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Application of Blind Source Separation Methods to Ion-selective Electrode Arrays in Flow-injection Analysis

Leonardo T. Duarte, *Member, IEEE*, João M. T. Romano, *Senior Member, IEEE*, Christian Jutten, *Fellow, IEEE*, Karin Y. Chumbimuni-Torres, and Lauro T. Kubota

Abstract—As shown recently, the interference problem typical of ion-selective electrodes can be dealt with via smart arrays adjusted by blind source separation (BSS) methods. In this letter, we resume this study and show that such an approach can be applied even when faced with a limited number of samples acquired through flow-injection analysis.

Index Terms—Chemical sensor arrays, blind source separation, ion-selective electrodes, signal processing.

I. INTRODUCTION

Although providing a simple solution for measuring ionic activity, an ion-selective electrode (ISE) often lacks selectivity, i.e., its response may be influenced by ions other than the target one. A possible solution to this problem is to set up an array composed of different ISEs. This allows the desired information to be recovered by signal processing methods that exploit the diversity provided by the array (diversity here means that each sensor responds differently). In this context, unsupervised signal processing methods can be particularly useful, since it works without calibration, or, at least, with a limited number of training samples. Such a feature can be interesting in ionic analysis since it avoids the need for performing calibration from time to time.

In the context of ISE arrays, an unsupervised approach for quantitative analysis leads to a blind source separation (BSS) problem [1], whose goal is to estimate a set of source signals by only considering mixtures of these sources. In ISE arrays, the sources and the mixtures are the activities of each ion within the solution and the responses provided by the ISE array, respectively. Among the difficulties in the application of BSS methods to ISE arrays is the fact that the mixing process is nonlinear. Indeed, ISEs are often modeled by the Nicolsky-Eisenman (NE) equation, in which the response of the i -th sensor within the array is given by:

$$x_i(t) = e_i + d_i \log_{10} \left(s_i(t) + \sum_{j=1, j \neq i}^{N_s} a_{ij} s_j(t) \right), \quad (1)$$

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where $s_i(t)$ and $s_j(t)$ are the activity of the target and interfering ions, respectively; e_i and d_i are constants and a_{ij} are the selectivity coefficients. N_s is the number of sources and can be estimated by model order selection methods.

In a recent work [2], a nonlinear BSS method based on a Bayesian approach was applied to ISE arrays. The results were encouraging and showed that BSS methods indeed provided good results for actual data. Herein, we extend this study by considering a more realistic scenario in which the data was acquired via a flow-injection analysis yielding a limited number of samples. Concerning the BSS method, we apply the Bayesian solution of [2], but also a BSS method based on independent component analysis (ICA) [3].

II. METHODOLOGY

A. Data acquisition

The data was acquired by an ISE array composed of two electrodes tailored to sodium (Na^+) and potassium (K^+) ions, respectively. Moreover, a flow injection analysis system (FIAs) was considered. In a FIAs, the solution under analysis is pumped through a tube system allowing them to be exposed to the sensors in a continuous sampling. There may be several successive injections of the same solution. There are several advantages in considering a FIAs. It presents a low-cost procedure in which a small quantity of reagent is necessary, and offers a more reproducible and rapid analysis compared to traditional beaker analysis.

In the performed experiments, 41 standard solutions were analyzed. The activities of Na^+ and K^+ for each of these solutions are shown in Figure 1 (these 41 samples can be represented as two signals which correspond to the desired sources). Concerning the FIAs, three successive injections for each standard solution were performed. There are thus three peaks associated with a given standard solution. The ISE array response for a given standard solution were obtained by averaging the three peaks associated with such solution. The obtained signals, which correspond to the mixtures in our problem, are shown in Figure 2.

B. BSS methods

Two BSS methods were applied to estimate the ionic activities depicted in Figure 1 from the mixtures of Figure 2: an ICA-based algorithm and a Bayesian algorithm. In ICA, the central assumption is that the sources can be modeled as statistically independent random variables [1]. Since the mixing process renders the mixtures dependent, ICA estimates the sources by adjusting a separating system whose inputs are

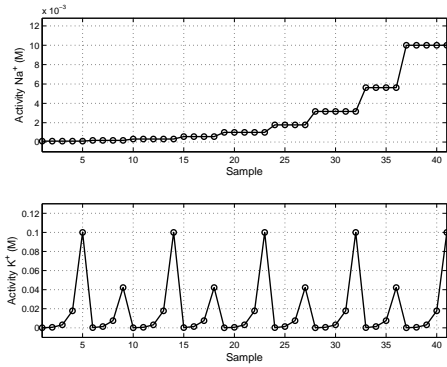


Fig. 1. Sources: activities of Na^+ and K^+ .

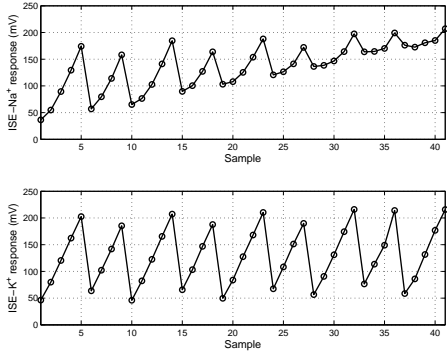


Fig. 2. Mixtures: responses of the Na^+ and K^+ ISEs.

the mixtures and the outputs are as independent as possible signals. We considered the ICA algorithm proposed in [3], which provides an efficient solution for the class of mixing systems known as Post-Nonlinear (PNL) models — when the valences of the ions under analysis are equal, the NE equation becomes a particular case of the PNL model [2]. The details of the ICA method adopted here can be found in [3].

In the Bayesian approach, BSS is rather seen as an inverse problem for which a good representation of the data is searched according to the Bayes' rule. In this letter, we adopted the Bayesian BSS algorithm proposed in [2], which is based on a Markov Chain Monte Carlo (MCMC) simulation and is also tailored to PNL models. A Bayesian method can be particularly useful when only a small number of samples is available and when the sources are correlated (see [2] for more details and for an example of correlated sources).

III. RESULTS

To compare the BSS methods, the signal-to-distortion (SDR) was considered [4]:

$$\text{SDR}_i = 10 \log \left(E\{s_i^2\} (E\{(s_i - \hat{s}_i)^2\})^{-1} \right), \quad (2)$$

where s_i and \hat{s}_i denote the source i and its respective estimation after correct scaling (the scale ambiguity, typical of BSS methods, was corrected by using 5 calibration points).

The sources retrieved by the ICA and Bayesian methods are shown in Figures 3 and 4, respectively (the actual sources are plotted in gray). The mixture SDRs, i.e. before any processing, were $\text{SDR}_1 = 1.2$ dB and $\text{SDR}_2 = 4.7$. The obtained SDRs

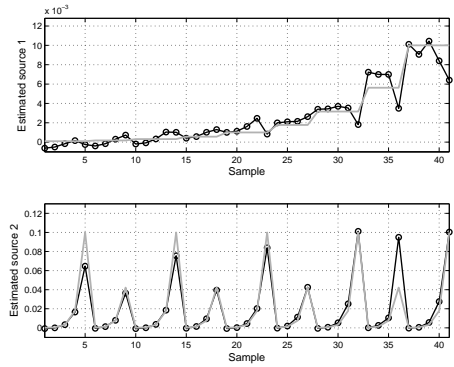


Fig. 3. Sources estimated by the ICA method.

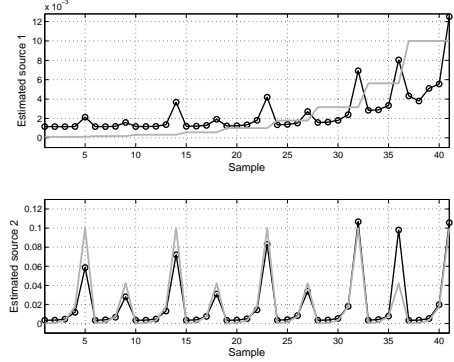


Fig. 4. Sources estimated by the Bayesian method.

for the two sources were $\text{SDR}_1 = 11.0$ dB and $\text{SDR}_2 = 10.6$ dB (ICA), and $\text{SDR}_1 = 4.4$ dB and $\text{SDR}_2 = 9.3$ dB (Bayesian method). The improvement was between 5 to 10 dB with ICA while only between 3 to 4.5 dB with the Bayesian approach.

IV. CONCLUSIONS

In this work, we applied BSS algorithms in ISE arrays operating in FIA. Despite the limited number of samples, a good estimation of the ionic activities was provided by BSS. However, in contrast to previous work [2], the ICA-based solution provided a better response in comparison to the Bayesian method. Indeed, differently from the data considered in [2], the sources in the present work were highly uncorrelated, which is in accordance with the main assumption of ICA methods. As a perspective for this work, we are currently studying its extension to scenarios in which the number of sources and sensors is greater than two.

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