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Water Quality Dynamic Monitoring Technology and Application Based on Ion Selective Electrodes

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1. Introduction

Water shortage and water pollution is become to a more serious problem in the world especially in developing country. Water pollution is mainly due to a large number of emissions from industrial wastewater, agricultural drainage, and urban wastewater to rivers, lakes and soil which is making surface water and groundwater quality deterioration. This water shortage is aggravated by the exacerbated water quality and thus to influence human health and society economy development [1]. In order to conserve water resources, prevent water pollution, and improve sustainable development of water environment and aquaculture production, water quality monitoring and control in dynamically and regularity is become more and more important. Water quality monitoring and control is not only able to understand the water quality changes and pollution migration patterns, but also provide scientific and reasonable technical support for water resources integrated planning, water environment assessment, water treatment and conservation technology [2]. Therefore, water quality monitoring is essential tool and basis foundation in water resource management and water pollution supervision and control for government administration.

Water quality monitoring of different water sources is difficult because of the intricate components and its mutual interference and thus depended mainly on chemical analysis and instrumental analysis. According to geochemistry, geographical and regional differences of water environment or water pollution, water quality monitoring is always conducted in instrument station and to construct a monitoring network for water quality management, assessment and planning via short-term monitoring, long-term monitoring, emergency monitoring, and dynamic monitoring [3, 4]. To supplement the instrument stations in laboratory level, water quality monitoring vehicle or shipping using flow sampling and online monitoring is used for water pollution tracking or iterative detection. Recent years, water quality dynamic monitoring using online sensors is applied for various applications and increasing with promoting commercialization of ions selective electrodes.

Since 1960, local, continents and federal agencies in the United State began to collect water quality data and gradually getting a unified specification data to establish STORET water quality system. 20 years later, the STORET water quality system is used to provide the water

quality scientific data and water pollution management support for federal, state and local water authorities [5]. Water quality file analysis system WAP2 (Water Archive Phase 2) is developed in UK after STORET water quality system constructed. WAP2 system is focusing on relationship between the hydrological cycle and impact of human activities, and described in detail for hydrology, meteorology, water supply, drainage, wastewater treatment, industrial, and water quality [6, 7]. Compared to advanced countries, water quality monitoring technology in developing countries is developed and applied from 1980s and almost conducted by regional or local government. the national water quality monitoring network is still not established such as China and Indian, because of the different sampling methods and expensive instrument import form the United States and Germany [8].

Water quality dynamic monitoring is integrated from chemical analysis, computer, sensing, and communication technologies for simultaneous detection of several water quality parameters, mass data processing, and automatic water treatment in designated regions. The sampling method and monitored data will be basis foundation to represent water quality for in the regional water environment. On the other hand, suitable sample distribution and contrast handy chemical analysis are important in water quality dynamic monitoring especially for rivers with serious floating debris and soil erosion [9, 10]. Therefore, automatic cleaning, calibration, diagnostics, and alarm functions, data remote transmission, and networking construction will be required in water quality dynamic monitoring. This chapter is focus on water quality sensors based on ion specific electrodes, water quality dynamic monitoring system based on web-server-embedded technology and its application in rivers and freshwater detection, aquaculture production and hydroponic plant production.

2. Principle and application of ion selective electrodes

Ion selective electrode is a kind of electrochemical sensor which determine the ionic activity or concentration by membrane potential. The membrane potential is directly related to the ionic activity or concentration by interface of the sensitive membrane when ion selective electrode contact with the ion solution. Sensitive membrane of the ion selective electrode is a layer of special electrode film which is selectively responded to the specific ions. The relationship between electrode membrane potential and the ion content is conformed to Nernst formula [11]. The ion selective electrode is most widely used in electrochemical analysis for wild automatic and on-site continuous monitoring because of the good selectivity and short balance time. With a hundred years of technology development, more than 20 kinds of ion selective electrodes were commercially produced in the present now (Table 1). On-line monitoring based on ion selective electrode has become an independent scientific branch in electrochemical analysis, and is widely used for gas, water, soil, biological, chemical, marine, geology, biology, medicine, food, environment monitoring, and other fields [12,13].

Ion selective electrode consists of ion electrode probe, internal reference probe, internal reference solution, and sensitive membrane (Fig. 1). To a particular ion selective electrode, the electric potential mechanism caused in the sensitive membrane may be different, because the membrane material is responded sensitively to a specific ion. The electric potential arises of main ion selective electrode is based on the membrane materials and the interface exchange of ion solution [11]. According to the sensitive membrane material such as glass film, solid membrane, polymer membrane, gas infiltration membrane, and ion selective electrode can be classified into glass electrode, solid electrode, polymer electrode, and gas induction electrode.
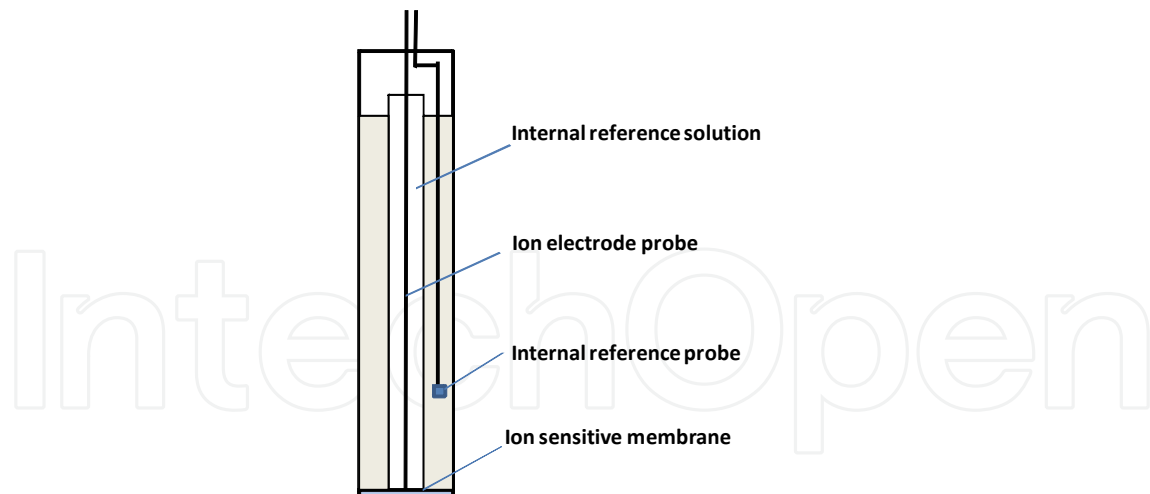
Fig. 1. Ion selective electrode

Glass film is made of silicon dioxide glass carrier which be added various chemicals, the common glass electrode includes pH electrode and Na+ selective electrode. Relatively unsolvable inorganic salts are used by solid electrodes membrane. The silver/sulfur ion, lead ion, copper ion, cyanide ion, thiocyanate ion, chloride ion, and fluorin ion electrodes are commonly commercialized. Polymer film is constituted by different ion exchange material which adding inert carrier such as PVC, PE, polyurethane or silicone rubber, potassium. The calcium ion, fluoride acid ion, nitrate ion, perchlorate ion, and water hardness are common produced by polymer electrodes. Gas sensing electrode including gas osmosis membrane and internal buffer liquid and without internal reference electrode for measuring ammonia, carbon dioxide, dissolved oxygen, nitrogen oxide and sulfur dioxide and free chlorine as dissolved gases.

Specific ion potential in solution is measured by ion selective electrode according to internal reference electrode with a constant potential. Electric potential difference of ion electrode and internal conference electrode depends on certain ions activity in the solution. However, the response of ion selective electrode will be affected by other ions in the sample solution. For certain ion selective electrode, impact of interfering ions can be quantitative corrected [14, 15]. If the sample solution is complex or contains large amounts of interfering ions, standard add method can be adopt [16]. Before the measuring, least 3 kinds of known concentrations of standard solution can be used to calibrate the ion selective electrode, and the sample concentration should be covered in the standard solution concentration. Sometimes, ionic strength adjustor (ISA) is used in order to ensure same ionic strength in the standard solution and sample solution. Usually, the ratio of sample solution and ISA is suitable in 50:1. Some ion selective electrode is used within certain pH range of solution, thus the pH of standard solution and sample solution can be adjusted by adding buffer to ionic strength adjustor. In addition, some chelating agent aiming to interference ion or preservatives aiming to antioxidant are added to ionic strength adjustor for dispelling interfering ions [17, 18].

Generally, ion selective electrode can be stabilized within 1 to 2 min, but more time will be needed when sensitive membrane is contaminated by solution with oil or particles. Electrode tip of glass electrode is washed by alcohol or a mild detergent such as laboratory cleaning detergent. Solid electrode is resumed by particles burnishing stick. Polymer electrode can be rinsed with freshwater [19]. The ion selective electrode needs to put in a low concentration of the standard solution for 2-4 h or more time. It is needed to calibrate after cleaning. The glass electrode can be stored in low concentration within the standard solution

Ion	Electrode type	Sensitive membrane material	Linear range	Interfering ions
Na^+	Rigid matrix electrode	NAS-11-18 glass	$1\sim10^{-6}$	H^+, Ag^+
Na^+	Rigid matrix electrode	ETH-157	$0.1\sim10^{-5}$	Li^+, Ca^+, H^+
K^+	Rigid matrix electrode	Valinomycin	$0.1\sim10^{-6}$	NH_4^+
K^+	Rigid matrix electrode	Di-tert-dibenz-30	$0.1\sim10^{-6}$	NH_4^+, Na_+
Ca^{2+}	Rigid matrix electrode	ETH-1001	$0.1\sim10^{-6}$	
Ca^{2+}	Mobile carrier electrode	Dioctyl-phenyl $Ca_3(PO_4)_2$	$0.1\sim10^{-5}$	Zn^{2+}, Mn^{2+}
Ag^+/S^{2-}	Homogeneous membrane electrode	Ag_2S	$1\sim10^{-7}$	Hg^{2+}
Pb^{2+}	Homogeneous membrane electrode	$PbS+Ag_2S$	$1\sim5*10^{-7}$	Ag^+, Hg^{2+}, Cu^{2+}
Cu^{2+}	Homogeneous membrane electrode	$CuS+Ag_2S$	$1\sim10^{-7}$	Ag^+, Hg^+
F^-	Crystalline membrane	LaF_3+EuF_2	$1\sim10^{-8}$	OH^-
Cl^-	Homogeneous membrane electrode	$AgCl+Ag_2S$	$1\sim5*10^{-5}$	S^{2-}, CN^-, I^-, SCN^-, Br^-
Cl^-	Homogeneous membrane electrode	Hg_2Cl_2+HgS	$0.1\sim5*10^{-5}$	S^{2-}, CN^-, I^-, SCN^-, Br^-
Br^-	Homogeneous membrane electrode	$AgBr+Ag_2S$	$1\sim5*10^{-6}$	S^{2-}, CN^-, I^-, SCN^-
I^-	Homogeneous membrane electrode	$AgI+Ag_2S$	$1\sim5*10^{-7}$	S^{2-}, CN^-, SCN^-
CN^-	Homogeneous membrane electrode	$AgI+Ag_2S$	$10^2\sim10^{-8}$	S^{2-}, I^-
NO_3^-	Mobile carrier electrodes	Trioctyl methyl ammonium chloride	$0.1\sim5*10^{-8}$	ClO_4^-, I^-, NO_3^-
BF_4^-	Mobile carrier electrodes	Triheptyl dodecyl amonium	$0.1\sim10^{-8}$	ClO_4^-, SCN^-
NH_3 molecule	Gas induction electrode		$1\sim10^{-6}$	Volatile amine
CO_2 molecule	Gas induction electrode		$10^2\sim10^{-4}$	

Table 1. General ion selective electrodes

without measuring. Solid electrode, polymer electrode, and gas induction electrode should be kept in a dry condition without measuring. Polymer electrode and gas induction electrode can store in a low concentration of the standard solution between the measuring.

3. Water quality dynamic monitoring parameters based on Ion selective electrodes

3.1 pH

pH as a basic parameter of water quality is to measure activity of hydrogen ion for indexing alkalinity or acidity of water. Component style and circulation of water are affected by pH value changed. The exorbitant or insufficient pH of water will cause serious consequence in the water cycling or aquatic biology. The exorbitant pH will interfere with carbon and iron utilization of phytoplankton and result in Illness or death of fish. The low pH value will restrict activity of nitrate reductase, and thus lead to nitrogen deficiency for hydrophyte [20, 21].

pH of water is usually measured by glass electrode with temperature compensation. pH glass electrode using doped glass membrane, glass H^+ ion sensitive electrode and additional reference electrode is sensitive to H^+ ion and active by the glass bubble tailored with varying amount of alumina (Al_2O_3) and other common constituent such as Na_2O, K_2O, B_2O_3. Inside of the pH electrode is usually filled with buffered internal filling solution of chlorides which is reference electrode usually made of silver wire covered with silver chloride (Ag/AgCl). Elective potential difference of the pH electrode is caused by H^+ activities of bubble on both thin glass sides and described by the Nernst formula. Since Nernst equation is a temperature-dependent function, temperature compensation is significantly required for measuring pH.

pH glass electrode is easy to be corroded because of fluoride in the water. Stibium (Sb) metal electrode could be adopted instead of glass electrode to measure pH in solution with fluoride. It is difficult to dissolve oxide membrane on the Sb electrode surface and issued in a reversible electron exchange between the oxide membrane and H^+ ion in the solution as follows:

$$2Sb + H_2O \Leftrightarrow Sb_2O_3 + 6H^+$$

$$Sb_2O_3 + 6H^+ \Leftrightarrow 2Sb_3+ +3H_2O$$
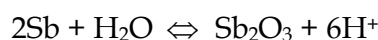
According to the Nernst formula, the elective potential difference between Sb metal and oxide membrane (Sb_2O_3) is measured for pH of the solution. In general, Sb metal electrode is widely used in solution containing cyanide, sulfide, fluoride, reduction sugar, alkaloids, etc. It shows measure accuracy in ±0.1 in the solution pH range from 2 to 7 and ±0.4 in the solution pH range from 7 to 12 [22].

3.2 DO

Dissolved Oxygen (DO) is amount of oxygen (O_2) dissolved in water. Since oxygen is needed for all forms of life including aquatic biology, DO measure is important in water quality monitoring of water environment. It is also produced by photosynthesis of plant byproduct and phytoplankton. DO is used in respiration and decomposition process of aquatic bacteria. A DO decrease is typically associated with an organic pollutant when organic matter such as animal waste or improperly treated wastewater entered to water, or algae growing increases [23]. DO of water is ranged from 0 to 18 mg/L, approximately 8

mg/L will be required for aquatic plant and animals, less than 5 mg/L will be taken biological stress. As DO levels constantly decrease, pollution intolerant organisms are replaced by pollution tolerant worms and fly larvae, and then result in water quality degenerating [24].

The dynamic monitoring of DO usually adopts membrane electrode which based on the membrane diffusion theory. This measure method is not affected by pH, salinity, oxidation-reduction substance, chromaticity, and turbidity, etc. Typical DO electrode contains a working electrode usually made of noble metal such as Pt or Au and a reference electrode of popular Ag/AgCl. Both electrodes are located in an electrolyte of KCl solution which is separated from the sample by a gas permeable membrane. The working electrode equaling to the cathode reduces the oxygen molecules to hydroxide ions occurred reaction following as $O_2 + 2H_2O + 4e \Leftrightarrow 4OH^-$. The anode occurred reaction following as $4Ag + 4Cl^- \Leftrightarrow 4AgCl + 4e$. In the above electrochemical reactions a current flows from the reference electrode to the working electrode. The current is generated directly proportional to the DO in the sample.

The DO measurement using ion selective electrode has the advantages of faster measurement speed, simple operation, and easy to automatically monitoring due to its gas permeable membrane easy to plug and the electrode aging. The maintenance of the DO electrode with periodical replacement of the membrane is needed. The solution flow with 0.2 to 0.3 m/s is required because of the oxygen contents decreased by cathode reaction during the measuring.

3.3 EC

Electrical Conductivity (EC) is used to indicate the purity of water and reflect the degree of the electrolyte existing in the water. Generally, the content of inorganic salt that is dissolved in the water can be estimated through measuring EC of the solution. EC means the ability to conduct electric current and equals the reciprocal of resistivity in physics. So according to the principle of electrolytic conduction, EC will be measured by the method of electric resistance measurement using metal electrode. Like the metal conductor, the electrolytic solution also obeys Ohm law, through the measurement of the electric current between the metal electrodes to get the EC of the solution. The resistance of the electrolyte is closely related with the concentration of solute in the solution [25]. In other words, the EC of the solution is closely related with the contents of inorganic acid, alkali, and slat in the solution.

The basic unit of the EC is Siemens (S). But S/cm is much more commonly used in the EC measuring because of the effect of electrode shape. At present, the 2-electrode based conductivity electrode also called as Kohlrausch electrode regularly is made of two metal plates or, metal cylinder fixed on the support holder with insulators. Its measuring range is usually 0 to 20 mS/cm, and the measuring range is different according to the different electrode constant, with conductivity reading accuracy of ±0.5%. In addition, another commonly used electrode is 4-electrode based conductivity electrode (Fig 2), which contains two coaxial current electrodes and two coaxial voltage electrodes. The current between the two current electrodes has a linear relationship with the conductivity of solution when measuring EC. The 4-electrode based conductivity electrode can avoid the influence by polarization effect usually occurred in 2-electrode based conductivity electrode. Its measuring range is usually 0 to 2000 mS/cm, and either the measuring range is different according to the different electrode constant, with conductivity reading accuracy of ±0.5%.

Fig. 2. 2-electrodes (a) and 4-electrodes (b) conductivity sensors.

3.4 NH$_4^+$-N

The ammonium nitrogen (NH$_4^+$-N) in water body consists of molecular ammonium (NH$_3$) and ionic ammonium (NH$_4^+$). High content of NH$_4^+$-N in water body will cause the eutrophication phenomenon of the water body, and produce toxic hazard to the fish and other aquatic life, and then even result in a series of environmental problems [26]. Therefore, the content of NH$_4^+$-N is a significant symbol for evaluating the pollution degree of water body, as well as an important parameter for the water quality monitoring.

The ammonium ISE used to measure the NH$_4^+$-N in water is a diaphragm gas sensing electrode, in which there is a flat-plate pH glass electrode as the indicated electrode, and Ag/AgCl as a reference electrode which is immersed in the internal reference solution of 0.01 M NH$_4$Cl commix with inertia electrolyte, such as NaCl, KCl. At the end of electrode, the sensitive membrane of pH electrode is covered with a very thin layer of hydrophobic semi-permeable membrane usually made of PTFE that allows the molecular NH$_3$ only to pass through, but block off other ions in the solution. When measuring of NH$_4^+$-N in water with gas sensing electrode, the NH$_4^+$ in the solution will transform into molecular NH$_3$ by adjusting pH>11, and the NH$_3$ will pass through the membrane. There occurred a reversible chemical reaction as follow: NH$_3$ + H$_2$O $\Leftrightarrow$ NH$_4^+$ + OH$^-$. Therefore, the NH$_4^+$-N content in the solution could be determined through measuring the change of electric potential utilizing the pH glass electrode in the gas sensing electrode. The ammonium ISE has the feature of high selectivity, and requires no titration and has no turbidity or color interferences, but is sensitive to the change of temperature [27]. At present, most commercial electrodes show the performance with the detection limit of 10^{-7}-10^{-6} M, measuring range of 10^{-7} - 1.0 M, and response time of 30 seconds.

3.5 ORP

Oxidation-Reduction Potential (ORP) is the measurement (in millivolt, or mV) of the oxidizing or reducing tendency of a solution. ORP is typically not a good method for measuring solute concentration, so it is not used to indicate the water quality independently, but used to integrate with other water quality parameters to reflect the ecological status of the water environment. When the ORP is positive, it means that the oxidation ability of water body is strong, that is the ability of the recursive organism which handles the biological metabolism is strong. If the pH, DO and temperature are suitable, the pollutants in the water will be decomposed fast and effectively [28].

The principle of ORP measurement is similar with the measuring of pH, which based on the selectivity of H$^+$ by glass electrode, while the principle of ORP measurement refers to the

electrons' acceptance or release of noble metal electrode. The structure of a typical ORP electrode is almost same as that of pH electrode, adopting Pt or Au as the working electrode and the Ag/AgCl as the reference electrode inserted in the KCl internal reference solution. In the case of measuring ORP with a Pt metal electrode, a layer known as Helmholtze electric double layer which is equivalent to a capacitance will be formed. One end of capacitance is inked with the Pt metal, and another end is linked with reference electrode. Because the capacitance is undertook charging, this capacitance, therefore, the ORP of the testing solution could be obtained by measuring electric potential of the capacitance.

3.6 F$^-$ Ion

In the case of the F- ISE, the selective membrane is a single crystal of Lanthanum Fluoride (LaF$_3$) doped with Europium Fluoride (EuF$_2$) which produces holes in the crystal lattice through which F- ions can pass [29]. When immersed in a fluoride solution and connected via a voltmeter to an Ag/AgCl external reference electrode immersed in the same solution, the F- ions in the solution pass through the crystal membrane by normal diffusion from high concentration to low concentration until achieves an balance between the force of diffusion and the reverse electrostatic force. On the other side of the membrane there is a corresponding build-up of positive ions. The potential between the analyte and internal reference solution faces of the crystal produced during the phase of F- ion exchange across LaF$_3$ is proportional to the logarithm of F- activities according to Nernst formula.

For the Fluoride ISE, the most important interfering species is OH-. The OH- complexes with the LaF3 crystal itself in much the same way as F- does, with the chemical equilibrium of (LaF$_3$ + OH- $\Leftrightarrow$ La(OH)$_3$ + 3F-) that produces additional F-. Subsequently, the potential across the crystal will be a function of [OH-] and will interfere with the fluoride determination. Another pH dependent effect is due to the basicity of F-. HF is effectively a weak acid and at pH less than 5, acid-base equilibrium of (2F- + H$^+$ $\Leftrightarrow$ HF + F- $\Leftrightarrow$ HF$_2$-) will reduce the concentration of F- in solution. To remedy these problems, proton and hydroxide concentrations are controlled by buffering the pH of measurement solutions to between 5 and 7. In addition, sodium citrate can be used as masking agent for eliminating the interfering of polyvalent cations, such as Fe^{3+}, Al^{3+}, Be^{2+}, Si^{4+}, etc. which easy to form up complexes with F- ion [30].

4. Water quality dynamic monitoring system and its application

4.1 Construction of the water quality dynamic monitoring system

Water quality dynamic monitoring system consists of water sampling module, water quality sensor module, data collection module, data processing module, communication module, and power supply module. Water sampling methods are usually used in pattern s of submerged style, flow circulating style, float style, and water logging style (Fig. 3). Submerged style sampling is combination of water sampling module and water quality sensor module which is fixed at a specific depth by mounting brackets for long-term dynamic monitoring of water quality. Water quality sensors are connected with water sampling module by using threaded bolt for sensors maintenance. Submerged style sampling is the most common pattern in water quality monitoring. Flow circulating sampling is widely used in poor or tanks in aquiculture and hydroponics. Flow circulating sampling module and water quality sensor module are fixed in main pipeline or bypass pipeline for water inlet or outlet. Float style sampling is widely used in water quality or

pollutes monitoring of river, lake and reservoir [31-33]. Hydrological sensors, meteorological sensors, and biochemical sensors are always integrated with water quality sensors. Water logging style sampling is widely used in freshwater and sewage treatment and industrial wastewater treatment. The water logging size and the water exchange are depended with water treatment system. For water quality dynamic monitoring, ion selective electrodes as water quality sensor are widely used, other online sensors based on photoelectricity principle, fluorescence principle, scattering principle, fibre-optical principle, and bioinstrumentation principle are also used. For example, turbidity is measured dynamically by scattering principle; oil content of water is measured dynamically by ultraviolet-fluorescence analysis; nitrate content of water is measured dynamically by UV absorption method; chlorophyll and DO are measured dynamically by fluorescent method [34, 35]. Data collection module can be independent, or integrated with data processing module or communication module or both. Data collection and processing modules are to transfer analogue data measured by the water quality sensor into digital data. The monitoring data analysis and database store, uploads and download of data, remote operation functions are required in water quality dynamic monitoring system. Communication protocols are reported in RS-232, RS485, LAN, and CAN with wire or wireless [36, 37]. Security and efficient encryption protocols are used to improve the system security level. In the power supply module, 220V AC supplied for pumps and electromagnetic valves, 12V or 24V DC is supplied for water quality sensors.
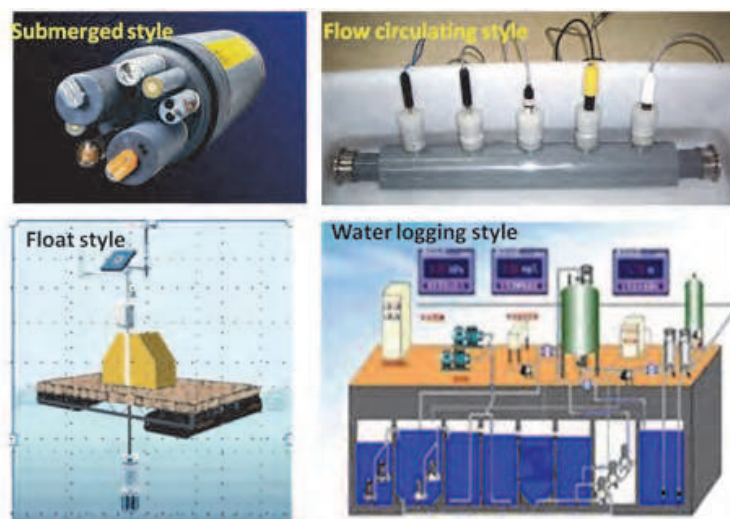
Fig. 3. Water sampling methods in water quality monitoring.

4.2 Water quality monitoring of Taihu Lake basin
4.2.1 Introduction of Taihu Lake basin
Taihu Lake is the third largest freshwater lake in China and covering Jiangsu, Zhejiang and Shanghai Province. The lake area is 2,338 square kilometers with 1.9 m mean depth of and 3.4 m greatest depth. Taihu lake basin including big cities of Wuxi, Suzhou, Changzhou, and Huzhou is about 3.65 millions square kilometers. It is also one of the most advanced industrial and agricultural areas in China. Water quality change of Taihu lake basin is related closely to surrounding water safe and Taihu regional economy development. Since the special geography heights decrease from west to east, excessive chemical fertilizer application caused soil nutrient excess, and a large number of industrial sewage, wastewater

urban drainage, water quality exacerbated and water pollution with nutrient-enrichment become to a serious problem in Taihu Lake basin.

In May to June, 2007, green algal blooms have broke out in Taihu Lake, thus source water quality deterioration directly influence freshwater quality to drink safety for surrounding threatened millions people. This emergency event was taken a great danger to human health and society economy. Water pollution in Taihu Lake is mainly due to nutrient enrichment with nitrogen and phosphorus. Past several years, water quality of Taihu Lake is always in the eutrophic condition [38]. Therefore, water quality monitoring and emergency warning in Taihu Lake basin has become an important problem for sustainable development of society and economy. In August 2009, water quality and disease monitoring platform around Taihu Lake basin funded by the China government was started in Wuxi, Suzhou, Changzhou and Huzhou city for water quality monitoring and disease warning [39-40].

4.2.2 Water quality and disease monitoring platform around Taihu Lake basin

Water quality monitoring in Taihu Lake basin is focus on source water and freshwater. In the water quality and disease monitoring platform around Taihu Lake basin, 15 instrumentation stations were deployed for source water quality monitoring and 14 instrumentation stations were deployed for freshwater quality monitoring (Fig. 4). Otherwise than water quality dynamic monitoring, standard measurement of water quality including algae amount, biomass of frustules, total nitrogen, total phosphorus, N/P ratio for source water, and chromaticity, turbidity, ammonia nitrogen, total phosphorus for freshwater were measured according same method at the first week of every month. On the other hand, shipping itineration detection with 15 sampling places is conducted once every month for source water quality monitoring by Wuxi Disease Control Center Cooperated with Wuxi Environmental Monitoring Station. Various water quality monitoring data will be update and issue to Jiangsu Province server for homepage publication. In addition, meteorological parameters such as wind direction, wind speed, air temperature, sunshine radiation rainfall are measured simultaneously.

Fig. 4. Water quality monitoring in Taihu Lake basin for source water and fresh water.

Water quality and disease monitoring platform around Taihu Lake basin is a data-share-and-exchange platform developed under J2EE environment. The web interface with B/S

construction is connected to Oracal database. All authenticated users can visit and manage the data. Using this platform, water quality change of source water and freshwater can be reported and alarmed automatically and clearly. Via the past two years operation, water quality parameters especially microcystin content were improved within national warning line

4.2.3 Water quality dynamic monitoring of Taihu Lake basin

Water quality dynamic monitoring in Taihu Lake basin based on multi-variables water quality monitoring instrument (YSI6820, YSI Inc., USA) were founded in 2004 for 13 invidious instrumentation station networked [41]. There are 13 stations of water quality/situation monitoring. It is succeed in monitoring and warning on water quality of Taihu Lake basin. Taihu Lake water situation monitoring determine water stage and rainfall with hydraulic remote-system stage gauge and rotary rain gauge every 5min. Water quality monitoring determine water temperature, pH, DO and ammonia nitrogen with electrode sensor every 5 min. There are 1 industrial personal computer, 1 I/O elevation model and 1 communication module in every station. Monitoring stations send data to the central station per hour, and examine data by central station or call phone at any time. The central station server can setup, dispose and synchronize monitoring station. There are 2 models to collect water sample: water quality sensor is set in water with PVC pipes surrounding; water quality sensor is set in water gauge that determining per 30 min. Water quality sensor applied with 12V D.C supply, sampling pump and other equipments applied with 220V A.C supply. Ammonia Nitrogen sensor has to be replaced every half a year, pH and DO sensor have to be replaced every year.

4.3 Water quality dynamic monitoring system based on web-server-embedded technology
4.3.1 Water quality monitoring problems in aquaculture production

Aquatic products play an important role in agricultural products. Aquaculture has becoming to an important industry in agriculture and the water quality monitoring is an important issue for improving aquatic production yield and its quality. Effective water quality dynamic monitoring are required for measuring and controlling water temperature, pH, DO, EC, and others in aquaculture production because of closer relationship between water quality parameters and aquatic organism (Fig. 5). In Europe, water quality variables were regulated by physical, chemical and biological methods to organize the aquaculture production by utilizing hazard analysis and critical control point operating rules. The computer-based process control technology proposed by United States for intensive aquaculture production was used in marine fish's growth environment control. Recently, water quality monitoring is trended to be smaller, more automatic and intelligent, and multi-functional automation. Although water quality monitoring technology has been researched in China at recent decade, there are still many problems such as the unstable sensor performance, less real-time monitoring parameters of water quality, low level of networked monitoring, and single system network monitoring. Many researches utilize new technology such as GPRS and neural networks to improve water quality monitoring level in China.

The aquaculture water pollution, aquatic production and quality issues, and the establishment of food safety traceability system make constructing effective dynamic monitoring network to obtain multi-parameters of water quality become an important issue

in aquaculture. Distributed networking, real-time remote monitoring, the dynamic controlling of water quality using web-server-embedded technology and the sensor node technology are future trend development for intensive aquaculture production. In this chapter, a water quality dynamic monitoring system using ion selective electrodes and web-server-embedded technology was introduced for aquaculture production. The water quality information was transported safely using wireless communications technology based on CDMA services, WiFi and virtual private network (VPN) technology.
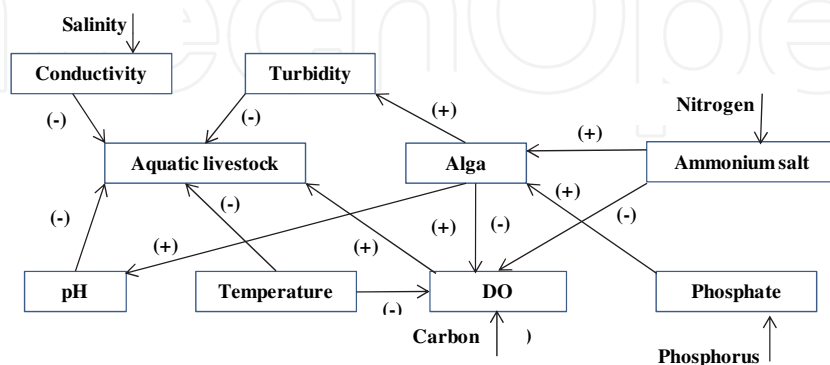
Fig. 5. Relationship between water quality parameters and aquatic organism.

4.3.2 Introduction of water quality dynamic monitoring system for aquaculture

The water quality dynamic monitoring system is composed of water quality dynamic monitoring devices and a remote information server. The water quality dynamic monitoring device consists of sensor module, data monitoring module, communication module, and power module (Fig. 6). The sensor module is composed of a water flow cell and water quality sensors including pH (ED201, Suzhou Han-star CO., China), EC (DJS-1T, Suzhou Han-star CO., China), DO (ED012, Suzhou Han-star CO., China), ORP (PC312, Suzhou Han-star CO., China), and temperature (STWB-1000, Beijing Saiyiling CO., China). The data monitoring module is a web-server-embedded chip (PICNIC2.0, TriState Co., Japan) to get water quality sensor signals. The communication module is composed of a Wi-Fi module (AirStation-G54, Buffalo Co., Japan), and a CDMA module with IPSec-based VPN function (InRouter210C, Beijing Inhand Co., China), for establishing wireless LAN network and achieving communication with local and remote information servers. The power module consists of 12V DC power supply and 220V AC power supply. The remote information server consists of an ADSL modem (DSL-300, D-Link Co., China), a VPN router (BV-601, Nesco Co., China), and personal PC as information server. The VPN router and information server connect to Internet via ADSL service. After the VPN router and CDMA device of the water quality dynamic monitoring device are connected to Internet, VPN connection is established via IPSec authentication.

The water quality dynamic monitoring system is an isolated local area network and can be used as a sensing network node. That means the system can be constructed to a large-scale wireless sensing network under CDMA signal covered areas. The system is easy to increase by 255 devices at most, and the monitoring device is also easy to increase sensor channels. Water quality data are transported by TCP/IP protocol and identified and stored in the remote information server. The CDMA module will be dynamically connected to the remote information servers via IPSec-based VPN security technology. In order to identify the

specified remote information servers, the remote VPN router have to use a dynamic domain or a fixed global IP to support the remote VPN calling. Therefore, the water quality dynamic monitoring system deployed anywhere can be constructed to be a large monitoring network if the IPsec-based VPN tunnels were connected. Within the network, the information captured by all devices could be used as a local information network to conduct secure access. Therefore, all authorized users could visit or manage the remote sensing devices anywhere and anytime under Internet environment.
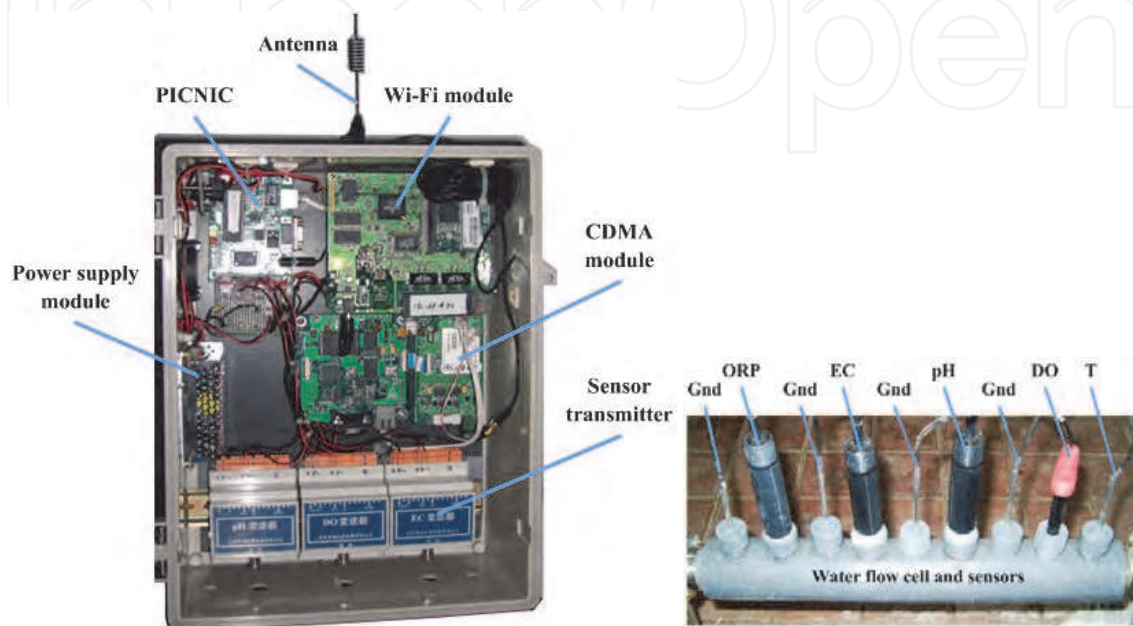
Fig. 6. Water quality dynamic monitoring system based on web-server-embedded technology.

4.3.3 Performance test of the water quality dynamic monitoring system

Two water quality dynamic monitoring systems were installed respectively in inlet and outlet in a seawater aquaculture farm (Fig. 7). The aquaculture production is using seawater and semi-circle mode for intensive aquiculture. In this testing, one remote information server with an IPsec-based VPN router is deployed in the China Agricultural University located in Beijing city. The testing experiments were conducted for three years.

The water quality data including pH, DO, EC, and water temperature throughout a week were dynamically storied or issued in webpage or Extensible Markup Language (XML) file by a special JAVA applet program in the remote information server (Fig. 8). In this testing, the 10-bit analog signals of the water quality sensors were obtained by the web-server-embedded chip without storage device. The water quality dynamic monitoring systems were communicated with the remote information server in Beijing by a 20-30 Kbps access speed with over 26-30 signal quality level of CDMA services. Under normal processing of Internet, 6 days data were randomly selected to analysis data loss via remote communication. As a result, high measuring accuracy of pH, DO, EC, and temperature and average packet loss rate is between 1.7 to 2.3% were reported. The water quality of seawater in inlet were relatively maintained in an appropriate level, but pH, DO and EC were changed greatly when rainfall. This is because the nature rainfall addition has decreased the EC and pH of seawater, thus led to low DO with drop in water temperature. In aquaculture

production, input water has to be processed regularly via settling and filtered treatment in tanks, thus periodical water quality change is because of periodical water exchange of tank water. The growth and development of aquatic products will be affected by water quality change with rainfall and season change. Therefore, water quality dynamic monitoring is available for aquaculture production.

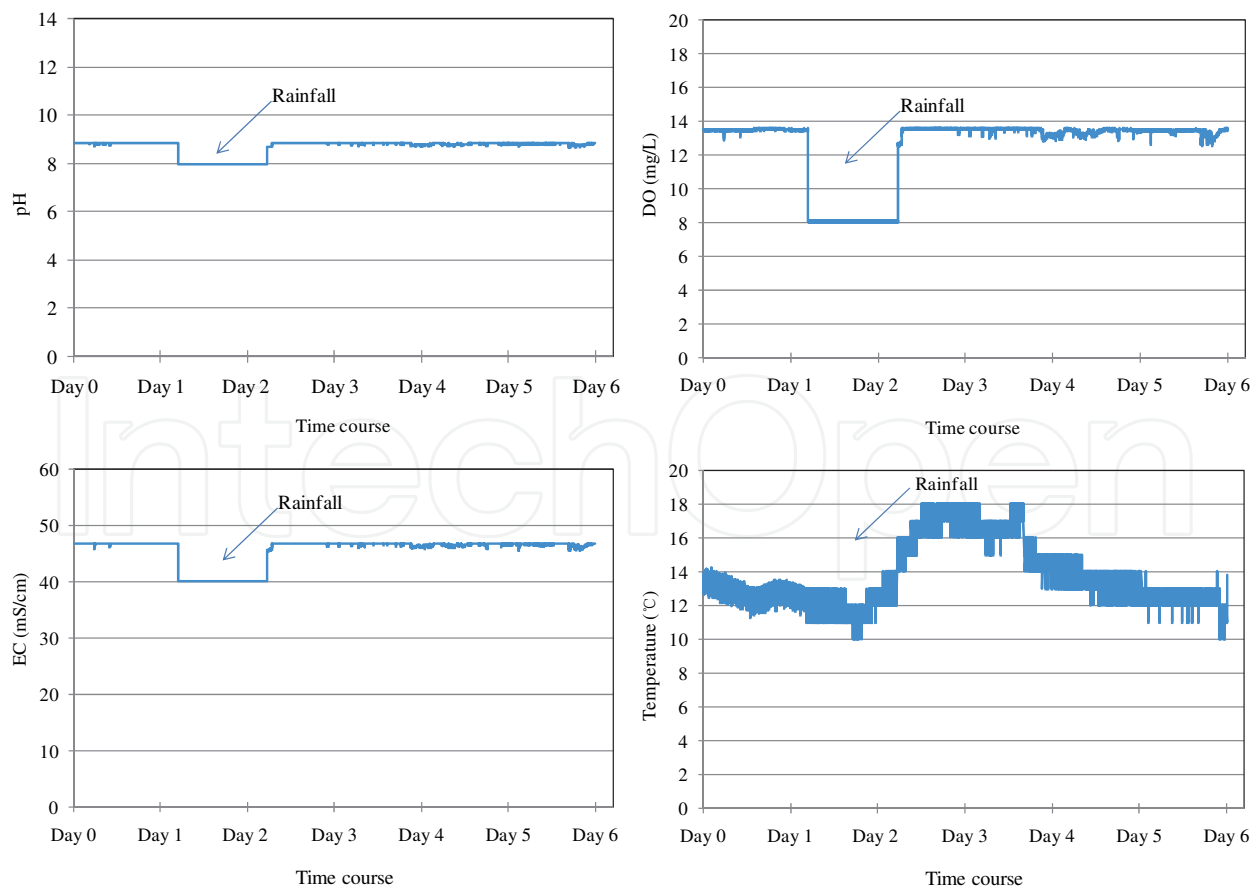Fig. 7. Water quality dynamic monitoring systems installed in an aquaculture farm.

Fig. 8. Time course of water quality in the seawater aquaculture farm.

4.4 Water quality dynamic control system for hydroponic production
4.4.1 Water quality monitoring problems in hydroponic production
Cultivation of hydroponic plants as a clean and efficient plant production has been widely used in protected horticulture. Nutrient solution supply and control are important in hydroponic plant cultivation because of nutrient solution regulation is related directly to plant growth and development. Since nutrient solution is configured by mother solution periodly, nutrition solution is adjusted and replaced timely even popular used hydroponic production with deep flow technique (DFT) and nutrient film technique (NFT). The inorganic nutrition absorption of plants growth is dynamic and selective, so water quality of nutrient solution is considerably changed in the process of circulation or maintaining. In order to make stable water quality in nutrient solution, water quality of supply nutrient solution need be dynamically adjusted and controlled. In this chapter, a water quality dynamic control system using ion selective electrodes and web-server-embedded technology for hydroponic production is described.

Fig. 9. Hydroponic production with deep flow technique (DFT) and nutrient film technique (NFT).

4.4.2 Introduction of water quality dynamic monitoring system for hydroponics
Water quality dynamic control system for hydroponics consists of nutrient solution supply module and nutrient solution control module. The nutrient solution supply module includes supply solution box, return solution box, mother solution box, and cultivation groove. There are 4 pipes which are assembled 4 electromagnetic valves respectively between supply solution box and mother solution box for automatic adding 2 kinds of mother solution, acid solution, and alkaline solution. There is connect pipe and overflow pipe which are assembled a check valve between supply solution box and return solution box. The supply solution circulation between supply solution box and cultivation groove is forced by submersible pump. The solution circulation between cultivation groove and return solution box is operated by submersible pump or water level natural circulation. The water adding is automatic controlled by electromagnetic valve. Bypass is under the supply solution box contact with square circulation style sampling device to ssembl water quality sensors including temperature, pH, EC. There are supply solution pump, solution circulation pump, PTC heater and water level sensor in the supply solution box. Water level sensor is used for controlling high water level and alarming low water level. Nutrient solution control module consists of water quality transmitter module, data processing module, LAN hub module, and power supply module. Water quality transducer module make up of temperature transducer (PT1000, Hayashi Elect. Inc., Japan), pH tranducer (E201, Nanjing Chuandi Inc., China), and EC transducer (DJS-1, Nanjing Chuandi Inc., China). Data processing module is a web-server-embedded chip (PICNIC2.0, TriState Co., Japan) using TCP/IP protocol. The web browser can be used to communicate with the water quality dynamic control system in any local or remote area via Internet. LAN hub module is used connect more data processing modules. 220 V AC power supply and 12 V DC power supply were used in the power supply module. The water

quality sensors and transducers are supplied by 12V DC, and submersible pump, electromagnetic valve, and other electrical equipment are supplied by 220V AC.
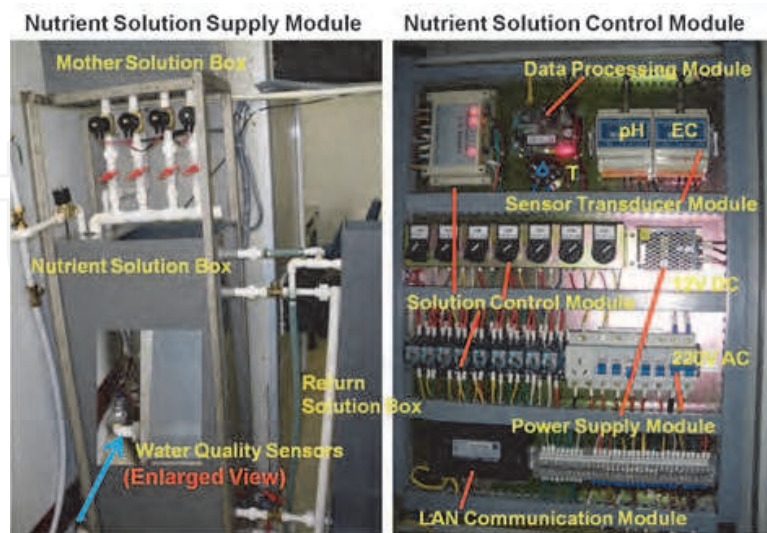

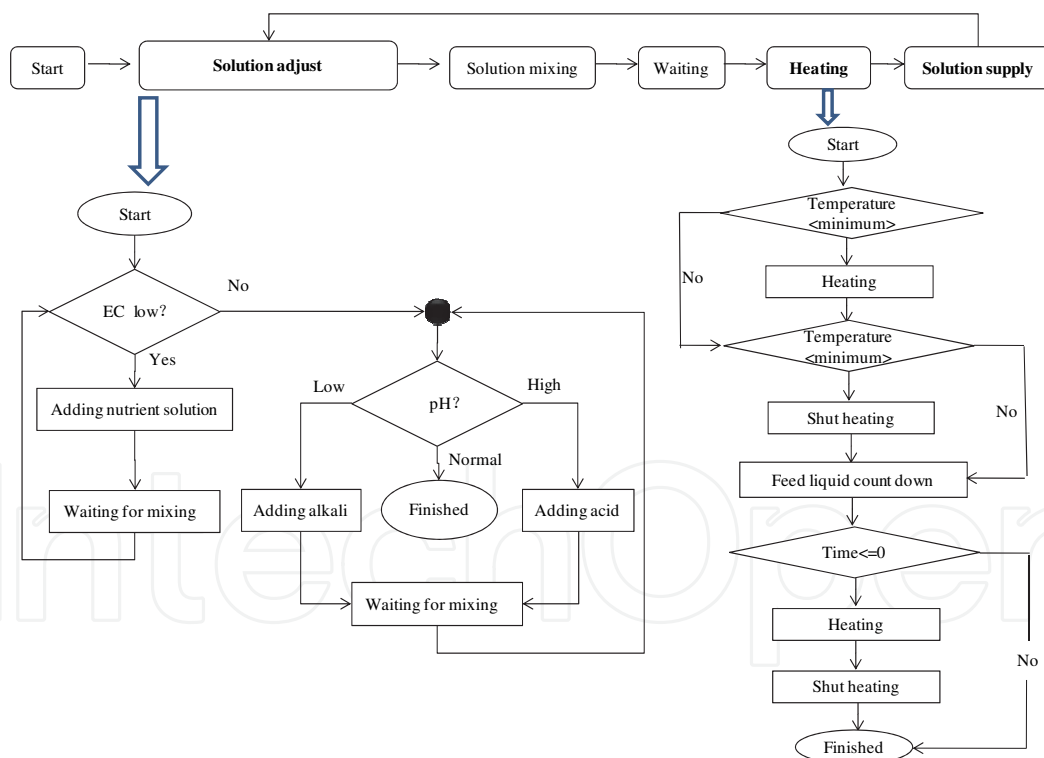Fig. 10. Water quality dynamic control system for hydroponics.

Fig. 11. Nutrient solution control process in the water quality dynamic control system for hydroponics.

The control process of nutrient solution in the water quality dynamic control system for hydroponics is always following the cycle as solution adjust, solution mixing, waiting, heating, solution supply (Fig. 11). Solution adjust process is following the cycle as water addition, mother solution addition, acid or alkaline solution addition. The mother solution

includes A mother solution and B mother solution. The water addition and mother solution addition are used to adjust EC of the nutrient solution. The acid and alkaline solution additions are used to adjust the pH of the nutrient solution. Heating process is used after solution adjusts and before solution supply. Therefore, temperature, pH, EC, and water level of the nutrient solution is controlled automatically and dynamically by the water quality dynamic control system. Nutrient solution control algorithm can choose ON/OFF mode or prediction algorism. The control strategy can be specified by users. The water quality dynamic control system is easy to construct a water quality monitoring network because of the web-server-embedded technology. For networking convenience, the water quality dynamic control system is set to priority server control and the machine can also be run independently itself.

4.4.3 Performance test of water quality dynamic monitoring system for hydroponics

A small closed plant production system with artificial lighting is used to test the system performance. The closed plant production system is equipped with plant culture module, environmental control module, nutrient supply module, web-server-embedded environment/nutrition control module (Fig. 12). The hydroponic plant cultivation generally requires the preparation of concentrated stock solution (mother solution) and work nutrient solution. In order to prevent precipitation when the mother solution in the preparation, the compounds of the nutrient solution have to divide to two or three kinds because of precipitation formed when some ions mixed. Generally, the compound which reacts with calcium without precipitation is perpetrated as A mother solution, and the compound which react with phosphate without precipitation is perpetrated as B mother solution. In this test, the 200 times concentrated A and B mother solutions are used.

Fig. 12. Closed plant production system with artificial lighting.

When nutrient solution control target as: temperature 28℃, EC 4 mS/cm, pH 6.5, supply solution box begin dynamic control test while adding water, then nutrient solution control was cycle supplied after 1.5h from the start testing (Fig. 13). The total testing time was 2.5h. As a result, the regulation of nutrient levels would stable after 1h in dynamic controlling, and water quality parameters of nutrient solution can basically maintain at the target levels.

Because plant will selective absorb nutrient inorganic ions, the EC decreased significantly and there is little change in solution temperature and pH when the nutrient solution is started to supply and cycle for plants. The cycle supplied over a period of time, plants also tend to selectively absorb a dynamic equilibrium, then the EC levels of nutrient solution gradually dynamic control to the target level. A contract measurement is using a portable multi-parameter water quality instrument (HQ40, Hach Inc., USA) at 4:30 and 5:30 respectively, the solution temperature were 28.3℃ and 27.6℃, EC were 3.9 mS/cm and 4.3 mS / cm, pH were 6.7 and 6.8 respectively.

When the control target of nutrient solution as: temperature 28℃ and pH 6.5 was unchanged and EC change from 4 mS/cm to 15 mS/cm, nutrient solution temperature and pH were basically stable after 30 min in the dynamic controlling (Fig. 14). EC stabled at the target levels after 1h after the target changed. After 20 min in the control target changed, solution temperature was 27.5℃±0.1℃; EC was 15 mS/cm±0.2 mS/cm; pH was 6.9±0.2. Therefore, the water quality dynamic control system can quickly correspond to the nutrient control change for different plant culture requirements.
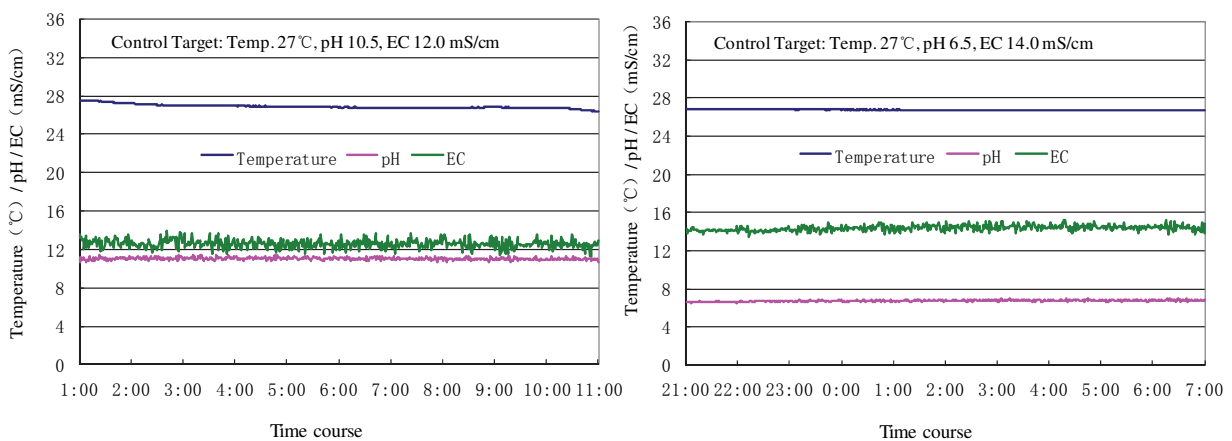
Fig. 13. Performance test of the nutrient solution dynamic control system for hydroponic plant production.
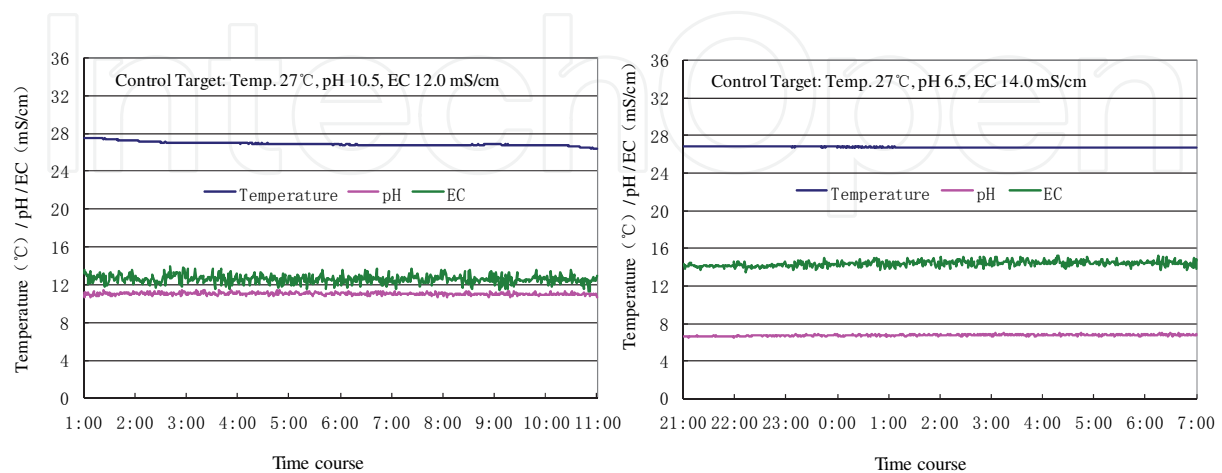
Fig. 14. Reliability test of the nutrient solution dynamic control system for hydroponic plant production.

In order for the 12h system stability testing, different level nutrient pH and EC were set up in two levels. The 10 h test data were resulted in temperature 26.9℃±0.2℃, pH 11.0±0.1, and EC 12.6±0.4 mS/cm for control target of temperature 27℃, pH 10.5, and EC 12 mS/cm; resulted in temperature 26.8℃±0.3℃, pH 6.7±0.1, EC 14.4±0.3 mS/cm for control target in temperature 27℃, pH 6.5, EC 14 mS/cm, respectively (Fig. 14).Therefore, the reliability of the water quality dynamic control system for hydroponics is available.

5. Conclusions

Water quality dynamic monitoring technology based on ion selective electrodes is an available toll for water quality monitoring in lake water and source water, in aquaculture and hydroponics production. Its system is used to achieve data collection in real time and data transmission in remote and wireless simultaneously. Except of the pH, EC, DO, ORP sensors, other water quality sensors in ion selective electrodes are not easy to apply in commercial applications. For the near future, development of water quality dynamic technology and application will be promoted by increasing commercialized ion selective electrodes.

6. Acknowledgments

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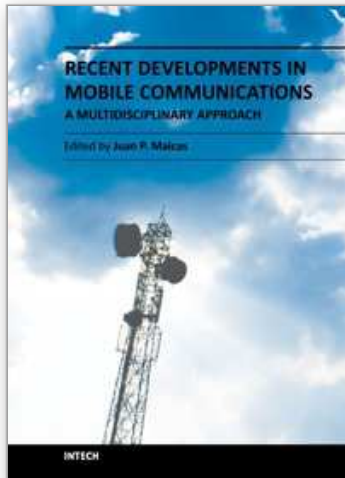
Recent Developments in Mobile Communications - A Multidisciplinary Approach

Edited by Dr Juan P. Maícas

Recent Developments in Mobile Communications - A Multidisciplinary Approach offers a multidisciplinary perspective on the mobile telecommunications industry. The aim of the chapters is to offer both comprehensive and up-to-date surveys of recent developments and the state-of-the-art of various economical and technical aspects of mobile telecommunications markets. The economy-oriented section offers a variety of chapters dealing with different topics within the field. An overview is given on the effects of privatization on mobile service providers' performance; application of the LAM model to market segmentation; the details of WAC; the current state of the telecommunication market; a potential framework for the analysis of the composition of both ecosystems and value networks using tussles and control points; the return of quality investments applied to the mobile telecommunications industry; the current state in the networks effects literature. The other section of the book approaches the field from the technical side. Some of the topics dealt with are antenna parameters for mobile communication systems; emerging wireless technologies that can be employed in RVC communication; ad hoc networks in mobile communications; DoA-based Switching (DoAS); Coordinated MultiPoint transmission and reception (CoMP); conventional and unconventional CACs; and water quality dynamic monitoring systems based on web-server-embedded technology.

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