

A CO₂ titration electrode

Part II: Development of the sensor

W. J. ALBERY, M. UTTAMLAL

*Molecular Sensors Unit, New Chemistry Laboratory, South Parks Road, Oxford OX1 3QT, Great Britain*M. S. APPLETON*, N. J. FREEMAN[†], B. B. KEBBEKUS[‡], M. D. NEVILLE[§]*Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AZ, Great Britain*

Received 5 February 1993; revised 4 May 1993

The construction and operation of a new titration electrode for measuring CO₂ are described. Typical results are presented including calibration plots and a comparison of results from the new sensor with those from an infrared analyser. Good agreement is found. Results using the sensor to measure CO₂ levels in a glasshouse and in the ambient atmosphere of the laboratory are presented.

1. Introduction

In the previous paper [1] we have developed the theory for a titration electrode to measure CO₂ and have shown that experiments are in good agreement with the theory. In this paper we report the development of the titration electrode as a sensor for CO₂ and its use to measure concentrations of CO₂ in a glasshouse.

2. Experimental details

The construction of the sensor is illustrated in Fig. 1. The sensor is similar to a Clark oxygen electrode [2] except that the electrode arrangement is more complicated. As shown in Fig. 1 there is a small central iridium oxide electrode which is used to measure pH potentiometrically [3]. This electrode is surrounded by a platinum generating electrode that is used to generate a known concentration of OH⁻ amperometrically. The generating electrode is surrounded by a platinum ring electrode that acts as a counter electrode. Finally there is a silver wire electrode which is used as a Ag/AgCl reference electrode. The electrolyte was 1 M NaClO₄ with 0.10 M Cl⁻.

In operating the sensor OH⁻ is generated at constant current for a time t_g . The current is then stopped and CO₂ diffusing through the membrane titrates the OH⁻. The time to the end point, t_t , is measured. The concentration of CO₂ is proportional to t_g/t_t . In the previous paper [1] we showed that if the initial pH is greater than 11.5 then two maxima in a trace of $d \ln(h)/dt$, where h is [H⁺], against time, t , will be observed; the second maximum occurs

close to a pH of 8 and therefore identifies the endpoint. In the work described in this paper we are measuring CO₂ in the gas phase. Instead of a membrane made of PTFE, used for solution work, in this work we use a membrane made of silicone rubber (Radiometer D606); the membrane has a thickness of 25 μm. The latter membrane is more permeable and is therefore more suitable for measuring the low concentrations of CO₂ found in the ambient atmosphere. A silicone rubber membrane cannot be stretched as tight as a PTFE membrane leading to a thicker electrolyte layer. This in turn means that on generating the same quantity of OH⁻ the pH rises less far. In practice the pH at the end of the generating period was below 11 and this is too low for the first maximum in the previous work to be observed. So in this work only one maximum close to a pH of 8 is observed.

For each determination fresh electrolyte is used behind the membrane. This renewal prevents a build up of HCO₃⁻ which by its buffering action vitiates the operation of the sensor. The fresh electrolyte is provided from the reservoir shown in Fig. 2. Liquid is driven from the reservoir by a peristaltic pump (Pharmacia P3). We have found that this renewal is valuable in other membrane electrodes. Figure 2 also shows how the gas is presented to the electrode. For calibration plots the concentration of CO₂ was controlled by a gas blender (Signal Instruments, model 852). The CO₂ was diluted with oxygen.

The electrode potentials, the gas blender and the peristaltic pump are controlled by an Imperial College Chemistry Microprocessor Unit (ICCMU) serial interface rack. We wish to find the maximum

Present addresses: * Hazard Evaluation Laboratories Ltd., Fire Research Station Site, Borehamwood WD6 2BL, GB; [†] Hirst Research Centre, GEC Marconi, East Lane, Wembley, Middlesex HA9 7PP, GB; [‡] Department of Chemical Engineering and Chemistry, Newark College of Engineering, Newark, NJ 07102, USA; [§] Applied Electrochemistry Department, INTEC, AEA Technology, Harwell Laboratory, Oxford OX11 0RA, GB.

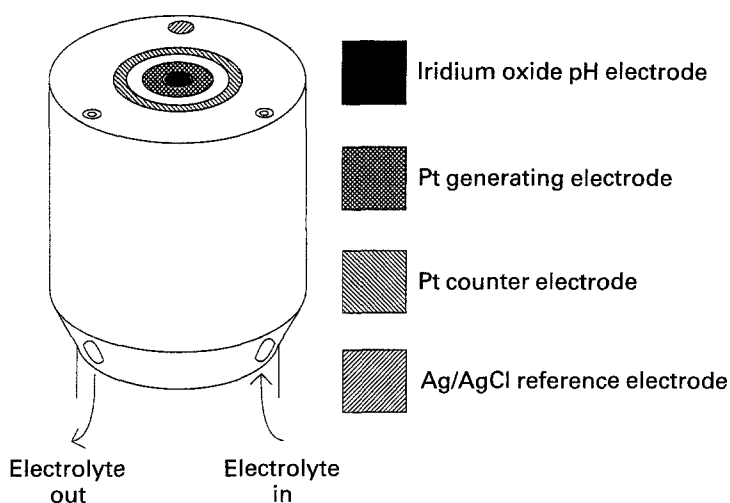


Fig. 1. The CO₂ titration electrode.

in dE/dt where E is the potential of the iridium oxide electrode. This is done by double differentiating the curve of E against t and finding the time when d^2E/dt^2 changes from being positive to negative. Each differentiation is done using the Lagrange three point method [4]. These calculations are performed by the rack.

Hence the complete sequence for a measurement is as follows.

- (i) Pump fresh electrolyte for 30 s.
- (ii) Generate OH⁻ with a current of $-15 \mu\text{A}$ for $t_g = 100$ s.
- (iii) Monitor E and measure time, t_t , to the point where d^2E/dt^2 goes negative.
- (iv) Calculate $[\text{CO}_2]$ from t_g/t_t and calibration constant.

All chemicals were of AnalaR quality. All gases were supplied by BOC. Concentrations of CO₂ in the glasshouse were also measured using an infrared analyser (ADC Series 225).

3. Results and discussion

Figure 3 shows a typical E against t trace and the three phases, pumping, generation and titration. During the titration phase traces of dE/dt and of d^2E/dt^2 are also shown.

Figure 4 shows two typical calibration plots. It is

satisfactory that in each case we obtain good straight lines. It is also highly satisfactory that concentrations as low as 250 p.p.m. can be measured; ambient CO₂ is 340 p.p.m. The difference between the two experiments is that in the case of B a double membrane was used. It is satisfactory that the ratio of the gradients is 2.0, showing that the diffusion of CO₂ through the membrane is indeed controlling the titration.

In Fig. 5 we compare results from the new electrochemical sensor with those from a conventional infrared analyser. It is satisfactory that a good straight line is obtained. Figure 6 shows typical results obtained in a glasshouse from the electrode and from the infrared analyser. Again it is satisfactory that reasonable agreement is obtained.

Finally in Fig. 7 we show typical results obtained for the atmosphere in our laboratory. From these results we can measure the times of arrival and departure of the research group and the length of its lunch break!

Acknowledgements

We thank the SERC Biotechnology Directorate and the AFRC for financial support. We thank AFRC Engineering for the use of the glasshouse and infrared analyser.

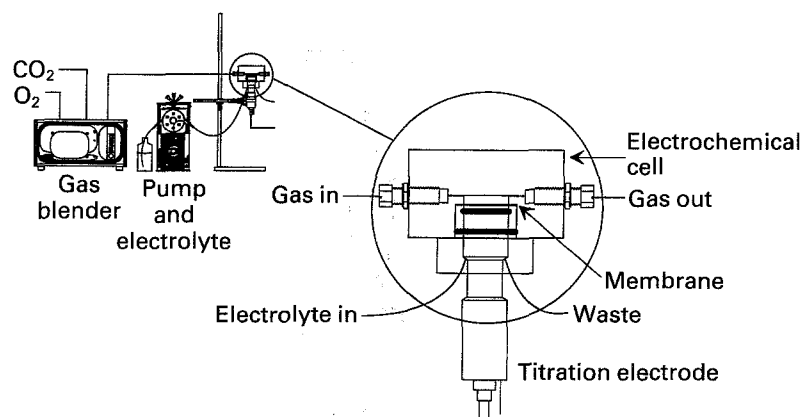


Fig. 2. Electrochemical workstation for the determination of CO₂.

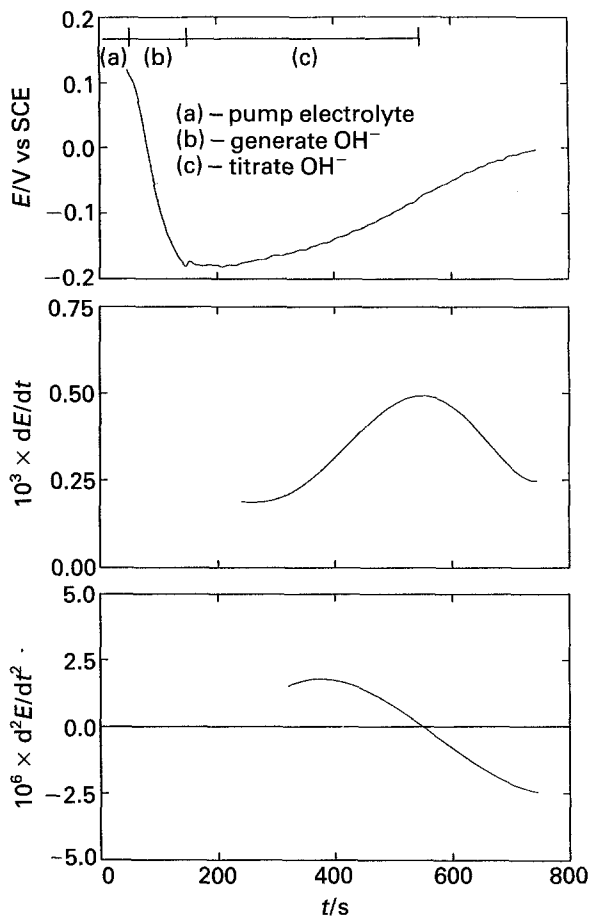


Fig. 3. (a) E/V against t/s trace of the potential of the iridium oxide electrode during a CO_2 measuring cycle (b) and (c) shows the corresponding plots of dE/dt and d^2E/dt^2 , respectively.

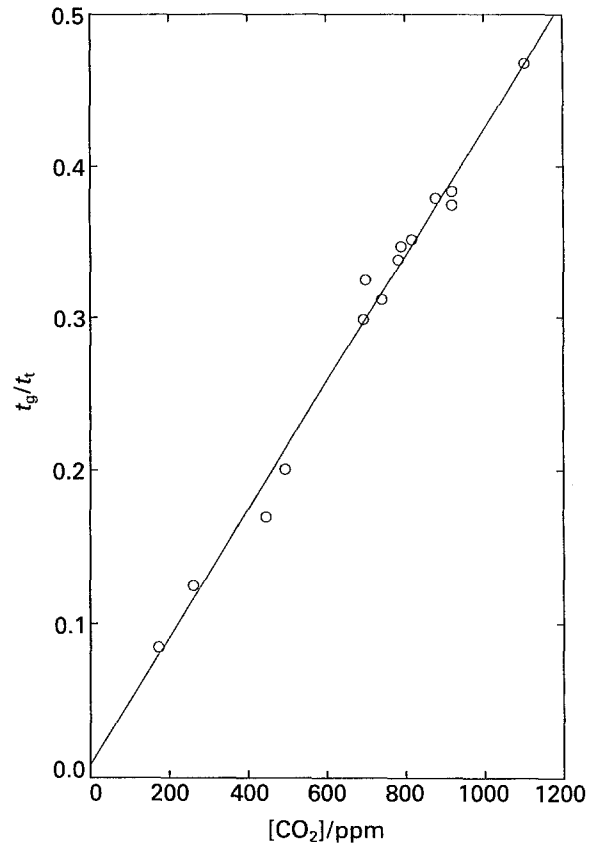


Fig. 5. t_g/t_i against $[CO_2]$ (infrared gas analyser) calibration plot.

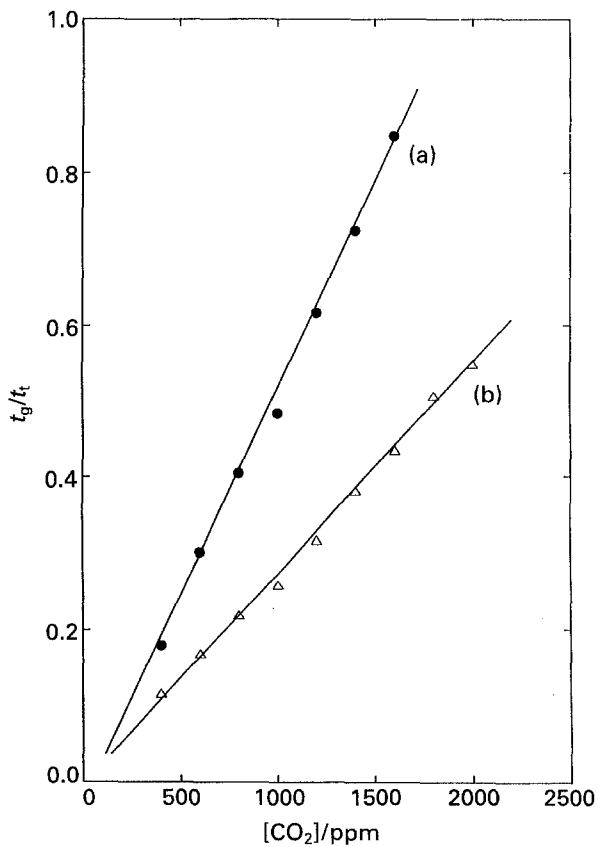


Fig. 4. Sensor calibration plots: (a) $1 \times 25 \mu m$ silicone rubber membrane, (b) $2 \times 25 \mu m$ silicone rubber membrane.

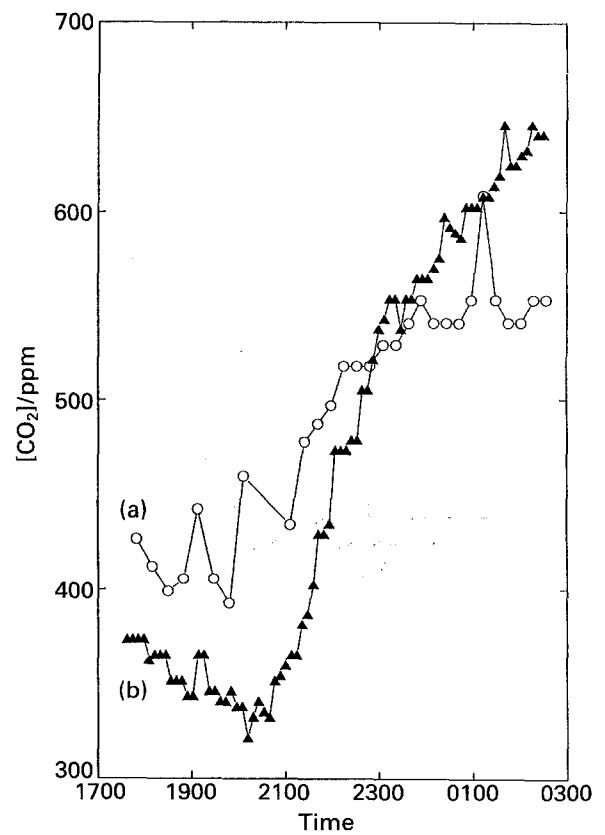


Fig. 6. CO_2 in a glasshouse: (O) titration electrode, (Δ) infrared gas analyser.

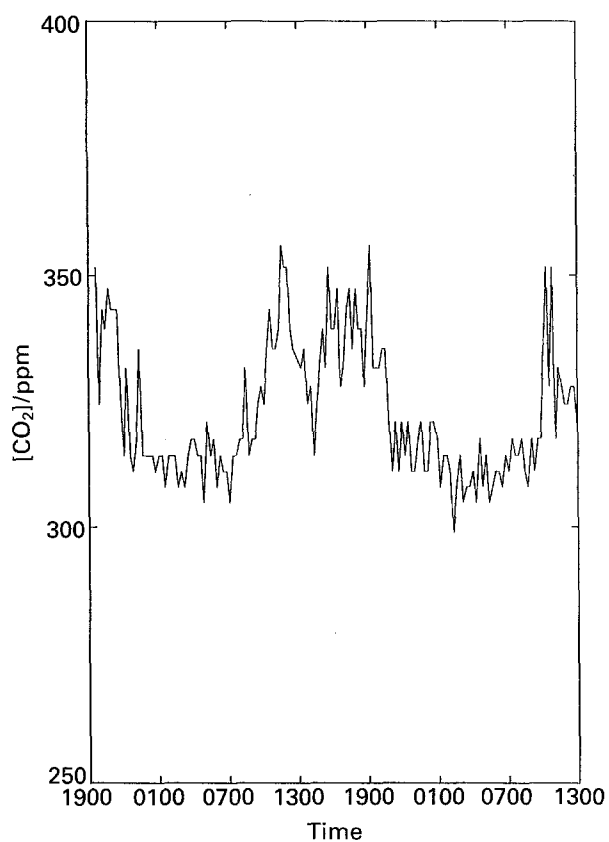


Fig. 7. CO₂ levels in a laboratory.

References

- [1] W. J. Albery and M. Uttamlal, *J. Appl. Electrochem.* (1993) this issue.
- [2] L. C. Clark, *Trans. Am. Soc. Art. Int. Org.* **2** (1956) 41.
- [3] M. L. Hitchman and S. Ramanathan, *Analyst* **113** (1988) 35.
- [4] M. Abramowitz and A. Stegun, 'Handbook of Mathematical Functions', Dover Publications, New York (1970) p. 879.