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Trace-metal Analysis in Hydroponic Solutions

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A wall-jet ring–disc electrode detector has been developed for the direct on-line monitoring of the trace metals manganese, zinc and copper at the micro- and submicro-molar level in hydroponic nutrient solutions. The technique employed is of anodic or cathodic stripping voltammetry with collection (a.s.v.w.c. or c.s.v.w.c.) at ring–disc electrodes. All three elements may be quantitatively determined by a.s.v.w.c. using *in situ*-plated thin-mercury-film electrodes. Interference effects and intermetallic compound formation are discussed. It is shown that manganese may be quantified alternatively by c.s.v.w.c. *via* its deposition as MnO_2. Results in test solutions and in nutrient solution agree well with theoretical predictions and the reproducibility is good. A method for determining the toxic trace-metal nickel by a.s.v.w.c. is also developed.

The quantitative estimation of trace metals at the submicromolar level is very important in many applications involving biological, environmental or industrial samples. This usually relies on spectrometric techniques, the analysis often taking place somewhere removed from the sample collection site. An ideal sensor would be an on-line monitor and would produce results quickly and frequently with the minimum of assistance. Flow-through amperometric electrochemical sensors are able to satisfy these criteria. As they are based on solid electrodes many of the difficulties experienced by non-electrochemists with the more classical dropping mercury electrode disappear. They can be placed anywhere in a flow system and computer automation is relatively easy to accomplish.

Here we describe the development of a flow-through sensor based on the wall-jet principle to determine trace-metal ions in hydroponic solutions based on the nutrient film technique. The plants are grown in a shallow stream of flowing nutrient solution in sloping troughs within glasshouses, the solution being continuously recirculated and slowly replenished.[1] The levels of beneficial or toxic trace metals can have a marked effect on plant growth and will vary according to the crop. Table 1 shows a typical set of concentrated nutrient solutions, which would be added to the circulating solution as necessary. In table 2 are recommended levels of trace elements for a tomato crop (which are not necessarily the optimum). We shall be concerned with the first three of these trace elements, namely manganese, zinc and copper. We will also consider the measurement of nickel, a particularly toxic trace metal which can appear by, for example, corrosion of monel heaters used to warm the nutrient solution in winter.

Electrochemical Detector

There are several different types of electrochemical flow-cell available, including thin-layer,[2] tubular[3] and wall-jet[4] types. The last of these has advantages with respect to the other configurations, owing to its higher sensitivity, ease in use and ease of maintenance and well defined hydrodynamics.

Table 1. A typical formulation for concentrated hydroponic nutrient stock solutions

solution I/dm^{-3}	solution II/dm^{-3}
100 g $Ca(NO_3)_2$ hydrate	160 g KNO_3
	100 g $MgSO_4$
	10 g Fe EDTA complex
solution III/dm^{-3}	0.25 g H_3BO_3
100 g HNO_3	1.2 g $MnSO_4$
42 g H_3PO_4	0.08 g $CuSO_4$
	0.1 g $ZnSO_4$
	0.02 g $(NH_4)_2MoO_4$

Table 2. Typical trace-element levels in nutrient solutions[a]

	concentration	
element	(p.p.m.)	/mol dm^{-3}
Mn	1.0	1.8×10^{-5}
Zn	0.08	1.2×10^{-6}
Cu	0.05	7.9×10^{-7}
B	0.15	1.4×10^{-7}
Mo	0.03	3.1×10^{-7}

[a] By dilution from table 1 formulation.

A fine jet issuing from a circular nozzle impinges on the centre of a disc electrode perpendicular to the jet: the solution then spreads out radially. It has been shown[5] that under laminar flow any species which reaches the disc electrode and subsequently leaves the diffusion layer cannot react again. This is very useful in practice, since it means that the volume of the wall-jet cell is not important for its efficient use. The wall-jet ring–disc electrode cell, analogous to the rotating ring–disc electrode, allows extra possibilities in studies of electrochemical reactions. We have used a wall-jet ring–disc electrode (w.j.r.d.e.) for this work.

Voltammetric Method

In order to increase the measured signal and to improve the signal-to-noise ratio, we generally use a preconcentration step to deposit the electroactive species on the electrode, followed by a stripping step for the actual measurement. Table 3 shows four methods for achieving this, the most widely used being stripping voltammetry (s.v.) and potentiometric stripping analysis (p.s.a.). P.s.a. has the advantage in some cases that the oxidant in the stripping step can be oxygen, obviating the need for deoxygenation.[10] The range of application of s.v. is large and therefore we have used this technique.

In stripping voltammetry there are a number of ways of carrying out the stripping step, the current for which contains Faradaic and non-Faradaic (mainly capacitative) contributions. The simplest is a linear scan, which for oxidation of a deposited metal will be in the anodic direction; the limit on sensitivity is the capacitative contribution, which means high scan rates cannot be employed. To obviate this, several more sophisticated waveforms have been invented such as differential pulse,[11] staircase,[12] phase selective a.c.[13] and subtractive stripping voltammetry.[14, 15]

Table 3. Principles of preconcentration methods for electrochemical detection of trace species

method	deposition (preconcentration step)	stripping step	measurement
stripping voltammetry[a]	potential control	potential control	*i vs. t*
adsorptive stripping voltammetry[b]	adsorption (no applied potential)	potential control	*i vs. t*
potentiometric stripping analysis[c]	potential control	reaction with oxidant or reductant in solution (no applied potential)	*E vs. t*
stripping chronopotentiometry[d]	potential control	current control	*E vs. t*

[a] Ref. (6). [b] Ref. (7). [c] Ref. (8). [d] Ref. (9).

We have used a method first described by Johnson and Allen,[16] namely anodic stripping voltammetry with collection (a.s.v.w.c.). It can be applied to any double electrode system and has been used at the r.r.d.e.,[16] at the double tube electrode[17] and at the wall-jet ring–disc electrode.[18] The ring potential is held constant in such a way that it collects the species stripped from the disc. We may write

$$q_{\mathrm{R}} = \int i_{\mathrm{R,L}}\,\mathrm{d}t \tag{1}$$

$$= -N_0\, q_{\mathrm{D}} \tag{2}$$

$$= -N_0\, i_{\mathrm{D,L}}\, t_{\mathrm{dep}} \tag{3}$$

where the integration is carried out over the whole transient. $i_{\mathrm{R,L}}$ and $i_{\mathrm{D,L}}$ are the limiting currents at ring and disc, respectively, q_{R} and q_{D} the respective charges involved and N_0 is the steady-state collection efficiency. The diffusion-limited current at a wall-jet electrode is given by[4]

$$i_{\mathrm{D,L}} = 1.38\, nFD^{\frac{2}{3}} v^{-\frac{5}{12}} V_{\mathrm{f}}^{\frac{3}{4}} a^{-\frac{1}{2}} c_{\infty}\, r_1^{\frac{3}{4}} \tag{4}$$

where D is the diffusion current of the electroactive species, v the kinematic viscosity of the solution, V_{f} the volume flow rate, a the nozzle diameter, c_{∞} the bulk concentration and r_1 is the disc electrode radius. Thus it is simple to check the accuracy of the technique in test solutions containing known quantities of trace metals by use of eqn (3).

Another important aspect is that whatever the type of stripping waveform used at the disc electrode, the ring response integrated over the whole current transient should be unaffected: here we use potential pulse.

In general, because of the rather negative deposition potentials involved, it is necessary to use a thin-film mercury electrode on a glassy carbon electrode substrate, which we prepared by *in situ* deposition.

A.s.v.w.c. with a linear scan stripping step using an r.r.d.e. with mercury films on both the glassy carbon disc and glassy carbon ring have been reported.[19]

Experimental

The wall-jet ring–disc electrode cell (Oxford Electrodes) was of the Fleet and Little design[20] and has been described previously.[18] The electrodes used were glassy carbon–

platinum and platinum–platinum disc–ring combinations in a Kel-F sheath. A glassy carbon–glassy carbon r.r.d.e. was also employed. After initial polishing with 6 and 3 μm diamond lapping compound, the electrodes were then hand polished with 1 and 0.3 μm alumina made into a slurry with triply distilled water and finally washed thoroughly with triply distilled water. The final polishing step was repeated every day.

In testing the procedures, analytical grade reagents were used and made into solution with triply distilled water. Nutrient test solutions were made up from laboratory grade reagents in order to conform with the commercial solutions. After mixing of the test solution and supporting electrolyte, deoxygenation was carried out using oxygen-free nitrogen (Air Liquide) presaturated in the supporting electrolyte. It has been shown that further purification of the oxygen-free nitrogen is unnecessary.[21]

The solution was pulled through the wall-jet detector by means of a Pharmacia P3 peristaltic pump placed downstream. To minimise pump pulsations a long length of Teflon tubing and a hollow glass ball between detector and pump provided damping. Flow rates were calibrated volumetrically every day.

The normal bipotentiostat was modified to enable integration of the ring transients. These were recorded either on a Gould Advance digital storage oscilloscope OS4020 with subsequent readout or on a Philips PM8120 XYt recorder.

Results and Discussion

The trace metals manganese, zinc and copper can all be determined by a.s.v. Relative to an Ag|AgCl reference electrode (wall-jet cell) we found the deposition potentials necessary to be -1.8, -1.2 and -0.4 V, respectively, on an *in situ*-deposited mercury film electrode (m.f.e.) with glassy carbon substrate. Owing to the large negative deposition potential for manganese we also investigated its deposition as MnO_2 and cathodic stripping with collection (c.s.v.w.c.).

An important parameter in this type of collection technique is the transit time between disc and ring, which will affect the shape of the ring-current transient. At the wall-jet (unlike rotating electrodes) the radial velocity decreases with radius. In order to have a reasonable transit time (*ca.* 0.3 s) the ring–disc electrode dimensions need to be quite small. Our electrodes have the approximate dimensions: disc radius, $r_1 = 0.17$ cm; inner ring radius, $r_2 = 0.18$ cm; outer ring radius, $r_3 = 0.19$ cm. In this way we were able to perform the a.s.v.w.c. and c.s.v.w.c. experiments with high reproducibility. The experimental value of N_0 was 0.160, independent of flow rate and was reproducible; the fact that it is slightly higher than the theoretical value has been ascribed to edge effects in the cell.[18]

Laser and Ariel[19] in their work on a.s.v.w.c. at the r.r.d.e. have noted that a minimum mercury plating time is necessary on the ring electrode in order to get the full response predicted by eqn (3). There are two reasons for this: one is the shielding factor caused by the disc electrode and the other is that a relatively thick film of mercury has to be deposited to accommodate the large quantity of metal ions reaching it from the disc stripping pulse. However, with judicious care and several minutes' plating time at the ring, good results are obtained.

For the a.s.v.w.c. experiments the supporting electrolyte employed was $NaClO_4$, added in sufficient quantity to give a 0.1 mol dm^{-3} solution. M.f.e. were formed *in situ* from Hg^{II} in the test solution, added to give 5×10^{-5} mol dm^{-3}.

We now consider results obtained for the individual trace elements, in 'ideal' conditions and in the nutrient solution. The a.s.v.w.c. (as opposed to a.s.v. with just a disc electrode) of Mn and Zn has not yet been carried out at the wall-jet ring–disc electrode as an electrode with a glassy carbon ring and glassy carbon disc is still under development. Although they will not be shown here, good results were obtained for all collection-type experiments at an analogous rotating ring–disc electrode. We will focus on the more interesting aspects of what we found.

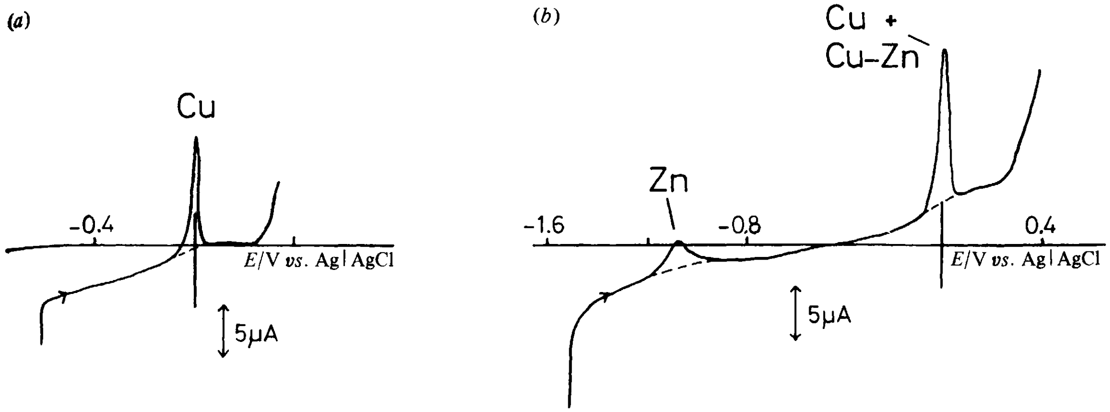

Fig. 1. The effect of Cu–Zn intermetallic compound formation shown by linear-scan stripping at the wall-jet m.f.e. Solution: 10^{-6} mol dm^{-3} Zn^{II}, 10^{-6} mol dm^{-3} Cu^{II}, 0.1 mol dm^{-3} $NaClO_4$, 5×10^{-5} mol dm^{-3} Hg^{II}. Deposition period 90 s; flow rate 0.040 cm^3 s^{-1}, stripping scan rate 100 mV s^{-1}. (*a*) Deposition of Cu alone at −0.6 V, (*b*) deposition of Cu and Zn at −1.5 V.

Copper

The technique of a.s.v.w.c. at the wall-jet ring–disc electrode has already been demonstrated for copper at the 10^{-8} mol dm^{-3} level,[18] the detection limit probably being rather lower. It functions equally well at glassy carbon and platinum electrodes, and also at the m.f.e.

Zinc

In order to determine zinc, applying a deposition potential of −1.2 V *vs.* Ag|AgCl deposits both copper and zinc. Cu–Zn intermetallic compound formation in mercury electrodes is well known, and several papers have been devoted to the resolution of the problem which arises owing to the copper and copper–zinc stripping peaks being virtually coincident. These have involved the use of a twin-electrode cell,[22] optimising the potential stripping waveform and preconcentration time[23] and addition of a third element which has a significantly higher formation constant for intermetallic compound formation with copper, such as gallium, to mask it totally.[24] We propose a simple procedure for resolving this problem: it involves a two-step experiment: (i) deposition of Cu alone at −0.4 V followed by its stripping; (ii) deposition of Zn and Cu at −1.2 V–first strip the Zn alone (at, say, −0.5 V) and immediately afterwards the Cu–Zn and Cu. Simple subtraction gives the correct Cu and Zn concentrations. If (ii) is carried out quickly and the deposition times are not very short then there is minimal error. This is illustrated in fig. 1 in a linear scan experiment for clarity. In linear scan stripping at the m.f.e., the peak height is proportional to the concentration of the species being stripped.[25] To ensure good reproducibility, we strip the mercury film after each of these experiments.

Manganese

Manganese(II) may be quantified by deposition on an m.f.e. at −1.8 V and subsequent anodic stripping. There is only the odd example[26] with reduced precision (owing to the very negative deposition potential and the fact that manganese tends to form a dilute amalgam).

We have investigated the deposition of MnO_2 and its subsequent stripping. C.s.v. of Mn^{II} has been described at the rotating disc electrode.[27] There is obviously a pH

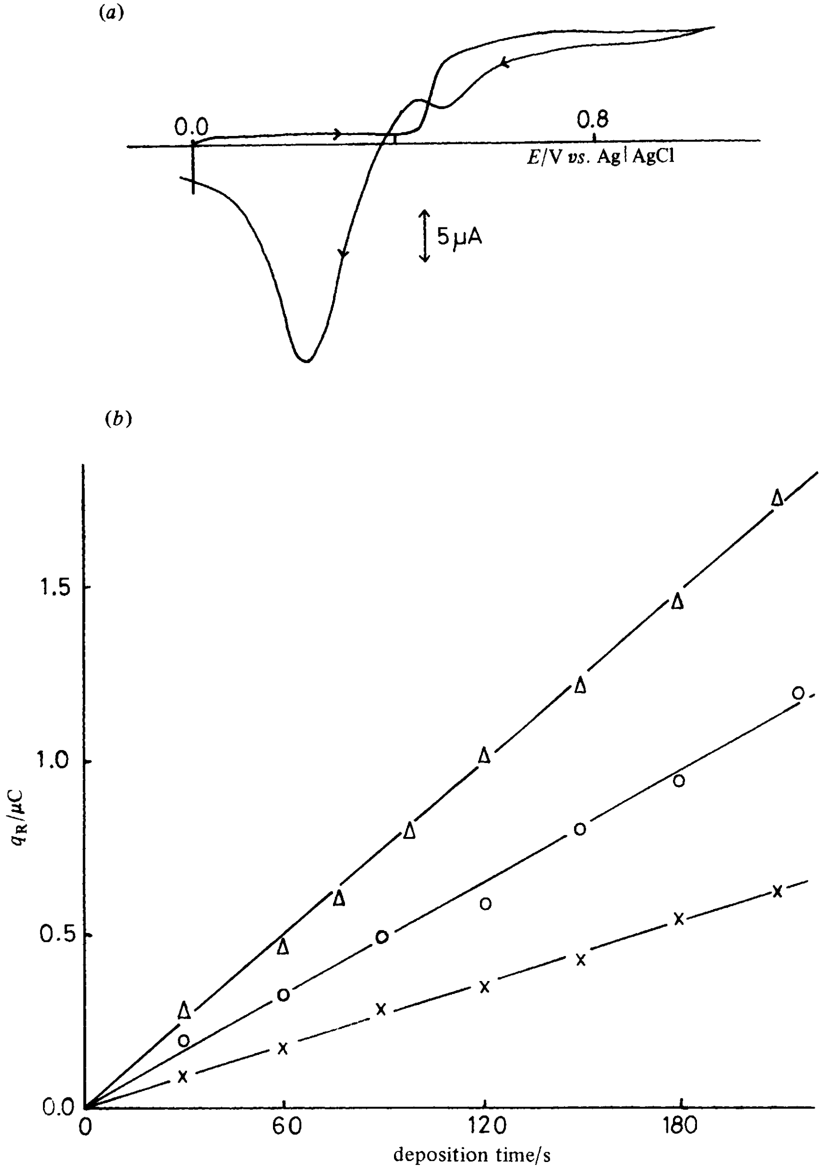

Fig. 2. Manganese analysis *via* electrode preconcentration as MnO_2. Conditions: Pt–Pt w.j.r.d.e., flow rate 0.04 $cm^3 s^{-1}$, 0.1 mol dm^{-3} KCl with borate buffer (pH 7.2). (*a*) Cyclic voltammogram at scan rate 5 mV s^{-1}. (*b*) Typical c.s.v.w.c. results. Deposition potential +0.75 V; stripping potential 0.0 V. Lines correspond to addition of (2, 4 and 6) × 10^{-7} mol dm^{-3} Mn^{II} to blank.

dependence in the deposition and stripping steps; we found, in accord with previous work, that a borate buffer with a pH slightly above neutrality worked most efficiently. The cyclic voltammogram in fig. 2(*a*) exhibits two peaks on the cathodic scan. The first of these is due to a change in oxide composition (MnO_2 is a non-stoichiometric oxide) and the second to reduction to Mn^{II}.[28] Nevertheless, if deposition is at +0.75 V and stripping at 0.0 V we find good agreement between experiment and theory [fig. 2(*b*)], so the oxygen:manganese ratio at +0.75 V must be very close to two.

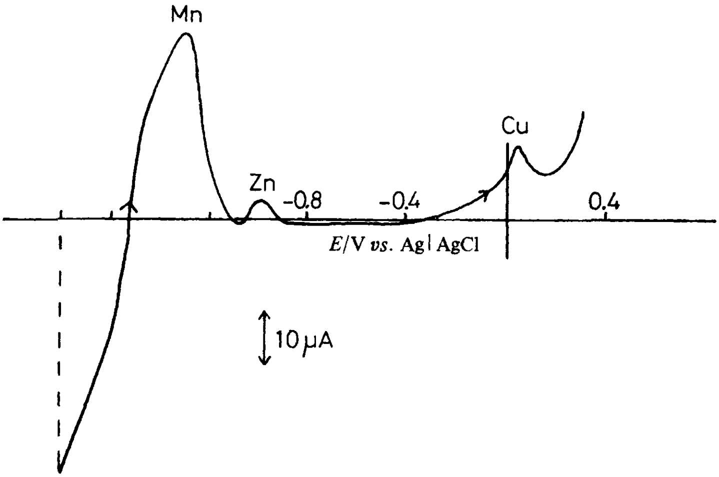

Fig. 3. Nutrient solution: linear scan stripping at wall-jet m.f.e. Electrolyte added to solution to give 0.1 mol dm^{-3} $NaClO_4$, 5×10^{-5} mol dm^{-3} Hg^{II}. Flow rate 0.040 cm^3 s^{-1}. Deposition time 120 s; stripping scan rate 100 mV s^{-1}. $E_{dep} = -1.8$ V.

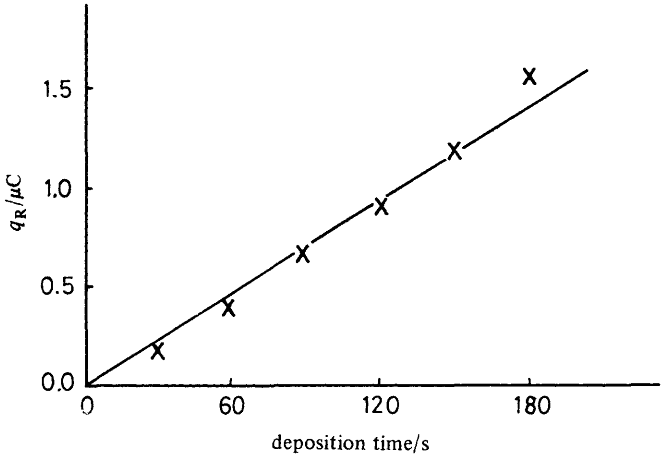

Fig. 4. Copper a.s.v.w.c. in nutrient solution at glassy carbon disc Pt ring w.j.r.d.e. with 0.1 mol dm^{-3} $NaClO_4$ and 5×10^{-5} mol dm^{-3} Hg^{II}. Deposition potential -0.4 V; stripping potential 0.0 V. (×) are experimental points and (——) is the theoretical prediction from eqn (3).

Nutrient Solution

A linear stripping scan for the nutrient solution obtained at the wall-jet m.f.e. is shown in fig. 3. It shows clearly the high manganese concentration and the effect of the Cu–Zn intermetallic compound formation, as discussed above. A typical response for copper is given in fig. 4. In mixing the nutrient solution with supporting electrolyte there is, of course, a dilution effect. Since the nutrient solution trace-metal levels are well above the detection limits, this presents no problems. No interferences were found either for a.s.v.w.c. or for c.s.v.w.c. of Mn.

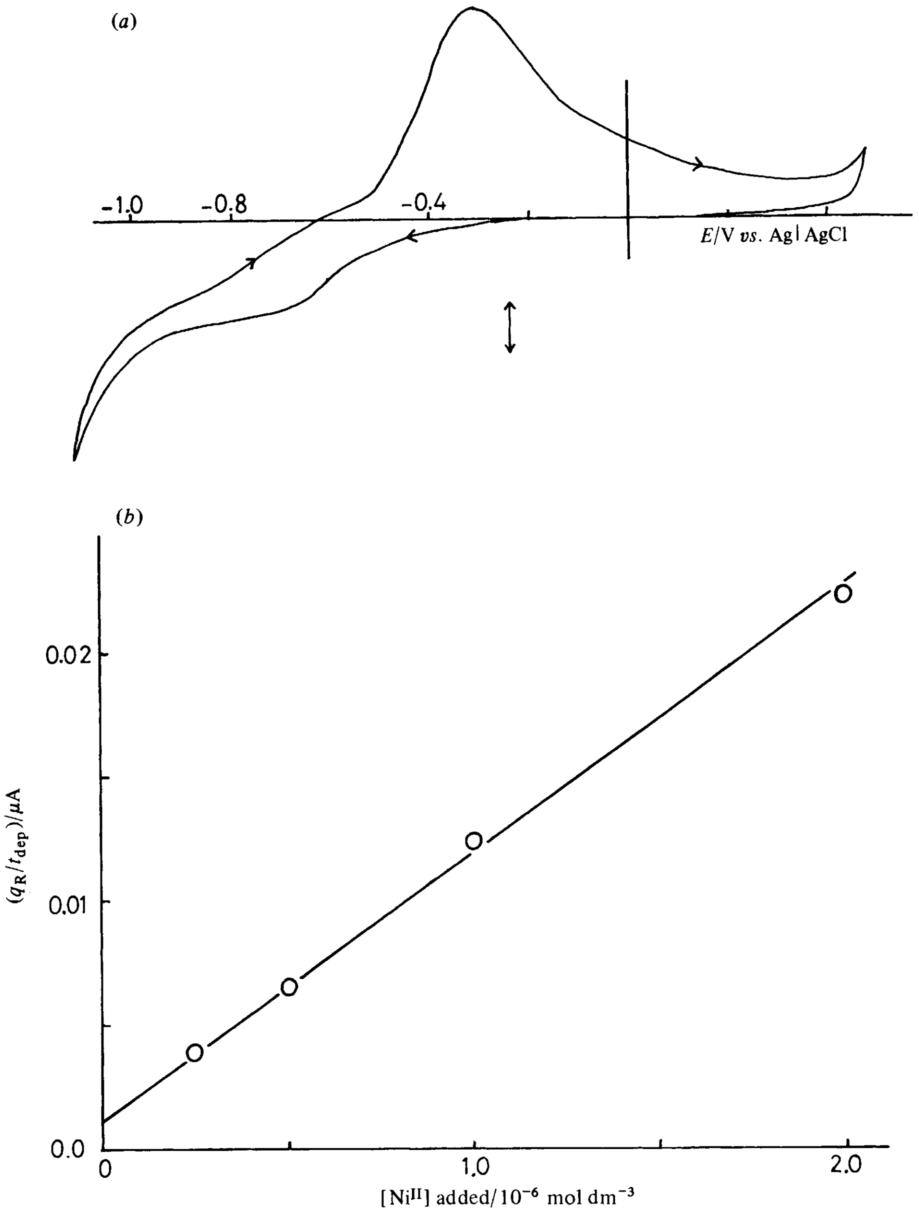

Fig. 5. Nickel results at a Pt–Pt w.j.r.d.e. in 0.1 mol dm^{-3} KSCN and 0.1 mol dm^{-3} KCl. Flow rate 0.040 cm^3 s^{-1}. (*a*) Cyclic voltammogram at scan rate 100 mV s^{-1}. (*b*) Typical plot from a.s.v.w.c. experiments. Deposition potential −0.9 V; stripping potential +0.3 V. Deposition times varied between 20 and 210 s.

Nickel

The very toxic trace-element nickel is relatively difficult to estimate quantitatively by stripping voltammetry owing to the slow electrode kinetics of the Ni^{II} aq|Ni^0 couple. It has been shown that the electrode kinetics can be improved by the presence of complexing species:[29] applications are in a.s.v.[30] and in adsorptive stripping voltammetry.[31] Following the earlier a.s.v. paper, we add 0.1 mol dm^{-3} KSCN and

0.1 mol dm^{-3} KCl to the test solution. Under such conditions there is $>50\%$ $Ni(SCN)^+$ and little free aqueous ion. Quantitative estimation down to $10^{-7} \text{ mol dm}^{-3}$ was possible with short deposition times (see fig. 5). We hope by optimising the solution composition, deposition and stripping potentials to lower the detection limit further and eliminate the non-zero intercept corresponding to a blank determination, probably linked with electrolyte impurities or with adsorption processes occurring on the electrode surface. Because the electrolyte and other experimental conditions are different from those used in the other trace metal determinations, there is no noticeable interference effect in analyses for nickel using nutrient solution. This masking is a very important advantage.

Conclusion

We have demonstrated the successful application of new electrochemical sensors to the monitoring of trace-metal levels in hydroponic solutions. In parallel with the glassy carbon–glassy carbon wall-jet ring–disc electrode to enable total on-line monitoring, automation is also being investigated. An approach to this in the laboratory has recently been described.[32] With computer automation operator assistance can be minimised. One can imagine a larger number of independent nutrient solution concentrates than in table 1, which could be dosed according to data obtained by the computer. The stored data could also be used for more fundamental studies of the mechanism of nutrient uptake by plants.

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