



Simultaneously determining multi-metal ions using an ion selective electrode array system



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HIGHLIGHTS

- Four metal ions and Cl have been simultaneously determined using ISE array.
- An open flow-through system for ISE array measurement was designed.
- PCA was applied as a data compaction technique to reduce the complexity of data.
- Patented method, *geneticICA*, was utilized to improve the accuracy of ANN.
- OED was employed for minimizing the number of samples for training the ANN.

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ABSTRACT

The electronic tongue (ET) system contains an ion selective electrode (ISE) array, with a signal recording system and data processing methodology. It is developed for simultaneous determination of multiple free ions dissolved in solutions for real-time *in situ* monitoring. This article outlines an application of the ET system to determine chloride (Cl) simultaneously, and multi cationic metal ions, including calcium (Ca), cadmium (Cd), copper (Cu) and lead (Pb). In this study, Principal Component Analysis (PCA) was applied as a data compaction technique to reduce the complexity of data from the ISE array without losing much information. A patent data preprocessing method, *geneticICA*, was utilized to improve the prediction accuracy of ANN. Moreover, Orthogonal Experiment Design was employed for minimizing the number of training samples without losing any quality characteristics for the specific ions. Using our methodology means that results can be obtained rapidly and accurately without disturbing the natural speciation. The robustness and appropriateness of the approach were assessed using the mean relative error (MRE). When configured and optimized, the ET system can quantify the concentration of the four desired metals and chloride with the average MRE being lower than 0.10.

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1. Introduction

Cadmium (Cd), copper (Cu) and lead (Pb) are highly toxic to ecological and human receptors, even in trace concentrations (Kader et al., 2016; Lamb et al., 2010). Heavy metals are found in significant quantities in industrial wastewaters where accurate techniques for online *in situ* monitoring of heavy metal concentrations is increasingly desirable during wastewater treatment (Smith, 2009; Stuetz, 2003; Aguado and Rosen, 2008). Calcium (Ca) is a dominant cation in natural waters, and is a key component of water, which has been shown to impact on heavy metals' environmental toxicity in soil and aquatic systems (Ayers and Westcot, 1994). Normally, these metals could be measured using inductively coupled plasma (ICP) mass spectrometry (MS) or ICP optical emission spectroscopy (OES). These instruments are lab-based, extremely heavy and importable. Furthermore, samples from the field have to be preserved and sent to a laboratory where ICP/MS or ICP/OES are located and measured by technicians, which is not suitable for online *in situ* monitoring. Compared to other analytical techniques, ISEs have the benefit of being relatively inexpensive, simple to use and exhibiting rapid responses, which are all essential for *in situ* monitoring of ions in environmental samples (Freiser, 1980).

ISEs are normally based on ionophores designed for complexing, interacting, and holding the analyte in a molecular cavity (Freiser, 1980). The main problem limiting the general utilization of these ISEs is interference from other undesired ions, often present in significant concentrations that respond similarly to the target analyte (Freiser, 1980). For example, both Cd and Pb ISEs indicate severe interference in the presence of Cu^{2+} ion (insert reference). Even at ultra-trace (ppb) levels of Cu^{2+} ion may cause significant interference to Cd and Pb ISEs (Manual of cadmium ion selective electrodes; Manual of lead ion selective electrodes). The reason is that Cd and Pb ISEs are normally a pressed pellet of silver sulfide (Ag_2S)/CdS and Ag_2S /PbS, respectively. Cu^{2+} ions form stronger complexes with sulfide than Pb^{2+} and Cd^{2+} (Bühlmann et al., 1998). Furthermore, for the Ca ISE, Cu^{2+} , Cd^{2+} , Pb^{2+} might cause significant interference when they are present at sufficient concentrations, such as ppm levels (Manual of calcium ion selective electrodes). Chloride (Cl) is widespread and is one of the major interfering ions for the Cu electrode (Neshkova et al., 1998; Gulens, 1987; Mackey and De Marco, 1997; Oglesby et al., 1977; Westall et al., 1979). Therefore, generally speaking, the concentrations of Ca^{2+} , Cd^{2+} , Cu^{2+} and Pb^{2+} cannot be determined by their ISEs simultaneously, especially in the presence of high Cl.

The cross-interference problem reported above can be minimized by applying an ISE array in combination with multivariate calibration methods. These methods can be separated as Mathematical Regression (MR) methods and Artificial Intelligent (AI) methods (Miller and Miller, 2005). Two of the most popular MR methods were Principal Component Regression (PCR) and Partial Least Squares Regression (PLS), Table 1 listed some of the applications of these two methods in both foodstuff and environmental samples. It is worth to mention that most of the MR methods are Multivariate Linear Regression. The quantitative prediction performance will be impacted, since the interferences from co-ions were non-linear in character (Baret et al., 2000). In the last decade, approaches using an ISE array with AI methods, especially ANN to solve the problem of non-linear interference have been widely studied (Mimendia et al., 2014; Wilson et al., 2012; Mimendia et al., 2010; Mueller and Hemond, 2013; Nuñez et al., 2013; Gutiérrez et al., 2007; Wang et al., 2015, 2014). An ANN is a nonparametric modeling algorithm which emulates biological neurons to understand the relationship between the input patterns and their targets (Miller and Miller, 2005). De Valle and his team, reviewed the applications of ISE array for remote environmental monitoring applications (Mimendia et al., 2010). In their case studies, ISE arrays were applied for the monitoring of heavy metals (Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+}) in water and soil samples (Wilson et al., 2012; Mimendia et al., 2010).

In this study, we utilized our recently patented method, *geneticICA*, to apply Independent Component Analysis (ICA) using the Genetic Algorithm (GA), to improve the prediction accuracy of ANN. In ICA, we denoted the independent component matrix as (1):

$$S = W^T Z \quad (1)$$

where:

- S —a mixture of independent components;
- W—the weight matrix for the whitened signal;
- Z —the whitened data matrix.

When the number of independent components is settled, *geneticICA* will start by randomizing the weight matrix W, then uses Genetic Algorithm symmetrically to orthogonalize every weight vector w in W using the mathematical formula (2):

$$w_{new} = E \left\{ z * (w^T * z)^3 \right\} - E \left\{ (w^T * z)^{3r} \right\} * w \quad (2)$$

where:

- w —the weight vector;
- z —the whitened data vector;
- I —identity.

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