AN ELECTROANALYTICAL TECHNIQUE FOR THE DETERMINATION OF
TOTAL IRON IN NUTRIENT SOLUTIONS

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Abstract

A new on line technique, the packed bed wall-jet electrode,
for the determination of total iron in hydroponic solutions
has been developed.To avoid interference from O_2 and to
convert Fe(III) to Fe(II) a packed bed electrode is inserted
upstream of a wall-jet electrode. The total iron is then
determined by the oxidation of Fe(II) on the downstream
electrode. The bed is shown to remove 99% of the O_2 present
in air saturated solutions, thereby removing the necessity
for deoxygenating the test solution by bubbling N_2. Linear
calibration plots have been obtained for iron concentrations
from 0.050 to 1.5 mmol dm^{-3} and the technique has been
tested in samples of nutrient film solution.

Introduction

The aim of this work has been to find a method to
determine total iron concentration in nutrient solutions
for hydroponics. Iron is a vital element for the growth of
plants and is present in nutrient solutions as a complex
of EDTA in concentrations of about 50 μmol dm^{-3} (1). The
plant till take up both the Fe(II) and Fe(III) complexes
and so the requirement is to determine the total iron
concentration. In our method this is determined amperometric
ally and the electrode of choice is a wall-jet electrode(WJE).
This is because, first it is one of the most sensitive on
line detectors and secondly it is a stationary electrode with
no moving parts and operates under forced convection in the

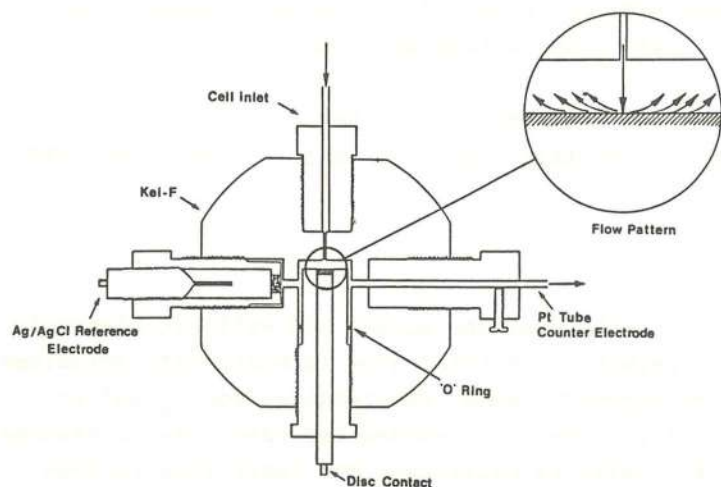*Now at CECUL,Cç Bento Rocha Cabral,14, 1200Lisboa, Portugal

Figure 1 - The Wall-Jet Disc Electrode (WJE).
The inset shows the flow pattern.

flowing solution(2). The electrode is illustrated in Figure 1.
The inset shows the flow due to a jet of fluid striking a
plane surface at right angles and spreading out radially over
the disc surface. Yamada and Matsuda(2) derived an expression
for the limiting current, i_L, at an electrode, under laminar
flow, where a jet issuing from a circular nozzle impinges
normally on the centre of a disc electrode:

$$i_L = 1.60 \ knFD^{2/3} \nu^{-5/12} \ V_f^{3/4} \ a^{-1/2} \ c_\infty \ r^{3/4} \qquad (1)$$

k is a constant determined by experiment to be 0.86(3), n is
the number of electrons transferred, F is the Faraday constant,
D is the diffusion coefficient of the electroactive species,
ν is the kinematic viscosity of the background electrolyte, V_f
is the volume flow rate, a is the diameter of the jet, c_∞ is
the bulk concentration and r is the radius of the disc electrode.

Albery and Brett(3) obtained the same expression but in
their derivation they found the streamlines shown in Figure 1.

In this work the wall-jet electrode is further improved
by adding a bed in the flow stream before the jet. This bed
electrode is designed firstly to remove oxygen and secondly
to convert Fe(III) to Fe(II) thereby allowing a determination
of total iron rather than either Fe(II) or Fe(III). The theory
of the packed bed wall-jet electrode (PBWJE) has been presented
elsewhere(4).

Experimental

Apparatus

The wall-jet electrode assembly has been described
previously, (5), (6). The packed bed addition is shown in
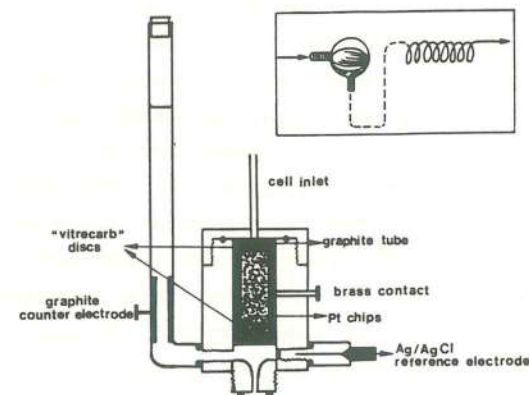Figure 2. It consists of three vitrocarb discs and the space

Figure 2 - The Packed Bed Wall-Jet Electrode (PBWJE).
The counter electrode for the packed bed
is located in a side arm to allow the
escape of O_2. The inset shows the pulse
damper for the peristaltic pump.

between them is filled with Pt chips (about 100 μ × 1 μm^2).

This assembly is fitted into a graphite tube and then platinised to increase the surface area. The porous vitrocarb (recticulated vitreous carbon) was supplied by Fluorocarbon. It has the following advantages. Firstly its resistance to solution flow is low. Secondly it is a material of low electrical resistivity, having a physically continuous structure, and a large surface area. The features lead to a high conversion efficiency. The counter electrode, also shown in Figure 2, was a graphite tube sealed into a vertical length of silicon rubber tubing filled with test solution. Oxygen bubbles formed on the counter electrode escaped into this side tube rather than blocking the electrical contact between the working and counter electrodes. The reference electrode was a silver-silver chloride electrode (E^O = 204 mV on the normal hydrogen scale). The solution was pumped through the electrode assembly by a Pharmacia P-3 peristaltic pump producing solution flow rates between 9 and 60 mm^3 s^{-1}. In each experiment the flow rates were calibrated volumetrically. All experiments were conducted at room temperature.

A peristaltic pump inevitably produces pulsations in the flow. They can be removed by a chamber and coiled length of tube as shown in the inset of Figure 2(8). The pump and pulse damper can be connected either upstream or downstream of the electrode assembly. In the upstream configuration (push mode) the oxygen is less likely to be sucked into the test solution but the test solution has to pass through the pump and pulse damper before being analysed, giving an undesirable time lag. In the downstream configuration (pull mode) this time lag is avoided but oxygen is more likely to be sucked into the system. As described below oxygen is removed by the packed bed filter. Therefore for nutrient solution determinations the system was operated in the pull mode. Preliminary experiments without the packed bed filter were conducted in the push mode.

Chemicals

Chemicals of Analar grade and doubly distilled water were used in the preparation of all solutions. Oxygen free

nitrogen used for deaeration was passed through Dreschel bottles containing Na 9,10-anthraquinone 2-sulphonate/zinc amalgam in sodium hydroxide solution. Samples of nutrient solutions from an NFT culture were provided by the Glasshouse Crops Research Institute (GCRI).

Results and Discussion

Reduction of $[Fe(III) EDTA]^-$ on a Pt WJE was carried out. As shown in Figure 3, well shaped voltammograms were obtained for a solution containing 10 mmol dm^{-3} $[Fe(III) EDTA]^-$ in 0.4 mol dm^{-3} K_2SO_4. As required by eqn (1) the limiting currents vary linearly with $V_f^{3/4}$. From the gradient the value of the diffusion coefficient ($D = 3 \times 10^{-6}$ cm^2 s^{-1}) agrees
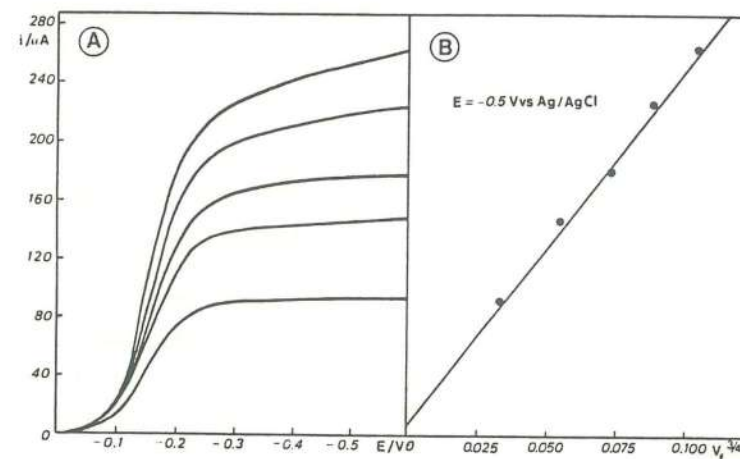

Figure 3 - Typical current voltage curves for the reduction of $[Fe(III) EDTA]^-$ (10 mmol dm^{-3}) on a Pt WJDE. Figure 3B shows the variation of the limiting current with flow rate plotted according to eqn 1 where V_f is measured in cm^3 s^{-1}.

with a value determined using the rotating disc electrode. As shown in Figure 4, at constant flow velocity the limiting current varies linearly with concentration in the range 1 to 50 mmol dm^{-3}. These results show that the wall-jet disc electrode performs well and has the correct hydrodynamics.
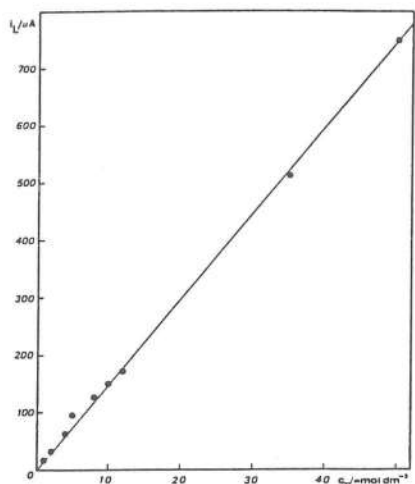

Figure 4 - Variation of limiting current, i_L, for reduction of $[Fe(III) EDTA]^-$ with bulk concentration, c_∞.

As reported by Gunansingham and Fleet(9) the nozzle of the jet must not be inside the hydrodynamic boundary layer. In our experiments we found that a distance of about 2.5 mm between the nozzle and the electrode gave satisfactory results. Although good results were obtained in solutions of 1 mmol dm^{-3}, the hydroponic solutions typically contain only 50 μmol dm^{-3}. For this concentration ill defined voltammograms were obtained. The reason for this was the interference from the reduction of oxygen. In addition some of the iron is present as Fe(II) and it is preferable to monitor total soluble iron. For these reasons the packed bed electrode was introduced:

Packed Bed Electrode $\quad$ Fe(III) + e^- → Fe(II)

$$O_2 + 4e^- + 4H^+ → 2H_2O$$
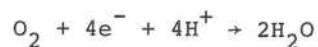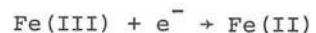
Disc Electrode $\quad$ Fe(II) → Fe(III) + e^-
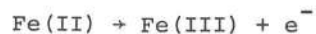
The packed bed electrode both removes the oxygen and converts all the Fe(III) to Fe(II). The total iron concentration is then found by oxidising Fe(II) on the

disc electrode. The removal of O_2 is important in order to prevent oxidation of Fe(II) in its passage from the packed bed electrode to the disc electrode.

Figure 5 compares the removal of oxygen by the pre-electrolyser, and by bubbling the solution with oxygen free nitrogen. In Figure 5A the bubbling method (broken lines) still leaves a significant quantity of O_2 which probably arises from operating the system with the pump in the pull mode, as discussed above. The cathodic part of
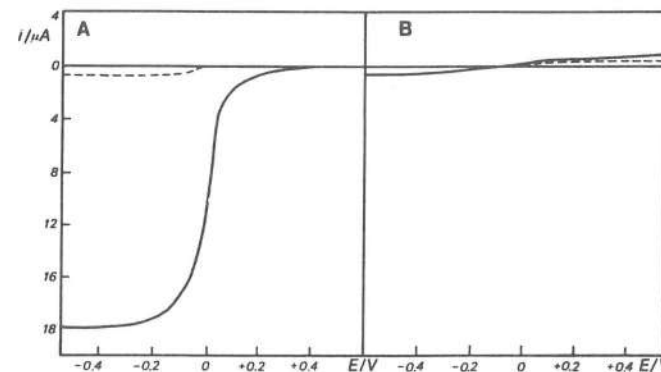

Figure 5 - The Packed Bed Oxygen Filter. Figures 5A and 5B show current voltage curves with the packed bed switched off and on respectively. In either case broken lines show current voltage curves where the test solution (0.4 mol dm^{-3} K_2SO_4) has been deoxygenated by bubbling with N_2, the solid lines show results where the solution has not been deoxygenated in this way. The flow rate was 9 mm^3 s^{-1} and when switched on the potential of the Packed Bed Electrode was -0.70 V.

Figure 5B shows that the packed bed removes 99% of the oxygen. Unfortunately there is a small anodic current. This current is not present if the solution is deoxygenated by bubbling

and the packed bed is switched on. This suggests that this small current is caused by a product of the O_2 reduction which may well be H_2O_2. However the results in Figure 5 show that the packed bed is an efficient filter for O_2 and this technique of removing O_2 should be useful for other applications involving on line flow through electrodes.

Figure 6 shows typical voltammograms for a solution deoxygenated by bubbling and containing 0.5 mmol dm^{-3} $[Fe\ EDTA]^-$. The upper voltammogram shows the behaviour with
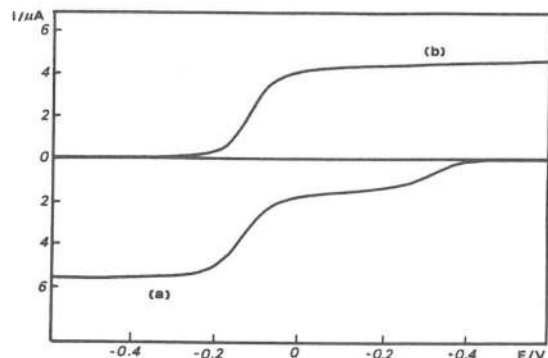

Figure 6 - Typical current voltage curves at the PBWJE for a solution deoxygenated by bubbling N_2 and containing 0.50 mmol dm^{-3} $[Fe(III)\ EDTA]^-$. In the upper curve the Packed Bed Electrode is switched off, while in the lower curve it is potentiostatted at -0.70 V. The flow rate was 9 $mm^3\ s^{-1}$.

the packed bed switched off. There is a wave due to residual oxygen reduction followed by a wave due to the reduction of Fe(III). The lower voltammogram shows the current voltage curve with the packed bed set to -0.70 V. A well behaved voltammogram for the oxidation of Fe(II) with insignificant interference from O_2 is observed. The variation of the limiting current with the concentration of Fe(III) in the range 0.05 to 1.5 mmol dm^{-3}, which is the range required for

the nutrient film, is shown in Figure 7. A good linear relationship is obtained. The technique was tested using
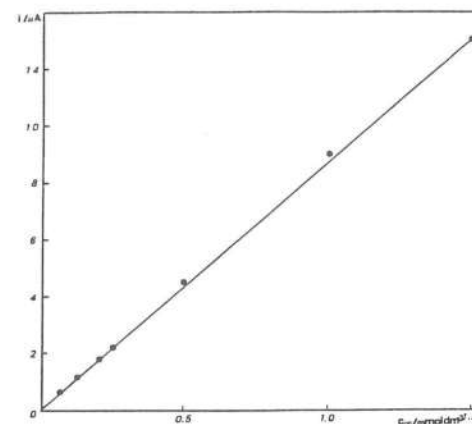

Figure 7 - Plot of limiting currents for the oxidation of $[Fe(II)\ EDTA]^{2-}$ as shown in Figure 6, against the concentration of $[Fe(III)\ EDTA]^-$ in the test solution.

samples of nutrient solution provided by GCRI. The samples were taken from an NFT culture which had been used to feed tomatoes for five months. The plants were showing good top growth and had good root systems. A typical voltammogram is shown in Figure 8. From the limiting current the concentration of total iron was found to be 0.9 mmol dm^{-3}
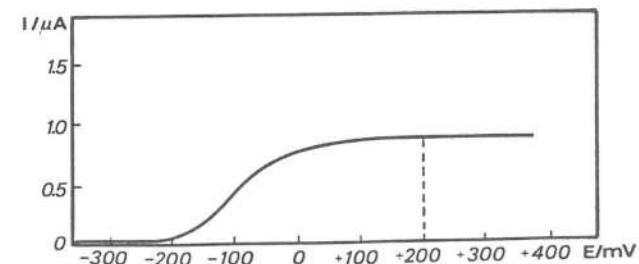

Figure 8 - Typical current voltage curve at the PBWJE for a nutrient solution with the Packed Bed Electrode set at -0.70 V.

and this result was in good agreement with that estimated
by atomic absorption spectroscopy at GCRI. Hence the packed
bed wall-jet electrode provides a cheap on line detector for
the measurement of total iron in nutrient film solutions.

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