

Estimating EC and ionic EC contribution percentage of nutrient solution based on ionic activity

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Abstract: The dynamic monitoring technology of inorganic ions using ion selective electrodes has some problems such as low precision, vulnerability to other ions, short service life, and high price. Due to the difficulty of dynamic control based on ionic concentration of nutrient solution, EC and pH values of nutrient solution are often used as feedback control indexes in hydroponic system. In this study, estimation algorithms of EC and ionic EC contribution percentage based on ionic activity were proposed to understand the quantitative relationship between ionic concentration and EC. With a view to predicting the EC accurately by mean ionic activities of specific salts in nutrient solution based on a specific formula, ionic concentration could also be calculated by the actual measurement of EC combined with ionic EC contribution percentage. With Japanese horticultural experimental nutrient formula and Yamasaki tomato nutrient formula, significant linear correlations between estimated EC and measured EC were found with determination coefficients over 0.99. Ionic EC contribution percentage was not affected by different relative concentrations of nutrient solutions. However, ionic EC contribution percentage changed significantly when adding specific salts with different concentrations, and different changes were found in each anions and cations of specific salt added. When the same K^+ concentration was added in different forms of KNO_3 , K_2SO_4 , KCl , and KH_2PO_4 , the changes of ionic EC contribution percentage of K^+ were similar, but those of other anions in potassium salts varied greatly. The relative errors of estimated EC of nutrient solutions based on ionic activities were only 1.3% in horticultural experimental nutrient solution and 1.8% in Yamasaki tomato nutrient solution with different relative concentrations compared to measured EC. The relative errors of estimated EC of nutrient solutions with specific salt added were only 0.1%-0.5% compared to measured EC in two nutrient solution. Therefore, the dynamic feedback control of ionic concentration of nutrient solution could be realized by using EC measurement combined with ionic EC contribution percentage to improve the ionic quantitative control in nutrient solution. The EC control of nutrient solution in automatic irrigation system might be upgraded to ionic concentration control by using algorithms above of ionic EC contribution percentage and EC estimation to meet dynamic demands of hydroponic crops for ionic concentration in different growth stages.

Keywords: hydroponics, nutrient solution, ionic activity, soilless culture, Debye-Hückel limiting equation, ionic EC contribution percentage, nutrient formula, solution dynamic control

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1 Introduction

Soilless culture is widely recommended by greenhouse vegetable industry because of its advantages of saving water, fertilizer, labor, and promoting production. The nutrient solution irrigation system based on feedback control of electrical conductivity (EC) and potential of hydrogen (pH) can roughly meet

the demands of plant growth and development. However, it is difficult to ensure the dynamic demands of greenhouse vegetables for specific inorganic ions in different growth stages^[1]. Therefore, how to accurately control the ionic concentration in nutrient solution according to the demands of crop growth is essential to achieve high yield and high quality production in greenhouse^[2]. However, there are a lot of problems in dynamic ionic detection technology by using ion selective electrodes such as low accuracy, vulnerability to other ions, short service life, and high price. As a result, the nutrient solution irrigation system based on ionic concentration control has not been applied to the actual production, and the main equipment is still based on feedback control of EC and pH of nutrient solution^[3]. Algorithms for estimating ionic EC contribution percentage and EC based on ionic activity in nutrient solution have been proposed for exploring quantitative relationship between its EC and the ionic concentration.

Nutrient solution for soilless culture belongs to a kind of strong electrolyte solution with extremely dilute concentration. Ion-pairs were formed because of attraction between anions and cations, and electrostatic interaction between ions is less than interaction

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affected by thermodynamic motion. Therefore, active force between ions except Coulomb force can be ignored. Ionic dielectric constant will not be changed with the dissolution of electrolyte in a continuous solution^[4]. However, effective concentration of ions is different from the interaction, charge number, ion volume, and electro-conductibility. Therefore, different ions have different effects on EC of nutrient solution^[5]. EC is the result of comprehensive interaction between the effective ionic concentrations of ions in mixed solution. The contribution of each ion to EC is not only related to molar concentration, but also closely related to the ionic characteristics^[5-7]. EC can indicate the change of total salt content^[8,9] or total ionic concentration^[5,10] in nutrient solution, but not the change of each ionic concentration^[2]. The pH of nutrient solution has an indirect effect on the effectiveness of many inorganic ions. High pH of nutrient solution will lead to precipitation of manganese, copper and zinc, especially iron, while low pH can cause the absorption restriction of calcium by crops due to the antagonism of hydrogen ions^[11].

In order to meet the dynamic demands of plant growth for the main inorganic ions in different growth stages, ionic concentration should be monitored and appropriately adjusted in nutrient solution. Therefore, ionic activity or mean ionic activity of specific salt in nutrient solution were proposed to precisely calculate ionic EC contribution percentage and EC of nutrient solution. Accordingly, quantitative relationship between ionic concentration and EC of nutrient solution can be determined, which provides a theoretical basis and technical support for the dynamic control of ionic concentration in nutrient solution.

2 Materials and methods

2.1 Compounds selection of nutrient solutions

According to the horticultural experimental nutrient formula and Yamasaki tomato nutrient formula for hydroponic production, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KNO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, H_3BO_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and DTPA-Fe were selected to prepare the target nutrient solution (Table 1). Distilled water with EC of 11 $\mu\text{S}/\text{cm}$ and pH of 5.82 was used in nutrient solution. In order to calculate the change of ionic EC contribution percentage of K^+ , different potassium salts such as K_2SO_4 , KCl , and KH_2PO_4 were added in nutrient solutions. The horticultural experimental nutrient solution and Yamasaki tomato nutrient solution were abbreviated as HENS and YTNS in this study.

Table 1 Japanese horticultural experimental nutrient solution (HENS) and Yamasaki tomato nutrient solution (YTNS) for soilless culture

Macro-element	HENS/ $\text{mmol} \cdot \text{L}^{-1}$	YTNS/ $\text{mmol} \cdot \text{L}^{-1}$	Micro-element	HENS/ $\text{mg} \cdot \text{L}^{-1}$	YTNS/ $\text{mg} \cdot \text{L}^{-1}$
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	4	1.5	Fe-DTPA (7%)	42.857	28.571
KNO_3	8	4	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	1.538	0.615
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	2	1	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.078	0.039
$\text{NH}_4\text{H}_2\text{PO}_4$	1.33	0.67	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.220	0.088
-	-	-	H_3BO_3	2.818	1.127
-	-	-	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	0.026	0.013

2.2 Preparation of nutrient solutions

Due to the different demands of greenhouse vegetables for relative concentrations of nutrient solutions in different growth stages, HENS and YTNS were prepared in 10 gradients as 0.20,

0.25, 0.33, 0.50, 0.67, 1.00, 1.33, 1.50, 1.80, and 2.00 times of standard concentration (Table 1). $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KNO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were weighed accurately and dissolved separately in 150-200 ml distilled water according to the concentration gradients mentioned above. All salt solutions in a concentration gradient were mixed in a volumetric flask with same concentration gradient microelements added, and then diluted to 1000 mL using distilled water as the nutrient solution to be tested.

In order to understand the EC changes of nutrient solution and ionic EC contribution percentage of different ions in HENS and YTNS, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KNO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, K_2SO_4 , KCl , and KH_2PO_4 with 12 different gradients with standard of cation concentration were added into standard nutrient solution respectively, and the concentration gradients were set as 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 times of cation in standard nutrient solution. Firstly, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KNO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, H_3BO_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and DTPA-Fe were weighed accurately according to the salt contents in 150 L standard nutrient solution, and dissolved separately in 20-25 L (The micro-elements were dissolved together.). Then the salt solutions were mixed and diluted to 150 L using distilled water as the standard nutrient solution. Secondly, the specific salts to be added were weighed accurately and dissolved separately in 500 mL standard nutrient solution, and diluted to 1000 mL using standard nutrient solution as the nutrient solution to be tested.

The nutrient solution with different relative concentration and the nutrient solution with different specific salt added were preserved in a dark and clean place for later measurement. All nutrient solutions mentioned above were prepared and measured in the laboratory at 25°C for three repeated experiments.

2.3 Measurement indexes and methods

Portable multi-parameter analyzer (HQ-40d, HACH Co., Ltd., USA) was used to measure the EC and pH of nutrient solution. Nitrate nitrogen concentration in nutrient solution was measured by ultraviolet spectrophotometer (UV-3150, Shimadzu Co., Ltd., Japan) at 210 nm^[12]. Ammonium nitrogen concentration was measured by ultraviolet spectrophotometer based on colorimetric measurement at 630 nm^[13]. Phosphate concentration was measured by ultraviolet spectrophotometer based on the molybdenum blue colorimetry at 680 nm^[14]. Sulfate concentration was measured by ultraviolet spectrophotometer based on barium sulfate precipitation method at 535 nm^[15]. Chloride ion was measured by silver nitrate titration method^[16]. Potassium was measured by atomic absorption spectrophotometer (AA-7002, Beijing East and West Analytical Instrument Co., Beijing) at 766.49 nm based on flame emission method^[17]. Calcium^[18], magnesium^[18] and iron^[19] were measured by atomic absorption spectrophotometer at 22.67 nm, 285.21 nm and 248.33 nm based on flame emission method, respectively.

Contribution of each ion to EC of nutrient solution is defined as the ionic EC contribution percentage (EC_i), which is calculated by ionic activities and equivalent ionic conductivity^[20]:

$$EC_i = \frac{|Z_i| T_i \lambda_{\infty}}{\sum (|Z_i| T_i \lambda_{\infty})} \quad (1)$$

where, EC_i is the ionic EC contribution percentage, %; Z_i is the charge number; T_i is the ionic activity, mol/L; λ_{∞} is the equivalent ionic conductivity, $\text{m}^2 \text{S}/\text{mol}$.

Because of the different ionic characteristics and the interaction between ions, each ion cannot play full role in

contribution to EC. The effective concentration that gives full play to EC is defined as ionic activity (T_i), which is determined by ionic concentration and ionic activity coefficient:

$$T_i = \gamma_i C_i \tag{2}$$

where, T_i is the ionic activity, mol/L; γ_i is the ionic activity coefficient; C_i is the ionic concentration, mol/L.

The anions and cations coexist in nutrient solution and attract each other. For a specific salt, the mean ionic activity (T) is expressed by the geometric mean of the ionic activities of cations and anions, indicating the comprehensive activity of specific salt^[4,21].

$$T = (T_j^{\nu_j} \cdot T_z^{\nu_z})^{\frac{1}{\nu_j + \nu_z}} \tag{3}$$

where, T is the mean ionic activity of specific salt, mol/L; T_j and T_z are the ionic activities of cations and anions of specific salt respectively, mol/L; ν_j and ν_z are the ion charge numbers of cations and anions of specific salt respectively.

The ionic activity coefficient (γ_i) is a thermodynamic parameter of electrolyte solution, which represents the deviation between the actual solution and the ideal solution. According to Debye-Hückel equation^[22], ionic activity coefficient is determined by ionic volume parameter^[20], ionic activity coefficient and ionic strength:

$$-\lg \gamma_i = \frac{AZ_i^2 \sqrt{I}}{1 + Br_i \sqrt{I}} \tag{4}$$

where, γ_i is the ionic activity coefficient; A is a constant related to temperature, 0.5091 at 25°C; B is a constant related to ionic size, 0.328 at 25°C; r_i is the ionic volume parameter; I is the ionic strength of nutrient solution, mol/L.

Ionic strength represents the electric field strength caused by ions in nutrient solution, which is calculated by ionic concentration and charge number^[21]:

$$I = \frac{1}{2} \sum C_i Z_i^2 \tag{5}$$

where, I is the ionic strength of nutrient solution, mol/L; C_i is the ionic concentration, mol/L.

2.4 Data analysis

Microsoft Excel 2010 and Origin 9.1 software were used to analyze the data and make charts. Relationships between EC/pH of nutrient solution and ion activities/mean ion activities of salt were conducted using multiple regression analysis; Relationships between measured values and estimated values of EC of nutrient solution were conducted using linear regression analysis.

3 Results and analysis

3.1 Effects of different ionic activities on EC and pH of nutrient solution

A significant linear correlation between ionic activity of inorganic ion and EC was found in two nutrient solutions (data was not shown), which agreed with the previous study^[23]. There was a significant quadratic correlation between ionic activity and pH of nutrient solution. The concentration and charge number between ions in nutrient solution tend to be stable and balanced, and the concentration of nutrient solution is extremely low. The short interactions between ions could be ignored. Therefore, effects of different ionic activities on EC of nutrient solution could be added^[24]. The multivariate linear correlations between ionic activities and EC were significant and the determination coefficients were greater than 0.99 in two nutrient solution. Significant multivariate linear correlations between ionic activities and pH of nutrient solution were also observed (Table 2). Therefore, EC and pH of nutrient solution could be calculated by ionic activities based on this multivariate linear correlation. This method could be applied to adjust the EC of nutrient solution according to the dynamic demands of greenhouse crops in different growth stages.

3.2 Relationships between mean ionic activities of specific salts and EC, pH of nutrient solution

All inorganic ions coexist in nutrient solution and keep in balance to avoid precipitation or antagonism. Significant multivariate linear correlations between mean ionic activities of specific salts and EC were found in two nutrient solutions with different concentrations (Table 3). Therefore, EC of nutrient solution can be estimated by mean ionic activities based on the multivariate linear correlation. Vice versa, ionic concentration can also be determined quantitatively by EC measurement of nutrient solution based on this correlation. Similarly, multivariate linear correlation between mean ionic activities of specific salts and pH of nutrient solution was significant (Table 3).

When a specific salt such as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KNO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, K_2SO_4 , KCl , or KH_2PO_4 was added in nutrient solution, mean ionic activity of specific salt was significantly related to EC in a linear mode. However, no significant correlation between mean ionic activity of the specific salt added and pH of nutrient solution was found under the same circumstance, with the exception of quadratic correlations between mean ionic activities of KH_2PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ and pH (Table 4).

Table 2 Multivariate linear correlation between ionic activities and EC, pH of nutrient solutions

Nutrient solution	EC/pH	Multivariate linear regression equation	R^2
HENS	EC	$\text{EC} = 0.02 + 0.057T_1 + 0.642T_2 + 2.135T_3 + 0.658T_4 + 0.220T_5 - 0.329T_6 - 2.251T_7 - 0.913T_8$	1.0000
	pH	$\text{pH} = 6.436 - 0.110T_1 - 2.568T_2 - 1.328T_3 + 5.621T_4 + 0.292T_5 - 0.366T_6 - 0.164T_7 - 9.569T_8$	0.9997
YTNS	EC	$\text{EC} = 0.001 + 0.172T_1 - 0.662T_2 - 0.926T_3 - 0.570T_4 - 0.079T_5 - 0.022T_6 + 0.738T_7 + 41.55T_8$	0.9999
	pH	$\text{pH} = 6.468 + 0.003T_1 - 0.417T_2 - 0.849T_3 - 0.953T_4 - 0.013T_5 + 0.191T_6 + 0.106T_7 + 33.18T_8$	0.9992

Note: T_{1-8} represent the ionic activity of NO_3^- , H_2PO_4^- , SO_4^{2-} , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , and Fe in the nutrient solutions, respectively.

Table 3 Relationships between mean ionic activities and EC, pH of nutrient solution with different relative concentrations

Nutrient solution	EC/pH	Multivariate linear regression equation	R^2
HENS	EC	$\text{EC} = 0.020 + 0.286T_{\text{KNO}_3} - 0.098T_{\text{Ca}(\text{NO}_3)_2} + 0.671T_{\text{MgSO}_4} - 0.213T_{\text{NH}_4\text{H}_2\text{PO}_4}$	0.9995
	pH	$\text{pH} = 6.376 - 0.170T_{\text{KNO}_3} - 0.027T_{\text{Ca}(\text{NO}_3)_2} + 0.419T_{\text{MgSO}_4} + 0.207T_{\text{NH}_4\text{H}_2\text{PO}_4}$	0.9837
YTNS	EC	$\text{EC} = 0.013 - 0.270T_{\text{KNO}_3} + 0.846T_{\text{Ca}(\text{NO}_3)_2} + 0.256T_{\text{MgSO}_4} + 0.106T_{\text{NH}_4\text{H}_2\text{PO}_4}$	0.9995
	pH	$\text{pH} = 6.484 - 0.105T_{\text{KNO}_3} + 0.165T_{\text{Ca}(\text{NO}_3)_2} - 0.161T_{\text{MgSO}_4} - 0.139T_{\text{NH}_4\text{H}_2\text{PO}_4}$	0.9946

Table 4 Effect of mean ionic activity of specific salt added on EC and pH of nutrient solution

Specific salt	HENS		YTNS	
	Linear regression equation	R ²	Linear regression equation	R ²
Ca(NO ₃) ₂	EC = 0.145T+2.318	0.9972	EC = 0.147T+1.159	0.9994
KNO ₃	EC = 0.145T+2.317	0.9989	EC = 0.148T+1.157	0.9995
MgSO ₄	EC = 0.159T+2.329	0.9977	EC = 0.177T+1.166	0.9995
NH ₄ H ₂ PO ₄	EC = 0.102T+2.332	0.9957	EC = 0.104T+1.163	0.9986
K ₂ SO ₄	EC = 0.156T+2.321	0.9996	EC = 0.168T+1.154	0.9992
KCl	EC = 0.156T+2.320	0.9994	EC = 0.151T+1.164	0.9992
KH ₂ PO ₄	EC = 0.101T+2.334	0.999	EC = 0.106T+1.163	0.9978
NH ₄ H ₂ PO ₄	pH=0.034T ² -0.280T+5.935	0.9477	pH=0.153T ² -0.485T+5.784	0.9734
KH ₂ PO ₄	pH=0.006T ² -0.146T+5.802	0.9705	pH=0.020T ² -0.254T+5.718	0.9801

Note: T in the table represents mean ionic activities of specific salts added in nutrient solution.

Table 5 Relationships between mean ionic activities and EC of nutrient solution after specific salts added

Nutrient solution	Specific salt	Multivariate linear regression equation	R ²
HENS	Ca(NO ₃) ₂	EC=1422-0.0119T-0.5781T _{Ca(NO₃)₂} +0.2657T _{KNO₃} -1358T _{MgSO₄} +341.5T _{NH₄H₂PO₄}	0.9999
	KNO ₃	EC=1508+0.0847T-0.2729T _{Ca(NO₃)₂} -0.1808T _{KNO₃} -1451T _{MgSO₄} +369.4T _{NH₄H₂PO₄}	0.9996
	MgSO ₄	EC=-9064+0.0094T+8507T _{Ca(NO₃)₂} -4562T _{KNO₃} -0.263T _{MgSO₄} -2130T _{NH₄H₂PO₄}	0.9972
	NH ₄ H ₂ PO ₄	EC=478.1+1.0418T-1841T _{Ca(NO₃)₂} +1394T _{KNO₃} +0T _{MgSO₄} +0.872T _{NH₄H₂PO₄}	0.9969
	K ₂ SO ₄	EC=340.9-0.0863T-111.8T _{Ca(NO₃)₂} -0.0807T _{KNO₃} -0.8521T _{MgSO₄} +97.49T _{NH₄H₂PO₄}	0.9996
	KCl	EC=-7731+2.5254T+1656T _{Ca(NO₃)₂} +2.2094T _{KNO₃} +2550T _{MgSO₄} -2060T _{NH₄H₂PO₄}	0.9996
	KH ₂ PO ₄	EC=-386.6-0.6181T-704T _{Ca(NO₃)₂} -0.8554T _{KNO₃} +2419T _{MgSO₄} -0.2049T _{NH₄H₂PO₄}	0.9991
YTNS	Ca(NO ₃) ₂	EC=494.78+0.1804T-0.0823T _{Ca(NO₃)₂} +0.0721T _{KNO₃} -978.5T _{MgSO₄} +538.3T _{NH₄H₂PO₄}	0.9998
	KNO ₃	EC=66.59+0.1184T+0.1721T _{Ca(NO₃)₂} -0.2016T _{KNO₃} -118T _{MgSO₄} +57.04T _{NH₄H₂PO₄}	0.9999
	MgSO ₄	EC=-2.6905+0.0078T+107.3T _{Ca(NO₃)₂} -63.58T _{KNO₃} -0.289T _{MgSO₄} +0.0961T _{NH₄H₂PO₄}	0.9999
	NH ₄ H ₂ PO ₄	EC=-121.9+0.1257T+0T _{Ca(NO₃)₂} -158T _{KNO₃} +779.4T _{MgSO₄} -0.0891T _{NH₄H₂PO₄}	0.9991
	K ₂ SO ₄	EC=84.57+0.1481T-74.45T _{Ca(NO₃)₂} -0.1214T _{KNO₃} +0.262T _{MgSO₄} +112.6T _{NH₄H₂PO₄}	0.9998
	KCl	EC=959.4+0.131T-27.5T _{Ca(NO₃)₂} -0.2202T _{KNO₃} -1824T _{MgSO₄} +1036T _{NH₄H₂PO₄}	0.9993
	KH ₂ PO ₄	EC=28.84+0.2328T+213.2T _{Ca(NO₃)₂} -0.0633T _{KNO₃} -552.1T _{MgSO₄} -0.2662T _{NH₄H₂PO₄}	0.9998

Note: T represents mean ionic activity of specific salt added.

For some salts such as Ca(NO₃)₂·4H₂O, KNO₃, MgSO₄·7H₂O, NH₄H₂PO₄, there were still significant multivariate linear correlation between ionic activities and EC of nutrient solution after specific salt was added. This correlation showed a linear response to the change of salt concentration added in nutrient solution. Therefore, the ionic concentration can be calculated by using different mean ionic activities and EC measurement based on multivariate linear correlation. Based on this theory, an automatic control of dynamic ion concentrations suitable for plant growth in different growth stages could be realized.

3.3 Response of ionic EC contribution percentage to amount of specific salt added in nutrient solution

The change of ionic EC contribution percentage of each ion was less than 2% except iron, when the concentration of HENS was adjusted from 0.2 to 2.0 times of the standard concentration. Ionic EC contribution percentage of iron was less than 5%. Similarly in YTNS, change of ionic EC contribution percentage of each ion was less than 2%, except iron (less than 4%) and phosphate (less than 6%) (Figure 1). However, ionic EC contribution percentage of each ion in two nutrient solutions was only about 1% in theory. This was due to the fact that composition of nutrient solution or specific salts in actual use might not be able to be in a balance or not reach the boundary condition of Debye-Hückel equation^[4]. However, ionic EC contribution percentage of ions in two nutrient solutions were also different because of the differences in ionic electro-conductivity resulted from different ionic concentrations, charge number, and ionic volume of each ion^[25]. In general, ionic

concentration of nutrient solution hardly went through great changes in soilless culture due to the extremely low concentration, and relative changes of ionic EC contribution percentage were neglectable when the concentration of nutrient solution was adjusted in a certain range. Therefore, the quantitative relationship between ionic activities and ionic EC contribution percentage could be clarified to calculate the ion concentrations with EC measurement based on this stability of ionic EC contribution percentage.

When specific salts with 12 different concentrations were added respectively into HENS and YTNS, ionic EC contribution percentage of added ions significantly increased, while ionic EC contribution percentage of other ions decreased correspondingly (Figure 2). The maximum relative change of ionic EC contribution percentage caused by addition of specific salt was NH₄H₂PO₄ when Ca(NO₃)₂·4H₂O, KNO₃, MgSO₄·7H₂O and NH₄H₂PO₄ were added separately in nutrient solution. The relative changes of ionic EC contribution percentage of cations and anions in MgSO₄·7H₂O and NH₄H₂PO₄ in nutrient solution after they were added showed the same trend. But relative changes of ionic EC contribution percentage of cations were 5-6 times that of anions in Ca(NO₃)₂·4H₂O and KNO₃ in nutrient solution after addition. The results above indicate that different ions had different effects on its ionic EC contribution percentage due to ionic characteristics^[26], which provided a theoretical basis for the way to choose specific salt in the dynamic control of nutrient solution.

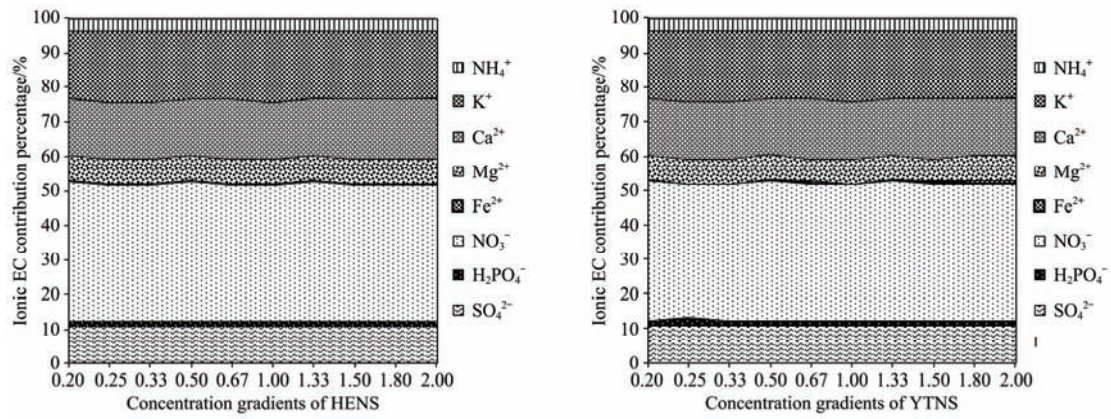


Figure 1 Changes of ionic EC contribution percentage of different ions with increasing concentration of nutrient solution

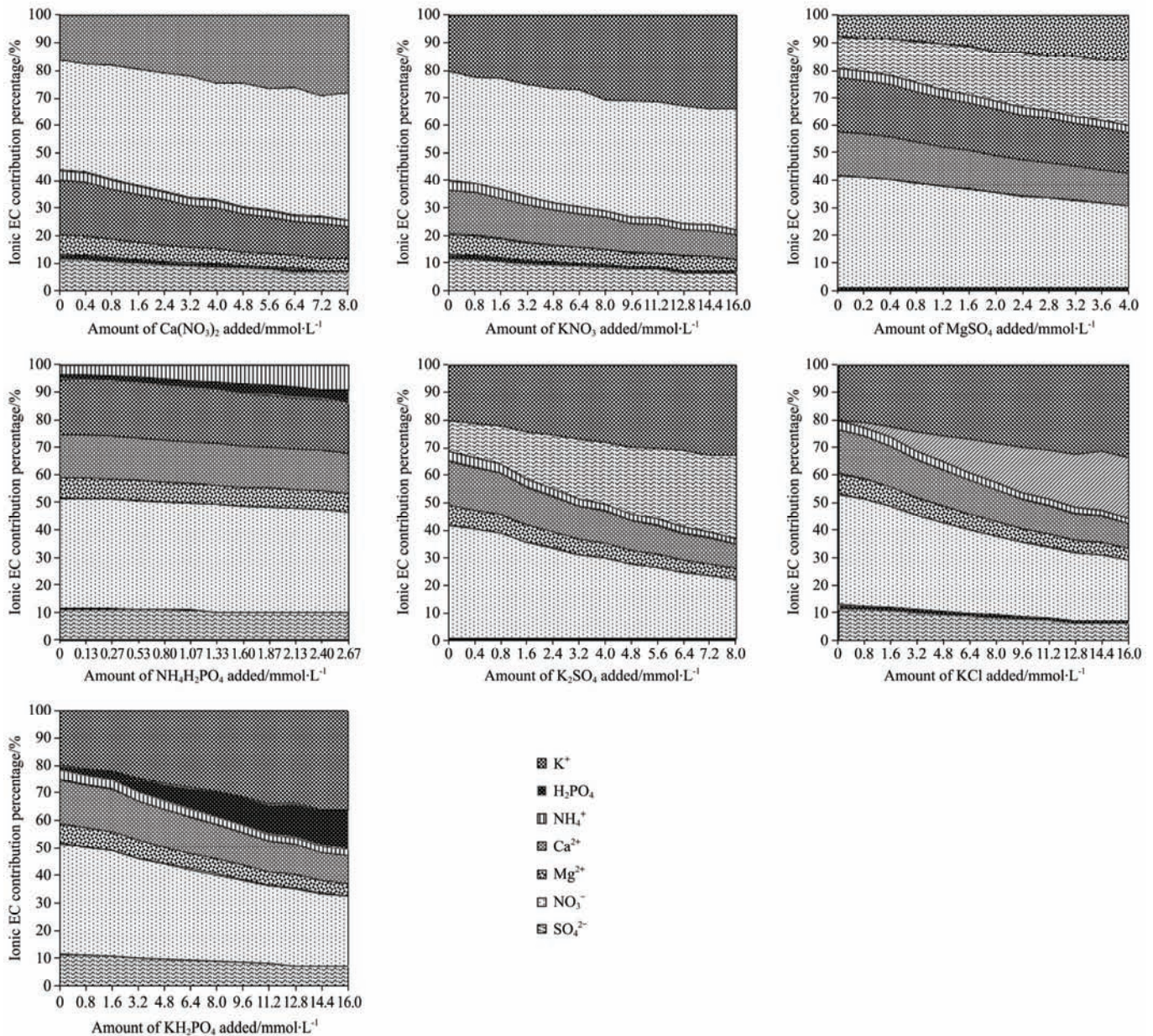


Figure 2 Changes of ionic EC contribution percentage of different ions in HENS with different salt added

When KNO_3 , K_2SO_4 , KCl and KH_2PO_4 were separately added in HENS and YTNS with same potassium concentration, relative changes of ionic EC contribution percentage of potassium in different nutrient solution were similar, while those of other ions in potassium salts were different. The maximum relative change of

ionic EC contribution percentage caused by specific salt added was Cl^- , followed by H_2PO_4^- , and relative change of ionic EC contribution percentage of NO_3^- was smallest. The results above also indicated that there was no short interaction between ions^[27]. Therefore, ionic EC contribution percentages of different ions were

not related only to ionic concentration but to ionic activities as well. Specific salts added in nutrient solution showed a different effect on ionic EC contribution percentage, so effect of specific salt added on EC should be fully taken into consideration in the process of dynamic control of nutrient solution.

3.4 Verification of estimated EC of nutrient solution based on ionic activity

EC of specific nutrient solution could be calculated by its multivariate linear correlation with mean ionic activities. The relative errors between estimated EC and measured EC were 1.33% in HENS and 1.84% in YTNS (Figure 3). In addition, Yamasaki lettuce nutrient solution (abbreviated as YLNS) and Yamasaki strawberry nutrient solution (abbreviated as YSNS) were used to verify this multivariate linear correlation, and the relative errors between estimated EC and measured EC were less than 1.49% in YLNS and 1.56% in YSNS. In a certain range of concentrations, each ionic activity or mean ionic activity had an additive effect on the changes of EC and pH of nutrient solution. Ionic EC

contribution percentage of each ion was not changed in nutrient solutions with different concentrations, since the proportions of different ions were fixed. Therefore, ionic concentration could be calculated quantitatively by regulating EC of nutrient solution.

However, the relative errors between estimated EC based on the multivariate linear correlation and measured EC were 0.10%-0.28% in HENS and 0.03%-0.33% in YTNS after specific salt was added (Table 6). The change of ionic EC contribution percentage of each ion caused by different specific salt added was significant different in nutrient solution. Therefore, concentration of ion or specific salt added could be calculated respectively by regulating EC of nutrient solution combined with ionic EC contribution percentage based on the quantitative relation. In conclusion, EC of nutrient solution could be accurately estimated by using ionic activities or mean ionic activities of specific salt, which provided theoretical basis and technical support for dynamic ion control based on EC measurement of nutrient solution.

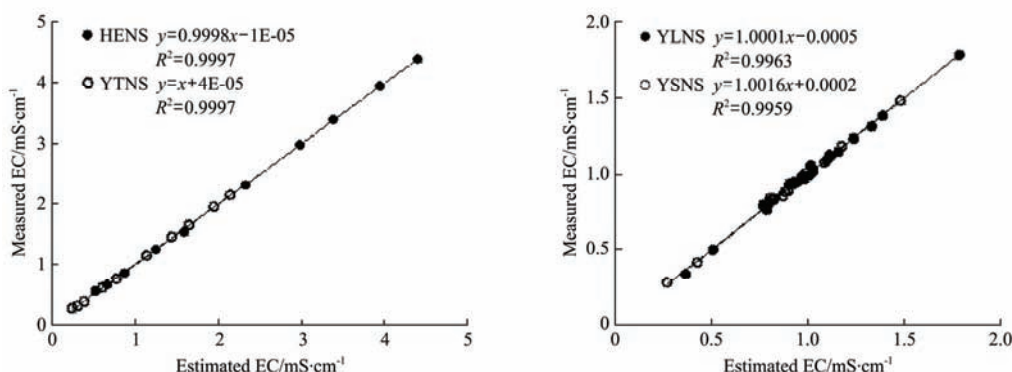


Figure 3 Comparison between estimated EC and measured EC in four nutrient solutions with different concentration

Table 6 Comparison between estimated EC and measured EC in two nutrient solutions after specific salt added

Specific salt	Estimated error of EC in HENS			Estimated error of EC in YTNS		
	Linear regression equation	R ²	Relative error/%	Linear regression equation	R ²	Relative error/%
Ca(NO ₃) ₂	EC _m =EC _e -4E-05	0.9999	0.10±0.08	EC _m =EC _e -3E-05	0.9999	0.14±0.09
KNO ₃	EC _m =EC _e	1.0000	0.27±0.21	EC _m =EC _e -3E-05	0.9999	0.14±0.08
MgSO ₄	EC _m =EC _e +6E-06	0.9985	0.23±0.12	EC _m =EC _e +5E-06	1.0000	0.03±0.02
NH ₄ H ₂ PO ₄	EC _m =EC _e +3E-12	0.9969	0.15±0.09	EC _m =EC _e -5E-13	0.9991	0.07±0.07
K ₂ SO ₄	EC _m =EC _e -3E-05	0.9998	0.21±0.19	EC _m =EC _e -4E-05	0.9999	0.13±0.11
KCl	EC _m =EC _e -3E-05	0.9998	0.26±0.20	EC _m =EC _e +3E-05	0.9996	0.33±0.26
KH ₂ PO ₄	EC _m =EC _e +2E-05	0.9995	0.28±0.18	EC _m =EC _e +5E-05	0.9999	0.13±0.11

Note: Linear relationships between estimated EC and measured EC were represented by the regression equation. And measured EC is represented by EC_m, estimated EC by EC_e.

4 Conclusions

The relative errors of estimated EC based on the multivariate linear correlation were less than 2% compared to measured EC in HENS and YTNS with different concentrations, and less than 0.4% in HENS and YTNS after specific salt was added. Therefore, the multivariate linear correlation analysis could be used to understand the quantitative relationship between mean ionic activities and EC, and accurately estimate EC of nutrient solution. In addition, the possibility of quantifying ionic concentration in nutrient solution by EC measurement and ionic EC contribution percentage based on ionic activity was proposed. The method in this study could improve the nutrition management from EC of nutrient solution to concentration of each ion, and also provide theoretical basis for future research on automatic control of ionic concentration to fulfill

the dynamic ion demands of greenhouse crops in different growth stages.

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