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A BLIND SOURCE SEPARATION METHOD FOR CHEMICAL SENSOR ARRAYS BASED ON A SECOND ORDER MIXING MODEL

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ABSTRACT

In this paper we propose a blind source separation method to process the data acquired by an array of ion-selective electrodes in order to measure the ionic activity of different ions in an aqueous solution. While this problem has already been studied in the past, the method presented differs from the ones previously analyzed by approximating the mixing function by a second-degree polynomial, and using a method based on the differential of the mutual information to adjust the parameter values. Experimental results, both with synthetic and real data, suggest that the algorithm proposed is more accurate than the other models in the literature.

***Index Terms*—** Blind source separation, chemical sensor arrays, ion-selective electrodes, quadratic mixing model

1. INTRODUCTION

The problem of blind source separation (BSS) is an important cornerstone in signal processing theory [1], with applications including audio signal processing, telecommunications, image processing, brain-computer interface design, analysis of seismic data, among others. To put simply, the BSS problem consists of estimating some signals, which we shall call sources, using measurements which are effectively a mixture of them, and possibly some *a priori* information on the nature of the desired signals and mixing process.

The common approach for solving the BSS problem starts with the hypothesis that the mixing process is linear and that the source signals are statistically independent, in which case successful algorithms such as the *independent component analysis* (ICA) [1] have been proposed and extensively studied over the last years. However, there are applications for which the linear model is insufficient, and a nonlinear mixing model is required. Among the nonlinear BSS mixing models that have been studied so far, it is important to mention the *post-nonlinear* (PNL) [2, 3], in which linear mixtures are further distorted by nonlinear functions before the measurement, and the *linear quadratic* (LQ) [4, 5] model, which represents the mixtures as a second-order polynomial on the sources.

In this work, we shall focus on the problem of source separation for ion-selective electrode (ISE) arrays [6–8]. ISEs are simple devices which are used for measuring the ionic activity (essentially the effective concentration of an ion) in an aqueous solution. An ISE consists of a sensitive membrane for which the electrochemical potential varies according to the concentration of a specific ion. A well-known example of ISE is the glass electrode used for measuring the pH value [9].

The problem of the ISEs, however, is that the membranes are not perfectly selective, which means that when trying to estimate the activity of a certain ion, the measurement will include an interference from ions different from the target one which are also present in the same chemical solution. Because the measurements are a mixture of the activities, a BSS paradigm can be used to separate the signals from each ion by using an array of multiple ISEs.

The problem of estimating the ionic activities based on ISE arrays has already been studied in the past, with the use of a Bayesian source separation method [10], sparsity-based methods [11] and a PNL model [3, 8]. In this paper, we will propose a different algorithm for the problem, in which we will model the data by a second-degree polynomial, and compare this approach with the PNL model previously mentioned.

In the paper, we will initially present, in section 2, a description of the BSS problem statement and how it relates to measurements with chemical sensor arrays. In section 3, we will then propose a solution to the problem, and present experimental results in section 4, as well as comparisons with previously analyzed methods. Finally, in section 5 a conclusion and future plans shall be presented.

2. PROBLEM STATEMENT

2.1. Blind Source Separation

Let us consider a set of N sources $\mathbf{s}(n) = [s_1(n), s_2(n), ..., s_N(n)]^T$ and M mixtures $\mathbf{x}(n) = \mathcal{F}[\mathbf{s}(n)] = [x_1(n), x_2(n),$

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$..., x_M(t)]^T$, where n is the temporal index and $\mathcal{F}[.]$ is the mixing function. The goal of the source separation problem is to obtain the sources $\mathbf{s}(n)$ given the mixtures $\mathbf{x}(n)$, and possibly some *a priori* information on the properties of the sources (e.g. independence, sparsity, non-negativity, etc) and/or on the mixing process. The problem is said to be *non-blind* if the mixing function $\mathcal{F}[.]$ is known, and it is otherwise said to be *blind*. If the function $\mathcal{F}[.]$ is linear, the mixing function can be represented by a matrix:

$$\mathbf{x}(n) = \mathbf{A}\mathbf{s}(n) \tag{1}$$

where $\mathbf{A}$ is a $N \times M$ matrix. For the linear case, there are several classical methods in the literature that can solve the BSS problem under different priors for the sources. A very well-known class of methods is the *independent component analysis* (ICA), which can successfully separate the sources provided they are statistically independent, at most one of them has a Gaussian distribution, and the mixing function is invertible [1].

For the nonlinear case, however, no general solution exists, and the problem has to be analyzed on a case-by-case basis [1], depending on the nature of the mixing function. Among the commonly studied nonlinear models are the post nonlinear (PNL) [3] and the polynomial model [12].

2.2. Chemical Sensor Arrays

For the problem of chemical sensor arrays, let us consider a solution in which we have N different ions and M ion selective electrodes (ISE) to measure their activity, which are our sources. However, due to the interference problem, the values measured are actually a nonlinear mixture of the activities of each ion. According to the Nicolsky-Eisenman (NE) equation [13], this interference can be approximately modeled by the equation below:

$$y_i(n) = e_i + \frac{RT}{z_i F} \ln\left(s_i(n) + \sum_{j=1, j\neq i}^{N} a_{ij} s_j^{z_i/z_j}(n)\right) \tag{2}$$

where e_i is the standard electrode potential (a scalar constant), R is the universal gas constant, T is the temperature, F is the Faraday constant, z_i is the valence of the ith ion, and a_{ij} are the selectivity coefficients. The $\frac{RT}{z_i F}$ slope is called the *Nernst slope*, and at room temperature of 25°C, it is approximately 26mV, or 59mV if the logarithm is converted to base 10 (which is the standard practice in chemical applications).

In this paper, we will treat the case in which we have two sources and two electrodes, and the ions have the same valence (for example, Na^+ and K^+). In this case, (2) becomes[1]

$$\mathbf{y} = \mathbf{e} + \mathbf{d} \circ \log(\mathbf{A}\mathbf{s}) \tag{3}$$

[1]The argument (n) has been omitted for clarity.

where A is such that $a_{11} = a_{22} = 1$, $\mathbf{d}$ is the vector containing the estimates of the slope for each ISE, and $\circ$ denotes the Hadamard (entrywise) matrix product[2]. While the slopes represented by $\mathbf{d}$ can be theoretically calculated directly by (2), the empirical nature of the NE equation cannot always accurately model the data, and better results can be obtained by giving the model an additional degree of freedom, allowing it to vary the slope.

3. PROPOSED SOLUTION

Starting from (3), it can be seen that by calculating

$$x_i = 10^{\frac{y_i - e_i}{d_i}} \tag{4}$$

we obtain the modified mixture set $\mathbf{x} = \mathbf{A}\mathbf{s}$, which is a linear mixture of the two sources and can then be solved by classical linear BSS algorithms. This results in the classical PNL approach in which the difficult part is to estimate the parameters that correctly cancel the nonlinearity - in this case the slopes $\mathbf{d}$. The electrode potentials $\mathbf{e}$ becomes only a scalar factor on each mixture, and is therefore unimportant. This amplitude ambiguity can usually be ignored in the BSS paradigm, since it is usually impossible to obtain the correct amplitude of each source without some additional information (because sources with different amplitudes can produce the same mixture set by adjusting the unknown coefficients).

An algorithm for estimating the Nernst slope has been proposed [10, 14] and was able to successfully separate the sources, though not perfectly. We propose here a different algorithm, in which instead of estimating the slopes $\mathbf{d}$, we simply use the theoretical value of the Nernst slope given by (2) of $d^* = 59$mV. Since the actual slope is close, but actually different from the theoretical value, by using d^* in (4) we obtain:

$$x_i = 10^{\frac{y_i - e_i}{d_i}\frac{d_i}{d^*}} \tag{5}$$

which leads to $\mathbf{x} = (\mathbf{A}\mathbf{s})^{\mathbf{d}/d^*}$, where the exponential is performed entrywise. We can see then that the mixture is no longer linear; but it should have a small measure of nonlinearity, since $d_i/d^* \approx 1$. Therefore, a promising idea is that by modeling it by a second-order polynomial, the approximation would be very close to the actual model. The quadratic terms of this new mixing model would also be able to eventually correct small flaws in the actual NE model (2). Thus, our modified mixture set $\mathbf{x}$ can be modeled as:

$$\mathbf{x} = \mathbf{A}\mathbf{s} + \mathbf{B}\mathbf{s}^{\circ 2} + \mathbf{c}s_1 s_2 \tag{6}$$

where $a_{11} = a_{22} = 1$ and $\mathbf{s}^{\circ 2} = [s_1^2, s_2^2]^T$. This mixing model encompasses the class known as linear-quadratic model, for which one can find several methods to deal with [12]. Since the mixing model is not as simple as the linear

[2]The logarithm operation is also performed entrywise.

case, inverting it is no longer trivial, and a recurrent network seems indicated solve even in the non-blind case [12].

3.1. Recurrent Network for Non-blind Model

The idea is that by rewriting the equation as

$$\mathcal{G}[\mathbf{s}] = \mathbf{A}\mathbf{s} + \mathbf{B}\mathbf{s}^{\circ 2} + \mathbf{c}s_1 s_2 - \mathbf{x} = \bar{\mathbf{0}} \tag{7}$$

where $\mathbf{s}^{\circ 2} = \mathbf{s} \circ \mathbf{s}$ and $\circ$ is the Hadamard product, we are able to use classical root-finding algorithms for nonlinear equation systems to solve the problem. One of the most popular such algorithm is the *Newton-Raphson method* [5], which converges to the solution by applying the following iteration

$$\mathbf{y_{k+1}} = \mathbf{y_k} - \mathbf{J}_{\mathcal{G}}^{-1}(\mathbf{y_k})\mathcal{G}[\mathbf{y_k}] \tag{8}$$

where $\mathbf{J}_{\mathcal{G}}$ is the Jacobian of the system, which in our case is

$$\mathbf{J}_{\mathcal{G}} = \mathbf{A} + 2\mathbf{B} \circ \left(\begin{bmatrix} 1 \\ 1 \end{bmatrix} \mathbf{s}^T \right) + \mathbf{c}\mathbf{s}^T \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{9}$$

3.2. Parameters Estimation

For the blind case, we need a method for estimating the parameters of the model. We used a gradient-based ICA method for this: starting with random parameters, we vary them according to the gradient of a cost function that should be minimized for the correct parameters. For independent sources, we can use the mutual information (MI) as cost function and will therefore need an estimate of the differential of the MI, as proposed in [15]. Let us start by defining what can be roughly interpreted as the "gradient" of the MI with respect to $\mathbf{y}$:

$$\beta_{y_i}(\mathbf{y}) = \left(-\frac{\partial \log p(\mathbf{y})}{\partial y_i} \right) - \left(-\frac{d \log p(y_i)}{d y_i} \right) \tag{10}$$

which is the difference between the ith component of the joint score function of $\mathbf{y}$ and the marginal score function of y_i. It can be proven that $\mathbf{y}$ has independent components if, and only if, $\beta_{\mathbf{y}} = 0, \forall i$ [15]. It is interesting to note that the score functions (i.e., the derivatives of the MI), and, by extension, the $\beta_{\mathbf{y}}(\mathbf{y})$ defined in (10) can be accurately computed by efficient methods as described, for instance, in [16]. The "gradient" of the MI with respect to the parameter vector $\mathbf{w}$, can be therefore calculated:

$$\frac{\partial I}{\partial \mathbf{w}} = E\left\{ \frac{\partial \mathbf{y}}{\partial \mathbf{w}}^T \beta_{\mathbf{y}}(\mathbf{y}) \right\} \tag{11}$$

and the iteration to find the parameters can be written as:

$$\mathbf{w_{k+1}} = \mathbf{w_k} - \mu \frac{\partial I}{\partial \mathbf{w_k}} \tag{12}$$

where μ denotes the learning rate[3]. When applied specifically to the case of the second order model, and $\mathbf{w} = [w_1, ..., w_8]^T$ the coefficients that appear in

$$\mathbf{x} = \begin{bmatrix} s_1 + w_1 s_2 + w_2 s_1^2 + w_3 s_2^2 + w_4 s_1 s_2 \\ w_5 s_1 + s_2 + w_6 s_1^2 + w_7 s_2^2 + w_8 s_1 s_2 \end{bmatrix} \tag{13}$$

the matrix of partial derivatives can be calculated as

$$\frac{\partial \mathbf{y}}{\partial \mathbf{w}} = \mathbf{J}_{\mathcal{G}}^{-1}(\mathbf{y}) \begin{bmatrix} y_2 & y_1^2 & y_2^2 & y_1 y_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & y_1 & y_1^2 & y_2^2 & y_1 y_2 \end{bmatrix} \tag{14}$$

Our proposed algorithm alternates between the iteration to estimate the parameters (12) and the recurrent network capable of solving the non-blind problem (8), until the parameters converge.

4. EXPERIMENTAL RESULTS

In order to measure the quality of the estimated solutions, the *signal-to-intereference ratio* (SIR) was used, which is defined as (in decibels):

$$\text{SIR} = 10 \log_{10} \frac{E\{\mathbf{s}^2\}}{E\{(\mathbf{s} - \mathbf{y})^2\}} \tag{15}$$

4.1. Simulated Data

For the simulated data, the sources were uniformly distributed in the $[0, 1]$ interval and the first one was sorted, to make it easier to see on the time domain. This does not affect the statistical properties of the sources. We used $e_i = 100$mV (typical electrode potential values), $\mathbf{d} = [55, 65]^T$ (typical slopes estimated by the PNL), and mixing parameters $a_{12} = a_{21} = 0.5$. The ion valences are both equal to 1.

The algorithm was presented with the mixtures as given in (3), and after using standard values of 100mV for the potential and 59mV for the Nernst slope, we obtain a modified mixture set which can be separated with the described network. The sources, mixtures and estimates obtained in this simulation can be seen in Fig. 1. The SIR values obtained were 22.9 dB and 27.8 dB respectively, which can be considered good enough for our source separation simulation, especially in view of the fact that the model only approximates the data.

Another simulation can be done with the addition of white noise to the data, where we incrementally change the noise variation and calculate the obtained SIR as a function of the SNR for the proposed method, and the PNL, which is the method that best performed in the comparisons analyzed in [7]. The results obtained can be seen in Fig. 2.

We can see that for high SNR (i.e., low noise) both methods obtain similarly accurate estimates, whereas for lower

[3] Smaller learning rates improve the algorithm's robustness at the expense of longer convergence times. In our simulations we used $\mu \in [0.001; 0.01]$.

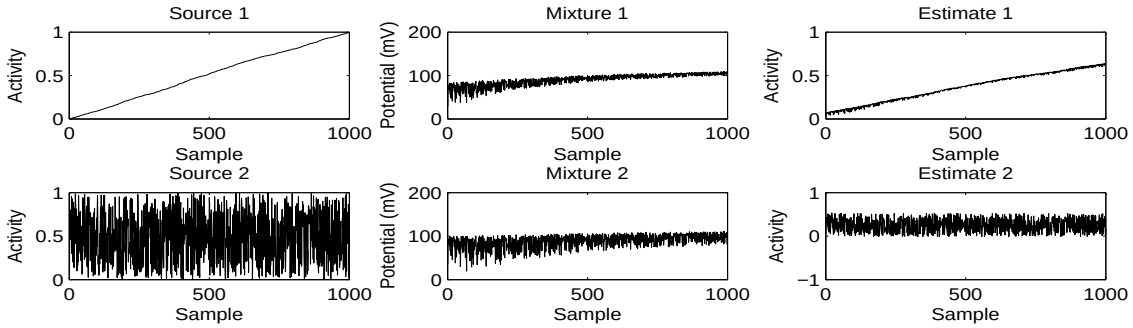

Fig. 1. Sources (left), mixtures (center) and estimates (right) for our simulation with synthetic data

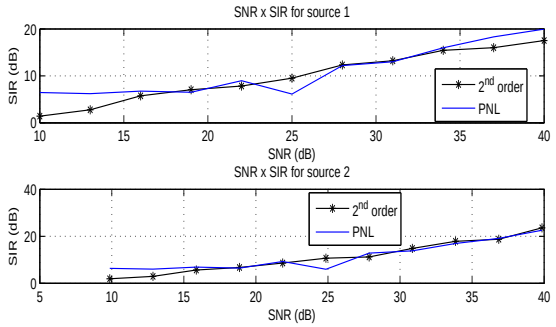

Fig. 2. SNR and SIR of each source for both methods

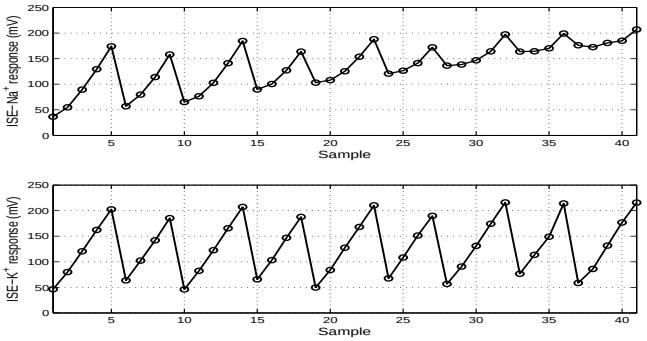

Fig. 4. Mixtures obtained for the FIA experiment

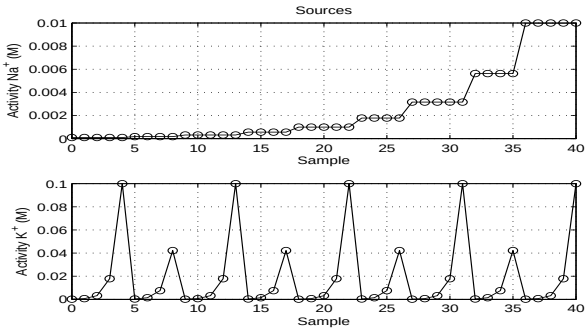

Fig. 3. Sources obtained in the FIA experiment

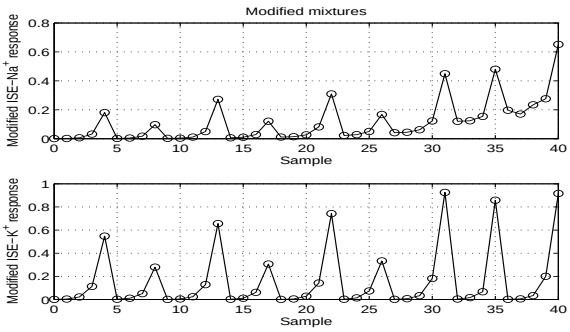

Fig. 5. Modified mixtures obtained for the FIA experiment

SNR the PNL obtains better result, though neither can be said to successfully separate the sources. This is expected, since in this simulation the PNL model characterizes the data exactly, unlike the quadratic network which just approximates it.

4.2. Real Data

For the real data, one of the limitations is that the set contains only 41 samples. Together with the fact that the NE equation used in the model is only empirical, it follows that the estimates will not be as good as the ones obtained for the synthetic data.

In Fig. 3, we can see the actual sources as the concentrations of Na^+ and K^+, in mol/L, measured during an experiment based on the FIA method for mixing the ions [7]. We can also see in Figs. 4 and 5 the mixture signals (as measured by the ISEs) and the modified version of the mixtures, after applying (4).

After using our algorithm on the modified mixture set, we obtain the estimates shown in Figs. 6 and 7. The SIR obtained were 16.3 dB and 11.1 dB, respectively. For comparison, the PNL network obtains SIR values of 11.0 dB and 10.6 dB [7], which shows a significant improvement for our proposed method on the first estimate, and a similar result for the

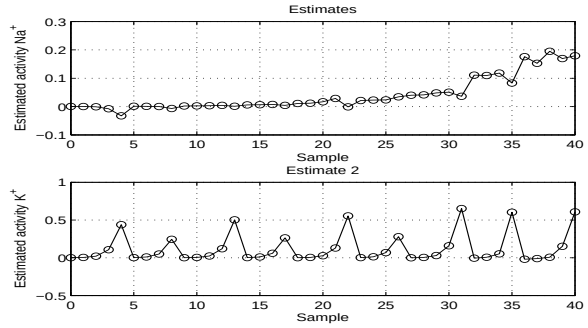

Fig. 6. Estimates obtained in the FIA experiment

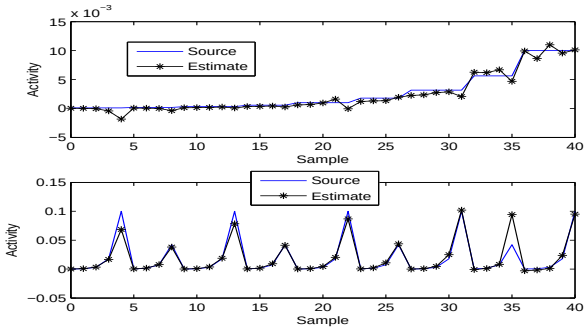

Fig. 7. Sources and estimates plotted after adjusting the amplitudes

second one. Again, the better performance can be explained by the fact that the NE equation does not accurately model the real data, emphasizing the importance of the additional degrees of freedom yielded by our method. Indeed, in [9] it has been discussed that the mixing coefficients can vary depending on the concentrations of the ions, unlike what is described by the NE equation.

5. CONCLUSION

In this paper, we have presented a new algorithm for solving the BSS problem associated with the estimation of ionic activity with an array of ion-selective electrodes. We have compared our proposed network with the previous solutions based on a PNL modeling, and experimental results seem to show an improvement in accuracy.

In the future, we would like to further study the quadratic model theoretically used in this algorithm, by investigating its separability conditions and stability of the solutions. Another interesting line of research is to include a method in the algorithm to estimate the Nernst slope $\mathbf{d}$ as well as the quadratic parameters, resulting in possibly better results. Finally, it is also possible to expand the proposed network for a greater number of sources and electrodes, or sources that have different valences, allowing the proposed network to be used in a wider variety of experiments.

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