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NOTA 222

THE USE OF ION-SELECTIVE ELECTRODES IN NFT SYSTEMS

door

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FOREWORD

The National Program for Crop Production on Artificial Substrates financed the project "Control of nutrient supply to plants in artificial substrates". This project (IB-402) was initiated in 1987 at the Institute for Soil Fertility. The idea was to study patterns of nutrient uptake by plants, using existing reliable measuring techniques. A measuring and control system for practical use in horticulture would be developed in a related project at the Institute for Agricultural Engineering (IMAG), Wageningen; project leader ing. Th. Gieling. Now, two years later, the (installed) measuring system consisting of ion-selective electrodes does not work satisfactorily, and, therefore, the emphasis of project IB-402 has shifted towards the development of a reliable measuring and control system.

In this report the theoretical background of ion-selective electrodes is presented. From this theoretical background it can be seen that measurements must be carried out under controlled conditions.

Together with results of future experiments this information will be published in an international journal.

SUMMARY

It follows from the theory on ion-selective electrodes that not only the sensitivity but also the zero-potential of the ion-selective electrode is temperature-dependent. Theoretical corrections can be made for the sensitivity of the electrode, but this cannot be done for the zero-potential, because in that case the ionic strength of the solution must be known. Therefore, ion-selective electrodes are only reliable at a constant temperature.

Another disadvantage of ion-selective electrodes is their drift. This calls for regular calibration. When ion-selective electrodes are used in an on-line system one could decide to use the double standard-addition method. However, this method has two opposing aspects, and, therefore, it is recommended to avoid this method. The best procedure is to calibrate the ion-selective electrodes before an experiment. During the experiment the sensitivity can be assumed to be constant and the zero-potential has to be adjusted on the basis of independent measurements of the solution in the laboratory. This procedure is justified by a pilot experiment.

When two ions are not measured in a system they can be estimated from the electrical conductivity measurement and the electroneutrality condition.

1. INTRODUCTION

One of the expected advantages of the introduction of artificial substrates in horticulture was that in these weak buffering systems (rockwool, Nutrient Film Technique (NFT)) a better control of crop growth (quantity and quality) would be possible than in soil-based systems (Heinen *et al*, 1990). To achieve this, uptake patterns of the nutrients must be known and a reliable measuring and control system is needed. In principle, the elements for such a system are available.

Water cultures have long been used in studies of uptake patterns of plants. A first publication stems from 1660 (Steiner, 1985). Nowadays, NFT systems (as described in e.g. Cooper, 1979; Graves, 1983; Hall and Wilson, 1986; Wild *et al.*, 1988; Winsor *et al.*, 1979) are commonly used in research studies of plant production and nutrient uptake. Most of these systems have recirculating nutrient solutions. Automatic systems have been developed to measure and adjust the concentrations of one or more nutrients. The aim may be to keep the concentration constant, or to adapt it according to a certain pattern. In these systems ion-selective electrodes (ISE) have been used widely (e.g. Albery *et al.*, 1986a; Bailey *et al.*, 1988; Blom-Zandstra and Jupijn, 1987; Clement *et al.*, 1974, 1978a,b; Hatch and Canaway, 1984). Although measurements using ISE are quick, easy, non-destructive, direct and cheap, there are also some serious problems involved (e.g. Cammann, 1980).

In chapter two of this report the theory, drawbacks, and calibration of the ISE are described briefly. In chapter three some practical results revealing the problems with in-situ calibration and with temperature effects are discussed. In chapter four a discussion is presented on the use of the electrical conductivity (EC) electrode to estimate the sulfate and magnesium concentrations in the experimental setup of Heinen *et al.* (1990).

2. THEORY

2.1. The Nernst equation

The theory of ion-selective electrodes (ISE) has been described in numerous places (e.g. Albery *et al.*, 1986a,b; Atkins, 1978; Bates, 1978; Cammann, 1973, 1980; Chang, 1981; PHILIPS, 1975, 1984). An ISE is a sensor which produces an electrical signal which is linear in the natural logarithm of the activity of a special ion. This linearity is expressed by the Nernst equation and reads for ideal behaviour

$$E = E_o \pm \frac{R \cdot T}{n \cdot F} \cdot \ln[a] = E_o \pm \frac{R \cdot T \cdot \ln[10]}{n \cdot F} \cdot \log[a], \qquad (1)$$

where:
E potential (V)
E_o zero-potential (V)
R universal gas constant (= 8.3144 $J \cdot mol^{-1} \cdot K^{-1}$)
T absolute temperature (K)
n absolute valence of the ion (-)
F Faraday's constant (= 96485 $C \cdot mol^{-1}$)
a activity of the ion (-)

The zero-potential, E_o, is the potential that belongs to one unit of activity, a. The plus-sign applies to cations and the minus-sign to anions. A plot of E versus log[a] yields a straight line, with intercept E_o and slope $(R \cdot T \cdot \ln[10])/(n \cdot F)$. The slope is also known as the sensitivity of the ISE. For mono- and divalent ions at T = 298 K the sensitivities are, respectively, 0.059 and 0.029 V per decade, i.e. per ten-fold change of a. According to Eq. (1) the sensitivity is proportional to the absolute temperature (figure 1). In the next paragraph it is shown that E_o is temperature-dependent also.

In practice measurements are carried out with a set including an

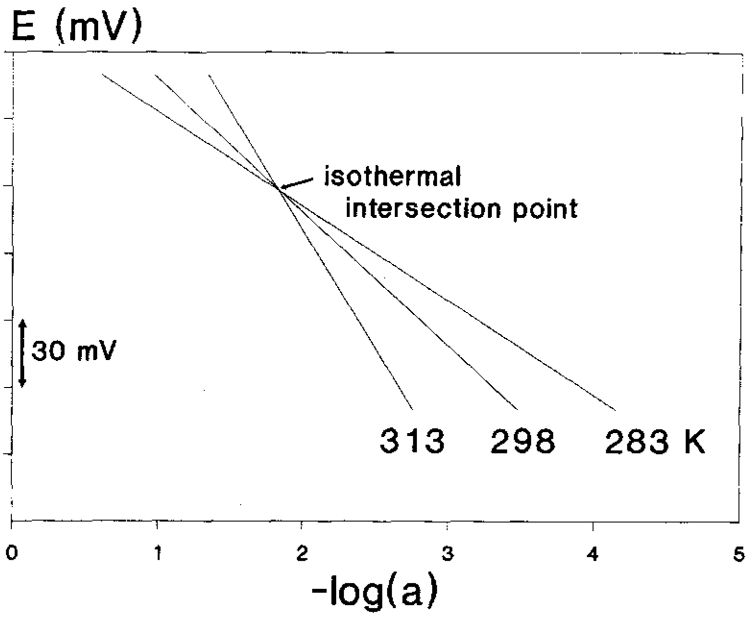

Figure 1. The influence of temperature on the slope and intercept of the calibration line. All calibration lines intersect at an isothermal intersection point (after PHILIPS, 1984).

ISE and a reference electrode. The purpose of the reference electrode is to obtain a stable reading, and to complete the electrical circuit. A potential difference is measured, which is the sum of six terms (Figure 2; PHILIPS, 1984):

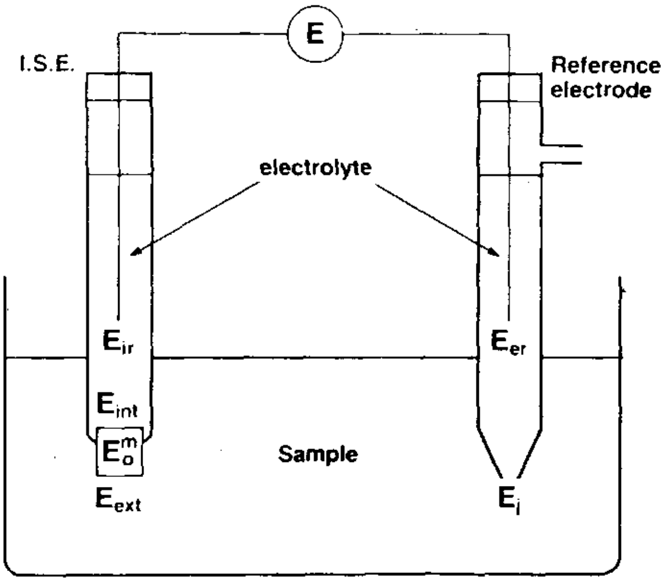

Figure 2. The electrode chain (after PHILIPS, 1984).

$$E = E_o^m + E_{ir} + E_{er} + E_j + E_{int} + E_{ex}$$
$$= E_a + E_{int} + E_{ext} \qquad (2)$$

where:

E	potential difference (V)
E_o^m	asymmetry potential of the membrane (V)
E_{ir}	contact potential of internal reference electrode in ISE (V)
E_{er}	contact potential of internal reference electrode in reference electrode (V)
E_j	potential at interface reference electrode and solution (V)
E_a	asymmetry potential of the measuring system $= E_o^m + E_{ir} + E_{er} + E_j$ (V)
E_{int}	internal phase boundary (or Donnan) potential of the ISE membrane (V)
E_{ext}	external phase boundary (or Donnan) potential of the ISE membrane (V)

E_{ir} and E_{er} have opposite signs, and their sum is independent of temperature; E_j is a constant (PHILIPS, 1984). For both E_{int} and E_{ext} Eq. (1) is valid. Both E_{int} and E_{ext} are temperature-dependent. Apart from this temperature-dependence, E_{int} is constant since the composition of the electrolyte in the ISE remains constant. Comparing Eq. (2) with Eq. (1) it follows that E_o is composed of E_a, E_{int} and the constant of the Nernst equation belonging to E_{ext}. Therefore, also E_o is temperature dependent.

2.2. The activity coefficient

Normally, the use of the concentration, c ($mol \cdot l^{-1}$ or $mol \cdot kg^{-1}$), is preferred to the use of the activity a. The concentration and activity are related to each other by the activity coefficient, f (-), according to (e.g. Atkins, 1978; Chang, 1981)

$$a = f \cdot c/1, \qquad (3)$$

where 1 represents unit concentration ($\mathrm{mol\cdot l^{-1}}$ or $\mathrm{mol\cdot kg^{-1}}$). The activity coefficient varies between one (for ideal solutions) and zero. Introducing Eq. (3) into Eq. (1) one obtains

$$E = E_o' \pm \frac{R\cdot T\cdot \ln[10]}{n\cdot F}\cdot \log[c/1], \tag{4}$$

where

$$E_o' = E_o \pm \frac{R\cdot T\cdot \ln[10]}{n\cdot F}\cdot \log[f]. \tag{5}$$

For a large range of c a linear relation exists between E and log[c/1]. In the new zero-potential E_o' an extra temperature-dependence (besides the one mentioned in section 2.1) is introduced, since the sensitivity is incorporated. The activity coefficient f depends on the total concentration of the solution, i.e. the ionic strength, I ($\mathrm{mol\cdot l^{-1}}$ or $\mathrm{mol\cdot kg^{-1}}$). This dependence is described by the (extended) Debye-Hückel theory (e.g. Atkins, 1978; Chang, 1981; Novozamsky *et al.*, 1981; PHILIPS, 1984)

$$\log[f_i] = \frac{-A\cdot n_i^2\cdot \sqrt{I}}{1 + B\cdot d_i\cdot \sqrt{I}}, \tag{6}$$

with (Atkins, 1978)

$$A = \frac{N_a^2\cdot e^3\cdot \sqrt{(2\cdot \rho)}}{8\pi\cdot \ln[10]\cdot (\epsilon_o\cdot \epsilon\cdot R\cdot T)^{3/2}}\quad (\mathrm{kg^{1/2}\cdot mol^{-1/2}}), \tag{7}$$

$$B = \frac{N_a\cdot e\cdot \sqrt{(2\cdot \rho)}}{(\epsilon_o\cdot \epsilon\cdot R\cdot T)^{1/2}}\quad (\mathrm{kg^{1/2}\cdot mol^{-1/2}\cdot m^{-1}}), \tag{8}$$

$$I = 0.5\cdot \Sigma\{c_i\cdot n_i^2\}\quad (\mathrm{mol\cdot kg^{-1}}), \tag{9}$$

where:
d effective diameter of the ion in solution (m)
N_a Avogadro's number (= $6.0220 \cdot 10^{23}$ mol^{-1})
e electron charge (= $1.6022 \cdot 10^{-19}$ C)
ρ density of solvent (kg$\cdot$m^{-3})
ϵ_o permittivity of vacuum or electric constant (= $8.8542 \cdot 10^{-12}$ C$\cdot$V$^{-1}\cdot$m^{-1})
ϵ dielectric constant of solvent (-)

The Debye-Hückel theory assumes that the electrolytes are completely dissociated into ions in solution, and that each ion is surrounded by ions of opposite charge, creating an ionic-atmosphere. Values for d for many ions have been tabulated, e.g. Novozamski *et al.*, 1981.

Also f is temperature-dependent (figure 3), since both A and B are temperature-dependent, adding an extra T-dependency to E_o'.

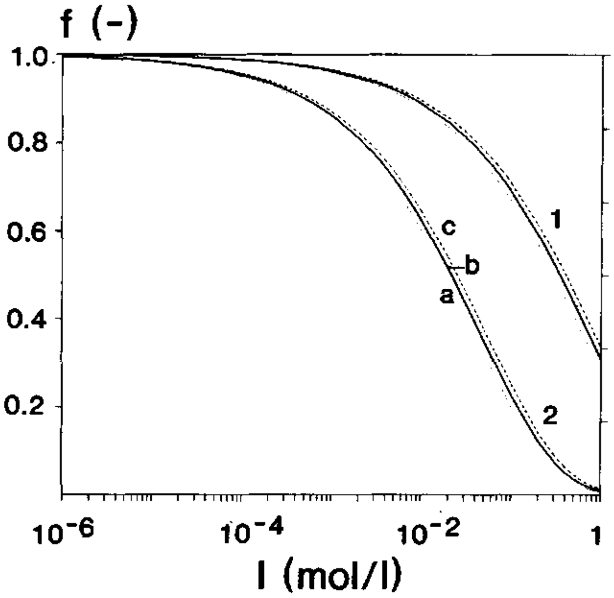

Figure 3. The relation between the activity coefficient, f, and the logarithm of the ionic strenght, I, according to the (extended) Debye-Hückel theory (Eq. (5), with $d = 3.10^{-10}$m), for mono- (1) and divalent (2) ions at temperatures of 283 (a), 298 (b) and 313 K (c).

For T = 298 K and water as solvent (ϵ = 78.54, ρ = 1000 kg$\cdot$m^{-3}) A = 0.510 kg$^{1/2}\cdot$mol$^{-1/2}$ and B = $3.3 \cdot 10^{+9}$ kg$^{1/2}\cdot$mol$^{-1/2}\cdot$m^{-1}. For very dilute solutions (I < 0.005 mol$\cdot$l^{-1} according to Bates, 1978; I <

$0.01\ \mathrm{mol}\cdot\mathrm{l}^{-1}$ according to Chang, 1981) or when the ions are assumed to be points (d = 0) one obtains the limiting Debye-Hückel law: $\log[f_i] = -A\cdot n_i^2\cdot\sqrt{I}$. In case d is assumed to be $3\cdot10^{-10}$ m for all ions in the solution, Eq. (6) can be approximated by $\log[f_i] = (-A\cdot n_i^2\cdot\sqrt{I})/(1 + \sqrt{I})$ (Günterberg approximation). For high values of I (say > $0.1\ \mathrm{mol}\cdot^{-1}$), one can use the Davies extension: $\log[f_i] = -n_i^2\cdot\{A\cdot\sqrt{I}/(1 + \sqrt{I}) - 0.1\cdot I\}$ (Bates, 1978). At high ionic strengths the activity coefficient again approaches unity because of ion-pairing which reduces the effective concentration of charge in the solution (Bailey *et al.*, 1988).

2.3. Calibration of the ion-selective electrodes and sources of error

Calibration

Even under conditioned circumstances the ISE shows drift, i.e. a change in zero-potential and sensitivity with time. Therefore, the ISE should be calibrated regularly, e.g. once a day or at least once a week. The standard procedure of calibration in laboratories consists of placing the ISE in two solutions of exactly known activity. The standard solutions should differ at least a factor ten in activity (PHILIPS, 1975, 1984), yielding for mono- and divalent ions at least a potential difference of 60 and 30 mV, respectively. From these two measurements the two unknowns (sensitivity and zero-potential) can be calculated from Eq. (1). For ideal Nerstian behaviour the least squares method can be used (Ebel and Becht, 1987). In practice one can use standards of known concentration (using Eq. (5)). On the other hand, the difference in c may not be too large, since then the ionic strength and the activity coefficient of the two solutions are different, and, therefore, the zero-potential E_o' does not remain constant. This can be avoided by adding to the two standard solutions a so-called TISAB-solution (Total Ionic Strength Adjustment Buffer). In that case the ionic strength of both solutions is determined by this TISAB solution, and accounted for by using an extended version of Eq. (1) or (5)), the unstable diffusion potentials, the influence of the flowing solution along the ISE, the influence of light and pressure on the ISE, instrument errors (such as resistance adaption, temperature compensation). Glass electrodes (e.g. K ISE) are pH-dependent (B. Veen, CABO, pers. comm.). All these factors imply that measurements should be carried out under the same controlled conditions as is done in laboratories. For use in practical experimental setups (e.g in glasshouses), the conditions (such as temperature, light intensity etc.) can hardly be controlled. Therefore, the specific measurement part of the experimental setup must be carried out under controlled conditions.

3. ION-SELECTIVE ELECTRODES IN PRACTICE

Two aspects of the use of ISE's have been determined in a on-line experimental setup, which is described by Heinen *et al.*, 1990. The first aspect is the calibration of the ISE in-situ, using a double-standard-addition method (as described in section 2.3); the second aspect is the influence of temperature on the measurements.

3.1. In-situ calibration

The double-standard-addition method, as mentioned in section 2.3, has been used several times to carry out an in-situ calibration of the ISE's. With the two opposing aspects associated with this method in mind, potential differences of 60 mV or less (down to 10 mV) were established. It was not possible to obtain equal calibration lines on one day, even when the short-circuited solution was kept at a constant temperature. The best result was a set of seven calibration lines, of which the maximum and minimum slopes differed about 6% (figure 4).

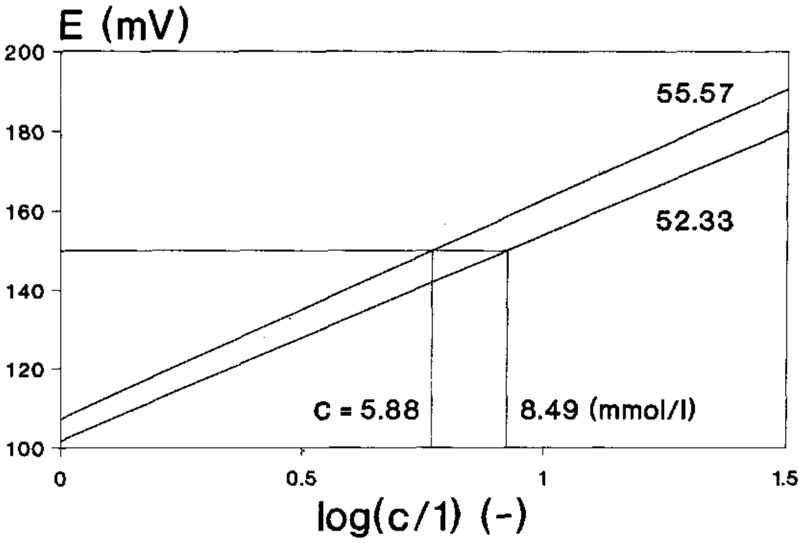

Figure 4. The calibration lines with minimum and maximum slopes from a set of seven consecutive calibration procedures.

Assuming that a potential of 150 mV is measured, this would yield a concentration obtained from both calibration lines which differ about 36%. For detailed studies in which concentration differences of less than 10% are required, this double-standard-addition method cannot be used to update the calibration lines.

These calibration procedures took 3 times 20 minutes. Each minute the potential was measured, enabling us to obtain intermediate values of the slopes and intercepts of the calibration lines. Mostly these intermediate values show a trend (figure 5), i.e. the signals from the ISE are slowly reaching an equilibrium value.

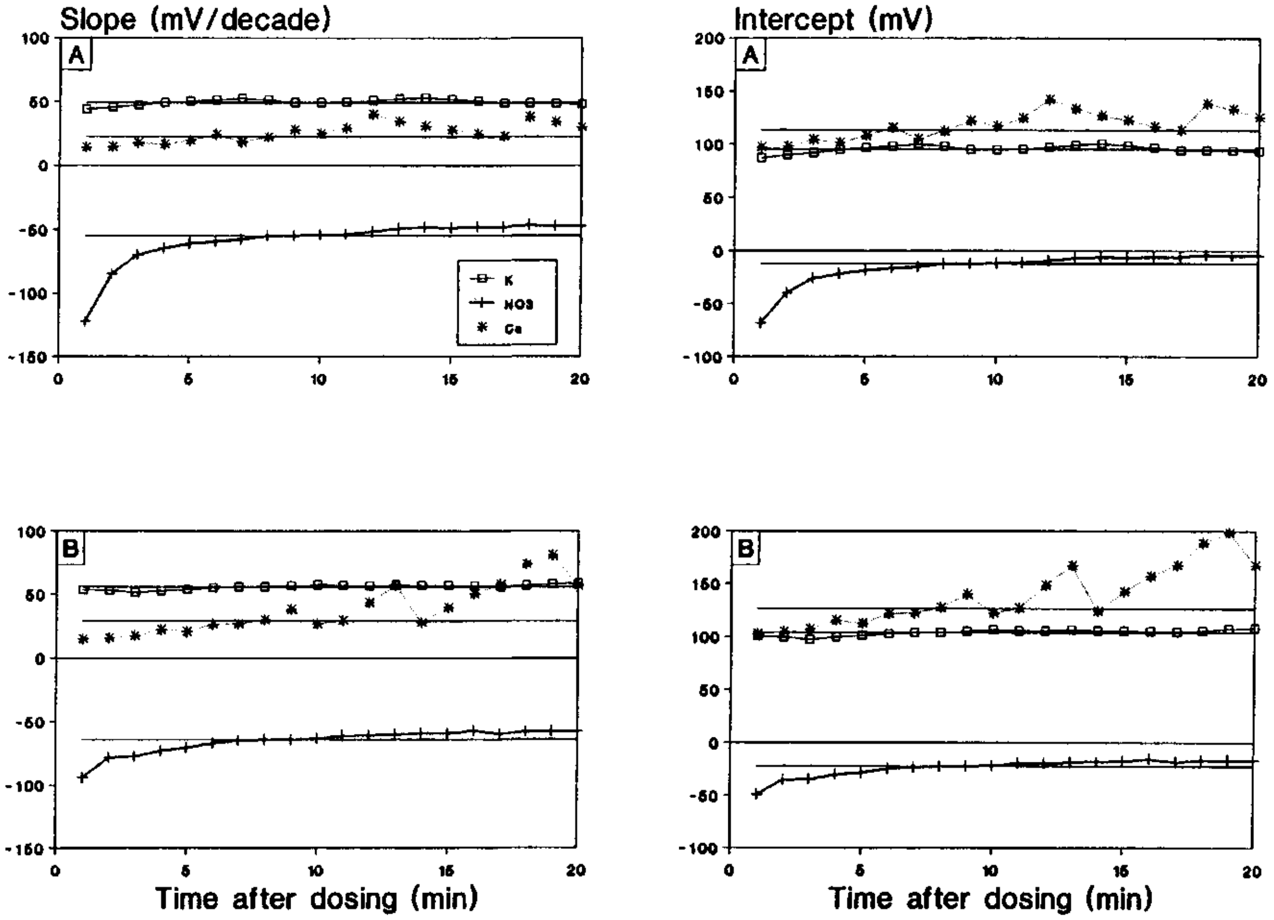

Figure 5. The change in slope and intercept calculated from intermedeate measurements during the calibration procedure, without (A) and with (B) one hour waiting after the start of the procedure. Calibration was carried out by adding KNO_3 and $Ca(NO_3)_2$. Horizontal lines represent averages.

One reason why this would happen can be the influence of the abrupt temperature change of the ISE. The nutrient solution had a temperature of about 285 K, while calibration was carried out at 293 K. The abrupt change in temperature may have caused the large gradient in the trends in figure 5A. A second reason might be the fact that the ISE had to adapt to the changing background concentration (I) after a standard addition (although the standard additions were kept relatively small). The influence of I on the signal of an ISE can be shown as follows. A calibration of the NO_3 and K ISE was carried out, but the concentration of Ca remained constant. However, the signal of the Ca-ISE changed during the calibration process (figure 6).

For these reasons we decided not to use in-situ calibration in project IB-402 (Heinen *et al.*, 1990).

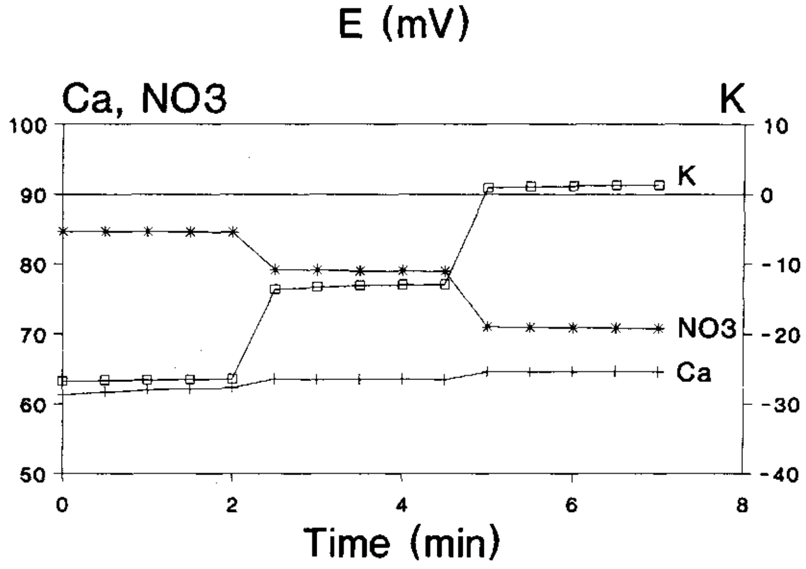

Figure 6. Change in potential of the NO_3, K and Ca ISE during a calibration procedure by adding KNO_3 only.

Instead, the ISE will be calibrated in the laboratory before a new experiment, using the nutrient solution of known concentration. The potential in this solution will be determined, followed by a standard addition of concentrated nutrient solution to obtain a second potential reading. From these two measurements the sensitivity and the zero-potential can be determined. The calibration will be carried out at the same temperature as at which the measurements in the experiments will take place. It will be assumed that during an experiment the sensitivity does not change (recommended by B. Veen, CABO, pers. comm.). The concentrations in the regularly taken samples of the nutrient solution will be determined in the laboratory. After comparing these concentrations with those measured with the ISE, the value of the intercept may be adapted.

3.2. Temperature effect

An experiment without plants has been carried out, in which the concentration of the nutrient solution was manually adapted. At any time the concentration of the nutrient solution was known, such that the measured concentrations by the ISE could be checked. The nutrient solution was continuously pumped through the measuring cell. The temperature of the nutrient solution was not controlled and was determined by the external environment. The ISE were calibrated in the laboratory according to a similar method as described at the end of section 3.1 at a temperature of 291 K. The sensitivity was determined from two solutions of known concentration at an ionic strength equal to that of the nutrient solution. The zero-potential was determined from a measurement in a sample of the nutrient solution (table 1).

TABLE 1. The slope, α, and intercept, β, of the calibration lines of the ISE at the start of the experiment.

ISE	α	β
NO_3	-59.02	144.56
K	57.64	-51.16
Ca	29.90	64.44

After installing the ISE in the measuring device and filling the system with the nutrient solution, the registration started. The measured concentration differed from the setpoints of the nutrient solutions (table 2).

TABLE 2. The measured concentrations (mmol·l-^{1}) by the ISE immediately after starting the experiment, and the difference (%) in comparison with the setpoints (mmol·l-^{1}).

ISE	Measured	Setpoint	Difference
NO^3	6.16	5.002	23.2
K	1.96	2.625	-25.3
Ca	1.16	1.172	1.0

Even after one day the concentrations differed from the setpoints, and changed with time (table 3).

TABLE 3. The measured concentrations (mmol·l-^{1}) by the ISE one day after starting the experiment at 16.00 and 20.00 h, and the difference (%) in comparison with the setpoints (mmol·l-^{1}).

	16.00		20.00	
ISE	Measured	Difference	Measured	Difference
NO$_3$	5.74	14.8	5.66	13.2
K	2.12	-19.2	1.90	-27.6
Ca	1.34	14.3	1.37	16.9

Tables 1 and 2 clearly show that one can hardly speak of absolute concentrations measured by the ISE. Instead, in the following only the relative changes in the signals will be discussed.

Four weeks after the start of the experiment the temperature of the nutrient solution, which was determined in the measuring device, changed from 283 to 292 K (figure 7). In figure 7 the change in concentration as measured by the ISE is presented for two cases. Firstly, the concentrations are given using the slope values of table 1, and secondly the concentrations are calculated using a temperature corrected slope value (according to the sensitivity definition in Eq. (1)). At low nutrient solution temperatures the temperature correction yields a higher concentration for NO$_3$. But even then the concentration changes in time, although the true concentration of the nutrient solution was constant.

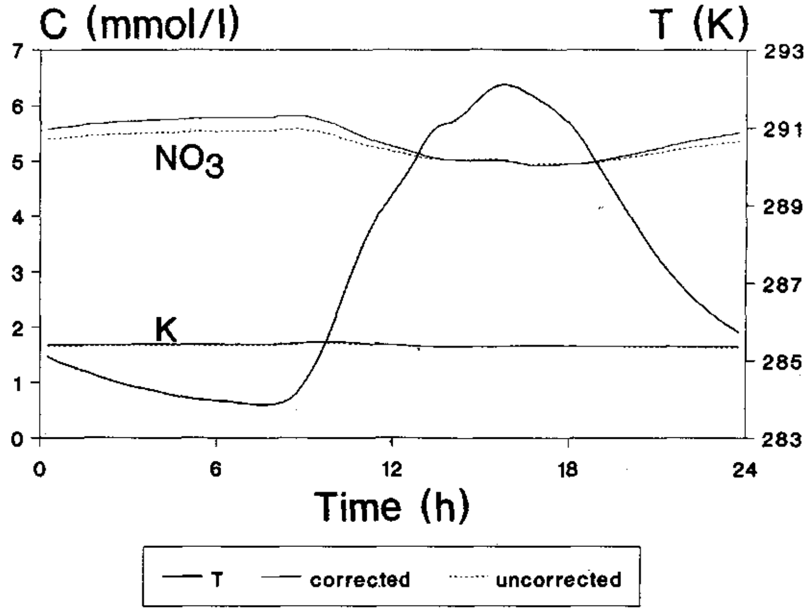

Figure 7. The measured concentrations of NO_3 and K and the temperature of the nutrient solution on 18 March 1989, 40 days after the start of the experiment. The concentrations are obtained with and without temperature-corrected values of the slopes of the calibration lines.

So the temperature correction on the sensistivity of the ISE alone does not diminish the temperature effect. It even enlarges the change in computed concentration. The temperature influence on the intercept of the calibration line is of great importance (see also sections 2.1 and 2.2). It follows from figure 7 that the measured extremes in concentration occurred about one hour after the temperature extremes were determined. This means that the ISE adapt slowly to the change in temperature. The temperature correction on the K ISE is hardly visible. This can be explained by the fact that the absolute value of the K concentration is smaller than that of NO_3.

The reaction time of the ISE to an abrupt change in concentration is faster than the adaptation time to the change in temperature. Four and a half weeks after the start of the experiment the concentration of the nutrient solution was suddenly lowered by 20%. The changes in temperature of the nutrient solution were relatively small (figure 8), so that the change in measured concentration can be attributed to this sudden decrease in concentration (figure 8). At the start of the dilution the measured concentrations of NO_3, K and Ca were 5.36, 1.64 and 1.16 $mmol \cdot l^{-1}$, respectively. Every 15 minutes measurements were made and after 45 minutes the concentration remained constant. Thus, within 30 and 45 minutes the whole system was well mixed. The new concentration levels for NO_3, K and Ca were 4.27, 1.32 and 1.02 $mmol \cdot l^{-1}$, respectively. The observed change in concentration for NO_3, K and Ca equaled 20.3, 19.5 and 12.1%, respectively. For NO_3 and K these changes compare very well with the expected value of 20%. The Ca ISE did not show the expected 20% decrease in concentration, probably because it had been used for too long.

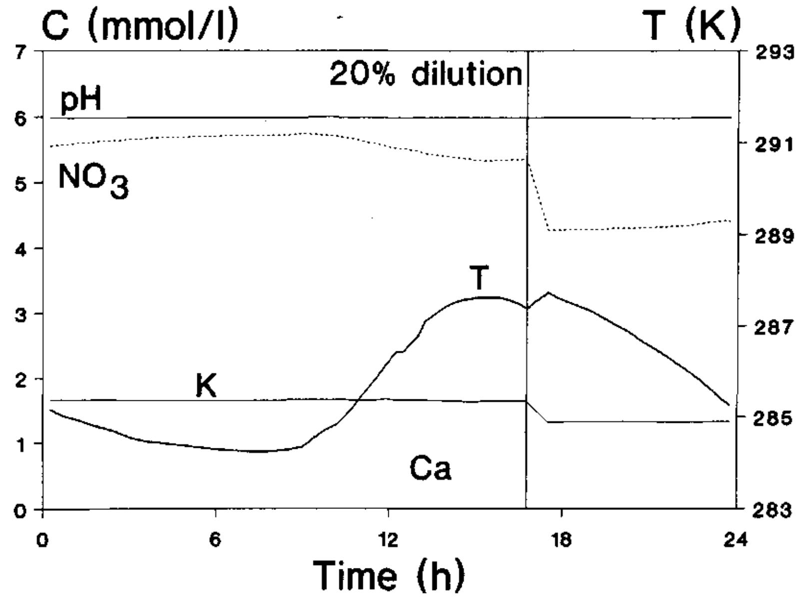

Figure 8. The measured NO_3, K and Ca concentrations and the temperature of the nutrient solution on 22 March 1989. At 16.50 h a sudden dilution of 20% was supplemented.

After 40 days the ISE were re-calibrated in the laboratory (Table 4).

TABLE 4. The slope, α, and intercept, β, of the calibration lines at the end of the experiment, and the changes (%) in respect to the values of table 1.

ISE	α	Change	β	Change
NO_3	-58.00	1.7	-33.07	123
K	53.25	7.6	99.46	294
Ca	19.00	36.5	141.59	-120

The slope of the NO_3 ISE has not changed very much, the slope of the K ISE has changed slightly more, but the slope of the Ca ISE has markedly changed. The Ca ISE apparently becomes less sensitive in a short time, and therefore, is not reliable for long-lasting experiments. The values of the intercepts for all electrodes have strongly changed within 40 days.

The proposed procedure at the end of section 2.3 (keeping α constant during an experiment and adapting β according to separate measurements) seems to be correct for the NO_3 and K ISE's. The membrane of the Ca ISE should be changed regularly.

4. THE USE OF THE EC ELECTRODE TO ESTIMATE THE CONCENTRATIONS OF Mg AND SO_4

Heinen *et al.* (1990) described an automatically controlled NFT system in which the concentration of the nutrient solution is monitored and kept constant. For this purpose the concentrations of NO_3, K, Ca, H_2PO_4 and H are measured. The decrease in concentration of all macro-nutrients must be known in order to use the salt-dosing scheme described in Heinen *et al.* (1990). Since the concentrations of Mg, SO_4, Cl and Na are not determined, the decrease in concentrations of these ions were related to the decrease in NO_3 concentration (Heinen *et al.*, 1990). In this chapter a method is proposed to estimate the ion concentrations of Mg and SO_4 from the EC measurement. This can only be done in case Cl and Na ions are absent or are only present in negligably small concentrations (e.g. at micronutrient level). An alternative is to measure Cl and Na with ISE's. The concentrations of the micronutrients are assumed to be negligably small, as are the contrations of H and OH. In the following discussion the temperature is considered to be 293 K, since this will be the temperature at which future measurements will be carried out. Subscripts n, p, s, k, c, m are used to represent NO_3, H_2PO_4, SO_4, K, Ca and Mg, respectively.

According to the theory of ionic mobilities and ionic conductance in electrolyte solutions (Atkins, 1978; Bard and Faulkner, 1980; Chang, 1981) the electrical conductivity (EC) of an electrolyte solution can be given as a function of the concentration. However, the conductance of a solution is in fact a function of the activities of the ions present in solution (Kamphorst and Bolt, 1981). In that case we can write

$$EC = F\cdot\Sigma(c_i\cdot n_i\cdot f_i\cdot \mu_i), \qquad (10)$$

where:
EC electrical conductivity ($mS \cdot cm^{-1}$),
F Faraday's constant (= 96485 $C \cdot mol^{-1}$),
c_i concentration of ion i ($mol \cdot l^{-1}$),
n_i absolute valence of ion i,
f_i activity coefficient of ion i,
μ_i ionic mobility of ion i ($cm^2 \cdot s^{-1} \cdot V^{-1}$).

The activity coefficient follows from the (extended) Debye-Hückel theory (Eq.(6)). Values for the effective diameter of the ions in the Debye-Hückel theorie can be obtained from Novozamski *et al.* (1981) (table 5).

TABLE 5. The concentration, c ($mmol \cdot l^{-1}$), of the ions in the nutrient solution used by Heinen *et al.* (1990). Per ion the valence, n, the effective ion diameter, d ($m/10^{-10}$), the activity coefficient (for nutrient solution without Cl), f (at T = 293), and ionic mobility, μ ($cm^2 \cdot s^{-1} \cdot V^{-1}/10^{-4}$) are given.

Ion	c	n	d	f	μ
NO_3	10.003	1	3	0.880	7.40
H_2PO_4	0.667	1	4	0.884	7.84*
SO_4	0.336	2	4	0.610	8.27
Cl	0.166	1	3	0.880	7.91
K	5.254	1	3	0.880	7.62
Ca	2.344	2	6	0.630	6.16
Mg	0.784	2	8	0.648	5.50

* Since no value is known it is assumed to be the arithmetic mean of NO_3 and SO_4

It is assumed that the ionic strength of the nutrient solution remains constant. For the nutrient solution of table 5 the ionic strength according to Eq. (9) equals $14.97 \cdot 10^{-3}$ $mol \cdot l^{-1}$. Note that the concentration of Cl is considered also. Then the values for f for each ion can be calculated according to Eq. (6) (table 5). The ionic mobilities can be found in Bard and Faulkner (1980) and Chang (1981). Their values are valid for T = 298 K, here it is assumed that these values are also valid for T = 293 K. For H_2PO_4 no value for μ is known, therefore it is given the mean value of those from NO_3 and SO_4. The error introduced will be small since the contribution of H_2PO_4 to the conductivity is small because of its relatively low concentration.

For known concentrations of NO_3, H_2PO_4, K and Ca, and for known EC, Eq. (10) has two unknowns, i.e. the concentrations of SO_4 and Mg. There is a second condition that has to be met. The nutrient solution is always electrically neutral

$$c_n + c_p + 2 \cdot c_s = c_k + 2 \cdot c_c + 2 \cdot c_m, \tag{11}$$

where c represents the concentration in $mmol \cdot l^{-1}$ or $mmol \cdot kg^{-1}$. Eq. (11) contains the two unknown concentrations of SO_4 and Mg, and the known concentrations of NO_3, H_2PO_4, K and Ca. From Eq. (10) and Eq. (11) the concentrations of SO_4 and Mg can be calculated according to

$$c_s = \frac{EC/F - D - f_m \cdot n_m \cdot \mu_m \cdot C}{f_s \cdot n_s \cdot \mu_s + f_m \cdot n_m \cdot \mu_m}, \tag{12}$$

$$c_m = c_s + C/2, \tag{13}$$

with

$$C = c_n + c_p - c_k - 2 \cdot c_c, \tag{14}$$

$$D = c_n \cdot f_n \cdot n_n \cdot \mu_n + c_p \cdot f_p \cdot n_p \cdot \mu_p + c_k \cdot f_k \cdot n_k \cdot \mu_k + \\ + c_c \cdot f_c \cdot n_c \cdot \mu_c. \tag{15}$$

To check the validity of Eq. (10) the EC of eleven nutrient solutions used by Steenhuizen (1987) were calculated using Eqs (6), (7), (8), (9) and (10) at T = 291 K (table 6). These solutions also contained Cl and NH_4. The effective diameters, d, of these ions are $3 \cdot 10^{-10}$ m, and the ionic mobilities, μ, of these ions are 7.91 and $7.61 \cdot 10^{-4}$ $cm^2 \cdot s^{-1} \cdot V^{-1}$, respectively. The differences between the measured and calculated EC values are less than 4%. The use of Eq. (9) seems to be justified by the results presented in table 6. However, using the proposed procedure to estimate the concentrations of SO_4 and Mg of these solutions, yielded estimates differing up to 50% from the exactly known concentrations. This can be explained by the fact that the contribution of SO_4 and Mg to the total EC is very small, so that the relative error in the calculated concentration may become large.

TABLE 6. The concentrations, c (mmol·l-¹), of 11 nutrient solutions used by Steenhuizen (1987) and the measured and calculated EC values (mS·cm-¹), EC_m and EC_c, respectively.

Ion	Solution 1	2	3	4	5	6	7
NO_3	10.000	8.000	6.000	10.000	6.000	10.000	6.000
H_2PO_4	0.667	1.556	2.444	0.667	2.444	0.667	2.444
SO_4	0.333	0.778	1.222	0.333	1.222	0.333	1.222
Cl	0.166	0.388	0.611	0.166	0.611	0.166	0.611
NH_4	0	2.000	4.000	0	4.000	0	4.000
K	5.227	4.318	3.409	5.227	3.409	5.227	3.409
Ca	2.353	1.943	1.534	2.689	1.754	2.895	1.888
Mg	0.784	0.648	0.512	0.448	0.292	0.242	0.158
EC_m	1.27	1.27	1.27	1.27	1.27	1.27	1.27
EC_c	1.28	1.30	1.32	1.28	1.32	1.28	1.32

Ion	Solution 8	9	10	11
NO_3	17.750	14.200	25.750	20.600
H_2PO_4	1.184	2.762	1.718	4.007
SO_4	0.592	1.381	0.859	2.004
Cl	0.295	0.689	0.427	0.999
NH_4	0	3.550	0	5.150
K	9.278	7.664	13.460	11.119
Ca	4.176	3.449	6.058	5.003
Mg	1.392	1.150	2.019	1.668
EC_m	2.13	2.13	3.00	3.00
EC_c	2.15	2.18	2.99	3.04

A simulation model is being developed to see how this procedure will affect the true concentration of the nutrient solution during a growth period. This model and its results will be published later. Preliminary results show that the concentrations of SO_4 and Mg do not remain at their setpoints, but level off to a value above their setpoints.

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APPENDIX 1

The double-standard-addition method to obtain a new calibration line for ion-selective electrodes (ISE).

In a known volume, V_1, the concentration of a certain ion, c_1, is unknown, since the old calibration line is not valid anymore. The potential reading, E_1, is correlated to c_1 according to the Nernst equation

$$E_1 = \alpha \cdot \log[c_1] + \beta, \tag{a1}$$

where α represents the sensitivity of the ISE (slope of the calibration line) and β represents the zero-potential (intercept of the calibration line).

Then the first standard of known volume, V_a, and of known concentration, c_a, is added to V_1. This yields a new potential, E_2

$$E_2 = \alpha \cdot \log[c_2] + \beta, \tag{a2}$$

with

$$c_2 = (c_1 \cdot V_1 + c_a \cdot V_a)/(V_1 + V_2), \tag{a3}$$

The second standard addition of known volume, V_b, and of known concentration, c_b, yields the third potential, E_3

$$E_3 = \alpha \cdot \log[c_3] + \beta, \tag{a4}$$

with

$$c_3 = (c_1 \cdot V_1 + c_a \cdot V_a + c_b \cdot V_b)/(V_1 + V_a + V_b). \tag{a5}$$

A set of three equations ((a1), (a2), (a4)) is obtained with three unknowns (c_1, α, β), which is solvable. Eq. (a2) minus Eq.

(a1), and Eq. (a4) minus Eq. (a1) yields, respectively

$$E_2 - E_1 = \alpha \cdot \log[c_2/c_1], \tag{a6}$$

$$E_3 - E_1 = \alpha \cdot \log[c_3/c_1]. \tag{a7}$$

Dividing Eq. (a7) by Eq. (a6) yields

$$e = \frac{E_3 - E_1}{E_2 - E_1} = \frac{\log[c_3/c_1]}{\log[c_2/c_1]}. \tag{a8}$$

Eq. (a8) can be rewritten as

$$(c_2/c_1)^e - c_3/c_1 = 0. \tag{a9}$$

Substituting Eq. (a3) and Eq. (a5) into Eq. (a9) under the conditions $c_a = c_b$ and $V_a = V_b$ yields

$$(f + g/c_1)^e - h - i/c_1 = 0, \tag{a10}$$

with

$$f = V_1/(V_1 + V_a), \tag{a11}$$

$$g = c_a \cdot V_a/(V_1 + V_a), \tag{a12}$$

$$h = V_1/(V_1 + 2 \cdot V_a), \tag{a13}$$

$$i = 2 \cdot c_a \cdot V_a/(V_1 + 2 \cdot V_a). \tag{a14}$$

The parameters f, g, h and i are known, and only c_1 in Eq. (a10) is unknown. c_1 can be solved from Eq. (a10) by means of standard mathematical iteration procedures, such as the Newton-Raphson method. If c_1 is estimated from Eq. (a10), then α and β can be calculated. α follows from Eq. (a6) and Eq. (a3)

$$\alpha = (E_2 - E_1)/\log[(c_1 \cdot V_1 + c_a \cdot V_a)/(c_1 \cdot (V_1 + V_a))], \tag{a15}$$

and β follows from Eq. (a1) using the new calculated α

$$\beta = E_1 - \log[c_1]. \tag{a16}$$

ERRATUM

In:

M. Heinen, 1990. The use of ion-selective electrodes in NFT systems. Institute for Soil Fertility, Nota 222, 29 p.

Due to a calculation error, wrong intercepts, β, are presented in Table 4 on page 20. Table 4 should read as follows:

TABLE 4. The slope, α, and intercept, β, of the calibration lines at the end of the experiment, and the changes (%) in respect to the values of table 1.

ISE	α	Change	β	Change
NO_3	-58.00	1.7	141.0	-2.5
K	53.25	7.6	-60.35	17.9
Ca	19.00	36.5	79.00	22.7

The change in intercept for the NO_3 electrode is small, but for K and Ca the change is large. The combined effect of change in slope and intercept, however, yields for all three electrodes large relative changes in concentration (see the discussion on figure 4, pp 13-14). For example, the potentials that correspond to the concentration setpointsof NO_3, K and Ca (table 2) using the calibration lines defined in table 1 are, respectively, 103.4, -27.1 and 66.5 mV. These same potentials using the calibration lines at the end of the experiment (the new table 4) would yield concentrations which differ, respectively, by about -10, 60 and -80% from the setpoints in table 2. (Note: these errors depend on the value of the potential).

PS: Note that in this report the intercept is defined as the potential at log[c] = 0, where c represents the concentration expressed in $mmol \cdot l^{-1}$.

29-03-1990, MH.