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Application of mathematical models and genetic algorithm to simulate the response characteristics of an ion selective electrode array for system recalibration

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ABSTRACT

With proper training procedures, including the use of a sufficiently large training sample set, ISE array with Back-Propagation Neural Networks (BPNNs) can be used to simultaneously determine the concentrations for multiple ions in environmental water. However, it is not practical for end-users to re-measure the whole training sample set – dozens of samples – to re-build the BPNN model every time after a long storage or measurement period, since both the sensitivity and selectivity of ISEs would be gradually degraded over time. In this study, instead of using BPNNs, we developed and patented some mathematical models to describe the based characteristics of the ISE array's response, including the sensitivity and selectivity. The developed mathematical equations can be used to simulate the response values of ISE array, and to determine the analytes' concentrations from unknown samples. By measuring only a couple of standard solutions, which are practical to the end users, the ISE array can be automatically recalibrated using genetic algorithm (GA). This research is based on an array of Prussian blue modified Carbon Paste Electrodes (PB-CPEs), and the interferences between nitrate (NO_3) and chloride (Cl) was used as a case study.

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1. Introduction

ISEs are normally based on ionophores designed for complexing, interacting, and holding the analyte in a molecular cavity [1]. These interactions are actually non-specific so that interference from other undesired analytes of a similar size and charge commonly appear [1]. In the last decade, approaches using an ISE array with Back-Propagation Neural Networks (BPNNs) to solve the problem of cross-interference between ISEs have been widely studied [2–11]. Recently, Mueller and Hemond, performed a comprehensive study of this application to simultaneously determine the major ions in environmental samples [2]. Del Valle and colleagues have also published significant research in this area [3–8]. However, our previous temporal stability experiment showed that both the sensitivity and selectivity of ISEs would be gradually degraded over time [9–11]. In this situation, using two or three single ion concentration points, to recalibrate a previously built-up BPNN model for an ISE array system would result in an inaccurate calibration, since the ISE response to the interfering ions would not be considered. On the other hand, it is not practical for end-users to re-measure the whole training sample set – dozens of samples – to re-build the BPNN model every time after a long storage or measurement period, even when an effective experimental design, such as an orthogonal experimental design, has been utilized [11,12].

In fact, the mathematical equations can be developed to describe the based characteristics of the ISE's response, which are not only based on the response of the ISE to their related ion, but also to that of the interfering ion. The developed mathematical equations can be used to simulate the response values of ISE array, and to determine the analytes' concentrations from unknown samples. We have to mentioned, there are several parameters in the equations which can be optimized using genetic algorithm (GA), to match the response characteristics of the ISE array. GA whose optimization principle relies on the biological theory of survival of the fittest that explains how genes on the chromosome vary by several biological means such as chromosome encoding and decoding, selection for offspring, crossover and mutation to adapt to the particular environment has been widely used for search and optimization of the problem [13,14]. As knowing that there are a lot of other optimization methods, such as Davidon Fletcher Powell method, Nelder–Mead method, Levenberg Marquardt method, Linear search method, etc.. However, most of these algorithms are suitable for linear input scenarios only. For the nonlinear scenarios,

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most of these algorithms will face the local maxima problem, which means the algorithm would just search in a much smaller sub-set of the multi-dimensional parameter space rather than in the whole parameter space [15]. GA can be used to avoid the local maxima problem by starting with a number of random matrices as multi-points in the PDF of the model. The parameters' values in the equations are adjustable following the degradation of the sensitivity and selectivity of ISEs. By using the built-up equations, it is possible to measure only a couple of selected standard solutions to calculate the parameters in order to recalibrate the ISE array system for determination.

In this study an array of solid state electrode, Prussian Blue modified Carbon Paste Electrode (PB-CPE), was applied to determine NO_3 concentrations in the presence of Cl. Prussian blue (PB) or iron (III) hexacyanoferrate (II) is an inorganic polycrystal with well-known electrochromic and electrocatalytical capabilities [16]. Mixing PB with graphite powder to prepare Carbon Paste (CP) is a cheap, simple and effective mixing technique to create the electrode body [17–22]. The well-known problem of using ISEs to predict Cl and NO_3 in the presence of cross-interference was selected as a case study. NO_3 is a common nitrogenous compound that results from the natural processes of the nitrogen cycle. However, anthropogenic sources, such as fertilizers and detergents, have greatly increased their nitrate concentrations in potable water supplies, particularly groundwater [23–26]. Chloride (Cl) is a major anionic constituent of surface and groundwater, and concentrations vary widely between water. Therefore, understanding the co-relationship between the ISEs and ions of Cl and NO_3 can improve the accuracy of predicting these two ions for monitoring water quality. In the present study, the characteristics of both NO_3 ISE and Cl ISE have been described mathematically. 30 different soil leachate samples collected from three different states in Australia were used for validation to demonstrate that Cl and NO_3 can be simultaneously and accurately determined using the proposed mathematical model.

2. Experimental design

2.1. ISE array

For making the PB-CPE body, iron (III) ferrocyanide powder (Sigma-Aldrich) was mixed with graphite powder (Aldrich) in a 1:9 ratio by weight [17,23]. This powder mixture was transferred to an agate mortar and mixed thoroughly for 5 min with 20 wt.% mineral oil (Sigma-Aldrich). The homogeneous paste was placed in the electrode holders, which were made from 10–100 μL pipette tips (Sigma-Aldrich), connected with a copper cable and sealed with epoxy (Araldite). The electrode paste surface was smoothed onto a glass plate. The geometric diameter of the electrode surface was 5 mm. The ISE array contained an Ag/AgCl reference electrode and 2 PB-CPEs. The ion-sensitive membranes were prepared by adding a solution (30 μL) drop-wise of a the formulation which consisted of: chloride-selective membrane: 2.0 wt.% of chloride ionophore (ETH 9009, Fluka), 0.05 wt.% of ionic additive (TDMACl, Fluka), 64.95 wt.% of plasticizer (Bis(2-ethylhexyl) sebacate, Fluka) and 33 wt.% of PVC (Fluka) [27]; nitrate-selective membrane: 1.0 wt.% of nitrate ionophore (Nitrate Ionophore V, Fluka), 0.6 wt.% of ionic additive (TDMACl, Fluka), 65.6 wt.% of plasticizer (oNOPE, Fluka) and 32.8 wt.% of PVC (Fluka) [28]. 400 mg of these chemicals was mixed into 3 mL of tetrahydrofuran (THF, from Fluka).

2.2. Reagents and solutions

All reagents employed were of analytical grade and used directly without further purification, unless otherwise stated. Deionized water (Milli Q plus System, Millipore, Bedford, MA, USA, with resistivity of 18.2 $M\Omega\ cm^{-1}$) was utilized in all experiments including the preparation of all aqueous solutions. The calibration solutions of NO_3^- and Cl^- were in the range of 0.1 μM to 0.1 M and were made by successive 10-fold dilutions from a 1 M solution of KNO_3 and NaCl, respectively. Generally, the major anions in natural water are chloride (Cl), sulfate (SO_4), bicarbonate (HCO_3) and carbonate (CO_3) [29]. It has to be mentioned that the NO_3 ISE experiences significant interference from Cl, HCO_3 and CO_3 whereas, the Cl ISE experiences significant interference only from NO_3. According to [30], the interferons HCO_3 and CO_3 can be reduced by lowering the pH to under 4. Therefore, background buffer solution, 0.1 M sodium sulfate and 1.25 mM sulfuric acid, where pH was adjusted to 3.2 (measured by an Orion pH electrode), was used to eliminate the interference from hydrogen carbonate and carbonate. There is no significant interference from sulfate to either of the two ISEs tested. All working standard solutions were prepared daily and stored in polyethylene containers. The laboratory-based instrument IC served to confirm the concentrations of these two ions for each solution.

2.3. Apparatus and measurement protocol

The potentiometric system consisted of 4 pH amplifiers (ADInstruments Co.) applied as signal amplifiers while the PowerLab (ADInstruments Co.) served to interface the computer with the amplifiers. Chart5 for Windows software (ADInstruments Co.) was used for the data acquisition and filtering phases. Data processing and analysis was undertaken in Matlab R2012b using the Statistical Analysis and neural network toolboxes. Microsoft Excel 2010 was applied for data recording and searching the regression lines. SPSS 20 for Windows generated the Orthogonal Experimental Design and Pearson correlation coefficients for interference analysis. The electrodes were connected to electronic amplifiers, sharing the same measuring conditions that included: the reference electrode and grounded earth. A 10 Hz low-pass digital filter eliminated the noise caused by signal granularity generated by electrodes. One Magnetic Stirrer (IEC, C876083V) with a spin bar, and several beakers (Schott Duran 250 mL) were used for sample and standard preparation.

Standards and samples containing various combinations of each ion were directly measured by ISEs using the standard addition method. All measurements were carried out at the same temperature (22 °C) in triplicate and the average values reported for processing. During measurement, electrode membranes were completely free from air bubbles after immersion into an analysis solution. The final electrode potential was only recorded when stable, i.e. at a constant potential of ±0.05 mV, over 30 s. Single point calibrations with standard solutions (1 mM of $NaNO_3$ and 10 mM of NaCl) were carried out every hour. After each measurement, all containers and electrodes were carefully rinsed with deionized water and blotted dry on tissue paper to prevent electrode cross-contamination.

3. Results and discussion

3.1. Electrode characteristics

The detection limit and linear detection range were estimated for each ISE using single ion standard solutions (NaCl and KNO_3) and each solution was measured in triplicate. The detection limit and linear response range were calculated according to the IUPAC recommendations [31]. Both the Cl ISE and NO_3 ISE have a detection limit of 10 μM, and a linear response range of 0.1 mM to 0.1 M. The slopes of the calibration curves for Cl-ISE and NO_3-ISE were 37.8 and 35.7, respectively. Both NO_3 and Cl ISEs' responses can be expressed using the Nikolsky–Eisenmann equation. Therefore, according to our theory, the response of these two ISEs to the major selected ions can be expressed as Eqs. (1) and (2):

$$V_{pC_{NO_3}} = P_1 \times pNO_3 + P_2 = 35.7 \times pNO_3 + 246.8 \tag{1}$$

$$V_{pC_{Cl}} = P_1 \times pCl + P_2 = 37.8 \times pCl + 274.2 \tag{2}$$

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