

# BLIND SOURCE SEPARATION FOR SOLID-STATE CHEMICAL SENSOR ARRAYS

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## ABSTRACT

Electronic noses and tongues are two recent examples in chemical sensing that employ statistical array techniques in order to overcome the intrinsic limitations of current solid-state chemical sensors like ion-selective field transistors (ISFET). In particular, ISFETs are sensitive to the concentration of a particular ion in a solution to be measured, but it can be also strongly affected by several interfering ions found in the solution. Hence, they must be employed in regions in which the effect of interferences is negligible thus limiting their range of operation. However, since ISFETs behave as non-linear mixers of main ion activities and interfering ones, an attempt to separate the original main ion activity and interferences from the mixed response is suitable with blind source separation (BSS) techniques and related methods like independent component analysis (ICA) methods. In this direction, several experiments with real ISFET measurements demonstrate the interest of employing BSS for dealing with the separation in ISFET responses, and further reconstruction, of ion activities in those operating regions in which interferences notably affect their response.

## 1. INTRODUCTION

In the last decade the use of the so-called smart sensor arrays arouse much attention [1]. Their key idea is the combination of poor selective sensors through a post-processing stage that performs some kind of intelligent processing that allows you to obtain an overall response that is better than that obtained by the individual sensors. Such a post-processing stage performs some statistical array processing [2] to overcome the intrinsic limitations of sensors by enhancing their output signals, which facilitate the extraction of relevant information in further stages. Notorious examples of these architectures are electronic noses and tongues [3] in the field of solid state chemical sensors [4], which perform analytical tasks to obtain qualitative or quantitative information about particular chemical components through the conversion of chemical information into an electrical signal using a transducer capable of recognizing some chemical

components. In particular, some combinations of ISFET [5][6] (or other related sensors) for the detection of ionic concentrations in solids and fluids are widely employed for this purpose.

In ISFET arrays, an intelligent post-processing stage, based on some kind of multi-sensor fusion, remains a necessary step not only to allow multi-component analysis but also: 1) to cope with their response to the activity of a particular component (the desired) and other secondary ones (the interferences), 2) to remove undesired sensor behaviors like non-linearity, hysteresis and drift. As a first step, our work is here restricted to study some solutions to the (first) problem of the sensor response to several ion activities, which limits in practice their range of operation only in regions in which the effect of interferences is negligible. In particular, we demonstrate how the single ISFET responses in an array, which is based on a non-linear weighted sensitivity to different (main and interfering) ion activities in a solution, can be separated into several reconstructed ion activities with the help of BSS/ICA techniques in combination with linear regression.

The paper is organized as follows: Section 2 presents ISFET operation as a non-linear mixing of several ion activities which serves as a basis for introducing how this mixing can be reverted with the help of BSS/ICA techniques. Finally, Section 3 some preliminary experiments, which employ data generated from real ISFET measurements, are presented to demonstrate the interest of our approach.

## 2. ISFETS AND BSS

### 2.1. ISFETs as non-linear mixers of ion activities

Ion-sensitive field-effect transistors (ISFETs) [5][6], one of the most appealing chemical sensors appeared in the last decades, are the result of the integration of the ion-

selective electrode (ISE) technology with semiconductors. They are built on metal-oxide-silicon field-effect transistors (MOSFETs) and, as any other electrochemical sensor, relate electrical and chemical domains to convert chemical information into an electrical signal through achieving selectivity to a particular ion activity in a chemical solution by replacing the metallic gate in a MOSFET with a structure of membranes (which can be formed by organic, inorganic and even biological elements). Different forms and materials of these membranes added to the basic structure (a pH-ISFET) gave rise to a plethora of related chemical solid-state sensors like: MEMFETs, REFETs, and most notably CHEMFETs [7]. However all these devices behave in a similar way.

The principle of operation in ISFETs is as any other potentiometric sensor: they produce an electrical potential related to the number of ions in a solution, which has been induced at the membrane surface when they are submerged in a solution containing ions which can be exchanged with the membrane. Accordingly, the steady-state drain current of an ISFET can be expressed in the linear range of operation using the MOSFET equations as follows:

$$I_d = \beta(V_r - V_{T'} - 0.5V_{ds})V_{ds} \quad \text{for } V_{ds} < V_r - V_{T'} \quad (1)$$

where  $V_r$  is the voltage applied to the reference electrode,  $V_{ds}$  is the drain-source voltage,  $\beta$  depends on several geometrical and technological parameters of the ISFET and  $V_{T'}$  is the chemically modified threshold voltage. This threshold voltage which can be modeled by two (relatively) uncoupled parts [7]:

$$V_{T'} = V_T - EMF \quad (2)$$

where  $V_T$  is the MOSFET threshold voltage and EMF is the electrochemically induced voltage. According to Nernst equation derived in electrochemistry and its straightforward extension proposed by Nicolsky when more than one ion is in the solution the EMF can be considered as:

$$EMF = E_i + \frac{RT}{n_i F} \ln \left( a_i + \sum_j K_{ij} a_j^{z_i/z_j} \right) \quad (3)$$

where  $a_i$  is the activity of the main ion,  $K_{ij}$  is the selectivity coefficient which relates the response to the interfering ions  $a_j$ ,  $Z_i$  is the valence of the main ion and  $Z_j$  is the valence of the disturbing ion  $j$  in the solution. Finally, (1) can be rewritten as

$$\begin{aligned} I_d &= \beta \left( V_r + E_o + \Phi \log_{10} \left( a_i + \sum_j K_{ij} a_j^{z_i/z_j} \right) - V_{T'} - 0.5V_{ds} \right) V_{ds} \\ &= A + B \log_{10} \left( a_i + \sum_j K_{ij} a_j^{z_i/z_j} \right) \end{aligned} \quad (4)$$

where  $\{A, B, K_{ij}\}$  denote the parameter set of the model to be determined from measurements (Note: the natural logarithm in (3) has been replaced by the base 10

logarithm  $\log_{10}$  including the scale conversion factor  $\ln 10$  in constant B). An alternative mode of operation is setting the drain current to a constant value and then measuring the electrochemically-induced potential in the reference electrode. If we then isolate  $V_r$  in (4) yields

$$\begin{aligned} V_r &= \frac{I_d}{\beta V_{ds}} + V_{T'} + 0.5V_{ds} - E_o - \Phi \log_{10} \left( a_i + \sum_j K_{ij} a_j^{z_i/z_j} \right) \\ &= C - D \log_{10} \left( a_i + \sum_j K_{ij} a_j^{z_i/z_j} \right) \end{aligned} \quad (5)$$

where now  $\{C, D, K_{ij}\}$  are the parameter set of the model.

## 2.2. The role of BSS in ISFET Arrays

A key point in ISFETs operation is their need of being calibrated before they could be employed. This calibration process consists in obtaining a signal linearly dependent on the ion concentration from the output of an ISFET conditioning circuit [8], which can be obtained through the application of some regression method, i.e. any supervised learning technique, as suggested in [9]. However, this fully supervised approach, which attempts to compute an inverse mapping from the mixed output through the estimation of selectivity coefficients, usually demands many calibration points (or supervised training samples) since ISFETs are sensitive, not only to a single ion but, to several interfering ions making their response a non-linear function of a mixture of ion concentrations found in the solution. Consequently, this need of many calibration samples limits the application of supervised methods in practice. However, it is possible to reduce this number with the inclusion of unsupervised learning algorithms, widely employed in the Neural Networks (NN) community, such as BSS [10] and ICA [11] approaches in order to estimate this inverse mapping.

If an I/V (or V/V) conversion circuit is employed for each ISFET in the array, which obtains an output voltage proportional to (4) or (5), and a steady-state pre-processing plus an A/D conversion is performed, the resulting voltages can be modelled by  $m$  discrete-time signals  $x_1[n], \dots, x_m[n]$  that correspond to a non-linear mixture of  $p$  source signals  $a_1[n], \dots, a_p[n]$  based on (5), i.e.

$$x_1[n] = b_{11} + b_{12} \log_{10} s_1[n] \quad (6)$$

$\vdots$

$$x_m[n] = b_{m1} + b_{m2} \log_{10} s_m[n]$$

with  $\{s_u[n]\}$  are the total ion activities defined as

$$s_u[n] = a_i[n] + \sum_{j=1}^{m-1} K_{ij}^u a_j[n]^{z_i/z_j}, \quad u = 1, \dots, m \quad (7)$$

where  $a_i$  denotes the main ion activity,  $\{a_j\}$  are the interfering activities,  $\{K_{ij}^u\}$  are the selectivity coefficient and  $m$  is the number of ISFETs in the array and  $(m-1)$  the number of interfering ion activities. In regions in which ion concentrations are equal to activities, according to the Debye-Hückel theory, activities can be considered independent variables so they can be recovered from the observed signals  $\mathbf{x}[n]=\{x_1[n], \dots, x_m[n]\}$  using ICA methods. In particular, non-linear ICA algorithms [12] would seem necessary since a non-linear mixing is produced. However, if  $\{s_u[n]\}$  can be first recovered through the estimation of  $\{b_{ij}\}$  then the mixing problem would be linear. Note that this estimation could be possible through a supervised learning process in regions in which interferences does not affect.

### 2.3. A simple BSS algorithm for ISFETs

Some sort of smart array processing in a collection of ISFETs would increase the multi-component analysis precision through enhancing array selectivity with interference cancellation. In order to do that, the construction of an inverse mapping with the help of an ICA algorithm could be attempted to obtain a separated quantitative measure (i.e. ion activities) from the mixed response of main and interfering chemical components. As noted before, if we take into account that through the estimation of  $\{b_{ij}\}$  is possible in high main ion activities in which interferences does not affect, then linear ICA could be employed in an ISFET array learning algorithm as follows:

1. *Pre-calibration*: perform some sort of linear regression, to estimate  $\{b_{ij}\}$  where the main ion activities must belong to a range in which inferences does not affect the ISFET response. In the ideal case, a simple two-point pre-calibration is possible.

2. *Non-linear transformation*: compute a linear transformation  $\mathbf{y}[n]$  of the original signals  $\mathbf{x}[n]$  with the estimated coefficients as follows

$$\begin{aligned} y_1[n] &= 10^{\frac{x_1[n]-b_{11}}{b_{12}}} \\ &\vdots \end{aligned} \quad (8)$$

$$y_m[n] = 10^{\frac{x_m[n]-b_{m1}}{b_{m2}}}$$

3. *Linear ICA*: compute a separating matrix  $\mathbf{W}$  with a linear ICA algorithm where the input signals  $\{y_i[n], i=1, \dots, m\}$  are computed through (8) and  $\{x_i[n], i=1, \dots, m\}$  are the outputs signal of ISFET array which now operated in a region where interferences considerably affect the response the sensors. A linear ICA algorithm (e.g. FastICA [11]) based on kurtosis or other high-order moments can be good candidates to compute  $\mathbf{W}$ . The reconstructed  $\mathbf{z}$  ion activities are then

$$\mathbf{z}[n] = \mathbf{W}\mathbf{y}[n] \quad (9)$$

4. *Recovery of scale factor ambiguity*: since ICA algorithms can recover a separating matrix from the original sources with a scale factor ambiguity, a linear regression could be performed to compute the scale relation between the original ion activities  $\mathbf{a}$  and the reconstructed activities  $\mathbf{z}$ .

## 3. EXPERIMENTS

In this section, we present some simple experiments with a 2 NO<sub>3</sub>-ISFET array using the learning architecture proposed in Fig.1.

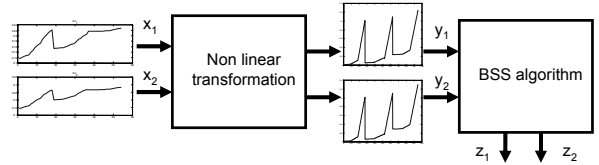


Fig. 1. Learning architecture based on: 1) 2 NO<sub>3</sub>-ISFET sensors, 2) a non linear transformation that recover mixed activities and 3) a BSS algorithm that separates main ion activities from interfering ones.

Interferences are reduced only to the Iodine ions and training data has been artificially created from real measurements where we have extracted the NO<sub>3</sub>-ISFET model parameters with a constant interfering iodine activity  $a_i=10^{-4}$ . Since these devices have a perfect Nicksolskian response, a population of 60 main ion activities with 3 constant interfering Iodine ions were generated (Fig.2) and then linear mixing of NO<sub>3</sub> and iodine activities were computed for obtaining the corresponding 60 steady-state output voltages for sensor  $E_{o1}$  and  $E_{o2}$ , which behave according to (5) (Fig.3). Fig. 4 displays the 60 reconstructed activities applying the BSS algorithm suggested in section 2.3 in these two output voltages, where a two-point pre-calibration was employed for the non-linear transformation and FastICA [11] was selected as a linear ICA algorithm. These results demonstrate that the reconstructed ion activities have a similar shape than the original ones except for a scale factor so the recovery of the original amplitudes (step 4 of the proposed learning algorithm) is possible.

## 4. CONCLUSIONS

We have presented a novel approach to the problem of recovering main and interfering ion activities in ISFETs arrays based on ICA. Experiments with artificial data generated from real measurements in 2 NO<sub>3</sub>-ISFET arrays demonstrate the viability of our proposal. Additionally, our approach could be adapted and then applied in other chemical sensors like solid-state gas sensors [13], since they exhibit a similar behaviour to interferences than ISFETs: their response is also a mixing of several (gas) components found in the air [14][15].

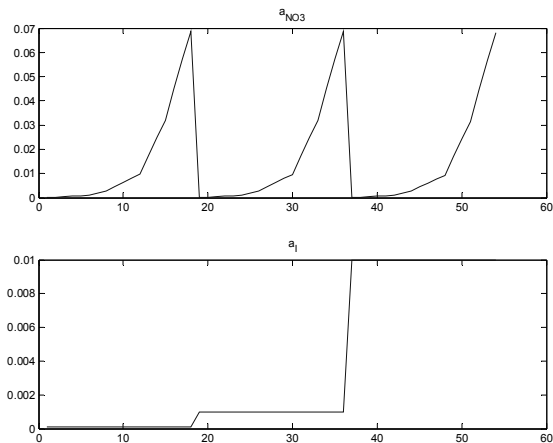


Fig. 2. Main ( $a_{NO_3}[n]$ ) an interfering ( $a_i[n]$ ) activities for  $n=1, \dots, 60$ .

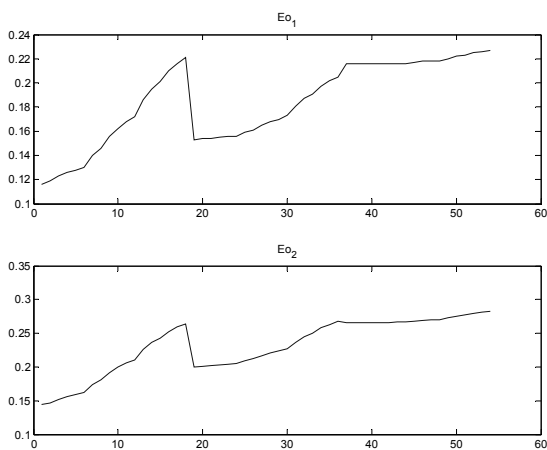


Fig. 3. Output voltages of 2  $NO_3$ -ISFETs,  $E_{o1}[n]$  and  $E_{o2}[n]$ , for the above activities.

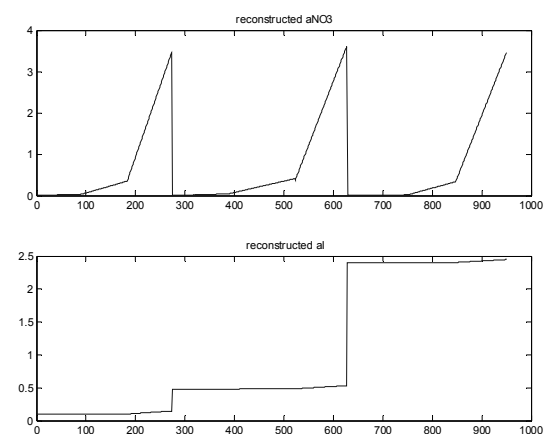


Fig. 4. Reconstructed activities ( $z_1[n]$  and  $z_2[n]$ ) applying the proposed learning architecture (Fig.1).

## 5. ACKNOWLEDGMENTS

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