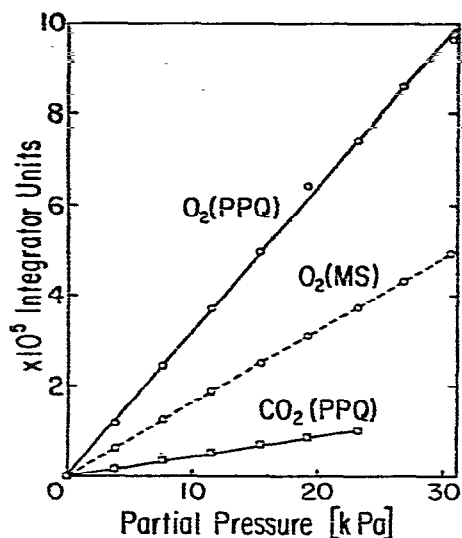


Fig. 5. Calibration curves for O₂ and CO₂. PPQ = Porapak Q. MS = molecular sieve.

CO₂ chromatographed on Porapak Q was linear over the test range up to 23 kPa. O₂ was tested on both Porapak Q and molecular sieve 5A. The response was fairly sensitive and linear up to the highest tested partial pressure of 30 kPa. As expected, the longer retention time on molecular sieve resulted in a decreased sensitivity of the detection.

Chromatograms of H₂, O₂ and N₂ on molecular sieve 5A are shown in Fig. 6. The sensitivity of the ECD to N₂ was extremely low and thus not further investigated. With argon-methane as carrier gas, H₂ caused a fairly sensitive response. But the peak tailed (Fig. 6A), which is not seen if it is detected by a thermal conductivity

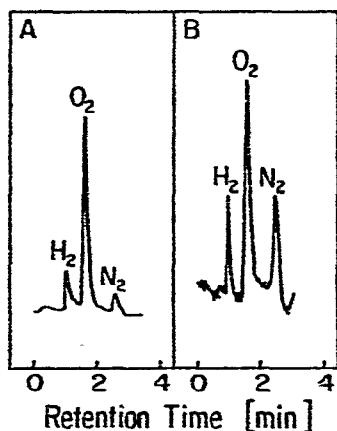


Fig. 6. Separation of gases on molecular sieve 5A and detection with ECD. Attenuation 16. Partial pressures in Ar-atmosphere: H₂, 0.2 kPa; O₂, 2 kPa; N₂, 20 kPa. Carrier gas: A, 95% Ar + 5% CH₄; B, 94% Ar + 5% CH₄ + 1% O₂.

detector. In a limited effort to improve the H_2 analysis, a carrier gas consisting of 1% O_2 , 5% CH_4 and 94% Ar was tested under the same instrument conditions. The result is shown in Fig. 6B. The tailing of the H_2 peak could be eliminated, and the sensitivity was slightly increased. However, the baseline was much less stable than with the conventional carrier gas, so that the use of the 3-component carrier gas did not improve the net sensitivity of the detector. Thus, the response of the ECD to hydrogen was tested with the conventional Ar- CH_4 carrier mixture. In the range from 0 to 20 kPa it was sigmoid and not always reproducible. The lowest part of the curve is shown in Fig. 7.

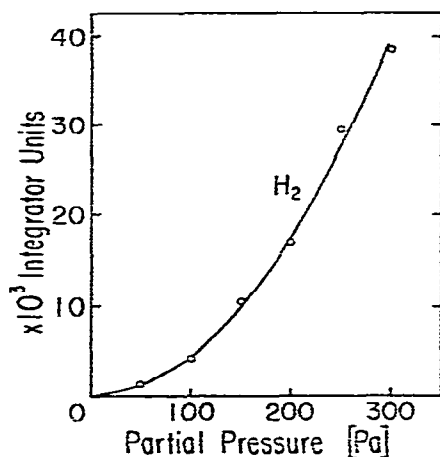


Fig. 7. Response of electron capture detector to low concentrations of H_2 . Molecular sieve.

DISCUSSION

Reproducible responses of the ECD were obtained for O_2 , CO_2 , NO and N_2O . In our laboratory these four gases are now routinely analyzed by ECD. H_2 gave a sigmoid and variable response curve. The sensitivity for this gas could not be improved by adding 1% O_2 to the carrier gas. The application of the ECD under the conditions used in this study for the H_2 analysis is therefore not feasible. However, it should be stressed that our effort to improve the sensitivity of the ECD for H_2 was limited. A thorough study of the chemistry of H_2 pertinent to this particular problem might result in very different detector conditions and carrier gas compositions. In general, we feel that the radical chemistry of many compounds could be exploited for a specific and sensitive detection by the electron capture principle, "selective electron capture sensitization"⁶.

Pellizzari¹⁰ illustrates the selectivity of the ECD with its relative responses to organic compounds which may vary by a factor of 10^6 . The same can be done with the gases investigated in this study. Table II summarizes the detection limits for all gases tested under the conditions given in Table I. It also shows the relative responses based on the response to N_2O . The ECD was extremely sensitive to both N_2O and NO. Its sensitivity to O_2 and CO_2 was much lower: 4 and 5 orders of magnitude,

TABLE II

DETECTION LIMITS IN 0.1-ml GAS SAMPLES, ASSUMING A MINIMUM PEAK SIZE OF 1000 INTEGRATOR UNITS

Detailed gas chromatographic conditions are given in Table I.

Gas	Column	Detection limit	Relative sensitivity
N ₂ O	PPQ	0.005 Pa	1
NO	PPQ	0.05 Pa	0.1
H ₂	mol. sieve	36 Pa	1.4 · 10 ⁻⁴
O ₂	PPQ	32 Pa	1.6 · 10 ⁻⁴
O ₂	mol. sieve	92 Pa	5.4 · 10 ⁻⁵
CO ₂	PPQ	205 Pa	2.4 · 10 ⁻⁵
N ₂	mol. sieve	28000 Pa	1.8 · 10 ⁻⁷

respectively. Yet this was still comparable to the sensitivity of a thermal conductivity detector for these two gases. The response to N₂ was at the other extreme end of the scale, 7 orders of magnitude lower than in the case of N₂O.

The detection limits for O₂ and CO₂ (32 and 205 Pa, respectively) are high compared to those for N₂O and NO and may discourage the use of the ECD for the analysis of these two gases. However, it should be remembered that the sample size was only 0.1 ml and that the sensitivity of the ECD to CO₂ can be improved by addition of O₂ to the carrier gas⁵. Thermal conductivity detectors may be slightly more sensitive to O₂ and CO₂, but the ECD has the advantage of coupling a fairly sensitive O₂- and CO₂-analysis with a highly sensitive analysis of N₂O and NO. This can be of great value in research concerned with the atmospheric chemistry of nitrogen oxides as well as with the chemical and biological conversions of these gases in terrestrial and marine environments, where the concentrations of gases are frequently reciprocal to the sensitivity of the ECD.

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