JOURNAL OF APPLIED ELECTROCHEMISTRY 24 (1994) 521–524

Development of an electrochemical workstation for monitoring the fermentation of beer

W. J. ALBERY, M. S. APPLETON*, T. R. D. PRAGNELL, M. J. PRITCHARD, M. UTTAMLAL‡
Molecular Sensors Unit, New Chemistry Laboratory, South Parks Rd, Oxford OX1 3QT, Great Britain

L. E. FIELDGATE, D. R. LAWRENCE, F. R. SHARPE
Whitbread Technical Centre, Park St, Luton LU1 3ET, Great Britain

Received 12 August 1993; revised 1 November 1993

An instrument with electrochemical sensors for measuring oxygen, carbon dioxide and glucose is described. The instrument has been used to monitor the variation of the three analytes in the fermentation of beer both in the laboratory and in a 1700 dm^3 vessel in a pilot plant. Typical results are presented. The control of oxygen levels at the start of the process is important. The concentration of glucose passes through a maximum. The time to this maximum and the initial rate of CO_2 production provide early indicators of yeast vitality.

1. Introduction

In the previous two papers [1, 2] the development of a novel titration electrode to measure CO_2 was described. In this paper the use of the CO_2 electrode, together with a conventional oxygen electrode [3] and a glucose enzyme electrode to measure online and in real time the variation of the concentration of these three analytes during the brewing of beer, is described. The new instrument has been used both in the laboratory and on a 1700 litre pilot plant fermenter at the Whitbread Technical Centre.

2. Experimental details

The construction of the CO_2 electrode has been described previously [2]. The membrane for dissolved CO_2 measurements in the 0 to 0.25 atm range was 12.5 μm PTFE. The complete sequence for a CO_2 measurement was:

(i) Pump fresh electrolyte (1 mol dm^{-3} $NaClO_4$/0.1 mol dm^{-3} NaCl) for 30 s.

(ii) Generate OH^- with a current of $-15\,\mu A$ for $t_g = 100$ s.

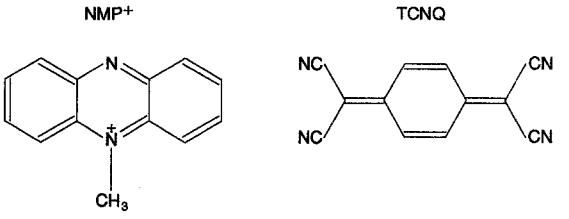
(iii) Switch from CO_2 free water to sample.

(iv) Monitor E and measure time, t_t to endpoint found as a point of inflexion.

(v) Calculate $[CO_2]$ from t_g/t_t and calibration constant.

(vi) Wash cell with CO_2 free water.

The oxygen electrode was a conventional Clark electrode [3] made of platinum with a 12.5 μm PTFE membrane supplied by Goodfellows Ltd. The electrode was held at −700 mV with respect to a Ag/AgCl reference electrode. The background electrolyte was a phosphate buffer (pH = 7.4) with 0.10 mol dm^{-3} NaCl. The glucose electrode has been described previously [4]; the electrode material was the conducting organic salt NMPTCNQ where NMP^+ and TCNQ are as follows:



The emzyme was glucose oxidase (E.C.1.1.3.4) supplied by Böhringer Mannheim Ltd and was used without further purification. The membrane was made of cellulose acetate, Spectra/Por 2 supplied by Pierce Warriner Ltd. The electrode was held at +50 mV with respect to a Ag/AgCl reference electrode. The electrolyte was the same as that used in the oxygen electrode. All other chemicals were of AnalaR grade.

At the start of this work the electrodes were controlled by the same instrumentation as that used in the development of the CO_2 electrode [2]. During the course of this work a new module, shown in Fig. 1, was developed. The electrochemical sensor, flow cell and peristaltic pumps are mounted on the front panel of each module. This gives a robust arrangement and minimises the distance between the sensor and the electronics, thereby reducing the pick up of noise in an industrial environment. The peristaltic pump heads were made by Pharmacia and each head was driven by electric motors supplied by RS Components Ltd. Switching between the test and

* Currently with Hazard Evaluation Laboratories Ltd, Fire Research Station Site, Borehamwood WD6 2BL, Great Britain
‡ Present address: Department of Chemistry, Tufts University, 62 Talbot Avenue, Medford, MA 02155, USA

0021-891X

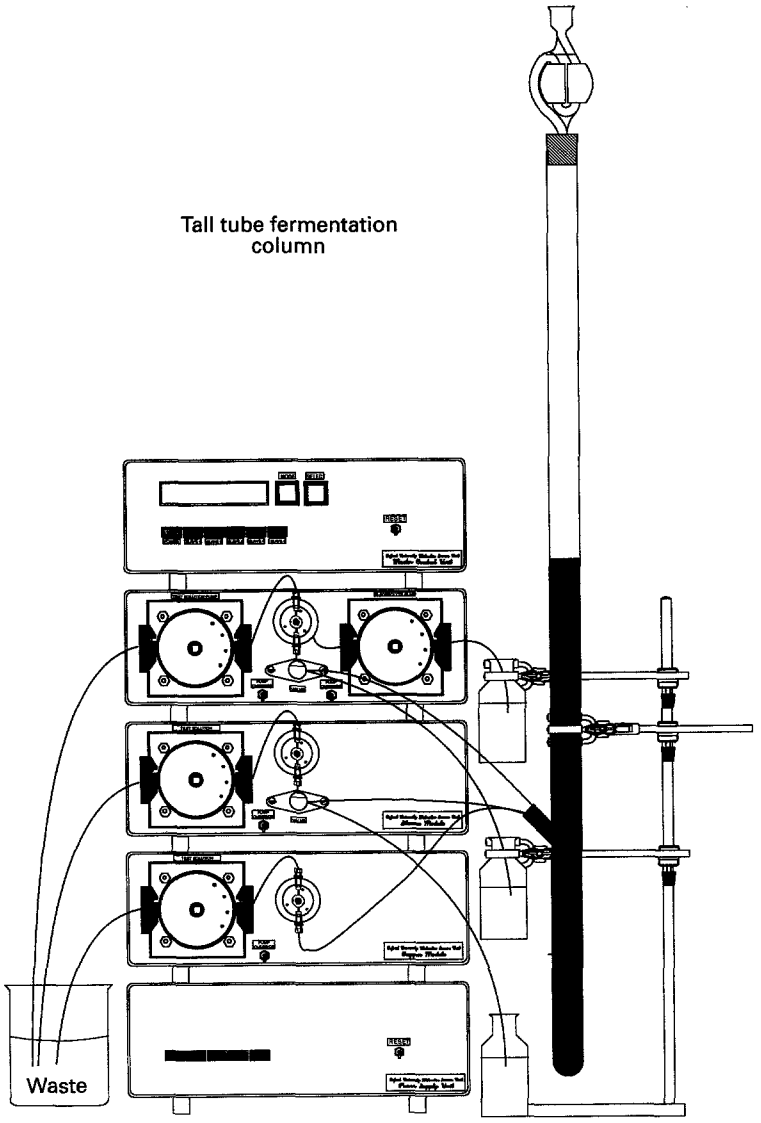


Fig. 1. Diagram of the electrochemical workstation.

calibration solutions was achieved using solenoid valves manufactured by Biochem Valve Corporation. Each analyte has its own module. Each module is connected in series and controlled through a Master Control Unit. Each module can store its own data and can be downloaded to a host microcomputer when desired. One Master Control Unit can govern up to eight modules. In the pilot plant all the modules, the Master Control Unit and the host microcomputer are housed in a Tecnopac Universal Case supplied by Schroff.

Beer was brewed in three different rigs. First, a $1\,dm^3$ tall tube fermenter made of glass was used. Secondly, we used a $30\,dm^3$ laboratory fermenter, and finally, a set of four $1700\,dm^3$ vessels in the pilot plant was used. The sensors were located outside the fermenter and the fermenting wort was bled at a flow rate of $0.10\,ml\,min^{-1}$ through the flow cell to waste.

For oxygen measurements the electrode was exposed directly to the fermenting wort. For glucose measurements the wort sample was diluted by a factor of 10 with a solution containing $0.1\,mol\,dm^{-3}$ NaCl and phosphate buffer at a pH of 7.4. This brought the glucose concentration to within the linear working range of the electrode (0 to $10\,mmol\,dm^{-3}$) and the optimum working pH. The beer and diluent were mixed continuously in the electrochemical cell using a magnetic stirrer. For CO_2 measurements the electrode was only exposed to the wort during the titration phase. At all other times wort was replaced with air saturated water. No serious problems with contamination were experienced using these procedures. The wort and yeast for brewing were supplied by Whitbread.

3. Results and discussion

3.1. *Oxygen electrode*

Brewers yeast requires oxygen in the initial part of the fermentation for the production of unsaturated lipids and sterols [5]. These are important constituents for the yeast cell membrane without which yeast growth is severely restricted.

Figure 2 shows typical results from the oxygen electrode for dissolved oxygen in wort. These results were obtained in the pilot plant. At point A the oxygen concentration is low. At point 8 yeast is introduced into the wort and the yeast rapidly consumes the available oxygen. Between points C and D oxygen is blown (sparged) through the wort. There is a specification for the initial oxygen content for each type of beer fermentation. Hence monitoring the oxygen level at this stage is important. At point E the oxygen is fully consumed leading to anaerobic conditions for the rest of the fermentation.

When the oxygen sensor was first used in the pilot plant it was found that for one vessel the oxygen levels appeared to be half of the value required. This problem was eventually traced to the sparge ring that had become partially blocked. After cleaning the ring the proper levels of oxygen were attained.

3.2. *Glucose Electrode*

A major source of energy for yeast propagation comes from the carbohydrates present in wort. Typical values for their proportions are glucose 14%, sucrose 6%, maltose 59% and maltotriose 20%.

Figure 3 shows typical results for the variation in glucose concentration obtained from the 30 litre laboratory fermenter. The glucose concentration passes through a maximum. This is because the yeast

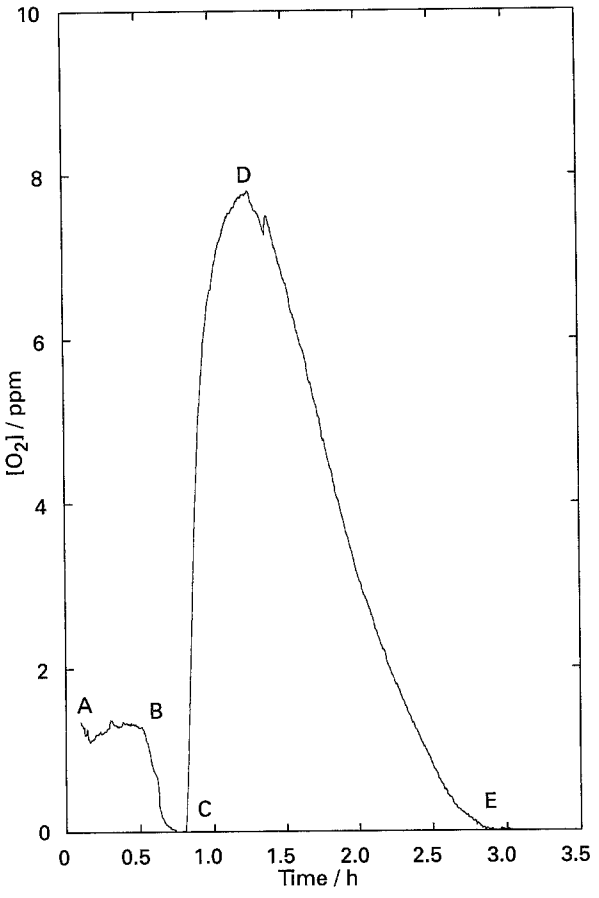


Fig. 2. Typical results for the variation of the concentration of oxygen in beer fermentation in the pilot plant.

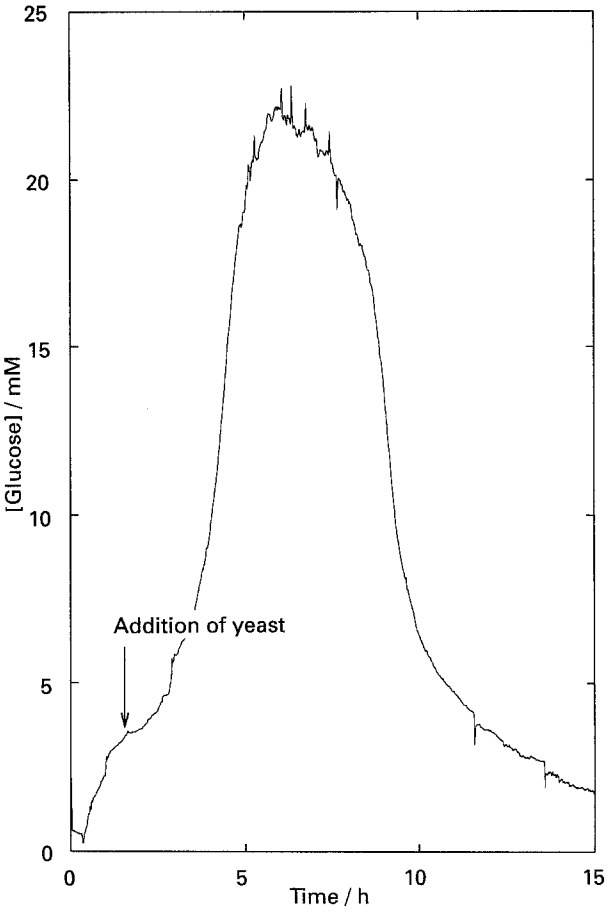


Fig. 3. Typical results for the variation of the concentration of glucose in beer fermentation in a 30 dm^3 laboratory fermentor.

starts by converting sucrose to glucose and fructose. Beyond the maximum the sucrose level has fallen so that now there is a net consumption of glucose.

3.3. *CO_2 electrode*

Previous work on the CO_2 sensor measured CO_2 in the gas phase [2]. The calibration plot in Fig. 4 shows that the sensor can also measure CO_2 in an aqueous phase. CO_2 production in beer fermentation can take place under aerobic conditions by the partial oxidation of glucose:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

Figure 5 shows typical results for the release of CO_2 for two different yeasts. The older yeast is less active. Such variation in yeast vitality means that the time for the same fermentation may vary, for instance, between two and four days. In managing a plant it is helpful to be able to predict the time the fermentation will take. The initial rates of CO_2 production and O_2 uptake and the time to the glucose maximum should provide an early indication of yeast vitality and fermentation performance leading to better control of the plant and of the fermentation process.

Acknowledgements

We thank the SERC Biotechnology Directorate

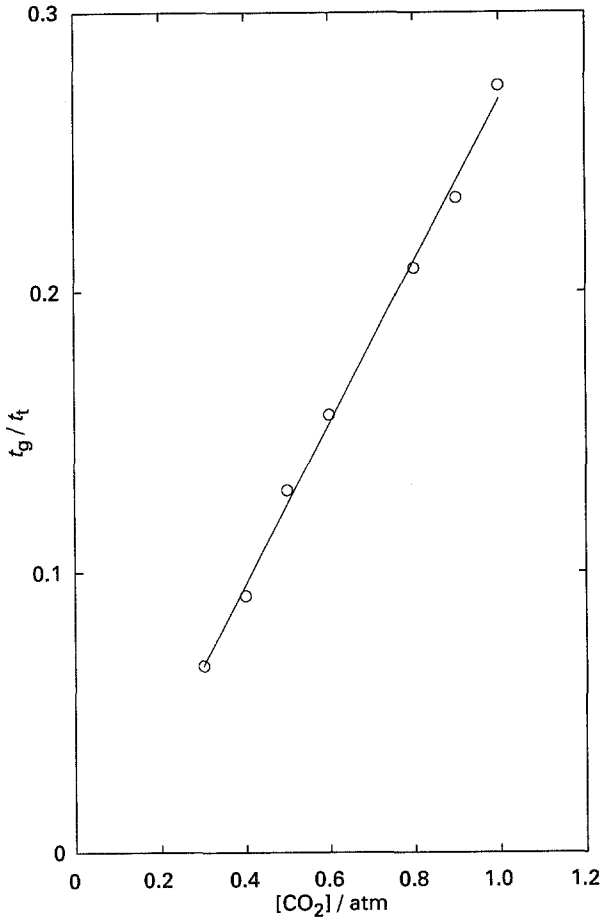


Fig. 4. Calibration plot for the measurement of CO_2 from an aqueous solution: t_g is the time for generation of OH^- and t_t is the time for the titration of OH^- by CO_2 diffusing across the membrane.

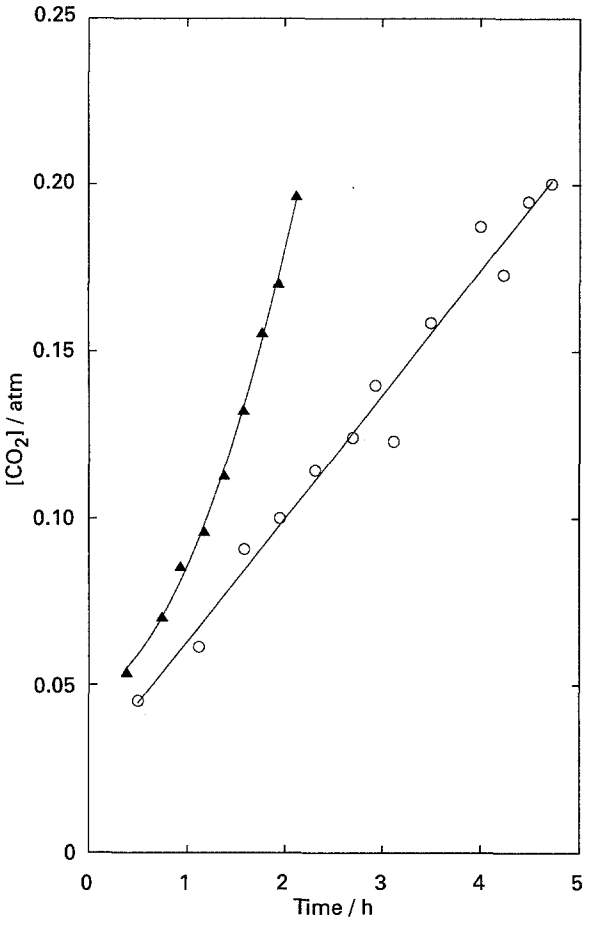


Fig. 5. Typical results for the variation of the concentration of carbon dioxide in an ale fermentation in the tall tube fermentor. (▲) Fresh yeast and (○) 15 day old yeast.

for a studentship for M. Uttamlal. We also thank the operators of the pilot plant for putting up with us.

References

[1] W. J. Albery and M. Uttamlal. *J. Appl. Electrochem.* **24** (1994) 8, in press.

[2] W. J. Albery, M. Uttamlal, M. S. Appleton, N. J. Freeman, B. B. Kebbekus and M. D. Neville, *J. Appl. Electrochem.* **24** (1994) 14, in press.

[3] L. C. Clark, *Trans. Am. Soc. Art. Int. Org.* **2** (1956) 41.

[4] W. J. Albery, P. N. Bartlett and D. H. Craston, *J. Electroanal. Chem.* **194** (1985) 223.

[5] B. H. Kirsop, *J. Inst. Brew.* **80** (1974) 252.